

**EFFECT OF NANOSIZED PHTHALOCYANINE ON THE PHOTOVOLTAIC
PERFORMANCE OF TITANIUM OXIDE/METAL ORGANIC FRAMEWORK
COMPOSITE**

By

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DEDICATION

This PhD THESIS is dedicated to my grandson LETHABO WANDILE RAMARIPA

DECLARATION

I declare that EFFECT OF NANOSIZED PHTHALOCYANINE ON THE PHOTOVOLTAIC PERFORMANCE OF TITANIUM DIOXIDE-METAL ORGANIC FRAMEWORK COMPOSITE thesis submitted to the UNIVERSITY OF LIMPOPO for the degree of DOCTOR OF PHILOSOPHY IN CHEMISTRY has not been previously been submitted by me for a degree at this or any other university, that it is my own work in design and execution, and that all material combined herein has been duly acknowledged.



RAMARIPA PS

3 APRIL 2023

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ABSTRACT

This thesis reports on the dye sensitized solar cell (DSSC), an unconventional opportunity for silicon solar cell owing to their flexibility, transparency and low cost. DSSC is one of the electrical production technology, which uses the photovoltaic effect. The necessity for DSSC to captivate more of the sunlight radiation was the motive force for the fabrication of semiconductor materials based on their high surface area. The main components in DSSC are the conducting substrate, dye, photoanode, catalyst and electrolyte. The photoanode is well known as an element that generates the energy conversion efficiency. There are different photoanode materials that were studied to date. Amongst photoanode materials, titanium dioxide (TiO_2) materials are extensively documented, explored and considered. In this work, efforts are made to survey the strategies to advance the energy efficiency of TiO_2 based photoanode with introduction of metal organic framework (MOF) in DSSC to suppress the recombination rate and electron loss. It was observed that to attain a high conversion yield in DSSC, it is vital to collect the produced ion carriers before electron recombination. This work is devoted to the TiO_2 and MOF photoanode, their properties and various improvement approaches using nanosized phthalocyanine for photovoltaic performance. A high surface area MOF was incorporated into TiO_2 network to form a TiO_2 -MOF composite using sol-gel method and was employed as a photoanode material for photovoltaic applications. X-ray Diffraction patterns (XRD), Fourier Transform Infrared (FTIR), thermal gravimetric analysis (TGA), differential thermal analysis (DTA) and Raman analyses showed the presence of MOF clusters in the TiO_2 aerogel network. The scanning electron microscopic (SEM) images revealed the smooth irregular shape of TiO_2 , octahedral shape of MOF and continuous arrangement of pore-solid network structure for composite. The TiO_2 -MOF composite showed a Brunauer, Emmett and Teller (BET) surface area of $111.10 \text{ m}^2\text{g}^{-1}$ as compared to the surface area of TiO_2 ($262.90 \text{ m}^2 \text{ g}^{-1}$) and MOF ($464.76 \text{ m}^2\text{g}^{-1}$). It was seen that an increase in average pore size of 3.40 nm for composite analogous with the pore size of TiO_2 (2.66 nm) and MOF (2.56 nm). Cyclic voltammetry (CV),

electrochemical impedance spectroscopy (EIS), and chronoamperometric were used to determine the energy level and suggesting a fast electron transfer as well as the high ionic conductivity. The overall power conversion efficiency of 0.722% along with a photocurrent density 0.46 mA cm^{-2} was achieved by TiO_2 -MOF composite. The other objective was to incorporate of phthalocyanine dye into TiO_2 -MOF composite to enhance the photovoltaic performance of DSSCs. The structural and morphological studies of the prepared CuPc dye and TiO_2 -MOF after dye adsorption were characterized with various analytical techniques. The ultraviolet visible (UV-vis) spectrum of CuPc showed absorption bands at 370 nm and 798 nm, which are attributable to the B-band or Soret band and the Q-band in H_2SO_4 solvent. The optical studies revealed the absorption of CuPc by TiO_2 -MOF composite. The XRD patterns have shown the anatase TiO_2 phases, MOF and CuPc phases in the TiO_2 -MOF after dye adsorption (TiO_2 -MOF/CuPc). Raman and FTIR spectroscopies have shown the N-Cu-N and O-Cu-O vibrational mode for both MOF and CuPc, N-Cu-N vibrational mode on CuPc, as well as the symmetrical and antisymmetric vibration mode O-Ti-O of TiO_2 in TiO_2 -MOF/CuPc. BET have revealed the decrease in surface area after CuPc adsorption in the composite. The SEM images of the final TiO_2 -MOF/CuPc revealed the rod structure of CuPc, agglomerated structure of TiO_2 upon the introduction of MOF and the octahedral structure of Cu-MOF. The Tauc plot of TiO_2 -MOF/CuPc, has shown that there are differences in band gaps of the materials. The band gap of the final composite is 2.7 eV. A maximum photocurrent and power efficiency of 1.80 mA cm^{-2} and 1.63% at 0.8 V were recorded for TiO_2 -MOF/CuPc composite under simulated light source, respectively.

Furthermore, Copper phthalocyanine derivative, copper phthalocyanine nanowire dye was synthesized from copper phthalocyanine molecule. This material was responsible for the dye material in the DSSCs technology. Copper phthalocyanine nanowire (CuPcNW) dyes are employed in DSSCs to generate low-cost devices, light-harvesting, fast electron transfer material, and prevent recombination process, as well

as conductivity improvement. In this study, investigation for the effect of CuPcNW dye on TiO_2 , MOF, and TiO_2 -MOF in photovoltaic performance were made. Electrochemical characterizations such as CV and EIS were used to determine the highest occupied molecular orbital (E_{HOMO}) and lowest unoccupied molecular orbital (E_{LUMO}) energies as well as the ionic conductivity. The E_{HOMO} and E_{LUMO} values were found to be -5.1 and -4.31 eV in the TiO_2 -MOF/CuPcNW ternary nanocomposite, respectively. The EIS behaviour showed the improved conductivity of the ternary nanocomposite with a value of 244 $\mu\text{S/cm}$. It was seen that the TiO_2 -MOF/CuPcNW ternary nanocomposite achieved a maximum power conversion efficiency of 6.467% at lower potential of 0.43 V owing to the presence of CuPcNW, which improved the photocurrent density. The impact of copper phthalocyanine nanotube (CuPcNT) dyes on performance of TiO_2 -MOF nanocomposite in the performance of photovoltaic applications was investigated. The CuPcNW was hydrothermally treated at 180 °C in order to produce a self-assemble rectangular CuPcNT. This material was introduced as dye for DSSCs into TiO_2 -MOF composite to form TiO_2 -MOF/CuPcNT ternary nanocomposite. The UV-vis revealed the smaller band gap of 2.62 eV, and absorbed at the region beyond the UV light with the wavelength of 798 nm. The x-ray diffraction patterns showed the TiO_2 , MOF and CuPcNT phases, and functional groups in the TiO_2 -MOF/CuPcNT nanocomposite. The CV showed the half wave peak potentials of the TiO_2 -MOF/CuPcNT ternary nanocomposite with the values of 0.38 and 0.10 V for the oxidation and reduction reversible reactions with the calculated HOMO and LUMO energies of -4.85 and -4.37 eV, respectively. The EIS for TiO_2 -MOF/CuPcNT ternary nanocomposite revealed lower conductivity of 1.39 $\mu\text{S/cm}$ with

a lifetime of 1.94 ms as compared to the TiO₂-MOF/CuPcNW material. Interestingly, the maximum photocurrent and power conversion efficiency of the TiO₂-MOF/CuPcNT ternary nanocomposite were 7.02 mA cm⁻² and 11.69 % at lower potential of 0.35 V under a simulated light source higher than in the TiO₂, TiO₂-MOF, TiO₂-MOF/CuPc, and TiO₂-MOF/CuPcNW. In conclusion, the role of nanosized phthalocyanine dyes may be used to improve photovoltaic performance of TiO₂-MOF composite and make the resultant composites to be excellent candidates for dye-sensitized solar cell applications.

RESEARCH OUTPUT

BOOK CHAPTERS

1. **Ramaripa, P.S.**, Molapo, K.M., Somo, T.R., Teffu, M.D., Hato, M.J., Maubane-Nkadimeng, M.S., Makgopa, K., Iwouha, E.I. and Modibane, K.D., 2020. Photovoltaic Performance of Titanium Oxide/Metal-Organic Framework Nanocomposite. In Metal-Organic Framework Nanocomposites (pp. 131-166). CRC Press. (See Appendix 1)
2. Makhafola, M.D., Hato, M.J., Ramohlola, K.E., **Ramaripa, P.S.**, Maponya, T.C., Monama, G.R., Molapo, K.M., Iwuoha, E.I., Katata-Seru, L.M., Makgopa, K. and Modibane, K.D., 2021. Synergetic Effect of Graphene Oxide and Metal Organic Framework Nanocomposites as Electrocatalysts for Hydrogen Evolution Reaction. In Carbon Related Materials (pp. 23-54). Springer, Singapore.
3. Ramohlola, K.E., Morudu, T.C., Maponya, T.C., Monama, G.R., Makhado, E., **Ramaripa, P.S.**, Hato, M.J., Iwouha, E.I., Khan, A. and Modibane, K.D., 2020. Metal-Organic Frameworks with Immobilized Nanoparticles for Hydrogen Generation. In Metal-Organic Framework Nanocomposites (pp. 291-332). CRC Press.

ARTICLES

1. **Ramaripa, P.S.**, Modibane, K.D., Somo, T.R., Maubane-Nkadimeng, M.S., Hato, M.J., Makhado, E., Katlego Makgopa, K., 2022. Recent applications of analytical techniques and electrochemical methods in characterizations of the titanium dioxide composites. Int. J. Electrochem. Sci., 17, Article Number: ID 170746. (See Appendix 2)

2. **Ramaripa, P.S.**, Modibane, K.D., Makgopa, K., Seerane, O.A., Maubane-Nkadimeng, M.S., Makhado, E., Hato, M.J., Ramoroka, M.E., Molapo, K.M., Balakrishnan, D. and Iwuoha, E.I., 2022. Fabrication, characterization, and photovoltaic performance of titanium dioxide/metal-organic framework composite. *Journal of Photochemistry and Photobiology*, p.100142. (See Appendix 3)
3. **Ramaripa, P.S.**, Modibane, K.D., Makgopa, K., Mpho S Ratsoma, Manoko S Maubane-Nkadimeng, Kamogelo D. Modisane, Mpitloane J Hato, Thabiso C Maponya, Edwin Makhado, Deepanraj Balakrishnan, and Sadanand Pandey. 2022. Effects of phthalocyanine dye on titanium dioxide/metal organic framework composite for the fabrication of dye-sensitized solar cells. *Materials Today Communications*, Under review. (See Appendix 4)
4. **Ramaripa, P.S.**, Modibane, K.D., Makgopa, K., Seerane, O.A., Maubane-Nkadimeng, M.S., Makhado, E., 2022. Influence of phthalocyanine nanowire dye on the performance of titanium dioxide-metal organic framework nanocomposite for dye-sensitized solar cells. *Chemical Engineering Journal Advances*, Under review. (See Appendix 5)
5. **Ramaripa, P.S.**, Modibane, K.D., Makgopa, K., Seerane, O.A., Ramohlola, K.E., Maubane-Nkadimeng, M.S., Makhado, E., 2022. Impact of copper phthalocyanine nanotube dye on photovoltaic performance of titanium oxide/metal organic framework nanocomposite. *Applied Sciences*, Under review. (See Appendix 6)

PROVISIONAL PATENT

1. Inventors: **Ramaripa, P.S.**, Modibane, K.D., Makgopa, K., Phthalocyanine nanowire decorated titanium dioxide/metal organic framework ternary nanocomposite photovoltaic system– Ref: ZA2022/10097. (See Appendix 7)

PRESENTATIONS

1. **Ramaripa, P.S.**, Modibane, K.D., Maubane-Nkadimeng, M.S., and Hato, M.J., Photovoltaic Performance of Titanium Oxide/Metal-Organic Framework Nanocomposite. NANOSMAT-AFRICA conference 19-23 November 2018, Cape Town.
2. **Ramaripa, P.S.**, Modibane, K.D., Makgopa, K., Maubane-Nkadimeng, M.S., Hato, M.J., Makhado, E. Influence of phthalocyanine nanowires on the photovoltaic studies of titanium dioxide–metal organic framework/ composite. Postgraduate Faculty of Science and Agriculture Research Day, Bilovia Lodge, Polokwane, Limpopo, South Africa, 21-23 September 2022.

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LIST OF ABBREVIATIONS

Ag/AgCl	: silver/silver chloride
ATR	: attenuated total reflection
BAU	: business-as-usual
BET	: Brunauer-Emmert-Teller
BIO	: biomass
CA	: chronoamperometry
CCD	: charge-coupled device
CF ₃ COOH	: tri-floro acetic acid
CH ₃ CN	: methylcyanite
CH ₃ OH	: methanol
CNTs	: carbon nanotubes
CO ₂	: carbon dioxide
CPE	: constant phase element
CsPbI ₃	: cesium lead triiodide
CuPc	: copper phthalocyanine
CuPcNT	: copper phthalocyanine nanotube
CuPCNW	: copper phthalocyanine nanowire
CV	: cyclic voltammetry
CVD	: chemical vapour deposit
D	: dimension

DMF	: N, N-Dimethyl formamide
DSC	: differential scanning calometry
DSSCs	: dyes sensitized solar cells
EDS	: energy dispersion spectroscopy
EIS	: electrochemical impedance spectroscopy
eV	: electron volts
FeS ₂	: iron disulphide
FF	: fill factor
FTIR	: Fourier Transform Infrared
FTO	: fluorine tin oxide
FWHM	: full-width at half-maximum
GA	: Gravimetric analysis
GHGs	: greenhouse gases
H ₃ BTC	: 1, 3 , 5 tricarboxylic acid benzene
HCl	: hydrochloric
HOMO	: higher occupied molecular orbital
HRTEM	: higher resolution transmission electron microscopy
HTM	: hole-transporting materials
I ⁻¹ /I ₃ ⁻¹	: iodide/tri-iodide
I ₂	: iodine
I _{sc}	: short circuit voltage
I-V	: current-voltage measurements

J-V	: current density-voltage
LiI	: lithium iodide
LiOH	: lithium hydroxide
LUMO	: lower unoccupied molecular orbital
MOF	: metal organic framework
MoS ₂	: molybdenum disulphide
MWCNT	: multi wall carbon nanotubes
Na ₂ SO ₄	: sodium sulphate
Nb ₂ O ₅	: niobium pentoxide
O ₂	: oxygen
OPC	: organic photovoltaic
OPV	: organic photovoltaic
P ₃ HJ	: poly-3-hexylthiophene
PCE	: power conversion efficiency
P _{max}	: maximum power point
PSCs	: perovskite solar cells
Pt	: platinum
PV	: photovoltaic
PVCs	: photovoltaic cells
PVD	: physical vapour deposit
QDs	: quantum dots
QDSSs	: quantum dot sensitized solar cells

RES	: renewable energy system
SAED	: selected area electron diffraction
SBU	: secondary building unit
SCE	: standard calomel electrode
SEM	: scanning electron microscopy
SiO ₂	: silicon dioxide
SnO ₂	: tin dioxide
SWV	: square wave voltammetry
TEM	: transmission electron microscopy
TGA	: thermal gravimetric analysis
TiO ₂	: titanium dioxide
TTIP	: tetra titanium iso-propoxide
UV	: ultraviolet
UVA A	: ultraviolet analysis A
V _{max}	: voltage
V _{oc}	: open circuit voltage
XRD	: x-ray diffraction
ZnO	: zinc oxide

LIST OF SYMBOLS

d_{hkl}	: Interplaner spacing of the crystal
$\Delta G_{\text{Hads}}, \Delta G_{\text{HX}}$	: Gibbs free energy of adsorbed hydrogen
A	: Absorbance
$\text{\AA}$	: Angstrom
A	: Electrode area
a	: Tafel constant
a	: Unit cell size
b	: Tafel slope (mV/dec)
c	: Speed of light ($2.998 \times 10^8 \text{ m.s}^{-1}$)
c, C	: Concentration (mol.dm^3) of the absorbing species
C_{dl}	: Capacitance double layer
D	: Particle size (nm)
D_i	: Diffusion coefficient
E	: Potential
E_{final}	: Final potential
E_g	: Band gap energy (eV)
E_i	: Potential where redox reaction is not occurring
E_{initial}	: Initial potential
E_K	: Kinetic energy
$E^{\circ'}$	: Formal electrode potential

E°_a	: Anodic equilibrium half-cell potentials at standard conditions
E°_c	: Cathodic equilibrium half-cell potentials at standard conditions
E_p	: Peak potential
$E_{p,a}$	: Anodic peak potential
$E_{p,c}$	: Cathodic peak potential
E_t	: Applied potential at a given time
$E_{1/2}$ Ox	: half wave peak potential for the first ring oxidation
$E_{1/2}$ Red	: half wave peak potential for the first ring reduction
eV	: Electron volt
ϵ	: Molar extinction coefficient ($\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$),
F	: Faraday's number ($96,485 \text{ C mol}^{-1}$)
h	: Planck's constant ($6.626 \times 10^{-34} \text{ J.s}$)
hkl	: Miller indices
$H\nu$	: Photon energy
I	: Current
I	: Transmitted intensity
I_0	: Original/reference intensity
i_o, j_o	: Exchange current density
I_p	: Peak current
$I_{p,a}$	: Current for the anodic reaction
$I_{p,c}$	: Current for the cathodic reaction
J_i	: Molar flux

l	: Optical path length or dimension (cm)
m	: Mass per square centimetre
M	: Mass percentage
n	: Number of moles
η	: Overpotential
n	: Transition probability
nm	: Nanometers
ϕ	: Work function
Q	: Charge
R	: Gas constant (8.31451 J mol ⁻¹ K ⁻¹) and
R_{ct}	: Charge transfer resistance
R_{th}	: Thermal resistance
T	: Thermodynamic temperature (K)
t	: Time
T	: Transmittance
T_c	: Temperature of the empty sample holder
T_r	: Reference temperature
T_s	: Temperature of sample
ν	: Frequency (Hertz)
V	: Scan rate
$\tilde{\nu}$	: Wavenumber
X	: Distance to the electrode surface

z	: Stoichiometric number of electron
α	: Absorptivity coefficient
β	: Band gap tailing parameter
ΔE	: Energy
θ	: Diffraction angle
λ	: Wavelength
λ_{onset}	: Onset absorption wavelength
ϕ	: Heat flow
ϕ_1	: Heat flow of sample
ϕ_r	: Heat flow of reference
i, j	: Current density
α	: Symmetry coefficient
β	: Full width at half maximum

CHAPTER 1: INTRODUCTION

1.1. BACKGROUND ON ENERGY

1.1.1. Global energy consumption and environmental safety

The challenges of global energy consumption and environmental safety brought attention to scientists and engineers to develop renewable energy resources [1]. According to the energy balance compiled by the Department of Energy, coal constitutes approximately 70% of total primary energy supply in South Africa followed by oil, natural gas; nuclear; and renewable with 22, 4, 3 and 1%, respectively [2]. Adebayo *et al.* [2] reported on the prediction of the development on energy consumption, the development of global primary energy supply and final energy use in 2010-2050. They projected a 50% increase in global energy demand driven by a 65% increase in building energy consumption, a 79% increase in electrical power generation, and a 40% increase in natural gas consumption. Pursiheimo *et al.* [3] further explained the total primary energy supply in each case of the energy source, the renewable energy obtained from the solar power constitutes nearly half of primary energy supply in year 2050. The industrial sector that shares electricity in final energy uses grows from 19% to 47%. The use of electricity in transport sector reached 34% share, which is the same as the share of synthetic fuels that grows up to 34% [3]. However, role of bio based fuels and district heat remains relatively unchanged. In addition, coal as non-renewable energy, has the highest percentage and produces carbon dioxide (CO₂) emission that has a negative impact towards the climate change.

1.1.2. Challenge and prospects on the current supply of energy

In South Africa, the most common available energy source is supplied from the non-renewable energy includes fossil fuel. The combustion of fossil fuels such as coal, oil and natural gases produces CO₂ emission, depletion, greenhouse gas emission that is toxic and harmful to the environment [4-7]. The fossil fuels cause approximately 70% of the total emissions of CO₂ on earth, and this contributes towards the largest climate change [8]. Renewable energy sources, such as biomass and nuclear energy, are sometimes touted as an alternative to fossil fuels to reduce CO₂ emissions. Biomass refers to all

organic matter existing in the biosphere, whether of plant or animal origin, as well as those materials obtained through their natural or artificial transformation [9-11].

The more advanced renewable energy source includes hydrogen evolution, lithium-batteries, super capacitors and solar energy. Strictly no production of CO₂ emission in those energy resources. Among these renewable energy sources, solar energy is the best energy source due to its outstanding properties such as low cost, optical, mechanical and chemical properties. Solar energy uses the photovoltaic technology to produce electrical energy.

1.1.3. Photovoltaic Technology

Solar energy is a type of energy source that uses photovoltaic effect to generate electricity. Photovoltaic effect is a phenomenon in which the photons from the sunlight is chemically converted to the electricity by the utilization of solar cells [12-16]. The first and second solar cells have shown 20% of the power conversion efficiency (PCE) was based on the multi-junction solar cells [17]. However, those solar cells use the toxic materials.

These materials must be handled and disposed of properly, to avoid with time serious environmental and human health problems. In addition, their fabrication technology is expensive due to the use of several expensive photolithography processes based on thick silicon wafers [17]. O'regan and Grätzel [18] developed the third generation solar cells devise based on the integrated dye sensitized and perovskite in order to minimise the disadvantages of the first and the second generation of solar cells devise. The device was named dye sensitizes solar cells (DSSCs). This solar cell have improved the performance of the solar cells photo conversion efficiency with 39.9 % [19]. The dye-sensitized solar cell is an effective alternative technology rather than to these p-n junction silicon-based solar cells [7]. The characteristics of dye- sensitized solar cells for their easy fabrication route, not very high purity of the raw material requirement have attracted the attention from all over the world. DSSCs use materials such as zinc oxide (ZnO), tin dioxide (SnO₂), molybdenum disulphide (MoS₂) and titanium dioxide (TiO₂) as photoanode/semiconductor [20].

1.2. PROBLEM STATEMENT

Energy is of a great global concern with increasing in population and industrialisation resulting in levitation of its demand [21-22]. The increase in energy demand accelerates the production of fossil fuels that are very harmful to the environment. As a result, renewable energy sources such as wind energy, hydrothermal energy and solar energy are candidates to meet the increase in energy demand and are anticipated to play an important role in taking the world to an environmental friendly, reliable and sustainable energy system [23]. Among these renewable energies, solar energy is considered as one of the most promising energy sources to replace currently used fossil fuel [24]. Solar cell technologies directly convert the sunlight photon energy into electricity through photovoltaic effect. Scientists have been working on the development of various kinds of cells that convert solar energy into electricity, and the cells have been developed include silicon crystalline solar cells, organic conversion solar cells, quantum dot solar cells, dye-sensitized solar cells (DSSCs). Currently in South Africa, silicon-based solar cells dominate the solar industry, however silicon based solar cells are extremely expensive [25]. Dye-sensitized solar cells contribute towards the improvement of the performance of photovoltaic solar cells [20, 26]. The interest in DSSCs on semiconductors is due to their properties such as low manufacturing cost, simple fabrication process, and environmental friendly and can even operate at low weather conditions [21]. The photo electrochemical solar cells in DSSCs is based on a sensitized material that act as a dye in the solar cells for the maximum absorption of the incident light [27]. The most widely used dye in DSSCs is the ruthenium dye. Ruthenium dye is a sensitizer that can harvest sunlight and produce photo-excited electrons [28]. However, it is toxic, expensive and has limited availability of the starting materials [29]. On the other hand, TiO_2 semiconductor is used as a working electrode in the DSSCs. TiO_2 was extensively studied due to its advantage of large surface area, high chemical and optical stability, nontoxicity and inexpensive [30]. However, TiO_2 has larger energy band gap of 3.2 eV that results in low power conversion efficiency (PCE) [31]. Hence, there is a need to develop composite based materials that can lower the energy band gap and improve the power conversion efficiency of the system. TiO_2 may be doped with metal-organic frameworks (MOFs) to improve the harvesting of sunlight and reduces the band gap [32]. MOFs are highly

porous network materials formed by coordination of metal ions and organic linkers [33, 34]. TiO₂-MOF composite was extensively studied [27]. However, TiO₂-MOF composite has a slow electron transfer and results in lowering of PEC as compared to the one for TiO₂ [35]. Furthermore, it was reported that introduction of copper phthalocyanine (CuPc) as a dye sensitizer into solar cell enhances the electric field of the devices but cannot harvest enough sunlight [36-38]. This encourages the use of copper phthalocyanine to TiO₂ and MOF in order to enhance their performance on the photovoltaic cells. All these materials, TiO₂ semiconductor electrode, MOF and CuPc dye have their competitive properties that supplement each other and improve the performance of photovoltaic cells. Incorporation of the MOF and CuPc dyes on the TiO₂ improved the performance of photovoltaic solar cell and increase the PCE of the system. The TiO₂ composite reported in the literature for clean energy, cheaper and non-toxic materials were not challenging enough, due to the fact that they can only produces low power conversion efficiency in the dye sinsitized solar cells. Composite materials such as titanium dioxide/ruthenium-metal organic framework (TiO₂/Ru-MOF) TiO₂/HKUS-1, titanium dioxide-copper-metal organic framework (TiO₂-Cu-MOF), titanium dioxide-zinc-metal organic framework (TiO₂-Zn-MOF), titanium dioxide –copper-metal organic framework/carbon nanotube (TiO₂-cu-MOF/CNT) and copper-zinc oxide (Cu-ZnO) were reported to produce low PCE %. TiO₂/Ru-MOF obtained 1.22 % [32], as compared to TiO₂/HKUS-1(0.26 % [39], TiO₂-Zn-MOF (0.67%) [40], TiO₂-cu-MOF/CNT (0.46%) [32] and Cu-ZnO (0.062%) [41]. Hence, we opted to investigate on the TiO₂, MOF materials and TiO₂-MOF composite with and without CuPc, CuPcNW or CuPcNT dye for the enhancement of the performance of DSSCs applications.

1.3. RATIONALE AND MOTIVATIONS

Suitable secondary organic materials for incorporation to the semiconductors are metal phthalocyanines as dyes, due to their chemical stability and they strongly absorb in the blue to green region of spectra and can be used in photosensitizing [36, 42-43]. Recent studies of copper phthalocyanine as an organic dye in most composite shows that it can delay electron recombination of photoexcited electrons on the surface of TiO₂. It helps

in the lowering of the energy band gap of the composite by absorption of energy, which are packets of light energy, and electrons,. The conglomeration of TiO₂-CuPc was also studied for more than a decade and reports show more desirable photocatalytic features resulting in ameliorated energy effectiveness of DSSCs [42,43]. Out of the improvement that were made in the DSSCs, the focus was on advancing the materials. MOFs are photosensitive materials and there are various straightforward procedure that can be used through their synthetic method. Nevertheless, MOFs were found to have steady electron transfer on when employed in the photovoltaics [33]. This is a point where there is a need of incorporation with secondary materials in order to improve properties of both TiO₂ and MOFs. TiO₂ solar cell have promising features, incorporating it with light sensitive MOF and CuPc dye to lower energy band gap of the TiO₂ and also improve the electron transfer. Furthermore, CuPc nanowires have excellent properties such as structure, electrical and optical [44]. Because, they are two dimensional aromatic molecules that can be able to self-assemble into stack. CuPc nanowire uses π - π stacking axes to the photocurrent flow and increases the interfacial layer-active contact area. In addition, CuPc nanotubes are remarkable electrical, thermal, and mechanical properties of carbon nanotubes. Hence, the novelty of this study is based on the incorporation of CuPc molecule, CuPc nanowire and nanotube dyes onto TiO₂-MOF film in a DSSC. This will provide more efficient electron transfer due to the outstanding electrical properties of the CuPc dyes by reducing the band gap.

1.4. AIM AND OBJECTIVES

1.4.1. AIM

The aim of this study is to evaluate the effect of nanosized phthalocyanine on the photovoltaic performance of titanium dioxide-metal organic framework hybrid composite.

1.4.2. OBJECTIVES

The objectives of this study are to:

- i. chemically and hydrothermally synthesise metal organic framework (MOF), copper phthalocyanine dyes (CuPc), copper phthalocyanine nanowire (CuPcNW) and copper phthalocyanine nanotube (CuPcNT);
- ii. chemically and sol-gel synthesise of titanium dioxide (TiO_2) and titanium dioxide-metal organic framework (TiO_2 -MOF) composite;
- iii. prepare TiO_2 -MOF composite, TiO_2 -MOF -CuPc, TiO_2 -MOF/CuPcNW- and TiO_2 -MOF/CuPcNT ternary nanocomposite through adsorption process.
- iv. prepare the working electrode (TiO_2 , MOF, TiO_2 -MOF, TiO_2 -MOF/CuPc, TiO_2 -MOF/CuPcNW and TiO_2 -MOF/CuPcNT) on the Nickel foam substrate.
- v. investigate optical properties and confirmation of the prepared materials using Ultraviolet-visible spectroscopy (UV-vis),
- vi. study structural characterisations of the prepared materials using analytical techniques such as Fourier transform infrared spectroscopy (FTIR), Raman Spectroscopy, X-ray diffraction (XRD), and Thermal Gravimetric Analysis (TGA),
- vii. interrogate morphological characterisations of the prepared materials using analytical techniques using Scanning and Transmission Electron Microscopies (SEM and TEM) coupled with Energy dispersive X-ray spectroscopy (EDS, EDX) detectors and Selected area electron diffraction (SAED),
- viii. study electrochemical properties and determine HOMO and LUMO energies of the prepared materials using Cyclic Voltammetry (CV).
- ix. investigate properties of materials and electrode reactions, ionic conductivity and lifetime of the prepared materials using Electrochemical Impedance Spectroscopy (EIS),
- x. determine power conversion efficiency and stability of the prepared materials using CV and Chronoamperometry (CA) techniques.

1.5. THESIS LAYOUT

This thesis attempts to develop a highly photovoltaic studies of TiO_2 , MOF, TiO_2 -MOF, TiO_2 -MOF/CuPc, TiO_2 -MOF/CuPcNW and TiO_2 -MOF/CuPcNT . The outline of the remaining chapters in the thesis are as follows:

- ✓ **Chapter Two:** Gives a comprehensive overview of the electrochemical DSSCs (principle, mechanisms and parameters to evaluate photovoltaic solar cells), followed by the review on the review of TiO_2 photoanode with the emphasis on its photovoltaic properties and strategies to enhance its activity.
- ✓ **Chapter Three:** Describes different analytical methods that can be used to study the surface and structural properties of nanomaterials. In addition, it comprehensively looks at the electrochemical methods used to study the photovoltaic study.
- ✓ **Chapter Four:** Focuses on the synthesis of titanium-metal organic framework and study their photovoltaic efficiency.
- ✓ **Chapter Five:** Investigates the effect of copper phthalocyanine dye on the performance of titanium-metal organic framework for the dye sensitized solar cells.
- ✓ **Chapter Six:** Investigate the influence of copper phthalocyanine nanowire dye on the performance of titanium-metal organic framework for the dye sensitized solar cells.
- ✓ **Chapter Seven:** Investigate the impact of copper phthalocyanine nanotube dye on the performance of titanium-metal organic framework for the dye sensitized solar cells.
- ✓ **Chapter Eight:** Summarise the important points obtained in the entire studies followed by recommendations.

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CHAPTER 2: LITERATURE REVIEW

PHOTOVOLTAIC PERFORMANCE OF TITANIUM DIOXIDE/METAL ORGANIC FRAMEWORK NANOCOMPOSITE

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ABSTRACT

Dye sensitized solar cell (DSSC) is an unconventional opportunity for silicon solar cell, owing to their flexibility, transparency and low cost. The necessity for DSSC to captivate more of the sunlight radiation was the motive force for the fabrication of semiconductor materials based on high surface area. The constituents of DSSC syndicate to form a solar cell device. The main components in DSSC are the conducting substrate, dye, photoanode, catalyst and electrolyte. The photoanode is well known element that generates the energy conversion efficiency. There are different photoanode materials that have been studied to date. Amongst photoanode materials, titanium dioxide (TiO_2) materials are extensively documented, explored and considered. In this Chapter, effort will be made to survey the strategies to advance the energy efficiency of TiO_2 based photoanode with introduction of metal organic framework (MOF) in DSSC for suppress the recombination rate and electron loss. It was seen that to attain a high conversion yield in DSSC, it is for collection of produced ion carriers very fast before electron recombination. This Chapter is devoted to the TiO_2 and MOF photoanode, their properties and various improvement approaches.

Keywords: Composite materials, dye sensitized solar cell, metal organic frameworks, photovoltaic cells, titanium oxide.

2.1. INTRODUCTION

Energy is of a great global concern with increasing in population and industrialization result in levitation of its demand [1-5]. The increase in energy demand accelerates the production of fossil fuels that are very harmful to the environment at large. Renewable energy sources are candidates to meet the increase in energy demand and are anticipated to play an important role in taking the world to an environmentally friendly, reliable and sustainable energy system [2]. Photovoltaic (PV) technologies are known to convert sunlight radiation into electrical energy [1,5]. They are type of energy which is renewable, clean and sustainable. In addition, they were introduced in a quest to limit or eradicate the combustion of fossil fuels [1]. Currently, PVs are used in small scale applications and showed a great potential to be used at a larger scale provided the power efficiency is above 10% [6]. The most commercialized photovoltaic solar cells are the silicon-based due to their high efficiency of up to 25% [7]. Even though, they show high efficiency some disadvantages such as high purity silicon single crystals manufacture uses expensive processes restrict their widespread use [7]. Gong *et al.* [8] have also indicated that high production and environmental cost restricts the terrestrial PV market. Silicon based photovoltaics have also shown to be expensive relative to other technologies and are generally used notwithstanding their changing cost factor and poor photovoltaic efficiency [7,8]. These disadvantages paved the way for intensive research in the quest to find an alternative in photovoltaic renewable energy production, therefore, leading to the development of dye sensitized solar cells (DSSC) [1]. The most attractive characteristic of DSSCs is its cost-effectiveness due to inexpensive materials and simple fabrication process [5]. DSSCs are good candidates to replace the conventional silicon-based solar cells due to their good performance in diverse light conditions as well as lightweight, flexible, and low toxicity [1, 5]. Daeneke *et al.* [9, 10] have also indicated that DSSCs are potential PV devices, because they are easy to be manufactured, and they have low cost materials as well as mechanical flexibility. Moreover, it was shown that DSSCs are mainly composed of five components [1, 5]. The photoanode is normally made of transparent conductive oxides where a semiconductor material may be coated to form film [1]. Currently, TiO_2 materials are used as photoanode materials due to their

wide availability, low cost, and non-toxicity [11]. The TiO_2 materials have ability to adsorb dye sensitizer for harvesting of light and generation of photo-excited electrons [12]. In addition, DSSCs have an electrolyte containing a redox mediator, usually triiodide/iodine in an organic solvent to transport electrons between photoanode and counter electrodes [5,12]. As a result, DSSC based on TiO_2 semiconductors were extensively studied due to its advantage of the large surface area, high chemical and optical stability [11, 12]. However, TiO_2 has the larger band gap of 3.2 eV and low power conversion efficiency of 3.08 % [13] that disadvantages it to harvest more energy. It was seen that the n-type anatase TiO_2 may be doped with metal-organic frameworks (MOFs) to improve the harvesting of sunlight and reduces the band gap owing to their high surface area [14-18]. MOFs are known to be porous polymers which are made from combination of metal cores and organic ligands through covalent bond [2, 3, 16, 17]. Therefore, in this Chapter reports on the recent position of improving the photovoltaic applications of TiO_2 with addition of MOFs. This is accomplished by considering the fundamental and mechanisms of photovoltaic cells (PVCs). Critical factors which are used to evaluate photovoltaic properties of semiconductor materials were discussed. Furthermore, the background, structural properties and synthetic methods of TiO_2 and MOFs were presented. To sum up, the challenges and approaches to address drawbacks of TiO_2 /MOF composite as photoanode material in dye sensitized solar cells were outlined.

2.2. PHOTOVOLTAIC CELLS

2.2.1. Background

Photovoltaic effect is a chemical process through which solar cells convert the sunlight radiation into electrical energy [19, 20]. It can occur in different kinds of solar cells (Figure 2.1(a)) such as nanocrystal (perovskite), organic (polymer), DSSCs and concentrated solar cells [20-22]. In addition, Figure 2.1(b) presents a conversion efficiency as a function of years for perovskite, and dye sensitized solar cells [21]. The figure shows that the efficiency progress of perovskite solar cells with other third-generation solar cells with up an enhanced of the efficiency over the years [21, 23, 24].

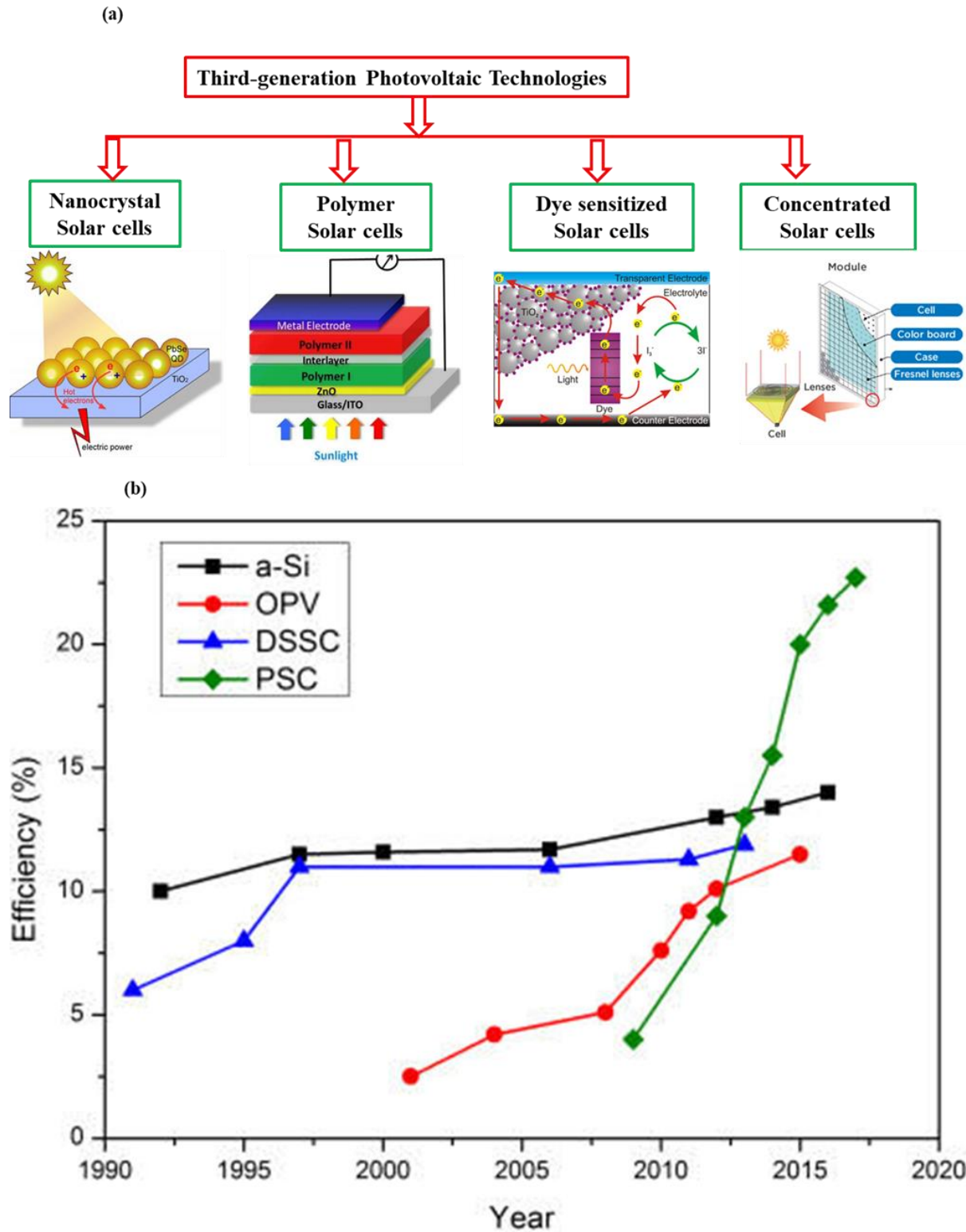


Figure 2.1: (a) Types of photovoltaic (PV) technologies and (b) the power conversion efficiency of different solar cells (a-Si = amorphous Si single layer, OPV = organic

photovoltaic solar cells, DSSC = dye sensitized solar cells and PSC = perovskite solar cells) against the years [21].

2.2.2. Key parameter evaluate photovoltaic

When solar cell panel interacts with light, the photocurrent can be measured. There are many factors that affect the value of the photocurrent such as the quality of the device, incident wavelength, and the surface area of the device being illuminated. Therefore, different parameters are employed to determine the energy efficiency of the PVCs such as the maximum power point (P_{max}), the energy conversion efficiency (η) and the fill factor (FF) [22].

The upper limit of V_{oc}

Open circuit voltage (V_{oc}) represents the maximum voltage at zero current. It was seen that the V_{oc} value rises logarithmically with increased sunlight radiation [1, 5, 22]. In addition, the band gap of the semiconductor material limits the increase in the V_{oc} value and maximum can only be achieved when bandgap is in the range 1.0 – 1.6 eV [25].

Short circuit current (I_{sc})

The short circuit current gives the maximum current density that can be obtained when the two leads are connected to each other. When analyzing a current-potential (I-V) curve, the I_{sc} value is obtained at zero voltage, as a result of generation and collection of carriers [22, 25].

Fill Factor (FF)

The fill factor is defined as the ratio of the curve under the maximum power point of the cell ($P_{max} = I_{max} \times V_{max}$) to the area associated with open and closed circuit ($P = I_{sc} \times V_{oc}$) [22]. The fill factor is referred to as a quantifying unit for the squareness of the I-V curve and calculated using Equation 2.1 [22]. This is also influenced by the materials morphology and stability of the materials [1]. The theoretical limit of a fill Factor (FF) is between 0.25 and 1 [1, 5].

$$FF = \frac{(P_{max})(V_{max})}{(I_{sc})(V_{oc})} \quad (2.1)$$

Power Conversion Efficiency (η)

Power Conversion efficiency (Equation 2.2) can be defined as the ratio between the maximum power output (P_{max}) and the power that is from the incident light (P_{in}) [22]. As stated, the power conversion efficiency greatly influenced by the V_{oc} and I_{sc} [5]. The power conversion efficiency is calculated as follows:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{(I_{sc})(V_{oc})(FF)}{P_{in}} \quad (2.2)$$

where P_{in} is the solar power input into the solar cell, and V_{oc} is the voltage across the open circuit.

2.2.3. Perovskite solar cells

It was documented that perovskite solar cells (PSCs) are made of materials that are described by the formula ABX_3 , where A represent organic material in large quantity; B is smaller amount of inorganic material (cations of different sizes); and X is an anion material, e.g. halogens [26]. In addition, it was shown that the perovskite solar cells exist in two forms as organic-inorganic and quantum dot sensitizes perovskite solar cells [27]. The organic-inorganic cells have been used as a light harvesting sensitizer [26, 27]. Whereas quantum dot sensitizer ones have been used as an electron transfer that is known as the third generation of the solar cells due to its distinguished optical and electronic properties [27]. The advantage of quantum dot sensitizer solar cells (QDSSCs), they have probability of light harvesting materials as well as the low cost in manufacturing [27, 28]. The principles of QDSSCs is similar to that one of DSSCs, but differ with the size which is larger than dye molecules [28]. Furthermore, lead-based material is usually known as the organometallic hybrid perovskites solar cells [29]. This kind of the solar cells has brought much attention to the researchers due to its outstanding structural properties of lead-based materials [29, 30]. The wide tunable band gap, high absorptivity coefficients, carrier mobility, and bipolar carrier transport make these solar cells to be

good [30]. The lead-based materials are highly versatile materials and show a high efficiency in solar cells, however, they are toxic and have a long term stability problem [31, 32]. To solve the problem of toxicity, other technology such as DSSC that are not harmful and qualifies for the clean energy should be employed. For example, Liu *et al.* [33], fabricated the PSCs by adding CsPbI₃ QDs as interface materials, as shown in Figure 2.2. They have observed the enhancement of the charge-transfer efficiency by CsPbI₃ QDs at the interface of the perovskite/ hole-transporting materials (HTM) layer. Their results predicted the energy level structure formed by interfacial material of the CsPbI₃ QDs improved the hole extraction and that led to increase in FF, I_{sc}, and PCE values. In addition, Yuan *et al.* [34] reported perovskite based quantum dot (QD) solar cells with introduction of CsPbI₃ and series of dopant-free polymeric hole-transporting materials (HTMs), as shown in Figure 2.3. Their device possessed a significant power conversion efficiency of ~13% with low energy loss of 0.45 eV.

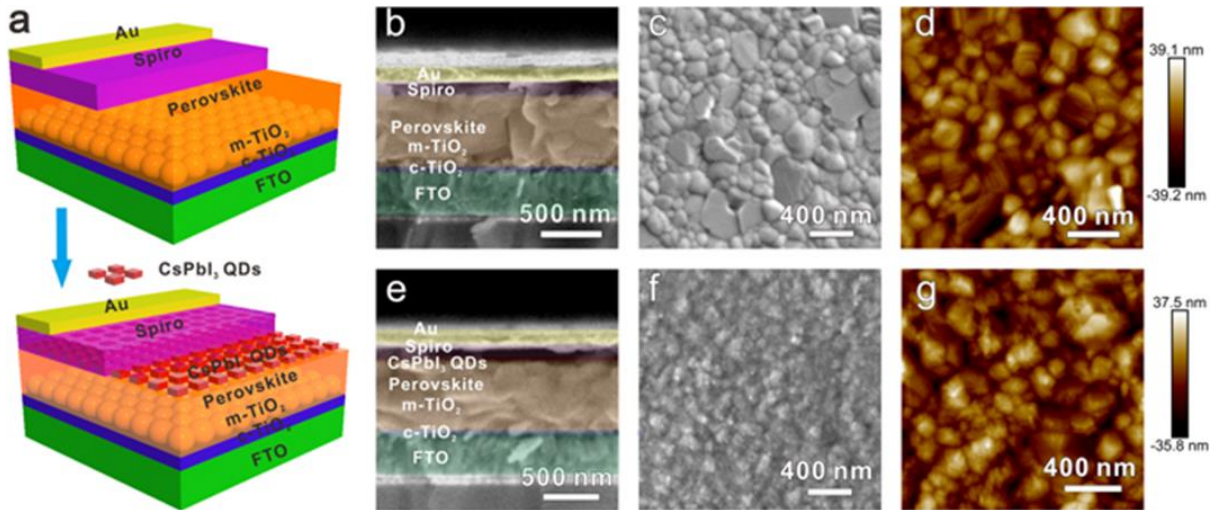


Figure 2.2: (a) synthetic route of CsPbI₃ QD interface, scanning electron microgram (SEM) cross-section of (b) non-deposited perovskite solar cells and of (e) CsPbI₃ QD-deposited perovskite solar cells, upper-view SEM image of (c) non-deposited perovskite layer and of (f) CsPbI₃ QD-deposited layer, as well as AFM images of (d) non-deposited perovskite layer and of (g) CsPbI₃ QD-deposited layer [33].

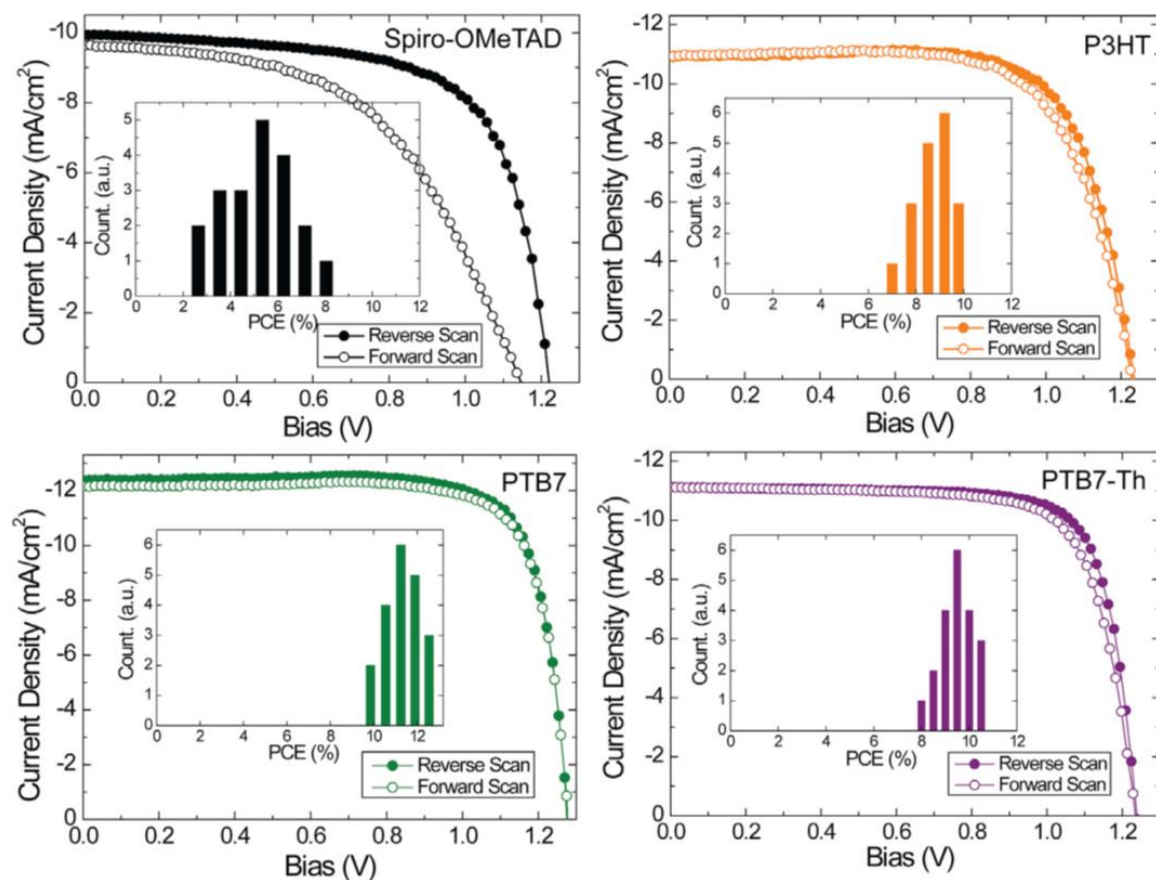


Figure 2.3: J-V curves from reverse and forward scan of optimized CsPbI₃ perovskite QD solar cells adopting 2,2,7,7-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9-bifluorene (Spiro-OMeTAD); poly-3-hexylthiophene (P₃HT); poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene-4,6-diyl] (PTB7); and poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)-carbonyl]-thieno[3,4-b]thiophene-4,6-diyl] (PTB7-Th) as the hole-transporting material (HTM) [34].

Moreover, the tunable band gap of the semiconductor materials improves the adsorption coefficient in QDSSCs that may lead to increase in short circuit current of the photovoltaic cells [35, 36]. It was reported that QDSSCs fabrication uses inorganic materials containing chalcogenide such as CdS, CdSe, CdTe, PbS and PbSe [36]. However, those materials are health hazardous due to their high toxicity [37].

2.2.4. Organic solar cells

The fundamental properties of organic (as well as organometallic) semiconductors differ from those of the inorganic counterparts; hence, organic photovoltaic cells (OPC) operate in different manner from inorganic solar cells. For example, Figure 2.4 shows the chemical structures of typical organic solar cell donor and acceptor materials with their corresponding energy levels [38]. The OPC device needs a bulk heterojunction (BHJ) that can be prepared from a mixture of an electron-donor (p-type semiconductor) and electron-acceptor (n-type semiconductor) (Figure 2.4). The p-type semiconductor material is made of π -conjugated polymer and a small molecule semiconductor. The n-type semiconductor material is generally a fullerene derivative [38]. In Figure 2.4, P₃HT (or PCBM), that is a solubility-enhanced fullerene, efficiently provides a bulk heterojunction [39]. It was shown in the figure that the MEH-CN-PPV provides a high open-circuit voltage with PCEs of 2.0% [38]. Moreover, it was reported that C70 derivative materials normally give higher power conversion efficiency as compared to C60 one, due to high light absorption [40].

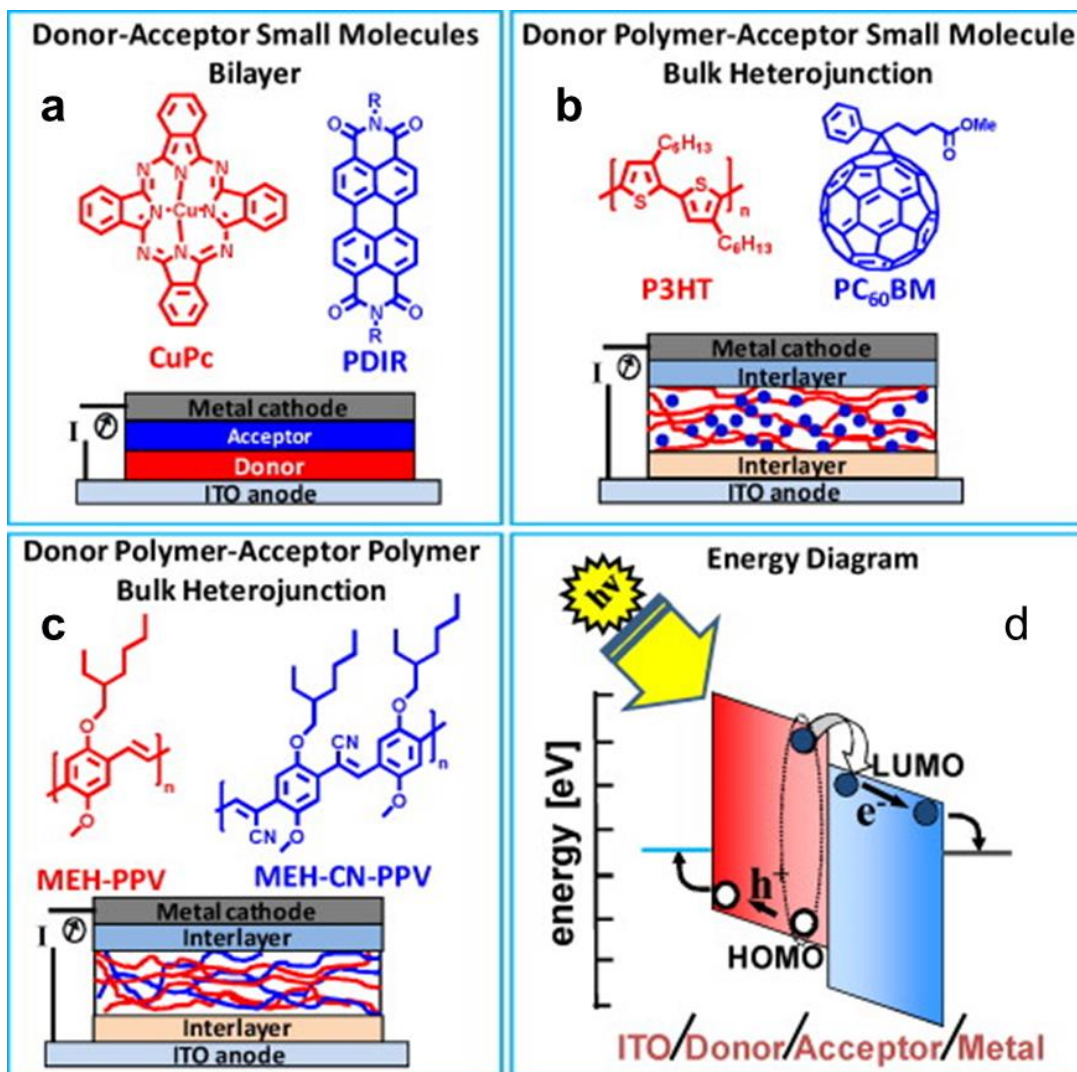


Figure 2.4: Structure and descriptive photoactive materials of (a) donor-acceptor small molecule single heterojunction, (b) donor polymer-acceptor small molecule bulk heterojunction, and (c) donor polymer-acceptor polymer bulk heterojunction photovoltaic cells. (d) Energy levels of the materials where light absorption/excitation dissociation/charge collection takes place [38].

2.2.5. Dye sensitized solar cells

The sensitization and photo-excitation of light absorbing material (e.g. dye) is the key element for the operation of DSSCs. Vogel and Berlin were the first scientists to discover the dye-sensitization technique in 1873 [41]. Although, it took a century to understand the

DSSC mechanism which was reported in photo-electrochemical studies of dye-sensitized single-crystal electrodes in 1970's [42]. Figure 2.5(a) shows the basic elements of DSSC, the components are conducting substrate, semiconductor active layer, dye sensitizer, electrolyte and catalyst [43]. In this figure, the dye sensitizer molecule absorbs energy from light radiation and gets excited, passing electron to the conduction band of semiconductor material. This passes the electron to the external circuit through conducting substrate .to generate excited electron from HOMO to LUMO of semiconductor [43]. Figure 2.5(b) shows the energy levels and the working principle of DSSC. It was seen that the dye's band energy level has to be higher than the one of semiconductor's conduction band [41-43]. On the other hand, electrolyte made of I^-/I_3^- receives an electron from the external circuit with the help of photocatalyst and donates its electron to the excited dye and [43]. The electrolyte plays important role as a bridge between photoanode and counter electrode where the migration of electron takes place from the anode to cathode [42, 43]. The photoanode electrode in DSSC consists of a semiconductor film of TiO_2 , sensitized with a monolayer of dye (normally Ru-complex) [43]. Exhibiting some TiO_2 based materials are broadly used as photoanode materials in DSSC due to unique properties such as cost-efficient, eco-friendly, larger surface area for the flow of electron and wide bandgap of 3.2 eV [44].

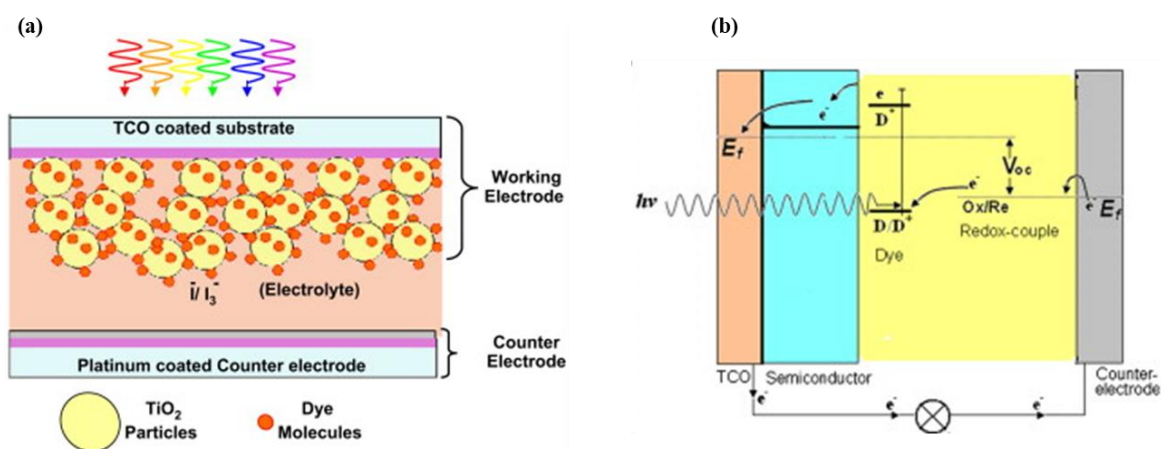


Figure 2.5: (a) Structure and (b) principle of a dye sensitized solar cell [43].

2.3. TITANIUM DIOXIDE

2.3.1. Background

Titanium dioxide (TiO_2) is a recognized and well investigated materials owing to its remarkable properties such as high strength, toxic-tolerance, and biocompatibility, photosensitive and electrical conductivity [45]. TiO_2 exists primarily in three distinct crystallographic forms which are rutile, anatase and brookite; as depicted in Figure 2.6 [46]. Rutile (Figure 2.6(a)) has proven to be the form of TiO_2 with the highest strength. and was discovered by Wermer [47] and the name rutile is derived from Latin meaning deep red colour transmitted light of the UV- visible spectroscopy. Anatase (Figure 2.6(b)) was earlier called octahedrite and named by Haüy in 1801 [47]. This word anatase is coming from the Greek, anatisis, meaning extention [48]. Figure 2.6(b) shows the Brooklite structure of TiO_2 and its name came in an honor of the English minorologist, HJ Brook in 1825 [49]. It was see that its crystal structure of brookite is darkbrown to greenish black [49]. Crystal forms include the typical tubular to platy crystal with psuedohexagonal structure [45-49]. After heating anatase and brookite forms of TiO_2 are converted to a thermal stable rutile form [50]. Table 2.1 presents some of the physical and structural characteristics of anatase and rutile form of TiO_2 [51].

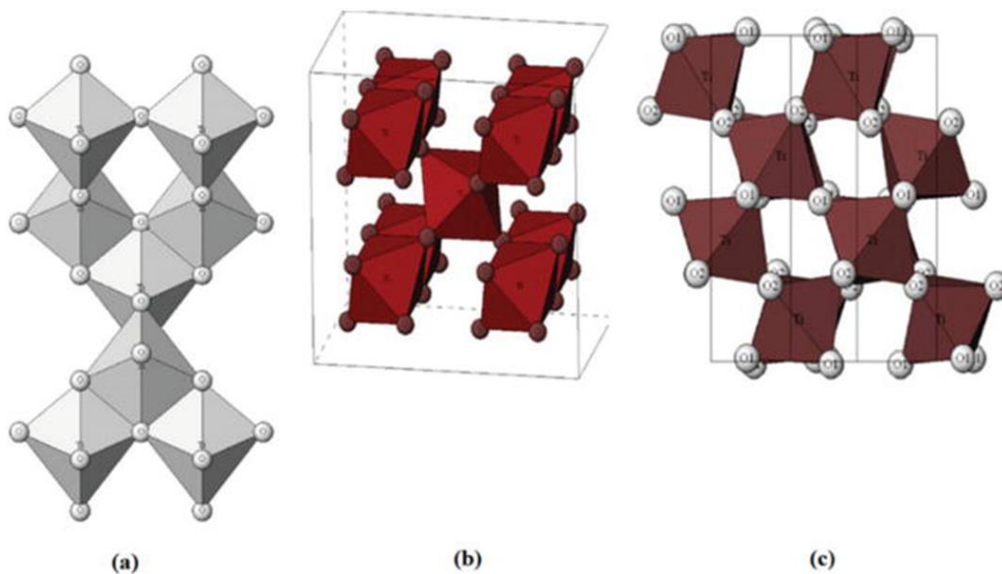


Figure 2.6: Crystalline structures of (a) anatase, (b) rutile, and (c) brookite forms of TiO_2 [49].

Table 2.1: Physical and structural characteristics of anatase and rutile phase of TiO₂.

Property	Rutile	Anatase
Molecular weight (g/mol)	79.88	79.88
Crystal structure	Tetragonal	Tetragonal
Density (g/cm³)	4.13	3.79
Light absorption (nm)	$\lambda \leq 415$ nm	$\lambda \leq 385$ nm
Specific gravity	4	3.9
Mohr's hardness	6.5 to 7	5.5
Refractive index	2.75	2.55
Dielectric constant	114	31
Melting point (°C)	1825	1825
Boiling point (°C)	2500–3000	2500–3000
Lattice constants (Å)	a = 4.5936	a = 3.784
	c = 2.9587	c = 9.515
Ti–O bond length (Å)	1.949 (4)	1.937 (4)
	1.980 (2)	1.965 (2)

2.3.2. Electronic absorption of titanium dioxide

Titanium dioxide is known to be a semiconductor, therefore, a suitable source of light can stimulate the transfer of electrons from the valence band to the conduction band [45]. The band gap energy is the energy required to encourage the photogeneration of electron–hole pairs [52]. The solar energy can be used as the primary source of radiation to activate TiO₂ catalyst when the band gap energy is small enough [53]. On the other hand, ultraviolet (UV) radiation may be used in a high band gap. It was reported that band-gap energy of TiO₂ is between 3–3.2 eV [52, 53], hence, light radiation (wavelength <400 nm), known as ultraviolet A (UVA), will be required for its activation. Therefore, using TiO₂ as photocatalyst under sunlight radiation leads into low performance because natural light comprises 4–5% of UVA radiation [54]. As a result, the TiO₂ band gap must be reduced

by using a suitable dopant in order to benefit of the remaining spectrum of sunlight radiation, the visible region in solar cells [53, 54]. For example, the electronic absorption properties of the pure TiO_2 and Fe-doped TiO_2 materials and the optical energy band gap of these materials were presented in Figure 2.7 [55]. As expected, it was seen that the Fe-doped TiO_2 possessed an increase absorption with a red shift with respect to pure TiO_2 . Additionally, the energy band-gap (E_g) of the TiO_2 and Fe-doped TiO_2 was measured using the Kubelka-Munk equation [55], as shown in the inset of Figure 2.7. The E_g value of Fe-doped TiO_2 was close to 3.15 eV, which was smaller than 3.26 eV of pure TiO_2 . These properties of red shift and smaller band gap of the Fe-doped TiO_2 material show that the absorption of light with a wider wavelength range (≤ 394 nm) was observed using Fe-doped TiO_2 sample while pure TiO_2 absorbed at ≤ 380 nm [55]. In addition, Momeni *et al.* [3] reduced the band gap of anatase TiO_2 by introducing Fe metal as an interesting dopant because its electronic configuration and ion radius is close to Ti^{4+} . They showed that Fe-doped TiO_2 decreased the band gap from 3.2 to 2.85 eV.

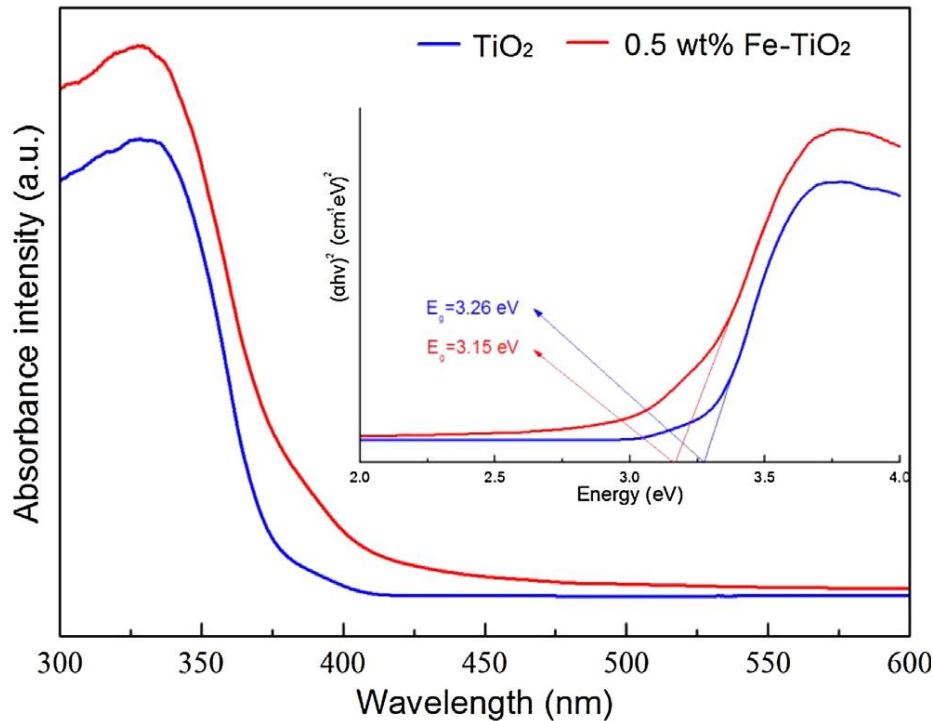


Figure 2.7: UV-vis spectra of TiO_2 and its doped derivative of 5% Fe- TiO_2 . Inset: Kubelka-Munk Plot [55].

2.3.3. Synthesis of titanium dioxide

Most approaches for the synthesis of different phases of TiO_2 have been investigated [45-56]. It was that the gas phase (physical) and solution (chemical) synthetic methods are the common ones in making TiO_2 nanostructures [56]. Physical route yields enormous amounts of material, however, their resolution is much finer from micrometres upwards [56]. Physical vapour deposition (PVD) procedure is one of the physical methods in making TiO_2 . It was reported in preparation of TiO_2 nanowires, a layer of TiO_2 nanopowders deposited on the substrate followed by growth of TiO_2 into nanowires [56]. For example, Figure 2.8(a) presents a model SEM image of nanowires of TiO_2 prepared via PVD method by Wu *et al.* [57]. They observed that TiO_2 nanowires with high density were uniformly grown over the entire substrate. Moreover, the image in the inset (Figure 2.8(b)) in Figure 2.8(a) indicated that the nanowires with diameters of 60–100 nm and lengths of 1–2 μm .

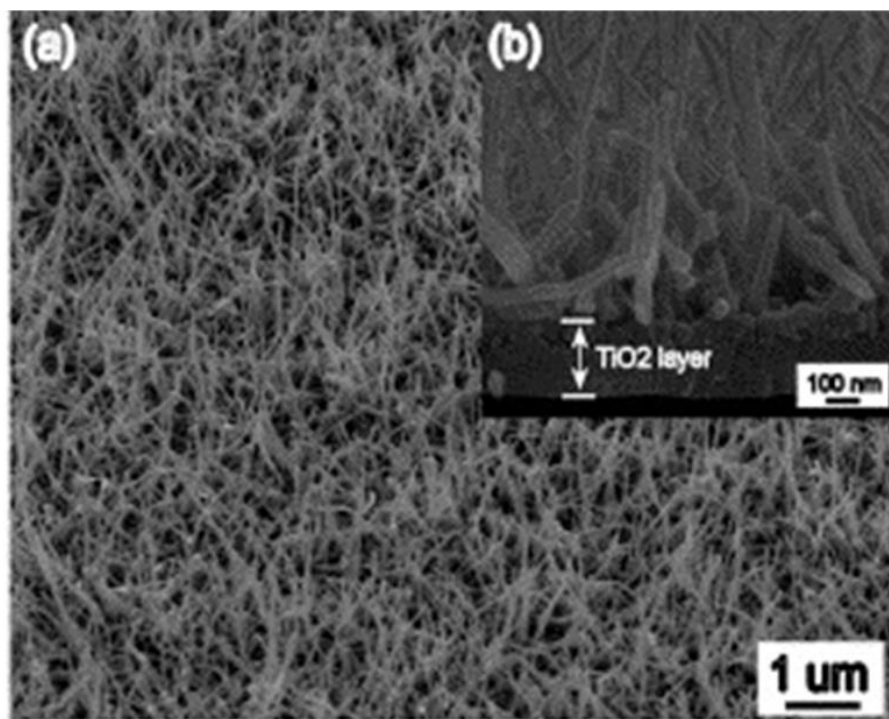
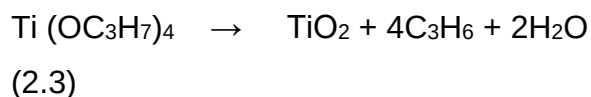


Figure 2.8: Morphological image of the TiO_2 nanowire arrays prepared by the PVD method observed by SEM technique [57].

Chemical vapour deposit (CVD) is also as a physical method, which is the promising processes of synthesizing rutile TiO₂. Due to its high quality film with controllability of micro and orientation at high deposit rate [56]. In addition, during the CVD process, the morphological orientation of the film is affected by various parameters such as laser power (P_i) and total pressure (P_{tot}) in CVD chamber for the film with random orientation [56].

They discovered that there are two reaction mechanisms for titanium (iv) isopropoxide that occurs in the reaction. The reactions are presented in Equation 2.3.

Pyrolysis



In this reaction, gases exposed to temperatures where the pyrolysis reaction can take place using liquid precursor and titanium tetraisopropoxide (TTIP) in a mixed gas (consisting of helium/oxygen atmosphere) leads to prepare bushy crystalline of TiO₂ [56].

The chemical methods are capable to coat complex shapes, govern on stoichiometry, and synthesis of composite materials [56]. They can approach the atomic layer limit through the preparation of nanostructure materials (in <100 nm or <10 nm scale) [56]. Chemical methods are easy to prepare cost effective and environmental friendly [51]. These methods include hydrothermal, solvothermal and sol-gel methods [56]. Hydrothermal synthesis of TiO₂ is generally conducted in an autoclave of steel pressure vessels and sometimes in the presence of Teflon liners. The synthesis is done under the control temperature and pressure in an aqueous solution. Solvothermal method is similar to the hydrothermal one, however, the former uses non-aqueous solvent. In the solvothermal methods, greater temperatures than those used in hydrothermal technique are utilized. They control morphology, size distribution and shape of TiO₂ nanoparticles a lot better than hydrothermal method [58]. Ramakrishnan *et al.* [58] synthesized TiO₂ nanoparticles using the modified solvothermal method for the photodegradation and photovoltaic applications (Figure 2.9). They showed that the synthesized TiO₂ nanostructures were used for photocatalytic and photovoltaic applications with

photodegradation efficiency of $\leq 97\%$ for organic dyes, respectively overall power conversion efficiency of 5.92% in DSSC (Figure 2.9).

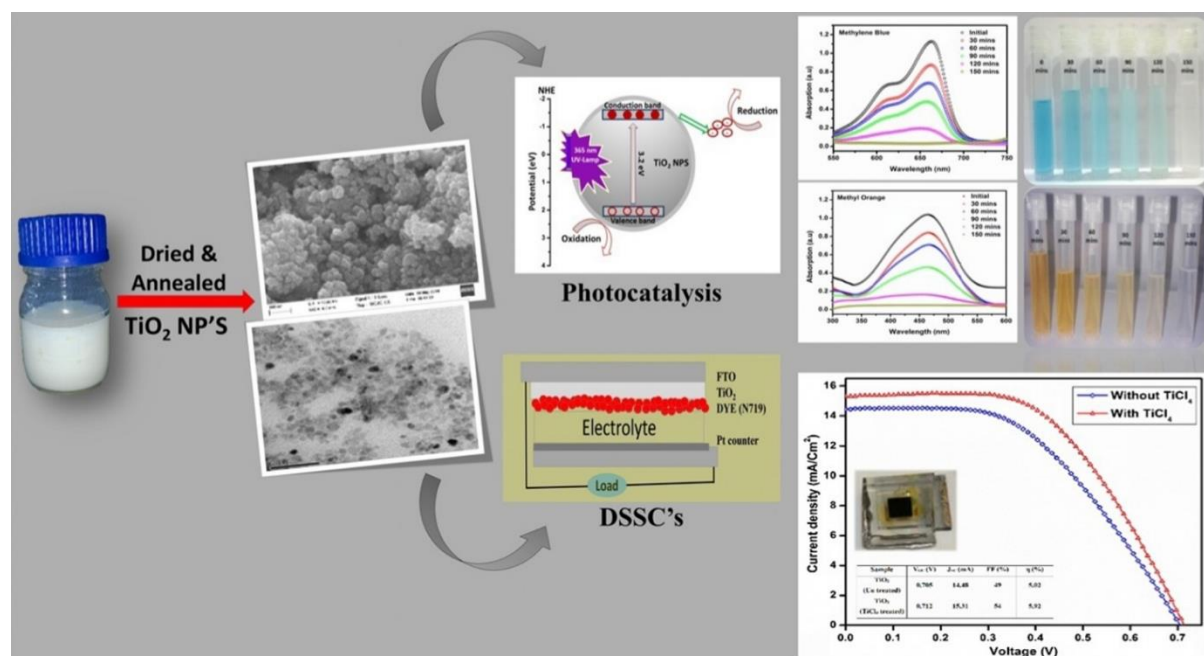


Figure 2.9: Synthesis and applications of TiO₂ using solvothermal method [58].

In sol-gel synthesizing methods, there are many sol-gel methods such as non-alkoxide and alkoxide routes. These sol-gel methods have advantages over other fabrication techniques for high purity, homogeneity, felicity, and flexibility [59]. In addition, these routes are the methods that are simple, they are easy to introduce dopants in a larger concentration, have stoichiometric control, control over the composition, ability to coat on larger materials and complexes [56, 59]. The synthesis involves the use of titanium tetra isopropoxide solution as a precursor in acidic catalyse hydrolysis (solvents such as hydrochloric, sulphuric and glacial acetic acids) and in the presence of distilled water or ethanol in order to speed up the hydrolysis processes, as shown in Equation 2.4 and followed by condensation polymerization reactions to give gels as shown in Equation 2.5 [56].

Hydrolysis:



Condensation:



It was seen that the sol particles size depends on the composition of solution, temperature and pH, and Ti–O–Ti chain development is preferred with little amount of water, additional titanium alkoxide in the reaction combination and stumpy hydrolysis rates [56].

2.3.4. Titanium dioxide composites

Doping TiO_2 using metals, non-metals and metal complexes is another way of improving the performances on photovoltaics solar cell. Higashimoto *et al.* [20] investigated the doping of nitrogen molecule on TiO_2 (for the photovoltaics application. They discovered that the formation of vacancies is exhibited to the n-type [60]. Duarte *et al.* [61] also investigated on the characterization of nitrogen doped TiO_2 thin film for the photovoltaic application (Figure 5.10). They observed that the cells attained with conventional DSSCs exhibit shorter short-circuit photocurrent as compared to cells attained through doping of TiO_2 with nitrogen.

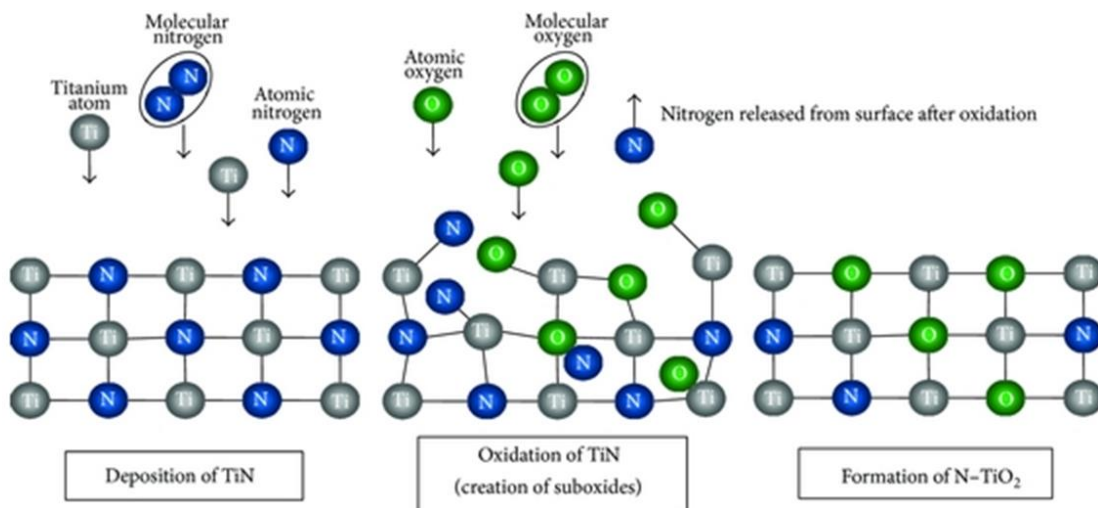


Figure 2.10: Tetrahedral structure of TiO_2 doped with nitrogen [61].

Furthermore, Wang *et al.* [62] reported on the influence of nitrogen doping on device preparation for TiO₂-based solid state dye sensitized solar cells. They showed that the PCE % of the material doped with 0.1 wt. % nitrogen content was 4.1 % (Table 2.2). On the other hand, carbon black dopants were used on TiO₂ to its abundance, low cost and high catalytic activities with chemical stability against iodine redox couple [63]. Lim *et al.* [64] reported on the study of counter electrode material made of TiO₂/carbon black composition for dye-sensitized solar cells. They presented that the surfaces morphologies of the synthesized materials suggested more active sites and high porosity of 75 nm sizes. Their material with low carbon black content performed better for photovoltaic activity with the PCE of 7.4 % (Table 2.2). In the case of metal and silicon dopants, the integration of transition metals and SiO₂ into TiO₂ contributes to the formation of new energy levels on the brink of the CB as a result of electrons in their d-orbitals [65, 66]. The transition metals such as Mg, Nb, Y, Al and Zr as dopants onto TiO₂ material have been used in solar cells [67]. The Mg-doping onto TiO₂ in DSSCs showed improved in V_{oc} value due to a higher CB energy and reduced recombination [68]. Nb-doping of TiO₂ solar cells led to increment of electron injection and transport, resulting in higher I_{sc} value with an overall 7.8% energy-conversion efficiency on 5.0 mol% Nb-doped TiO₂ [69].

A high PCE of 15.1% with a good fill factor of 76% was achieved at 2 mol% Zr doping onto TiO₂ as compared to 12.3% of the pure TiO₂ [70]. The Mott-Schottky bandgap showed that the elevated V_{oc} value was owing to the upshifting of flat band potential of TiO₂ from -4.15 eV to -4.02 eV after doping [70]. The dopants of gallium doping and yttrium in the TiO₂ material showed a noticeable increment of the power conversion efficiency 8.1% for Ga doping and 9.0% for Y doping with simultaneously increase in other PV parameters (Table 2.2) [71]. Ko *et al.* [72] reported that Al-dopant has ability to decrease the number of oxygen vacancies, and recombination as well as improving conductivity. They showed that introducing Al doping onto TiO₂ DSSC resulted with an overall increase in I_{sc} value and also with enhancement of the long-term stability. An'Amr *et al.* [73] investigated the photovoltaic behaviour of DSSCs based on Bi-TiO₂ materials. They obtained the V_{oc} values of 0.59 V with the I_{sc} value of 7.71 mA/cm², and the efficiency of 2.11% as an increase of 77% with respect to pure TiO₂ materials. Under optimized conditions, 0.1 at.% Ta doped TiO₂ nanotubes in DSSC possessed power

efficiency of 2.99 as increased of 25% compared to non-doped TiO₂ nanotubes [74]. In addition, MgO coated on TiO₂ surface material showed increase in the power conversion efficiency of 4.5% (Table 5.2) [75]. This indicates 45% increment as compared to the uncoated TiO₂ electrode due to improved specific surface area [75]. The Nb₂O₅ coated between FTO and TiO₂ nanocrystalline film as a potential blocking layer showed improvement of Voc that led to a better conversion efficiency of dye-sensitized TiO₂ solar cells [76]. The increment of photovoltaic parameters indicated that Nb₂O₅ layer was a good blocking layer at FTO and TiO₂ interface to suppress the recombination processes [76]. The photovoltage-current response of SrTiO₃ doped TiO₂ possessed an increase with overall conversion efficiency of the solar cell of 15% [77]. Lee *et al.* [78] reported that nanoporous CaCO₃-doped TiO₂ with higher specific surface area led to the larger amount of dye adsorption that increased the photovoltaic parameter of the DSSCs (Table 2.2). Yum *et al.* [79] investigated the nature of the improvement of photovoltaic parameters on Mg(OH)₂ coated TiO₂ DSSCs, whereby little influence of Mg(OH)₂ coating on diffusion coefficient was observed in relationship with the rise in Voc value to 0.76 V, and efficiency of 3.7%. Moreover, Hu *et al.* [80] presented the current–potential (I-V) curves of graphite based TiO₂ DSSCs. They observed that the increment of Voc_c value from 0.821 V to 0.835 V with addition of graphite from 0.00 wt% to 0.02 wt% in the composite. The Isc of 12.59 mA/cm² was obtained only 0.01 wt% graphite content with power efficiency of 5.76 (Table 2.2) [80]. The effect of graphene oxide was also investigated on TiO₂, the photoelectric conversion efficiency of the DSSC based on graphene/TiO₂ composite film increased from 5.52% to 6.49%, with an increase of η by 17.6% [81]. This showed that graphene reduces the charge recombination rate and electrolyte–electrode interfacial resistance as well as improvement of the transport of electrons that led to rise in the power efficiency [81].

Table 2.2: Photovoltaic parameters of TiO₂ composites in DSSCs.

Dopant	I_{sc} (mA/cm²)	V_{oc} (V)	FF (%)	η (%)	Ref.
N	8.31	0.79	62.0	4.1	[62]
C	15.5	0.71	67.4	7.4	[64]
Zr	19.35	1.02	76	15.1	[70]
Nb	17.7	0.70	63.0	7.8	[69]
Ga	13.4	0.76	79	8.1	[71]
Y	15.9	0.74	77	9.0	[71]
Bi	7.71	0.59	46.0	2.11	[73]
Ta	8.17	0.79	46.3	2.99	[74]
SiO₂	0.55	0.60	54	0.18	[66]
MgO	11.7	0.72	53.5	4.5	[75]
Nb₂O₅	9.32	0.71	68	4.5	[76]
SrTiO₃	10.2	0.71	58.4	4.39	[77]
CaCO₃	21.9	0.67	66.1	9.68	[78]
Mg(OH)₂	6.61	0.76	74.0	3.7	[79]
Graphite	12.6	0.82	54	5.76	[80]
Graphene oxide (GO)	13.7	0.69	69	6.49	[81]
Reduced GO	18.4	0.68	61	7.68	[82]
MWCNT	15.3	0.73	71	7.9	[83]

Cheng *et al.* [82] reported the preparation of anatase TiO₂@reduced graphene oxide hybrids for high performance of DSSCs applications. They observed that the PCE became lower at the low reduced graphene content and showed a high PCE of 7.68 % for the hybrid 1.6wt. % reduced graphene content. Dembele *et al.* [83] investigated the double layer multiwall carbon nanotubes (MWCNTs) -TiO₂ composite for DSSCs. They observed a high PCE of 8.1% at 0.010 wt. % MWCTs concentration. An increase in

concentration from 0.010 to 0.250 wt %, resulted in decrease in PCE to 1.1% [83]. Moreover, it was reported that the conversion efficiency of MWCNT/TiO₂ DSSCs with conventional Pt counter electrode was increased from 6.51% to 7.00% as compared to pure TiO₂ [84]. On the other hand, MWCNT/TiO₂ mesoporous based DSSCs with FeS₂ counter electrode possessed a high solar conversion efficiency of 7.27% as a result of higher surface area and good catalytic activity of FeS₂ as compared to the conventional Pt counter electrode [84]. As stated previously, TiO₂ based photoanode has the disadvantages of weak interconnectivity, and poor light scattering capillarity [85]. This may overcome incorporation metal organic framework (MOF) into TiO₂ photoanode in order to improve structural properties [86].

2.4. METAL ORGANIC FRAMEWORKS

2.4.1. Background

MOFs are a class of inorganic-organic materials and made from metal cation and organic linkers [87-95]. As shown in Figure 2.11, the metal cores serve as connecting points and the organic ligands function as bridging molecules [96]. These two constituents are connected together by covalent bonds in the formation of MOF structure [91-93]. The MOFs were first discovered through the study of Zeolites [96]. The name Metal-Organic Framework was given by Yaghi during synthesis of copper-4,4'-bipyridal compound that unveiled lengthy metal-organic interactions [96,97]. Basically, MOFs fit in to the family of coordination polymers. They are polymers of two- or three-dimensional crystallized networks and possess high porous properties with respect to other coordination polymers [92,96]. It is well known that MOFs are porous solids and the precise positions of all atoms in the MOF structure can be recognized and associated with the dignified properties [92-96]. In porous solids, permanent pores are created and they saturate the structure of the material. The pores are large enough to require guest molecules to diffuse into the structure or to be removed from the channels by heating or vacuum [98].

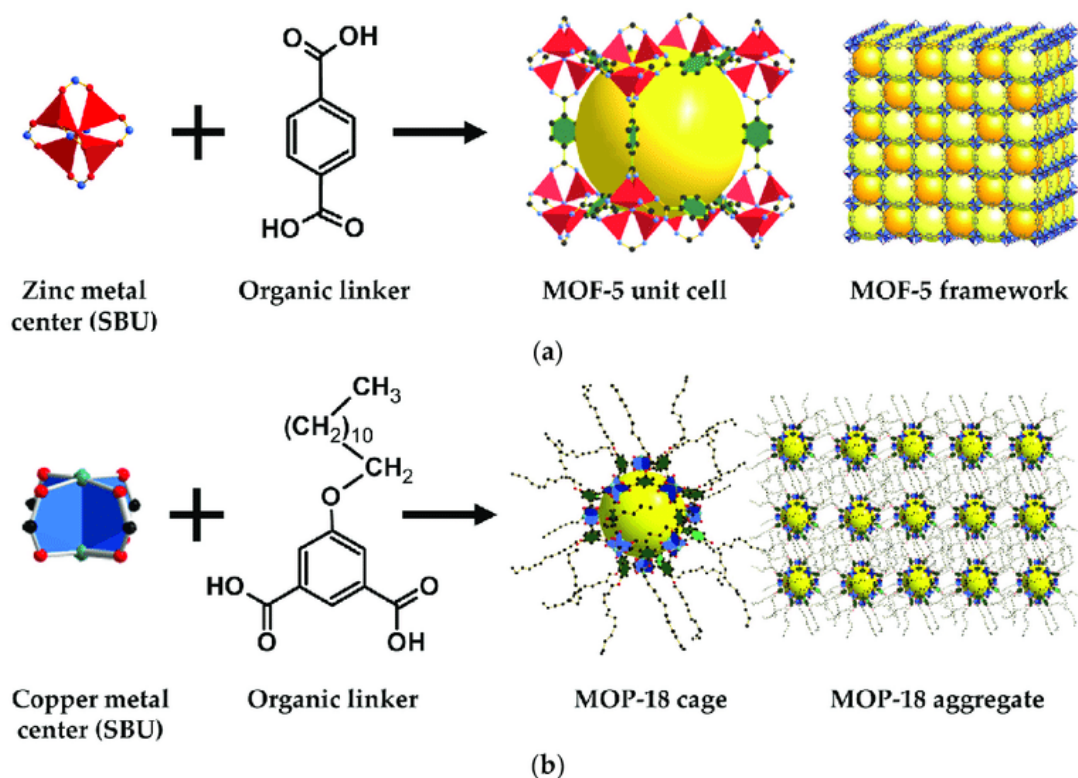


Figure 2.11: (a) Preparation of metal-organic framework from a zinc metal salt and organic linker of terephthalic acid; (b) preparation of metal organic framework from a copper dimer and alkylated isophthalic acid [96].

In addition, the MOF polymers are extremely tunable by altering the metal cores or organic linkers to attain an appropriate MOF material with the allowed structures and functionalities for definite applications [92]. It was seen that the porosity of the reported MOFs varies between 20 and 95 percent [98]. Figure 2.12 shows some MOF materials with different pores. Their porosity associated to high surface areas, permitting for improved adsorption capacity of guest molecules. As a result, MOFs have attracted significant attention owing to structural properties [92].

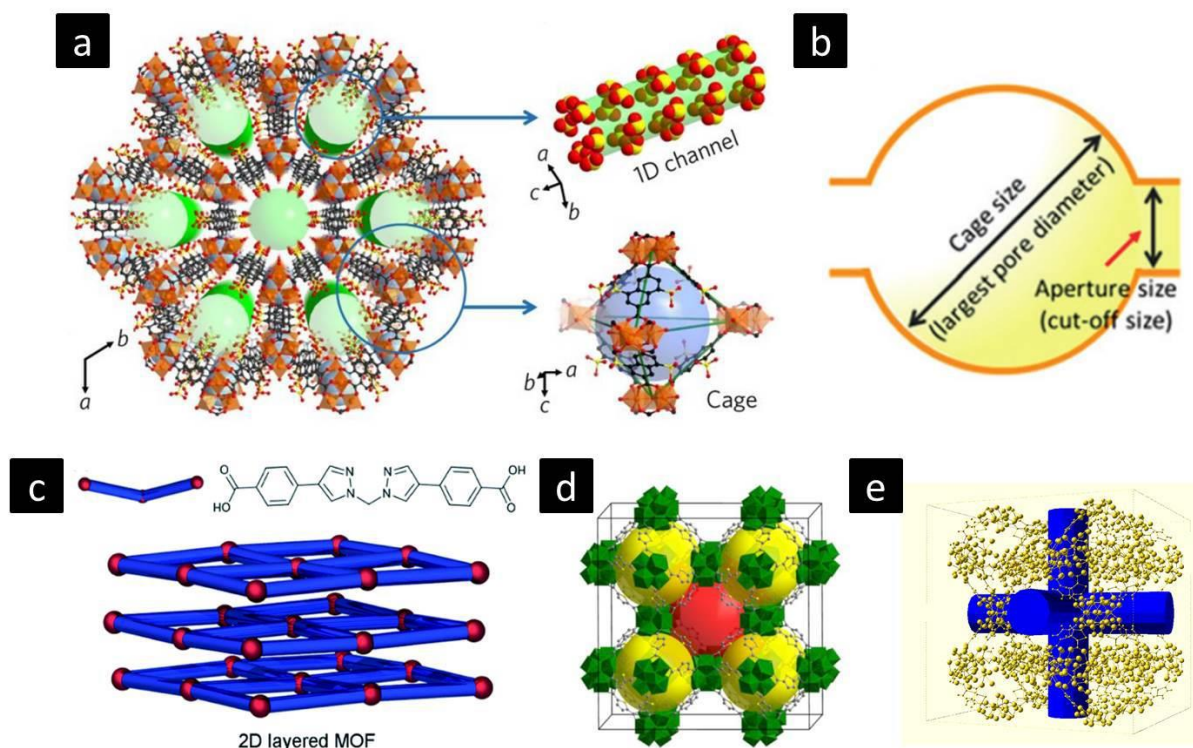


Figure 2.12: MOFs with different pore geometries: (a) BUT-8(M) contains the 0D cavity (light blue) and paralleled 1D channel (light green);(b) A schematic illustration for the 0D cavity showing the cavity diameter (i.e. cage size) and opening aperture size (i.e. window size);(c) A schematic diagram for 2D layered MOF showing interlayer spaces; (d) Two types of cavity (red and yellow) contained in a DUT-67 unit cell; and (e) Intersecting channels (blue) along $\langle 100 \rangle$ in a DUT-67 unit cell [100].

At beginning of the 21st century, there is exponentially growth of interest in the synthesis of MOFs and their publications are shown by the Figure 2.13(a) as compared to zeolitic materials [101]. These large numbers of reports, about 40 000 papers for MOFs and their amounts of increase rationalize the significance of the overview based on bibliometrics in this report with respect to each aspect. Moreover, Figure 2.13(b) shows that over 69 000 number of MOF have been reported in the Cambridge Structural Database (CSD) from 1970 to 2016 [102]. This intensify research interest to concentrate on MOF design and applications such as hydrogen, gas sensing and storage [87-95]. In the meantime, the pore dimension of MOFs can be bigger than inorganic nanoporous materials in general

and approaches 100 Å [103] Amongst the synthesized MOFs, MOF-5, ZIF-8, HKUST-1, UiO-66 and NU-1000 have been widely known and extensively investigated due to their low cost and easiness of preparation [104].

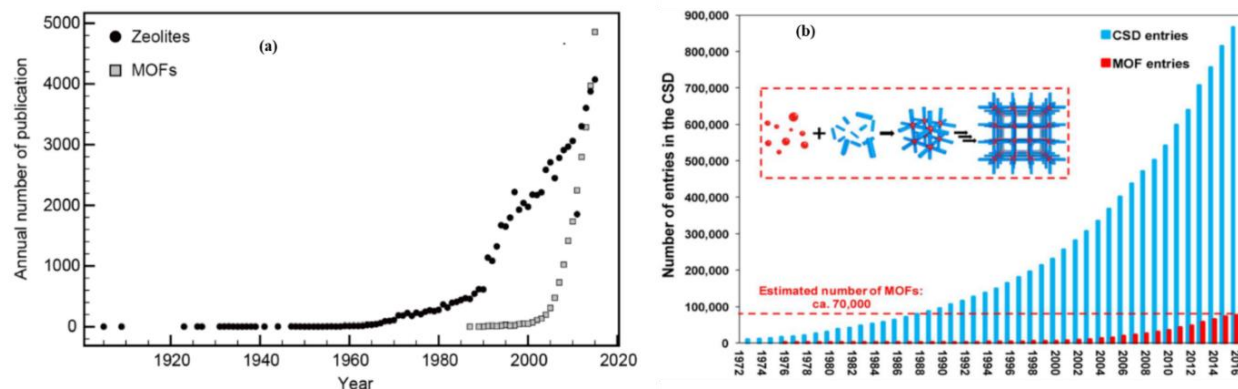


Figure 2.13: (a) Graph of number of MOFs (as compared to zeolites) published per year [101]; and (b) the reported MOF crystal structures in the CSD since 1970 [102].

2.4.2. Properties of MOF

The unsaturated metal sites in MOF materials have remarkable influence on their structural properties. The metal elements as the center connector are customarily chosen from copper, zinc, manganese, chromium, cobalt, etc [100]. The metal ions of MOFs act as Lewis acids and activate the attached organic substrate for successive organic transformation [105]. The partial positive charges of the metal cores in MOF structures have been shown to possess the ability to increase adsorption properties [101,102,105]. The organic linkers (Figure 2.14 and 2.15) used in the formation of MOF are usually multidentate organic molecules with O- and N-donor atoms. It is unusual for linkers in coordination polymers not to contain aromatic rings [106]. It was seen that the aromatic rings based organic linkers in MOFs help to maintain the structural integrity of the complex and direct the geometry of the frameworks [106,107]. The surface area and pore volume of MOFs can be controlled by modifying organic ligands which act as spacers and create an open porous structure [107]. A recipe of inorganic and organic structures can lead to materials with unique properties [106]. Alternatively, the choice of the primary building units makes it possible to vary some parameters, including the pore size (to increase pore

diameter to 98 Å), density (to decrease to 0.126 g cm⁻³), as well as the specific surface area (up to 1000 ± 10 000 m²g⁻¹). This opens up new ways to produce materials with tailored physical and chemical properties [100-106]. Based on porous structure, larger specific surface area, stability and ability to be functionalized, MOFs are currently good candidates for practical applications such as gas separation, catalysis and ion exchange reactions [987-95].

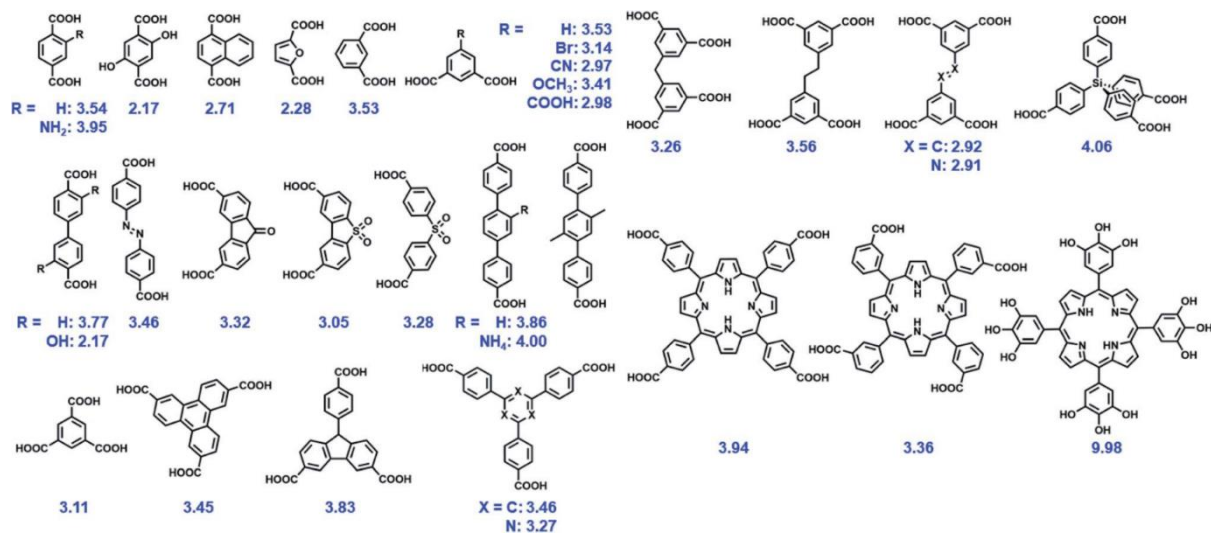


Figure 2.14: Some of organic linkers using in the preparation of MOF with O donor ligands and their pKa values [106].

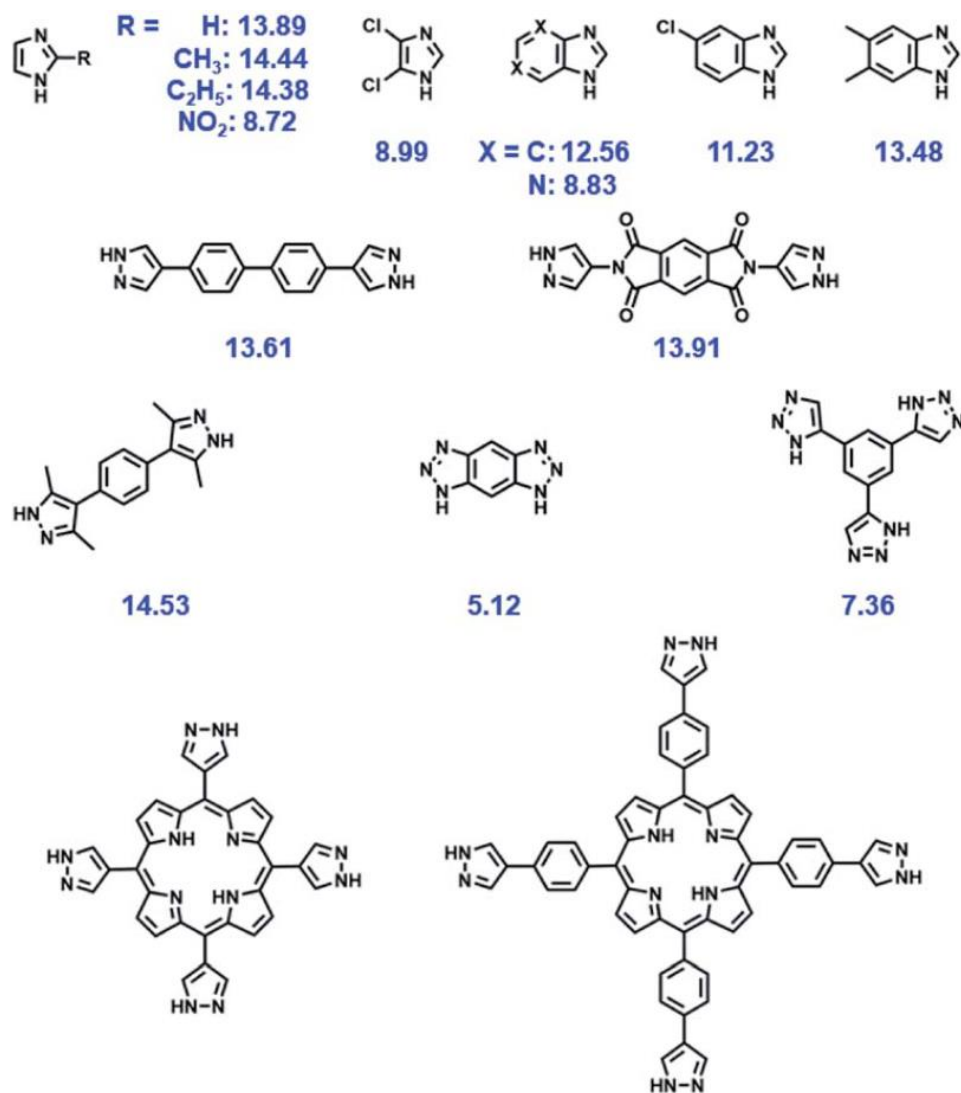


Figure 2.15: Some of organic linkers using in the preparation of MOF with N donor ligands and their pKa values [106].

Moreover, secondary building units (SBUs) play significant part as it dictates the final topology of MOFs. The geometry and chemical characteristics of the SBUs and organic ligands lead to the prediction of the design and preparation of MOFs [108]. Ren *et al.* [109] reported that under some conditions, multidentate linkers could aggregate and lock metal ions at certain position, forming SBUs. The SBUs will subsequently merged by rigid organic linkers to yield MOFs that exhibit high structural stability [108,109]. Zhao *et al.* [110] and Huang *et al.* [111] reported a comparative study of MOF nanosheets based on

the design and theoretical calculations. Huang *et al.* [111] attained an MOF of high stability under the thermodynamic and kinetic conditions (Figure 2.16(a)). Figure 2.16(b) presents the electrostatic surface potential (ESP) diagrams calculated using density functional theory (DFT)-, the activities of the three-coordinated Cu (0.056 au) with more σ -holes were higher than those of pristine four-coordinated Cu (0.040 au) [111]. Furthermore, the frontier molecular orbitals (MOs) in Figure 2.16(c) shows that the 3-coordinated Cu sites have the smallest band gap) of 1.38 eV [111]. On the other hand, the 4-, 2- and 1-coordinated Cu sites have band gaps of 1.43, 4.51 and 3.02 eV, respectively [111].

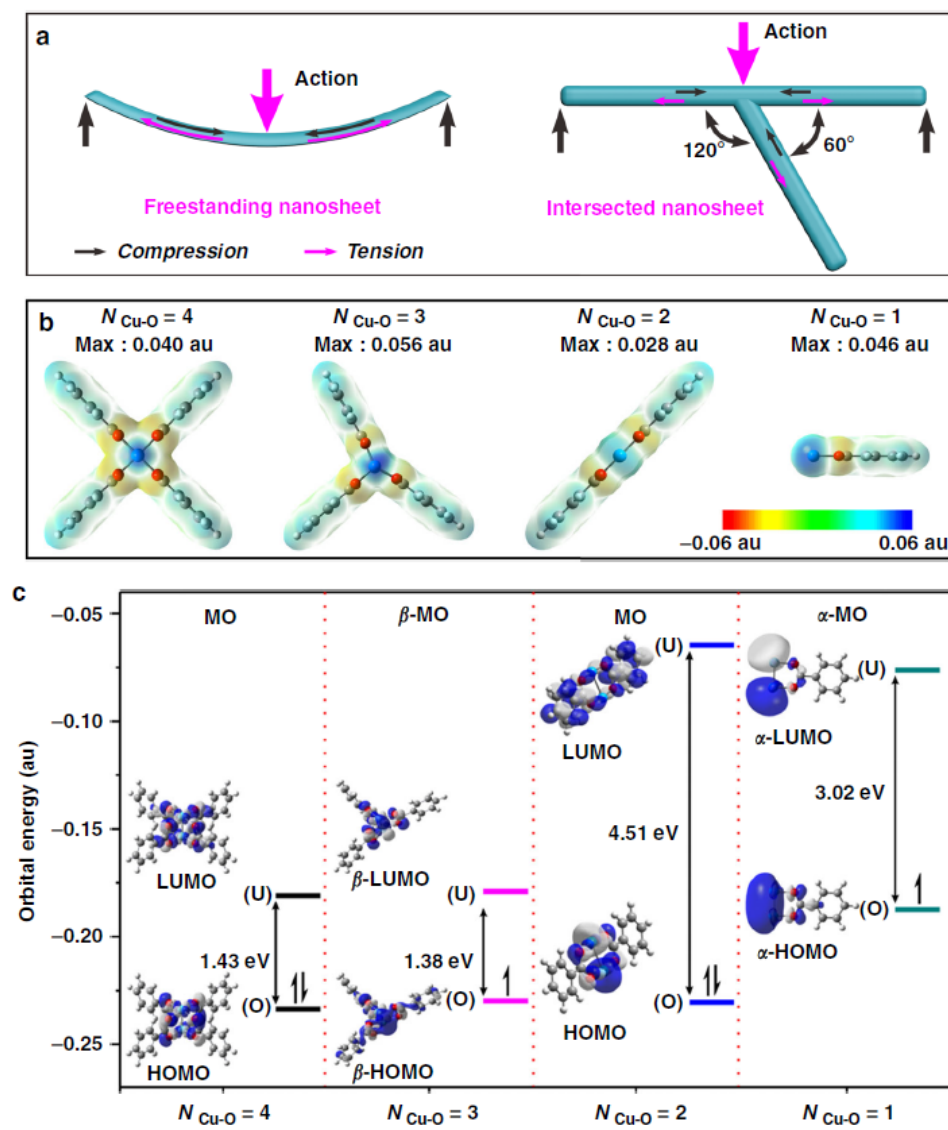
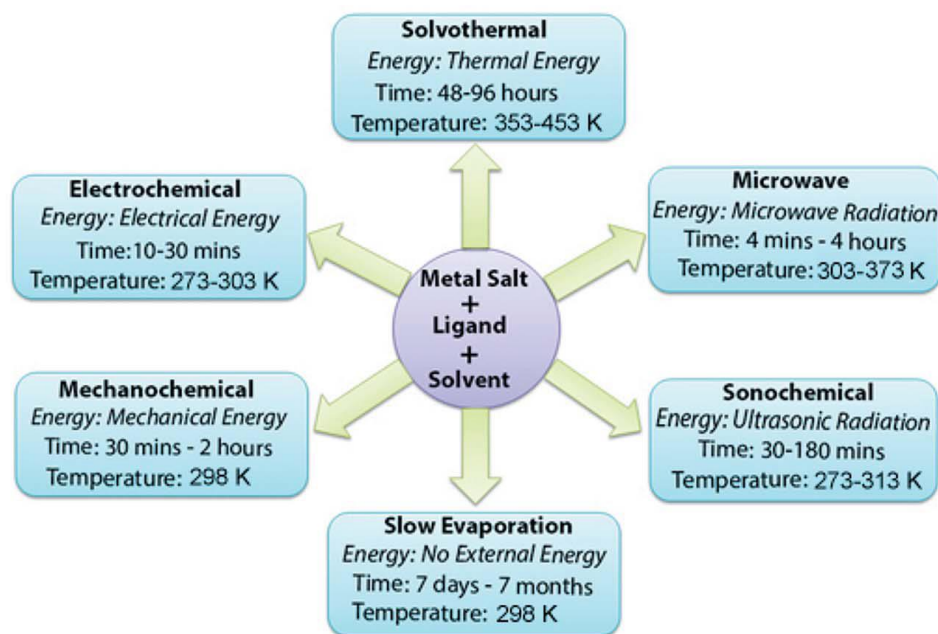


Figure 2.16: (a) comparison between displacements for MOF nanosheet and intersected nanosheet when force is applied to them; (b) ESP maps of paddlewheel Cu_2 clusters in MOF structure where $N_{\text{Cu-O}}$ stands for the paddlewheel Cu_2 clusters with different coordination numbers (CNs) of Cu–O (4, 3, 2, 1); and (c) the theoretical calculated frontier orbital energy levels and molecular orbital (MO) diagrams in MOF structure [111].

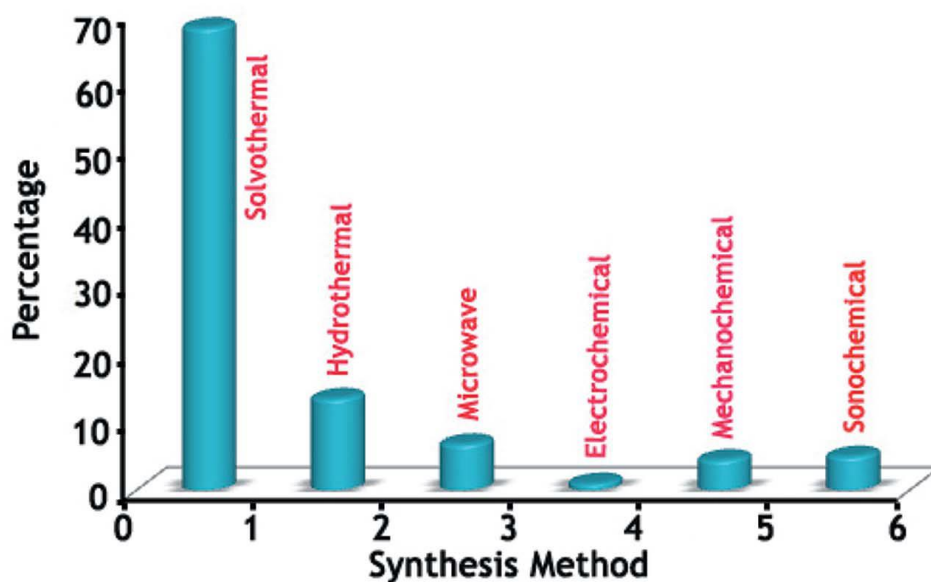
2.4.3. Synthesis of MOFs

Figure 2.17(a) illustrates a summary of several synthetic methods for MOF preparations. The main aspects of MOF preparation are to institute preparation conditions that can

produce a defined inorganic building blocks without decomposition of the organic linker [112]. In this Chapter, the focus will be given to the selected preparation of the MOF structures illustrated in Figure 2.17(b) [113].



(a)



(b)

Figure 2.17: (a) Preparation conditions for synthesis of MOF; and (b) percentage of MOFs synthesized using the various preparation methods [113], reproduced with permission of the International Union of Crystallography (<http://journals.iucr.org/>).

MOFs have been prepared effectively through solvothermal method [114]. During the heating process, coordination of the primary carboxylate linkers and metal ions can result in many metal-oxygen-carbon clusters, known as SBUs, as discussed above and settle into final orderly MOF network [108]. The imperative parameters in the synthesis of MOF are concentration, temperature, metal salt, organic linker and suitable solvents [114]. The metal cores are coordinated covalently through organic linker to form a so-called paddle wheel unit in a three-dimensional porous cubic network [106]. The solvothermal method (a method of producing chemical compounds using a stainless steel autoclave) is presented in Figure 2.18, it allows for precise control over the shape and size of the material to be synthesized, unlike hydrothermal method [114].

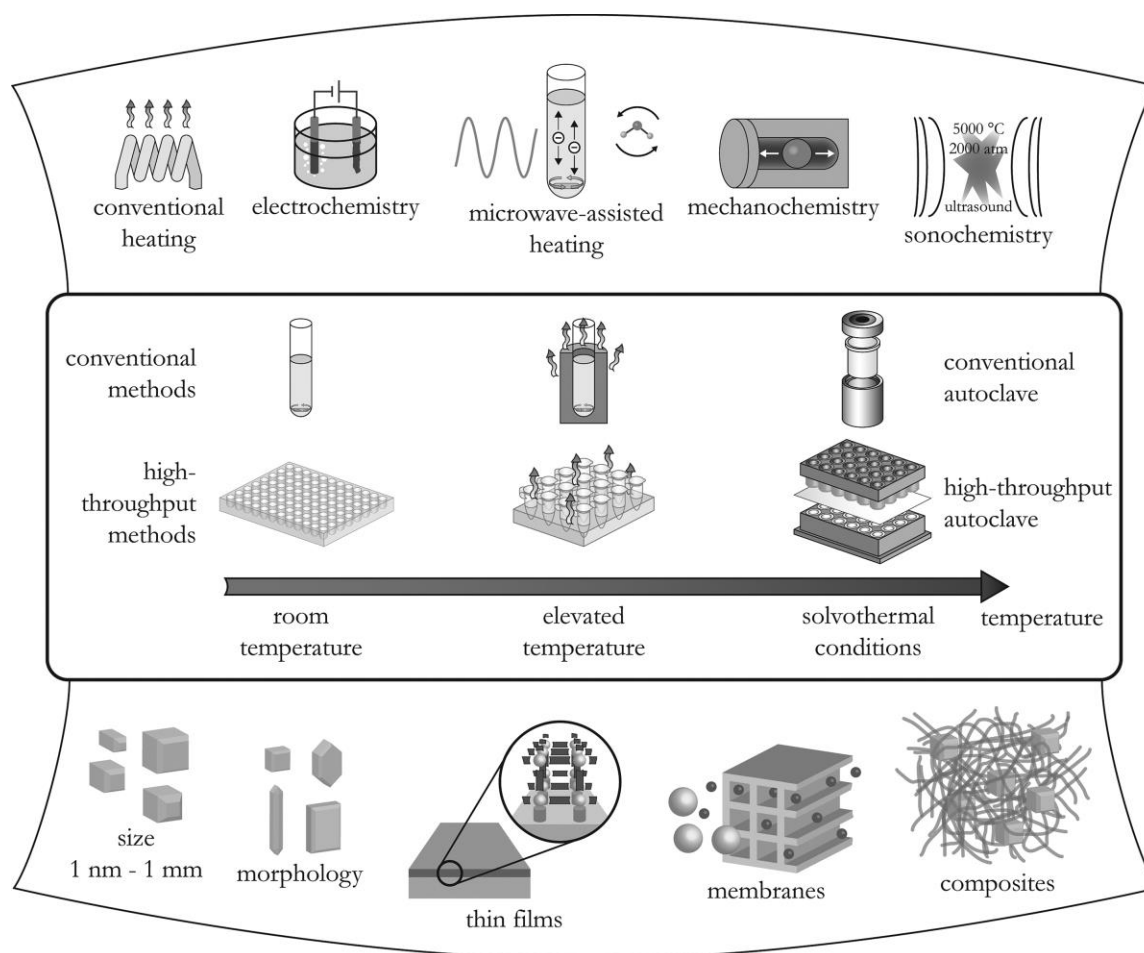


Figure 2.18: Various synthetic routes of MOF structures, operational temperatures related to each method and their final reaction products [114].

Microwave- method has demonstrated to be an appealing route for quick preparation of nano-porous materials under hydrothermal conditions [114,115]. Besides fast crystallization, high efficiency, potential advantages of this technique include phase selectivity, narrow particle size distribution, and facile morphology control [114]. In microwave method, the process involves applying heat to solution mixture of the substrates with microwave for a period of about an hour to produce nanosized crystals (Figure 2.18). This method produces excellence of the crystals which are normally the same as those by the regular solvothermal processes, but the synthesis is much quicker [115].

Mechanochemical method is a method used to prepare MOF in a solvent-free environment (Figure 2.18). Mechanical breakage of intramolecular bonds followed chemical transformation takes place in a mechanochemical synthesis [116]. Qualitative yields of small can be obtained in short times, normally in the range of 10-120 min [114]. Occasionally, metal oxides are selected as starting materials in mechanochemical method over metal salts due to the former producing H₂O as a by-product [114,116]. Currently, mechanochemical synthesis have been efficiently used for the rapid preparation of MOFs using liquid-assisted grinding (LAG), where a small amount of solvent is added into a solid reaction mixture [114,117]. This liquid could also work as structure directing agent and ion-and liquid assisted grinding (ILAG) was used as to be highly efficient for the selective construction of pillared-layered MOFs [118]. Though, the mechanochemical preparation is limited to specific MOF types only and large amount of product is difficult to obtain [114]. The electrochemical preparation of MOFs (Figure 2.18) uses metal ions continuous arranged as the anodes in an electrochemical cell with the organic linker dissolved in methanol as solvent and a metal cathode. In case of HKUST-1, trimesic acid dissolved in alcohol and copper cathode were used in electrochemical synthesis for period of 150 min at a voltage of 12-19 V and a currency of 1.3 A, to attain a greenish blue precipitate [114]. After activation by heat, a dark blue colored powder of octahedral crystals structure in nature with 0.5 to 5 μm size) possessing surface area of 1820 m^2/g was obtained [119]. Currently, HKUST-1, ZIF-8, Al-MIL-100, Al-MIL-53, and

Al-MIL-53-NH₂ were reported to be prepared through anodic dissolution in an electrochemical cell [114]. The experimental parameters such as solvent, electrolyte, voltage-current density, and temperature on the preparation of MOF are vital in obtaining a desired structure [120].

2.4.4. Titanium oxide/metal organic framework composite for DSSC

It was seen that MOFs are promising crystalline materials and received attentions in energy storage and conversion applications, because of their high surface area, variable pore sizes and low density [13]. Currently, the concepts of MOFs based solar cell are emerging and some reports on application of MOFs as candidate active materials in photovoltaics can also be found [13,121-126]. However, a fully devised solar cell based on MOFs as active material for harvesting solar energy has been rarely investigated [123]. The performance of these cells based on commercial TiO₂/MOF and functionalized TiO₂/Al-MOF (BDC= organic linker) with 1,4-dimethoxybenzene (DMB) is summarized in Table 5.3. The device with constructed with DMB@TiO₂/Al-MOF of lowest thickness, had Isc value of 0.36 than TiO₂/Al-MOF cells prepared without DMB [126]. The feasibility of the Ru-MOF film as a sensitizer in a solar cell was investigated by Lee *et al.* [123] and it was demonstrated that the cell performance of Isc = 2.56 mA cm⁻², Voc = 0.63 V and efficiency = 1.22%. The thin layer of Cu-based metal-organic frameworks (copper(II) benzene-1,3,5-tricarboxylate, HKUST-1) was fabricated using a layer-by-layer technique in TiO₂-based solar cells and it demonstrated the excellent performance with Voc = 0.49 V, Isc = 1.25 mAcm⁻², and power conversion efficiency = 0.26% [125]. Furthermore, Lee *et al.* [125] made a comparative study with the device without HKUST-1 sensitization under similarly conditions, the device showed only 0.37 mAcm⁻² of Isc and 0.06% of conversion efficiency. This was supported by EIS analysis, example in Figure 2.19(a-d) showing the Nyquist plots of the above cells under open circuit condition. The EIS revealed that iodine doping of MOF is very essential to reduce the charge-transfer resistance of the TiO₂/MOF/electrolyte interface, hence higher power efficiency was obtained [125].

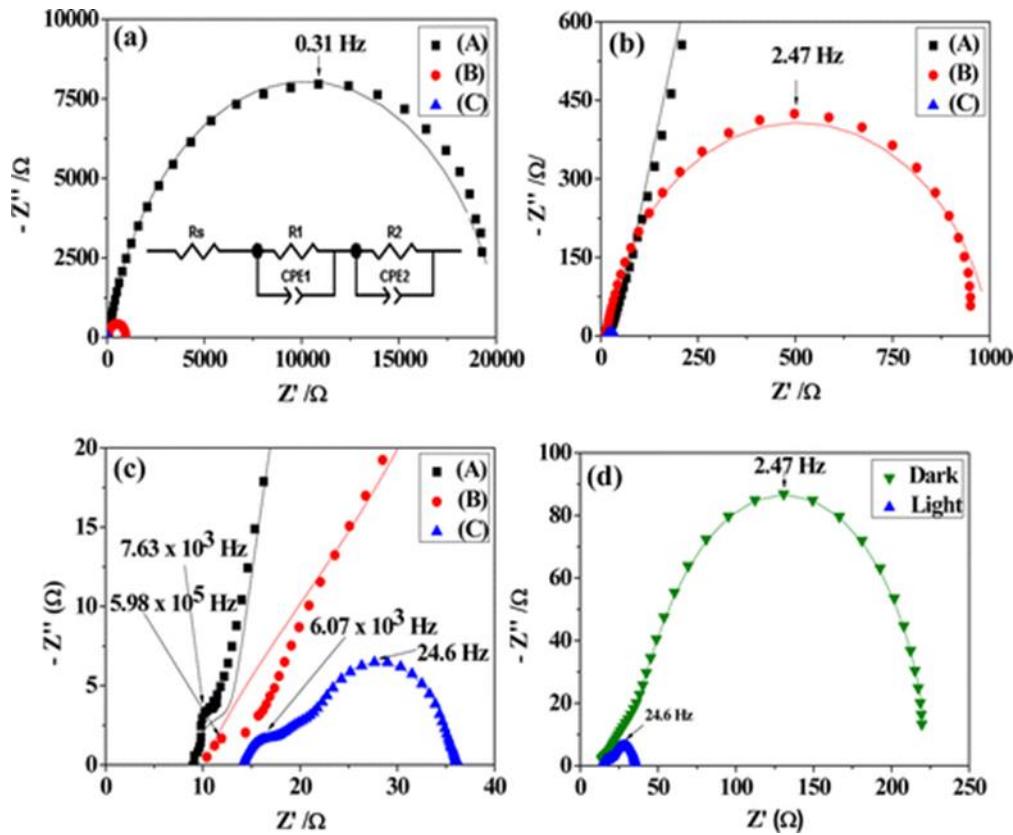


Figure 2.19: (a) Equivalent circuit model and the impedance spectra of the cell at open-circuit condition under illumination with simulated AM 1.5 solar radiations: (A) FTO/TiO₂/Cu-MOF undoped, (B) FTO/TiO₂, and (C) FTO/TiO₂/Cu-MOF iodine doped. (b) and (c) are zoomed impedance spectra of (a) at a higher frequency region. (d) Impedance spectra of the cell consisting of FTO/TiO₂/Cu-MOF iodine-doped photoanode under dark and illumination conditions. Squares, circles, and triangles are the experimental data, whereas the solid lines are the fitted curves [125].

On the other hand, Li *et al.* [121] reported for the first time fabrication of zeolite imidazolate framework (ZIF-8), a metal–organic framework reticulated using a nitrogen-containing ligand, 2-methylimidazole, and zinc metal, on top of the TiO₂ layer for DSSCs. They controlled the growth time of the MOF in order to vary the thickness of the MOF layer that was demonstrated by linear relationship of V_{oc} and thickness of ZIF-8 layer on top of TiO₂. The I–V curves under dark conditions showed a higher voltage requirement for the motion of electrons for ZIF-8-coated TiO₂ electrodes [121]. This was supported by the

charge transfer resistance determined using electrochemical impedance spectroscopy (EIS) possessing a higher resistance for TiO₂/ZIF-8 [121]. In addition, there was a decrease in both the I_{sc} and η was achieved as the thickness of ZIF-8 layer increased even though the V_{oc} was enhanced [121]. Gu *et al.* [122] prepared a thin blocking layer of a metal organic framework ZIF-8 coated on the surface of mesoporous TiO₂ films for DSSCs using MK2 dye and tris(2,20-bipyridine) cobalt(II)/(III) redox in acetonitrile as an electrolyte. They observed that dye-sensitized solar cells with TiO₂/ZIF-8/dye possessed increment of V_{oc} value by 3% and I_{sc} value by 21% with 9.42% power conversion efficiency (Table 2.3). Alwin *et al.* [13] reported for photovoltaic performance of TiO₂ aerogel–Zn-MOF (Zn (I-LCl)(Cl)/TiO₂) nanocomposite. The TiO₂ aerogel–Zn-MOF nanocomposite was used as photoanode in DSSC and an overall power conversion efficiency 2.34% along with a short-circuit current density 6.22mAcm⁻² was achieved using N719 dye [13]. Ramasubbu *et al.* [127] fabricated DSSC based on 3-dimensional TiO₂-Ni-MOF composite aerogels that was prepared through sol–gel method. They observed an enhancement of photovoltaic performance of TiO₂-Ni-MOF cell with respect to pure TiO₂-based QSDSCs using N719 dye (Figure 2.20). The maximum photo-conversion efficiency of the fabricated photoanode was obtained 8.846% for 0.5% composite aerogel, which is ~30% higher than that of pure aerogel-based ones (6.805%) (Table 2.3) [127]. The enhanced in power efficiency enhancement were due to increased photocurrent density, reduced charge-transfer resistance, and suppressed electron recombination was confirmed by photocurrent density–applied voltage curves and electrochemical impedance measurements as seen in Figure 2.20(a-d). Furthermore, Vinogradov *et al.* [128] applied a single-step hydrothermal preparation for the first time to produce a MIL-125@TiO₂ composite for DSSC application. They have seen that the analysis of the photopolarization measurements for determination of optimal MOF concentration, the greatest photocurrent response of 39 μ Acm⁻² observed in 3% MOF–TiO₂ [128]. The MIL-125@TiO₂-based device showed high stability over time with a power efficiency of about 6.4% [128].

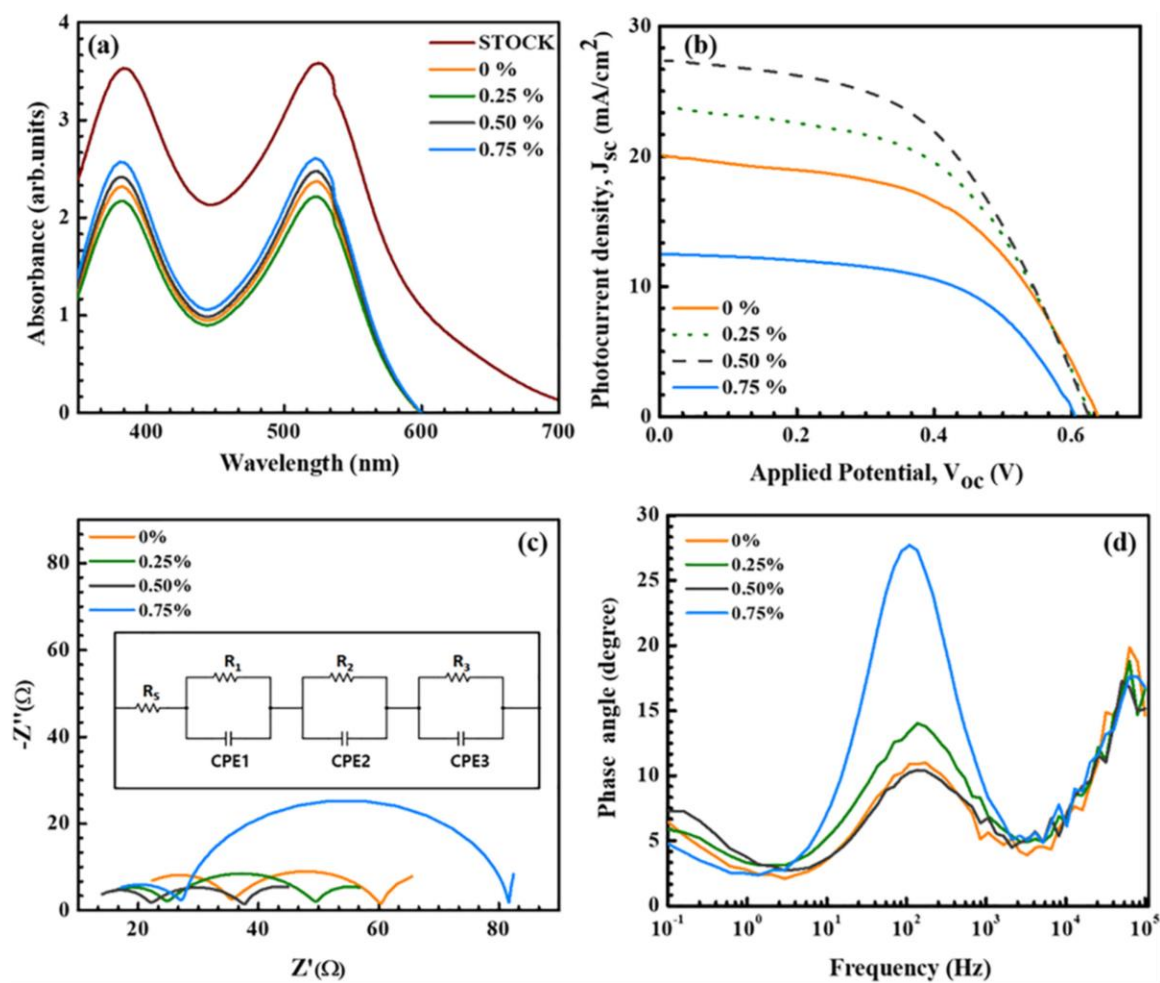


Figure 2.20: (a) Comparison between dye adsorption exhibited by pure TiO_2 aerogel, aerogels coated photoanodes and the blank. (b) Photocurrent density–applied voltage curves (J–V) and c) Nyquist plot of all the prepared QSDSCs and (d) bode plot of all the prepared QSDSCs [127].

Table 2.3: Photovoltaic parameters of TiO₂ composites in DSSCs.

Photoanode material	Dye	Electrolyte	Voc (V)	Isc (mAcm ⁻²)	η (%)	Ref.
TiO ₂ /Al-MOF	-	-	0.27	0.023	-	[126]
TiO ₂ /Al-MOF-DMB	-	-	0.36	0.036	-	[126]
TiO ₂ /Ru-MOF	-	I ₃ /I ₋ redox	0.63	2.56	1.22	[123]
TiO ₂ /HKUST-1	-	I ₃ /I ₋ redox	0.49	1.25	0.26	[125]
TiO ₂ /ZIF-8	N719	1DMPImI/LiI,/ I ₂ /AN/TBP	0.75	10.28	5.34	[121]
TiO ₂ /ZIF-8	MK2	[Co(bpy) ₃](TFS) ₃ /LiTFSI/tert-butylpyridine (tBP) /AN	0.90	14.39	9.42	[122]
TiO ₂ /Zn-MOF	N719	PEGOPEG/NaI/ I ₂ /EMITFMSI /AN	0.68	6.22	2.34	[13]
TiO ₂ /Ni-MOF	N719	PEGOPEG/NaI/ I ₂ /EMITFMSI /AN	0.62	27.32	8.84	[127]
TiO ₂ /MIL-125	N219	PEGOPEG/NaI/ I ₂ /EMITFMSI /AN	0.85	10.9	6.4	[128]

N719=Di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II); MK2= 2-Cyano-3-[5'''-(9-ethyl-9H-carbazol-3-yl)-3',3'',3''',4-tetra-n-hexyl-[2,2',5',2'',5''',2''']-quater thiophen-5-yl] acrylic acid; AN=acetonitrile; TBP=4-tertbutylpyridine; DMPImI=1,2-dimethyl-3-n-propylimidazolium iodide; PEGOPEG=poly(ethylene oxide)-poly(ethylene glycol); and EMITFMSI= 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide

2.5. CONCLUSION

In conclusion, photovoltaic cells have exhibited to be alternative source of energy and used in many fields, such as mobile commerce, building integrated photovoltaics (BIPVs), and vehicles. It was seen that development of PVCs has reached efficiencies of over 14%, however, recombination losses, poor stability, and leakage of the electrolyte (in liquid-state devices) have hindered the enhancement of the device performance and commercialization. Recently, numerous hard works have been made to reduce the recombination losses within the PVC devices. Particularly, dye sensitized solar cells based on TiO_2 have shown to possess higher power conversion efficiency due to high surface area and ability of dye molecule to transport electron fast. However, TiO_2 materials have large bandgap value of 3.2 eV that is higher to absorb radiation at visible region for practical usage which is utilized sunlight. In terms of low cost and lightweight, organics, inorganics, and hybrid materials have brighter prospects than the semiconductors. In TiO_2 hybrid materials, photovoltaic cells have been prepared with the advantages of organics or inorganics selectively. However, it is not easy to increase the energy conversion efficiency. One potential solution is to use 3-dimensional nanostructures, such as nanotubes, nanowires, composite films with metal, or metal organic frameworks. As of today, MOFs in photovoltaic cells still yield the higher energy conversion efficiency by supplying larger surface areas for the sensitizer adsorption. However, the electron transport and flexibility are sufficiently high in 3-dimensional nanostructures. To improve the energy conversion efficiency of 3-dimensional nanostructure based solar cells and take both advantages of organic- or inorganic-dye and MOF on TiO_2 , the light harvesting ability must be reinforced. One way of achieving the better light harvesting ability is to look at other molecules such as phthalocyanine and polyaniline that can be adsorbed on the in the cavities of 3-dimensional MOF structure and TiO_2 which is another currently active field of study.

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CHAPTER 3:

RECENT APPLICATIONS OF ANALYTICAL TECHNIQUES AND ELECTROCHEMICAL METHODS IN CHARACTERIZATIONS OF THE TITANIUM DIOXIDE COMPOSITES

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ABSTRACT

This work reports on the characterisation techniques of titanium dioxide (TiO₂) and its composites for photovoltaic studies. TiO₂ is a good semiconductor material owing to its low-cost, superior thermal and chemical stability. The synthesised TiO₂ material needs to be analysed and characterised to check if they are suitable for the entire applications. As such, there is a need to study their structural, optical, morphology, thermal and electrochemical properties. Titanium dioxide (TiO₂) composites are regarded as photoanodes in the dye sensitized solar cells application. As such, they have received a great

interest in energy applications due to its exceptional properties such as stability, high surface area, conductivity, and catalytic activities. TiO₂ photo-anode has the drawback of high band gap of ~ 3.2 eV. To decrease the band gap of TiO₂ photo-anode, metal organic framework (MOF) nanomaterials are incorporated TiO₂ to form a TiO₂-MOF composite that enhances the TiO₂ photo-anode property. Herein, we report literature survey on characterization techniques used to analyse TiO₂ nanomaterials and TiO₂- composites. Hence, this review will comprehensively discuss detailed literature survey on analytical techniques that can be used to study the chemical, physical and surface properties of TiO₂ and its composites, namely ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction, scanning and transmission electron microscopies energy dispersive X-ray spectroscopy, thermogravimetric analysis, differential scanning calorimetry and electroanalytical methods which include linear sweep voltammetry, cyclic voltammetry voltammetry, chronoamperometry, electrochemical impedance spectroscopy and current-voltage measurement.

Keywords: Analytical techniques, composites, titanium dioxide, photoanode, photovoltaic.

3.1. INTRODUCTION

Nanomaterials have long held a strong fascination for scientists. Due to its biological, chemical, and physical properties, nanomaterials have received considerable attention. Nanomaterials has opened another alternative nanotechnology which are employed in various research fields such as material science, physics, biochemistry, and chemistry [1–4]. In addition, nanomaterials have opened a new step in the evolution of understanding and utilization of materials and composites. In the 16 centaury, scientists discovered the material science, and realized that the chemical composition of material is the main factor that determines what a material is [5]. The particle size of nanomaterials

falls within dimensions of 1nm to 100 nm. The overall shape of these nanomaterials depend on dimension of the material such as 0D,1D, 2D or 3D [6]. Among the materials dimension, 1D nanomaterial such as metal oxides are preferred for the excellent performance in the dye sensitized solar cells (DSSCs). The most common 1D nanomaterials are for enhancement of dye-sensitized solar cells efficiency using mixed-phase TiO_2 , ZnO and NiO_2 nanoparticles as photo-anodes [7]. These photo-anodes differs in characterizations such as the size, purity, surface properties, stability, solubility, shape and reactivity and there is a need to improve the quality of the materials. In cooperating one material by another material enhanced the performance of material in various applications [8]. Several nanomaterials are composed of three different layers which include the surface layer, which may be functionalised easily, shell layer which differs from the core of the materials, and core layer which is the central part of the nanomaterial [9].

In addition, nanomaterials can be categorised according to the material composition. These categories include carbon, inorganic and organic based materials. Carbon-based materials are predominantly carbon such as carbon nanotubes (CNTs), fullerenes (C_{60}), graphene oxide (GO), and carbon onions (CO)). Inorganic based materials include metal oxides such as titanium dioxide (TiO_2), zinc oxide (ZnO), tin dioxide (SnO_2) etc. Organic based materials are mostly from organic matters with less amount of the carbon atoms [7 –9]. Looking at the properties of the nanomaterials, such as crystallinity, suggests whether materials are good for a particular application. A number of these applications include water purifications, conversion of carbon monoxide to carbon dioxide as well as the solar cells fabrications. Inorganic based metal oxide nanomaterials have received more interest in research due to its remarkable outstanding properties such as photophysical and photochemical properties. TiO_2 is one of the metal oxide nanomaterials which it is mostly studied owing to its low cost, low toxicity, high thermal and chemical stabilities [10]. TiO_2 has also played a key role in many applications as a photocatalyst and semiconductor in photovoltaic applications [11]. The term photocatalyst means a process which takes place when a light source come into contact with the surface of semiconductor materials. It was in the 1960s, when scientists investigated the photoinduced process occurring on solid materials for photovoltaic

studies [12]. It was seen that nanomaterials accumulate the low power conversion efficient (PCE) due to the larger band gap. This circumstance has been described and understood using the band gap theory of photocatalyst [12-13]. Many researchers such as incorporated TiO_2 with other materials such as metal organic framework (MOF) to develop a TiO_2 -MOF photocatalyst. The metal organic frameworks such as Ni-MOF and Zn-MOF were employed in the dye sensitised solar cells [13]. In addition, TiO_2 /carbon black, TiO_2 /graphene [14–15] and TiO_2 /polymers composites were also reported for dye-sensitised solar cells applications. [14–18]. Therefore, we discuss the importance of various analytical techniques in characterization for TiO_2 composites. These techniques include optical characterization using ultraviolet-visible spectroscopy (UV-vis) for electronic properties, morphological evaluation utilizing scanning electron microscopy (SEM) and transmission electron microscopy (TEM), functional group and phase determination by the aid of Fourier transform infrared spectroscopy (FTIR)/Raman spectroscopy and x-ray diffraction (XRD), thermogravimetric analysis (TGA/DTA) for thermal stability and also employing electrochemical methods. Representative results for TiO_2 nanomaterials and nanocomposites are employed to confirm the information of the entire materials and suggested from various analytical and electrochemical techniques. The good understanding and knowledge of TiO_2 phenomena stemming from the development of these analytical and electrochemical techniques. These techniques can lead to the advancement in design of TiO_2 composites for photovoltaic studies.

3.2. BRIEF FUNDAMENTAL OF TITANIUM DIOXIDE

Titanium dioxide (TiO_2) nanomaterials have unique structural properties with agglomerated shapes. Approximately, 50 % of TiO_2 nanoparticles have the same number of particle size distribution size of 1D dimensions and the size range 1–100 nm [19]. TiO_2 nanomaterials are regarded as good examples of transition-metal dioxide and derived from the linkage between a metal centre and oxygen atoms as ligands [19–21]. The coordination structure of Ti and two O atoms in TiO_2 are bonded chemically and forming O-Ti-O functional group which occurs as a sandwiched-like structures [22–24].

It is known that TiO_2 is a 1D nanomaterial, and in between the atoms of the molecules, a weak van der Waals bonds resulting in a formation of a trigonal or octahedral structure that hold the layers on TiO_2 together. Generally, TiO_2 consists of three crystal structures which are one octahedral and two trigonal structures, those structures are shown in [25–28].

The defects of TiO_2 crystal structures provide an information about the band gap that corresponds to the electrons localized in the d-orbital of Ti^{3+} centres. The formation of the O vacancy in TiO_2 rutile phase are produced by two excess electrons occupying 3d orbitals on the Ti atoms neighbouring the vacancy. Similarly in the TiO_2 anatase, two 3d subshells are filled by the electrons from oxygen atoms [29]. The length of TiO_2 nanomaterial is about 5 μm and the pore diameter is about 100 nm [30]. However, it was seen that the 2H- TiO_2 can be converted to 1T and 3R phases upon annealing, electric doping and controlling strains. Moreover, the central octahedral TiO_6 unit has a large particles enclosed by lower coordination sites [11]. Typically, structure of TiO_2 in Figure 3.1(a) is classified into three phase, high surface area (brookite), tetragonal more thermodynamically stable phase (rutile) and tetragonal stable phase (anatase) [31 – 32]. Among the TiO_2 phases, anatase has been consider as one with best phase because of its high stability, surface area and crystallinity. TiO_2 is a 1D-monocrystalline structure and is selected as photoanode. TiO_2 has the probability of attaching dye to enhance its photovoltaic performance [7].

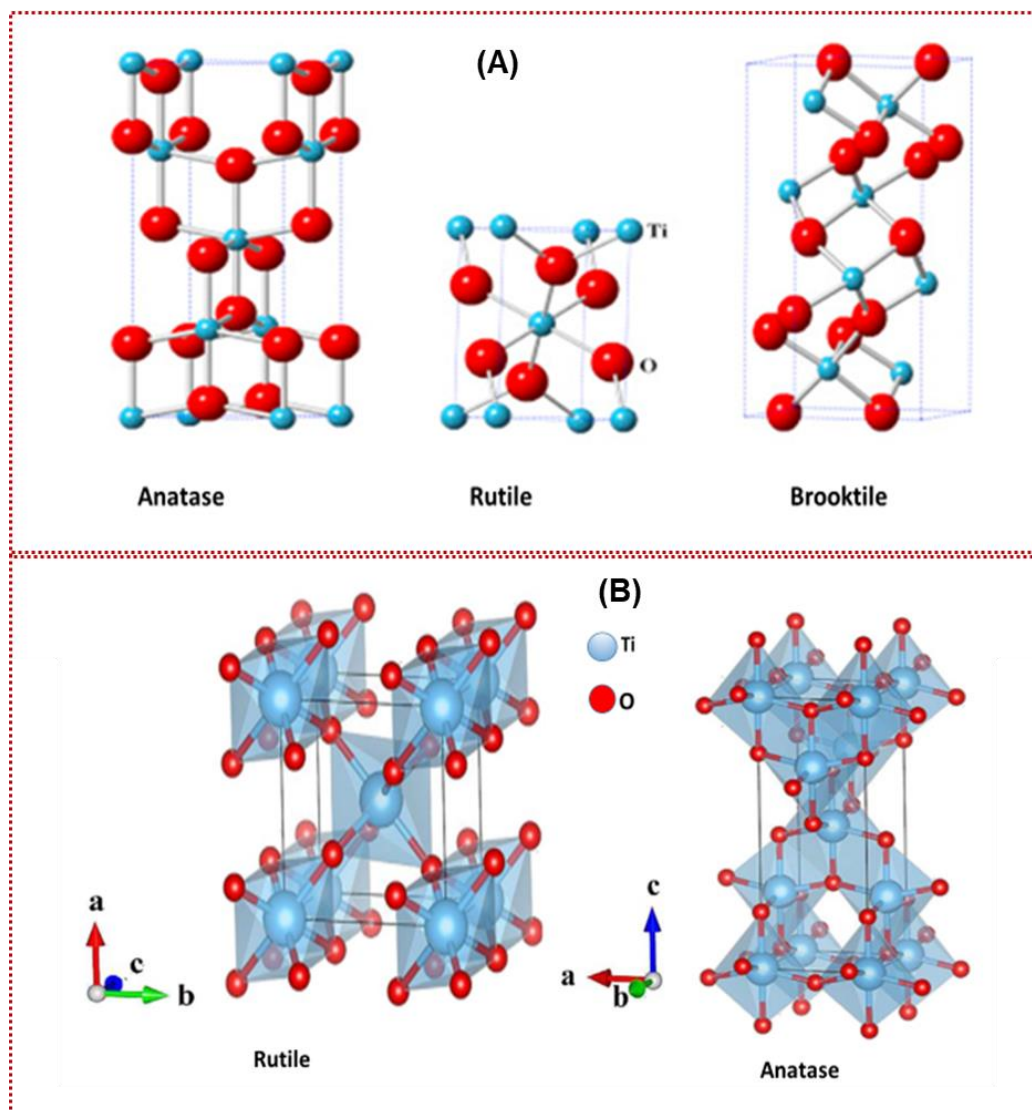


Figure 3.1: (a) and (b) Crystal structure of anatase, rutile and brookite [31, 32].

Moreover, the TiO₂ polymorphs have a crystal structure which describes the various spatial arrangements of TiO₆ octahedra geometry (Ti⁴⁺ ions attached oxygen ligands). It was seen that the major differences in 3 crystal structures are explained by various degrees of distortion and the assembly of 3-D in the octahedral of TiO₆ (Figure 3.1(b)). The crystal structure of TiO₂ differ according to the arrangement of their phases. The anatase TiO₂ phase has tetragonal geometry with $a = b = 3.78 \text{ \AA}$ and $c = 9.50 \text{ \AA}$ and

have octahedron geometry that shares corners to form (001) planes [31]. Rutile TiO_2 phase has the tetragonal geometry with ($a = b = 4.58 \text{ \AA}$ and $c = 2.95 \text{ \AA}$) [32]. The brookite TiO_2 phase has an orthorhombic geometry with the crystal structure of $a = 5.43 \text{ \AA}$, $b = 9.16 \text{ \AA}$ and $c = 5.13 \text{ \AA}$. This crystal structure consists of the edge sharing octahedrons forming the (001) planes [33]. However, anatase TiO_2 phase has a larger band gap of about 3.2 eV that is disadvantageous to it in performing well in the DSSC application [34 – 35]. TiO_2 can only absorb at a wavelength that is less than 400 nm in the ultraviolet region. Proper material is needed to enhance the properties of the TiO_2 in the DSSC application and can absorb in both visible and ultraviolet regions. TiO_2 anatase are synthesized using different methods such as aero-gel, hydrothermal process [36], solvothermal [37], combustion [38], ball rolling, chemical vapour deposit [39], spray pyrolysis [40] and sol-gel [41 – 42].

3.3. CHARACTERIZATION TECHNIQUES FOR TiO_2 COMPOSITES

Analytical instruments are normally used to analyze most of the nanomaterials and their composites synthesized in various research fields. In this field of research in nanotechnology and material science, titanium dioxide- composites are characterized and analyzed using various analytical techniques. These analytical techniques can be divided into several methods like microscopy, spectroscopy, thermal and physical instruments, and electroanalytical method that are explored by many researchers.

3.3.1. Structural characterization

The structural characterization are the primary methods for characterization of TiO_2 nanomaterials and they are used to investigate the formation of composite formed and its composition as well to provide information about the nature of bonding occurred. Spectroscopy is one of the analytical techniques used to investigate light interacting with material of interest. It can be utilized for both quantitative and qualitative analysis to identify or determine number of species present. The interaction of light and matter results

in the electronic properties (UV), functional groups (FTIR and Raman), phase identification (XRD), elemental composition (EDS/X and XPS) and particle size and the surface area (BET) [43-64].

3.3.1.1. Ultraviolet visible spectroscopy

Ultraviolet visible spectroscopy (UV-vis), is an analytical optical technique used to determine electronic properties through the interaction of ultraviolet-visible light with material [44 – 45]. The UV-vis is commonly applied in many fields such as research, production and quality control for the classification and study of substances. In principle, it provides an important information, such as the purity of the sample depending on the amount of light and its wavelength absorbed by the sample. In quantitative analysis, the absorbance is related to the amount of species present in the analyte [46 –47]. In addition, this spectroscopy is used to determine the band gap of a nanomaterials. Band gap will determine the activeness of the nanomaterials in electrocatalysis, photocatalysis and photovoltaic applications. For example in photovoltaic solar cell, a small band gap indicates that the molecule is more active and high percentage of power conversion efficiency is expected [48-51].

The optical band gap values of the nanomaterials are calculated using Tauc plots in Equation 3.1 [51-53].

$$(\alpha h\nu)^n = B (h\nu - E_g) \quad (3.1)$$

the absorption coefficient is denoted by α , $h\nu$ represents the photon energy, B stands for a constant relative to the nanomaterial, E_g represents the energy band gap, and n shows a value that depends on the nature of the transition ($n = 2$ for a direct allowed transition, and $2/3$ for a direct forbidden transition, and $1/2$ for an indirect allowed transition).

Yang and co-workers [54] reported a UV-vis absorption studies (Figure 3.2(A, a)) of TiO₂ nanowires (NWs) nanomaterials with CdS quantum dots (QDs) assembled, and this shows that the introduction of CdS resulted in the emerging of energy bands in the visible to the TiO₂ absorption. The spectra showed an absorption band which is broad in

the visible region, and it is well known to assist in the enhancement of the photocatalytic degradation activities [54]. Furthermore, TiO₂ nanomaterial absorption at the edge and CdS nanoparticle absorption at the edge were measured, as presented in Figure 3.2(A)c and d, possessing a bandgap 2.58 and 2.44 eV, respectively. The resulted composite CdS (6)-TiO₂ NWs had a bandgap of 2.25 eV, as given in Figure 3.2(A) e.

In another studies, Gopal and Basha [55] reported that the UV-Vis for the three materials namely TiO₂ starting material, nanowire and nanoflakes. The nanowires showed a blueshift with an edge of absorption at 398.73 nm with respect to the one at 412.58 nm for starting material and a redshifted of nanoflakes at 416.74 nm. The authors showed that the bandgap values of prepared TiO₂ starting material, nanowires and nanoflakes were found to be 3.00 eV, 3.10 eV and 2.97 eV respectively. Park *and co-workers* [56] investigated on the carbon doped TiO₂ (C-TiO₂). It was seen that the C-TiO₂ nanomaterial was effective to absorb more light in the range of 400–550 nm in comparison to pure TiO₂. The determined band gaps were found to around 2.90 and 3.08 eV for the C-TiO₂ and TiO₂ nanomaterials, respectively. Tang *and co-workers* [57] reported the UV-vis spectra of A-TiO₂, Ag/A-TiO₂, and hierarchical Ag/TiO₂ microspheres and observed that A-TiO₂, and TiO₂ microspheres doped with silver possessed a distinct red-shift to visible region with respect to other TiO₂ nanomaterial. The spectrum of Ag/A-TiO₂ showed an increment of absorption in the visible and near-infrared regions with wavelengths greater than 450 nm. It was seen that the Ag/TiO₂ microspheres showed a shallow peak with absorption bank at 500 nm [57].

Ramakrishnan *and co-workers* [58] reported that the optical band gab energies of TiO₂ nanomaterials and nanotubes can also be determined using the Equation 3.2.

$$hv = \frac{1240}{\lambda(\text{nm})} \quad (3.2)$$

They noticed that the absorption range of the synthesized TiO₂ nanomaterial and nanotubes were seen to be blueshifted due to a wide bandgap of the TiO₂. The absorption bands were found to be at 385.5, 391.4, 390.8 and, 392.8 nm for the TiO₂ nanoparticles,

TiO₂ nanoflakes, and TiO₂ nanotubes, respectively. The band gap values were calculated using Equation 1 and were found to be 3.22 eV for TiO₂, 3.167 eV for TiO₂ nanoparticles, 3.172 eV for TiO₂ nanoflakes and 3.156 eV for TiO₂ nanotubes [58]. Apart from evaluating the absorption properties of TiO₂ composites, ultraviolet visible spectroscopy can be applied to give insights into the interaction of these materials. For example, Jhuang *and co-workers* [59] employed UV–Vis to monitor the formation of silver nanoparticles on TiO₂ and it was observed that conversion of Ag⁺ ion on the dispersed TiO₂ in a solution of ethylene glycol and alkaline using ultrasonic wave as an autocatalytic reduction reaction. For application purposes, Cinelli *and co-workers* [60] investigated the photocatalytic degradation of a model textile dye induced by carbon-doped titanium dioxide using UV-Vis. The obtained kinetics data showed that a high degradation rate and substrate concentration dependence.

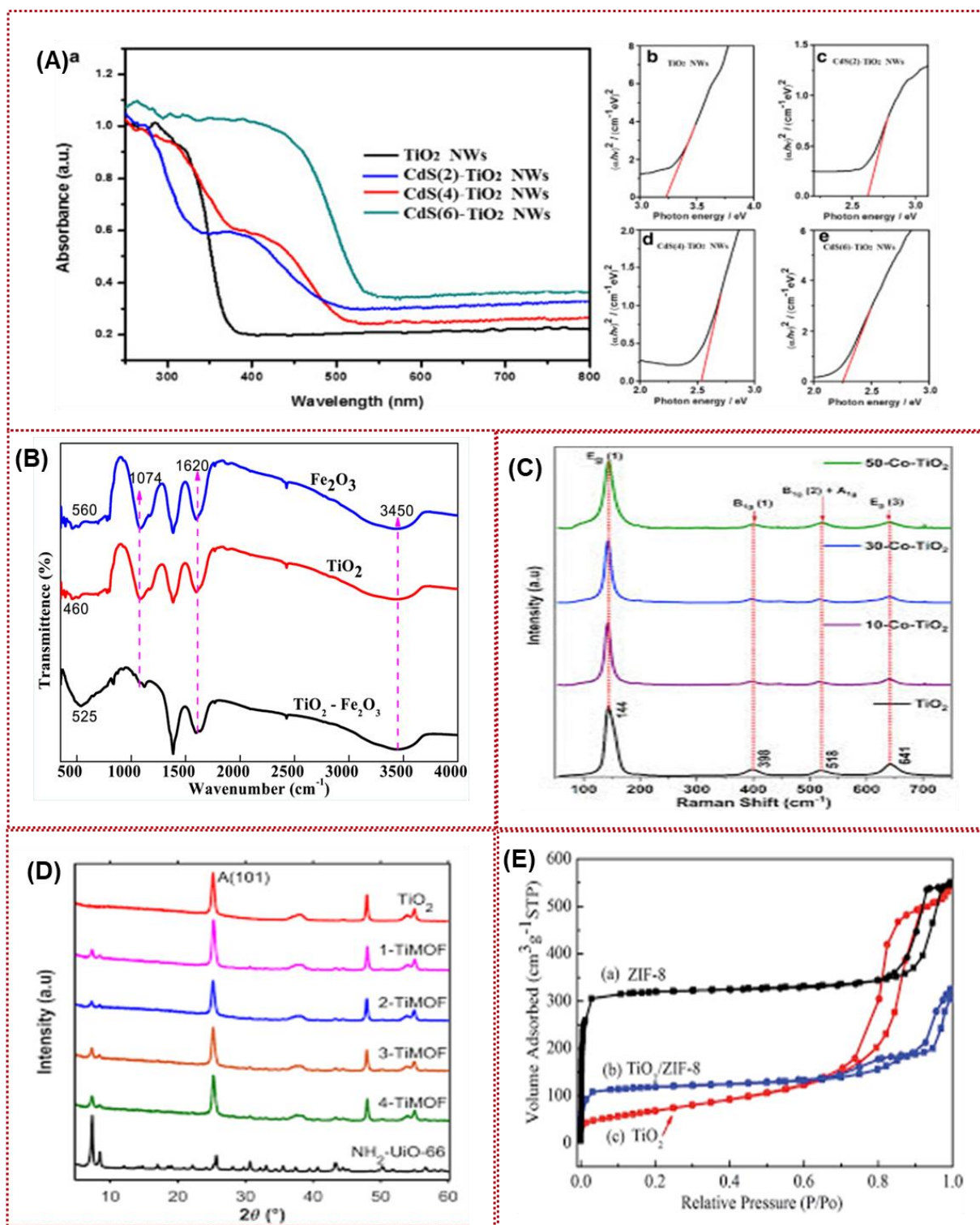


Figure 3.2: (A, a and b) UV-Vis and the band gaps of TiO_2 nanowire and CdS-TiO_2 nanowire [54], (B), FTIR for TiO_2 and $\text{TiO}_2\text{-Fe}_2\text{O}_3$ nanocomposite [61], (C), Raman

spectroscopy of TiO₂ and Co-TiO₂ nanocomposite [62] (D), phase identification using XRD for TiO₂, NH₂-UiO-66 and TiO₂/NH₂-UiO-66 nano composites (x-TiMOF) [63] and (E) The BET isotherms of TiO₂ beads, MOF (ZIF-8) and TiO₂/ZIF-8 hybrid [64]

3.3.1.2. Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is an analytical technique, which identifies the vibrational of the bond to bond in between the atoms known as the functional groups. Bonding type and molecular conformation of organic and inorganic molecules are described in this phenomenon [59, 60]. In principle, a material is reflected from irradiated infrared light source, the chemical bonds that attached the atoms together in a molecule and absorb the radiation at a certain frequency that match their vibration modes. The vibration modes occur when radiation stimulates the vibrational motion by depositing every photon into vibrational mode. This includes stretching, twisting, bending, rocking, wagging, or out-of-phase or in-phase deformation which adsorbs at the wavenumbers of 400–4000 cm⁻¹ [67]. The change in vibrational modes produce spectra with bands, in which each spectral band represents different chemical environment [61].

In the FTIR instrument, there are vital components, one of them is the interferometer. The interferometer is the one making FTIR to be different from traditional IR dispersive spectroscopy [61]. It is made of fixed and movable/translating mirrors and the beam splitter. In operation, the interferometer splits light into two portions when it comes. The one portion is reflected to the fixed mirror and then mirrored to the beam splitter where it can be detected. The other portion is redirected to the movable mirror and then back to the beam splitter and to the detector. These two portions meet to produce, constructive or destructive interference [62]. The FTIR have various operation modes like the attenuated total reflection (ATR), nujol, and potassium bromide (KBr) [70].

The ATR is the best operational modes, and it is used because there are no sample preparation difficulty, no issue of handling, and it avoids spectral irreproducibility [69, 71].

Li *and co-workers* [687] reported the FTIR spectra for TiO₂ nanoparticles, with peaks at 3400 and 1631.78 cm⁻¹, for the bending and stretching vibrational mode of the –OH functional group. The peaks at 435.91, 466.77 to 700 cm⁻¹ are assigned to the stretching and bending vibrational mode of Ti-O-Ti functional groups. The FTIR demonstrated that the disappearance of the peak at 2900 cm⁻¹ due to the removal of all unwanted organic compounds from the TiO₂ network after calcinations. Moreover, Ramalingam *and co-workers* [69] reported on the use of FTIR instrument for characterization of the synthesized nanosized TiO₂. The nanosized TiO₂ had an FTIR spectrum showing characteristic peaks at around 3651.25 & 3674.39 cm⁻¹, 1541.12 & 1558.48 cm⁻¹ for the stretching and bending vibration of the O-H functional group, respectively. In addition, Figure 3.2(B) presents the FTIR spectra of TiO₂-Fe₂O₃, measured in the range of 400–4000 cm⁻¹. It was seen that the peak at around 460 cm⁻¹ was associated to Ti-O bond [61]. The peak was observed to be shifted to 525 cm⁻¹ after the decoration with Fe₂O₃ and showed the appearance of Fe-O stretching mode [61]. Alwin and co-workers [76] presented the FTIR spectra of the TiO₂-Ni-MOF composite aerogels with the vibration band at 457–700 cm⁻¹ owing to the vibrational mode of Ti-O vibration and the bands were assigned to the carboxylic groups (1372 and 1610 cm⁻¹). They have shown that the vibrational bands at around 3100 and 3400 cm⁻¹ were due to C-H stretching (sp² carbon.). A broad peak at the wavenumber 3460 cm⁻¹ was assigned to the O-H functional group and indicated the presence of MOF incorporated in the TiO₂-Ni-MOF nanocomposite [76].

3.3.1.3. Raman spectroscopy

Raman spectroscopy focuses on the inelastic scattering of photons from the light source, known as Raman scattering. In principle, a nanomaterial is irradiated with monochromatic light of a certain frequency. Probably, the monochromatic light from a laser in the visible, near infrared, or near ultraviolet range is used, even X-rays can be used. The laser light comes into contact with molecular vibrations, and excited electrons from the system results in the upper energy level of the electrons from the molecule, as such the energy of the laser photons are being shift up and down [71 –72] This allows the electromagnetic light from the illuminated spot to be collected with a lens through a monochromator.

Elastic scattered light of a particular wavelength corresponds to the laser line called Rayleigh scattering which is filtered out by either a notch , edge pass , or a band pass filter, and the collected light is distributed and measured by a detector [73]. This provides an information about the modes of chemical vibration [72].

Another type of scattering is called spontaneous Raman scattering. Typically, this scattering is very weak; as a such, it results in hard in the collection of Raman spectra. This Raman spectra shows the separation of the weak inelastically scattered radiation from the laser rejection [74]. The high degree of laser rejection is achieved by using multiple dispersion stages and holographic gratings in Raman spectrometers [75]. There are several types of Raman spectroscopy such as resonance, surface-enhanced, polarized , tip-enhanced, stimulated, spatially-offset, transmission and hyper Raman spectroscopies [74]. Among various Ramans, the transmission Raman is popular and considered by many researchers [76-84]. This is due to its outstanding properties such as providing information of vibration fast. Sigh published about the discovery of Raman spectroscopy in 1923 [83]. Five years later, Norman Raman realized the scattered incidences on the operation of spectroscopy, and the spectroscopy was named after him called Raman spectroscopy [83]. Raman spectroscopy consists of two types of instrumental techniques. This includes Raman spectrometer and FT-Raman spectroscopy [84]. Dispersive Raman spectroscopy was associated with a diffraction of grating in order to disperse the scattered light from the nanomaterial. Generally, the radiation is detected upon multichannel detectors including the photomultiplier tube (PMT) or charge-coupled device (CCD) [85]. While in FT-Raman spectroscopy deals with the interferometer similar to FTIR [78] whereby the light is produced from a laser shine on the edge filter and directs it to various paths (lens) [85]. Light is directed to the first lens and interacts with the molecule and light from the second lens is directed to the slit of the spectrometer. The spectrometer has mirrors, collimating mirror which transfers light to the monochromator for wavelength selection. The monochromator centers the light to the focusing mirror and charge-coupled device (CCD) which will be generated [64, 76].

Krishnapriya *and co-workers* [62] presented the Raman spectroscopic analysis in order to understand the crystallinity, dopant-induced structural variations and also to

investigate the molecular vibration properties of all TiO₂-MOF nanocomposites, and the spectra are shown in Figure 3.2(C). It was seen from group theory that anatase TiO₂ has a tetragonal structure that consists of six Raman active modes. Those active modes include A_{1g}+ 2B_{1g}+ 3E_g [62]. E_g peak originated from O–Ti–O symmetric stretching vibrational mode in TiO₂, whereas B_{1g} is due to the O–Ti–O symmetric bending vibrational mode and A_{1g} originated from O–Ti–O anti-symmetric bending vibrational mode.

3.3.1.4. X-ray diffraction.

In order to identify the crystalline phases of the nanomaterial, X-ray diffraction (XRD) is employed as an analytical instrument. The main purpose of this technique is to identify the phases and crystallinity of nanomaterial. In addition, it used to give an information about unit cell dimensions. The X-ray diffraction was firstly discovered by Max Van Lowe in the late century [86]. A year after, William Lawrence Braggs discovered an X-ray crystallography, and their work was reported in 1912 and 1913 [86]. It was suggested that X-ray beam subjected to the material, passes through the crystal, and the process of diffraction takes place on the photographic plate. This technique is basically using an interaction of incident light from constructive interference of monochromatic X-rays and a material to induce constructive interference in order to satisfy the Bragg's law as given in Equation 3.3:

$$n\lambda = 2d\sin\theta \quad (3.3)$$

λ denotes the wavelength of the radiation beam, d represents the interlunar spacing between two diffracting lines, θ designates the diffraction angle, and n stands for an integer which is equal to 1. Furthermore, the crystallite size of the nanomaterials can also be predicted from the X-ray patterns. It is determined using Derby-Scherrer relationship in Equation 3.4.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3.4)$$

Where K is the Scherrer constant, β represents the full width at half maximum (FWHM), λ is the wavelength of Co radiation, and θ is the angle between the incident and reflected rays.

For example, Crake and co-workers [63] presents the XRD analysis of the pure TiO_2 and MOF ($\text{NH}_2\text{-UiO-66}$) nanomaterials and the TiO_2/MOF (x-TiMOF) nanocomposites as given in Figure 3.2(D). They demonstrated that the materials possessed a good crystallinity, however, only anatase TiO_2 with (101) phase was obtained, and $\text{NH}_2\text{-UiO-66}$ showed the typical diffraction pattern of MOF. As given in the XRD patterns of the x-TiMOF nanocomposites, there was no major change in the phase composition and crystallinity of TiO_2 after the incorporation of MOF into the TiO_2 network [63]. In a different study, Kanta and co-workers [87] used XRD technique to quantify the structural transformation of TiO_2 nanotubes in anodized amorphous phase to crystalline anatase when the materials were subjected to 500 °C anneal treatment for two hours.

3.3.1.5. Brunauer-Emmett-Teller (BET)

Brunauer-Emmett-Teller is an important tool dedicated for the analysis of surface area and pore size on a solid material using adsorption-desorption of N_2 gas isotherm. Wei and co-workers [78] showed determination of surface area and pore size of TiO_2 nanomaterial found to be in the ranging from 4 to 30 nm. They observed the similar intra nanoparticles pores as compared the analysis made using TEM. They further reported the surface area of the synthesized TiO_2 nanomaterials to be 250 m^2/g . This confirms that materials with larger surface area are likely to have more active sites [79]. In addition, Liu and co-workers [64] reported on the nitrogen adsorption–desorption isotherms of TiO_2 beads, MOF (ZIF-8) and $\text{TiO}_2/\text{ZIF-8}$ hybrid nanospheres as shown in Figure 2(E). They indicated that TiO_2 beads incorporated with ZIF-8 nanoparticles showed a higher BET area of 397 m^2/g as compared to the one of 250 m^2/g for TiO_2 beads, On the other hand, ZIF-8 (Figure 3.3.2(E)a) represents a typical type I isotherm, which fitted very well with the microporous frameworks of ZIF-8 [64].

3.3.2. Morphology/Microscopy Characterizations

Microscopic techniques are described as a set of analytical methods viewing of objects which cannot be detected by naked eye. Microscopy is comprised of three main sections that includes

- a) Optical microscopy focuses on the material that use visible light to enlarge images.
- b) Scanning probe microscopy that deals with a probe to scan object.
- c) Electron microscopy that utilizes an electron beam to create an image of a material.

3.3.2.1 Scanning Electron Microscopy

To view the surface morphology of the nanomaterials, scanning electron microscopy (SEM) is used which utilizes a focused the beam of electrons to provide a high-resolution imaging. Particularly, an electron beam is produced from the electron source. The beam is accelerated towards the specimen through a positive electrical potential. Then the electron beam is confined and focused using metal apertures and magnetic lenses and its electrons come into contact with the atoms of the specimen. Their interactions produce signals containing information about its surface composition, topography, and other electrical properties [81]. The detector in the SEM collects the electric signal using its cabinet for quantification which provides images as results output [82 -84]. The SEM detects three signals as such backscattered electrons for atomic number, secondary electrons for characterization of specimen, and Auger electrons for the luminescence property of the specimen [85-86]..Furthermore, SEM techniques are classified into two categories used to characterize the specimen. These are field emission scanning electron microscopy (FESEM) and the environmental scanning electron microscopy (ESEM) [87-96]. The FESEM gives a clearer, less electrostatically distorted image of a better spatial resolution/ magnification than the one of traditional SEM. While the ESEM is mostly utilized to analyze wet specimen, uncoated one, or both by letting for a gaseous environment in the specimen chamber [88].

Liu and co-workers [87] synthesized $\text{TiO}_2/\text{MOF}/\text{PPy}$ (PPy=polypyrrole) nanocomposite and used SEM to reveal the morphology of the nanocomposite. Figure 3.3(A)(a) indicates the morphology of TiO_2 nanoparticles with agglomerated type structure and Figure 3(B)b suggests that in nanocomposite containing PPy, the image is well dispersed by providing a well-established plate form of MOF [87].

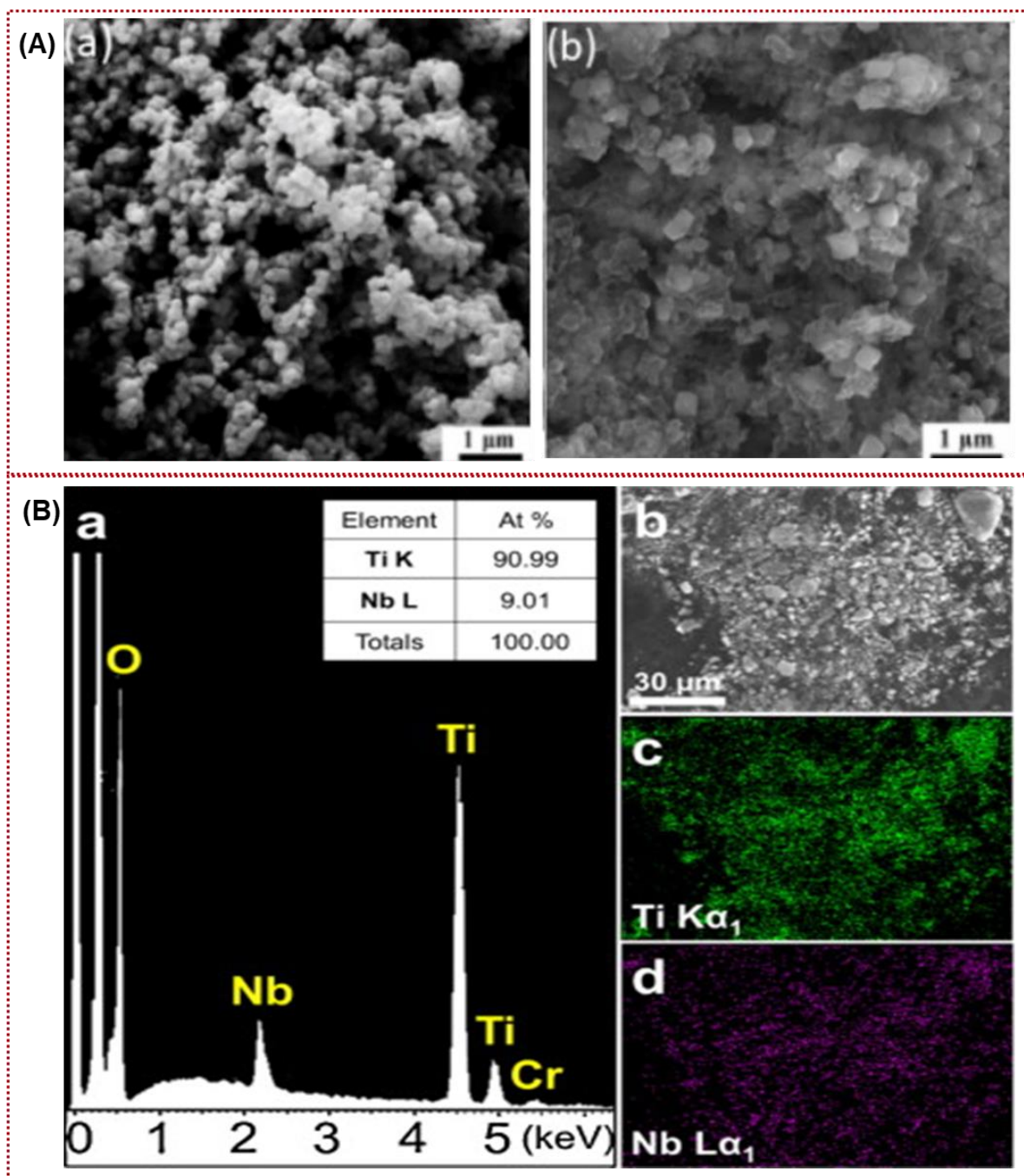


Figure 3.3: (A, a and b) SEM and (B, a, b, c and d) EDS spectra a, EDS, b, SEM at magnification of 30 μm for TiO_2 , c, and d. Figures reproduced with permission from [97].

In addition, the SEM may be coupled with energy X-ray dispersion spectroscopy (EDS) as important technique in the characterization and determination of elemental composition [89-93]. In principle, the incident electron interacts with an atom of the nanomaterial and produces an electron from the K-shell of the metal and create a vacancy or hole. It is reported that an electron from another shell may fill in that vacancy to emit X-rays [88-93]. This migration of electrons create electron transitions which represent a chemical composition of each elements [94-96]. For example, SEM/EDS analysis was used to confirm the Nb^{5+} substitution into the TiO_2 nanoparticles by Lim *and co-workers* [97]. Their results as shown in Figure 3.3(B), presents a typical EDS spectrum (Figure 3.3(B)a), where the peaks for Ti K1 were observed at ~ 4.5 and ~ 4.9 keV and for Nb L1 peaks were at around ~ 2.2 keV as indication for presence of Nb nanoparticles in the TiO_2 . The inset table in the figure showed a quantitative elemental analysis for TiO_2 composite possessing 9 at. % of Nb^{5+} and 91 at. % of Ti [97]. Furthermore, they investigated the uniformity of the Nb^{5+} distribution by conducting an elemental mapping analysis with SEM/EDS (Figure 3.3(B)b–d) and presented that the Nb^{5+} was observed at almost same region where Ti^{4+} was located in nanoparticles without segregation [97]

3.3.2.2. Transmission electron microscopy

In order to determine the growth of the layer on the material surfaces, the composition as well as the defects in the material, transmission electron microscopy (TEM) is used as an effective instrument. In addition, this instrument provides a high-resolution images and can be able to examine the shape, size, quality and density of quantum wells, wires and dots of the material especially the semiconductor. Generally, an intense beam of electrons is reflected to the material, and the interchange between the electrons and atoms in the material takes place. As such, the morphological

characterizations for the crystal structure and features in the structure like dislocations and grain boundaries are determined. Practically, the electron passes through multiple electromagnetic lenses to interact with the screen and to be in to light and to produce an image [89, 90].

Furthermore, the image can be controlled by regulating the voltage of the gun to increase or decrease the speed of electrons as well as altering of the electromagnetic wavelength using the solenoids [90]. The images are focused onto a screen or photographic plate using coils. As the transmission occurs, the speed of electrons is proportional to wavelength of electron. It was seen that the faster electrons move, the shorter electron wavelength and the better the quality and detail of the image [90]. On the image, the lighter areas shows that electrons were able to pass through that places whereas the darker areas represent the dense areas of the object. These differences give an information about the texture, structure, shape and size of the material [91 - 94]. The nanomaterial acquires the outermost properties such as a high crystalline structure in order to get a high resolution of TEM.

TEM can be coupled with selected area electron diffraction (SAED) or EDS to investigate crystallites and elemental composites of the materials [93].

The information gathered from the SAED patterns supply the information such as comparative values of the intensities between the central and other diffraction spots, distance R between the central spots and other diffraction spots and lastly angle c between the central spots to each diffraction spots [98-100]. In addition, TEM can provide a high-resolution images (HRTEM) based on the interference between two or more diffracted beams from the electron beam after the interaction with a thin sample.

For example, Krishnapriya and *co-workers* [62] reported the morphological and crystalline make-up of MOF-derived Co^{2+} -doped TiO_2 nanoparticles using TEM, HR TEM and SAED analyses given in Figure 3.4(a–f). From the figure, it is observed that pristine TiO_2 nanomaterial possessed an average size of $0.5\mu\text{m}$ (Figure 3.4(a,b) and its corresponding SAED pattern (Figure 3.4(c) presented a clear, distinct rings as indication of the polycrystalline nature [62]. They further indexed the rings in SAED pattern to have (101), (200), and (201) planes of tetragonal anatase TiO_2 nanomaterials using a d-

spacing. Furthermore, it was seen that the lattice fringes in TiO_2 were not identified in HRTEM due to high thickness of the particle.

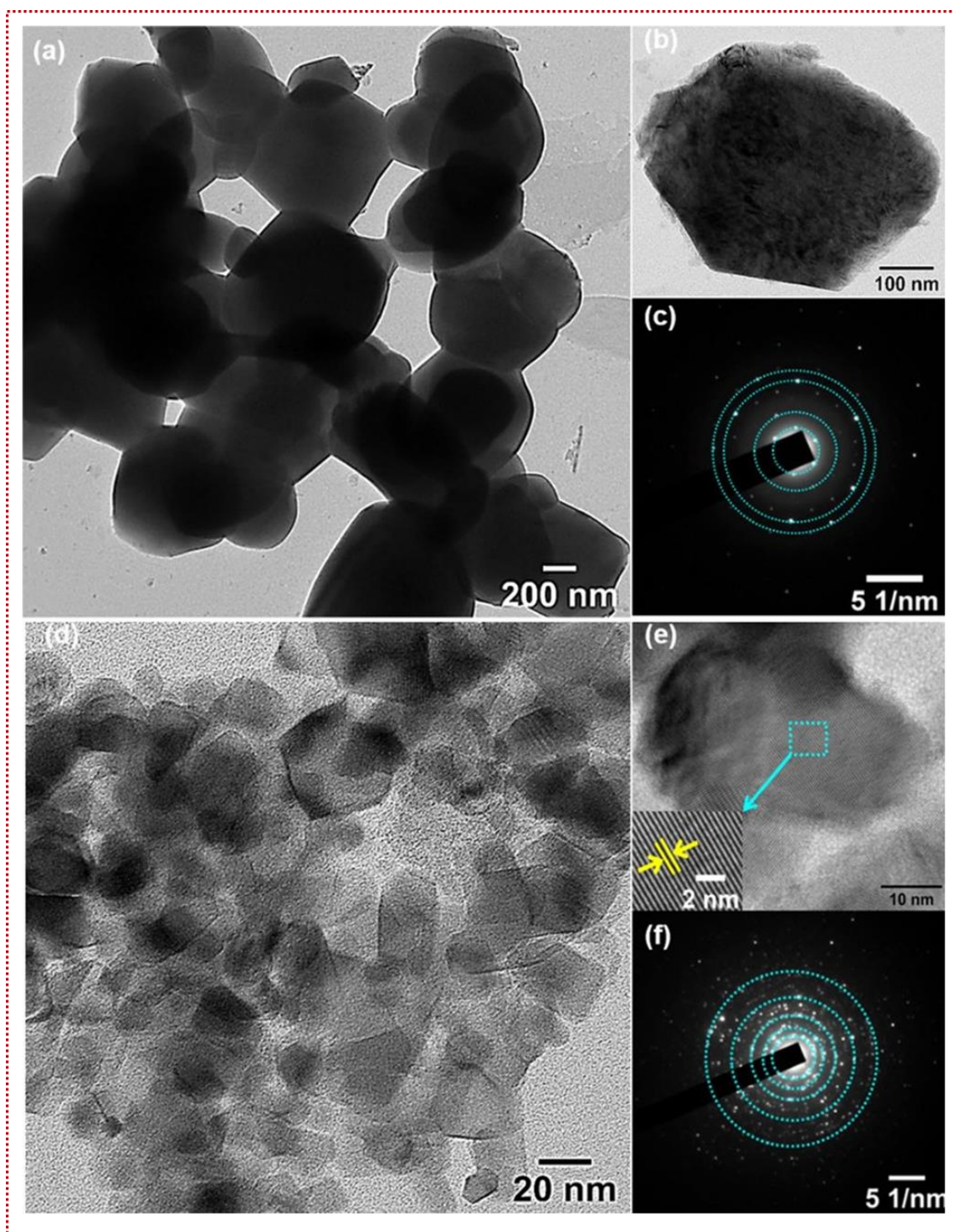


Figure 3.4: Morphology (a) HR-TEM at 200 nm magnification, and (b) HR-TEM at 100 nm magnification, (c) SAED for TiO_2 , (d) HR-TEM at 20 nm magnification, (e) HR TEM at

10 nm magnification and (f) SAED analyses for MOF-derived Co^{2+} -doped TiO_2 nanoparticles [62].

However, the introduction of MOF on TiO_2 nanomaterials as shown in Figure 3.4(d), resulted in with reduction of particle size to ~25 nm with clear lattice fringes (Figure 3.4(e)). The HRTEM images showed clear lattice fringes with d-spacing of 3.5 Å (inset figure of Figure 3.4(e)) with (101) plane of tetragonal anatase phase of TiO_2 [62].

3.3.3. Thermal Analysis differentiate scanning

Crystalline structure nanomaterial needs to be more stable to perform well in their applications. Thermal Analysis (TA) is an excellent instrument to determine the stability of the nanomaterial through thermal interactions. This determines the relationship between a nanomaterial property and its temperature as the nanomaterial is heated or cooled in a controlled manner. There are several thermal techniques used in processes of heating or cooling the nanomaterial such as thermogravimetric (TGA), differential thermal analysis (DTA) as well as differential scanning calorimetry (DSC).

The most used analytical techniques to examine the thermal analysis is TGA. This technique is there to support the stability of the material and gives the changes in chemical and physical properties of nanomaterials. It shows that at constant heating rate, there will be a change in mass of the material in relation to an increasing temperature. It discloses the information about physical aspect including adsorption, vaporization, desorption, and sublimation. Hence, it also discloses information about chemical aspects including desolvation, chemisorption, and decomposition [101]. Furthermore, TGA technique is regarded a supportive instrument basically used to determine the chosen features of nanomaterials that show either mass loss or gain due to decomposition, oxidation, or loss of volatiles. Its applications includes for determination of organic content in a material, the studies of degradation mechanisms as well as reaction kinetics and for CO_2 capture monitoring [102]. The main purpose of TGA technique is to determine and evaluate the thermal stability of a material. This technique is more advantages because

there is no instrumental error and does not require a multiple of standard preparation to determine unknown concentration [104-106]. TGA has its corresponding differential thermal analysis (DTA) which measures heat or mass differences over a temperature range.

Zhu *and co-workers* [103] presented thermal behaviour and the degradation of weight loss curves of pure TiO_2 and 10% Sn– TiO_2 nanocomposite (Figure 3.5(a and b)). They observed three degradation steps owing to the evaporation of physically adsorbed water, the combustion of organic compounds, and dehydroxylation, respectively. And this shows the improved thermal stability in the nanocomposite. The results of TGA suggested similar observation corresponding to DTA curves such as the endothermic and exothermic transitions of pure TiO_2 and 10% Sn– TiO_2 nanocomposite occurred from the water and organic compounds lost at a temperature below 450 °C. It was shown that the exothermic peak in the DTA curve at about 581 °C, showed the transformation of phases to rutile from anatase TiO_2 . However, the exothermic peak of 10% Sn– TiO_2 composite was shifted to 481 °C, as the results of reduction in the phase transformation temperature from anatase to rutile with introduction of Sn dopant.

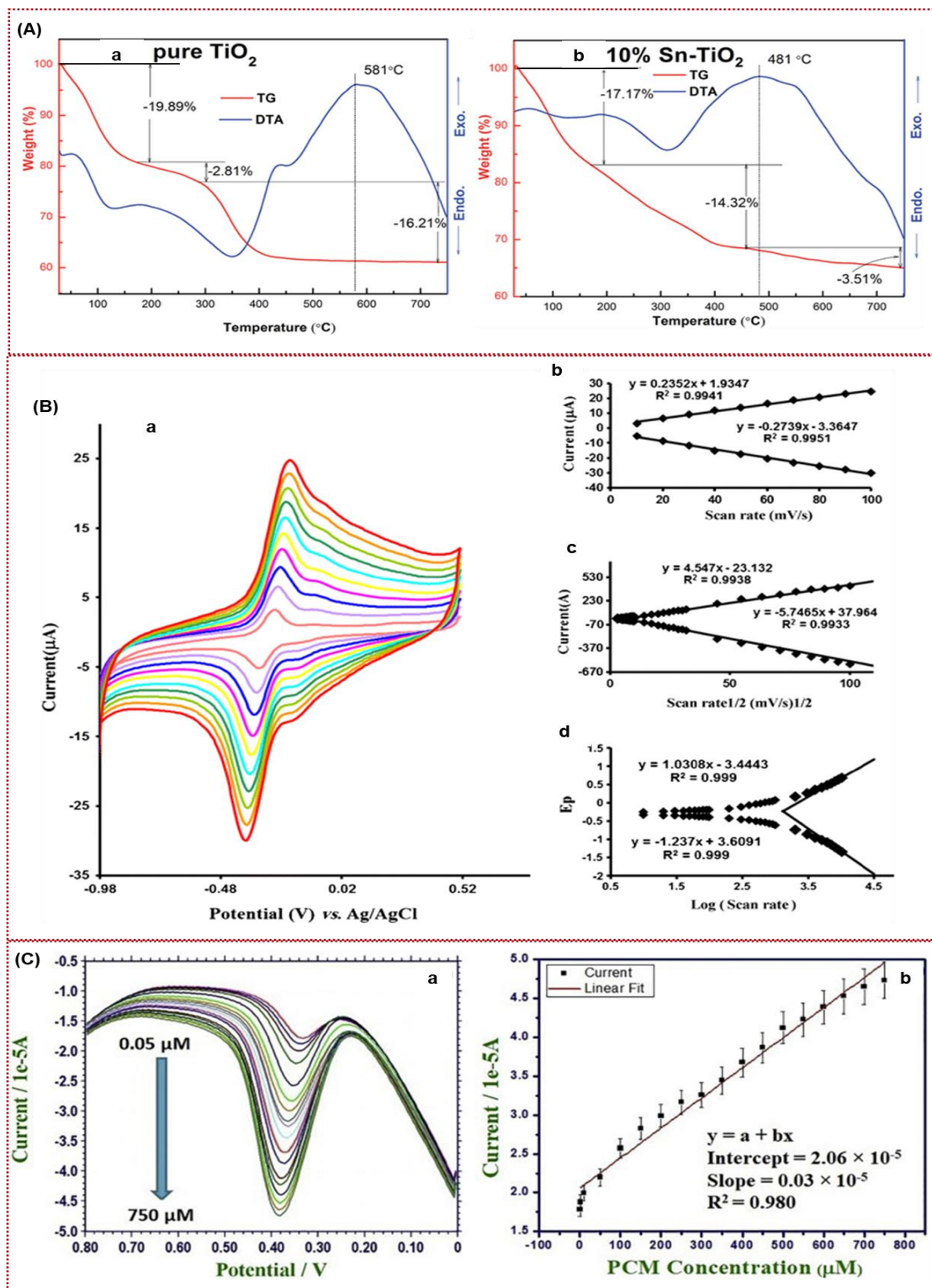


Figure 3.5: (A), TGA/DTA of (a) Pure TiO_2 and (b) 10 % Sn-TiO_2 [103], (B), (a) CV and (b) calibration curve at different scan rate [107], (C) Square wave Voltammetry response of $\text{MoS}_2/\text{TiO}_2$ NC/GCE as a function of (a) Linearity curve and (b) PCM concentration [108].

On the other hand, differential scanning calorimetry (DSC) determines the phase diagram of the nanomaterials such as crystallization and melting transitions, solid-solid reaction, and specific heat of a sample similar to DTA. In addition, DSC technique differs with TGA and DTA in a way that it can complement both structure and stability of nanomaterials, and can also confirm the transition in the nanomaterial composition [101]. This technique gives the difference in heat flow between a reference and material as a function of sample temperature [102]. The change in enthalpy is directly proportional to the area underneath the peak, and this is an indicative of thermal event in the process of exothermic or endothermic reaction [103].

3.4. ELECTROCHEMICAL CHARACTERIZATION OF NANOMATERIALS

A crystalline semiconductor nanomaterial such as ZnO, NiO₂, SnO₂ and TiO₂ have the excellent properties towards many applications such as sensing, hydrogen evolution, water cleaning, water splitting, photocatalyst and photovoltaic solar cells. In order to check the performance of the crystalline semiconductor nanomaterials, it is needed to use the electrochemical systems that determines whether the nanomaterial is good for the particular application. Electrochemical systems include the two electrode or the three electrode systems. The major role of those systems is to investigate the properties of an analyte by measuring the potential (volts) and current (amperes) in an electrochemical cell. The type of the electrochemical techniques employed in these systems are classified into three main categories. These include potentiometry, coulometry and voltammetry. Potentiometry deals with measuring of the difference in electrode potentials. In coulometry, the current is measured over time. Voltammetry is considered to be the electrochemical system, in which the current is measured as a function of applied potential [107-109]. Electrochemical techniques follow the basics of electrochemistry whereby redox reactions occur during operations and use the electrochemical cell principles. In principle, an electron is lost and gained between the species, and this experiment is conducted in the electrochemical cell. In case where two electrode system is operated, the electrochemical cell consists of a working and counter

electrode) which are immersed in an electrolyte solution and separated by a salt bridge. Chemical reactions mostly take place on the surface of the electrodes giving several half reactions. If the three electrode system is used, the working, reference and counter electrodes are used in an electrolytic solution in a glass [108]. The reactions take place on the working electrode's surface or in solution interface. There are different types of working electrode which are employed such as gold, aluminium, glassy carbon and mercury working electrodes. In the reference electrode, it is where a standardization process takes place. The reference electrode has a fixed potential and it assist in measuring the potential change on working electrode. The saturated calomel electrode (SCE) and silver/silver chloride (Ag/AgCl) are the commonly used reference electrodes. Then lastly there is a counter electrode which is known as an auxillary electrode such as platinum, or copper wire. Its purpose is to sink electrons so that the current can move through from the external circuit. The electrochemical technique used for TiO_2 and its composite are voltammetry, chronoamperometry, electrochemical impedance spectroscopy and current-potential curve.

3.4.1. Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the electrochemical techniques used to measure the relationship of current and potential. This takes place under conditions in excess voltage as predicted by the Nernst equation [109, 110]. The CV is achieved by monitoring the resulting current during the potential cycling of a working electrode. It is frequently employed to investigate a variety of oxidation and reduction processes, to determine the HOMO and LUMO energies as well as the stability of reaction products, to check the presence of intermediates in electrochemical reactions, electron transfer and reaction kinetics; and to monitor the reversibility of a reaction [109]. The CV is also utilized to determine the electrochemical properties of the nanomaterials in the dye sensitized solar cells applications.

Hallaj and Haghighi [107] reported the redox behavior of the anatase TiO_2 /graphene oxide composite using the cyclic voltammetric in the potential region as

indicated in Figure 3.5(B). It was seen that there is a linear relationship between the half peak reactions (anodic and cathodic) and scan rate (Figure 3.5(B)(a)). This showed that the electrochemical reaction from the anodic to cathodic peak current ratio is equal. Figure 3.5(B)(b) demonstrated that the half peak potentials related to the scan rate at higher scan rates as indicative of the slow diffusion of ions into the electrode surfaces. On the other hand, the effect of pH on the electrochemical behavior of anatase TiO_2 /graphene oxide composite electrodes was also studied as shown in Figure 3.5(B)(c) [107]. This indicated that the peak potentials shifted to less positive values with increasing the pH. Typically, , the TiO_2 electrode behaved the same way in both aqueous LiOH electrolyte and LiClO_4 non-aqueous electrolyte [14, 15, 17, 96,110, 111].

3.4.2. Square Wave Voltammetry

Square wave voltammetry (SWV) is one of the linear potential sweep voltammetries. The SWV has gained much more attentions in different fields [109, 112]. It works similar to CV to measure current of the working electrode as a function of the potential. It is advantageous over CV because it can be used to perform an experiment much faster and it is more sensitive [112]. . Belkhamisa *and co-workers* [112] investigated the voltammetric by monitoring the Pb (II) using TiO_2 incorporated with carbon paste electrode using SWV. Finally, the behaviour from the voltammogram of Pb (II) was recorded on the composite TiO_2 /CPE. For example, Figure 3.5(C)(a) shows SWV of $\text{MoS}_2/\text{TiO}_2$ NC/GCE electrode [108]. The half peak current for oxidation process becomes higher as the concentration of PCM increase. This causes the number of electrons to be more in the processes during the electrochemical reaction. Considering the dynamic linearity range was obtained from 0.5 μM to 750 μM . In Figure 3.5(C)(b), it was clear that the linearity curve of oxidation peak current vs. PCM increased with an increase in concentration [108].

3.4.3. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is one of the powerful and reliable methods to investigate the physical and chemical processes which occur in the electrolyte/electrode interface [113, 114]. This analytical technique is performed by gathering information on electrochemical characteristics including diffusion impedance, double-layer capacitance, rate of charge transfer, electron lifetime, charge transport processes, stability, conductivity, and solution resistance [115, 116]. EIS depending on the application of an applied current (AC) to the electrochemical cell provides a relationship of response and frequency [117-121].

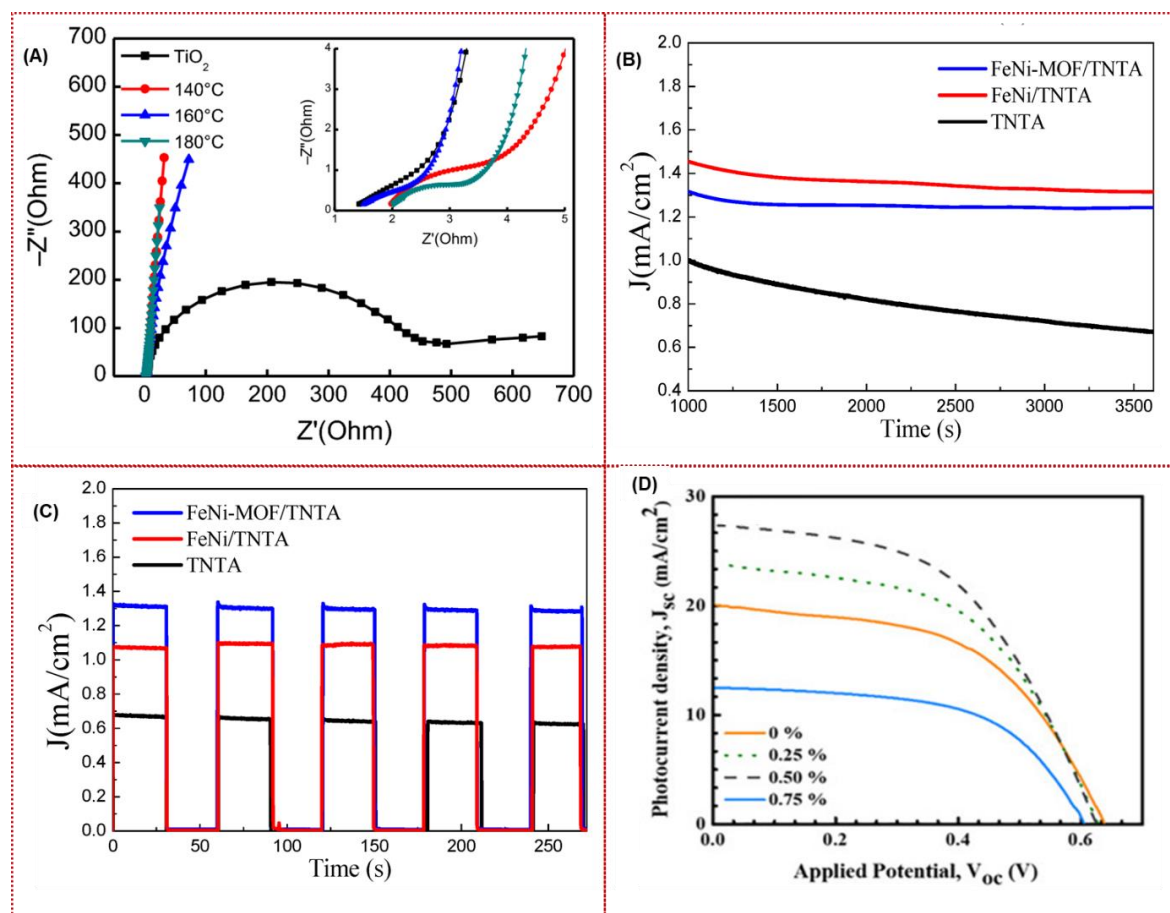


Figure 3.6: (A) Electrochemical Impedance spectroscopy, (B) Chronoampermetry of FeNi-MOF/TNTA, FeNi/TNTA and TNTA, current as a function of long time, (C) FeNi-

MOF/TNTA, FeNi/TNTA and TNTA current as a function of short time. (D) I-V curve of TiO₂-Ni-MOF. Reproduced with permission from [123] and [124].

It was seen in the work of Li and *co-workers* [122] reported on evaluation of the resistance as a function of the electron transfer of the TiO₂ powder, TiO₂/Graphene through the activation process using EIS at different temperatures as given in Figure 3.6(a). It was known that the semicircles of high-frequency were due to the resistance like the charge-transfer impedance on the electrode– electrolyte interface and the transfer and ohmic resistance [122]. It was noticed in Figure 3.6(a) that the TiO₂/graphene at 160 °C possessed a smaller semi-circular diameter than that of the TiO₂. This was attributed to a small charge-transfer resistance and an increment of conductivity.

3.4.4. Chronoamperometry

Chronoamperometry (CA) is an important electrochemical technique employed to evaluate the chemical reaction kinetics, diffusion processes, electrochemical stability and adsorption. This technique is a time-dependent technique whereby a potential is applied to the working electrode. The current of the electrode is measured against time. The fluctuation of the curve is due to the diffusion of an analyte from the bulk solution towards the material's surface. The CA can also be utilized to measure current as a function of time dependence in a diffusion-controlled process which occurs at working electrode. You and co-workers [123] reported on the experiment conducted using CA that is related to the determination of stability of the Fe/Ni bimetallic organic framework deposited on TiO₂ nanotube. They observed that the stability of FeNi/ anodized TiO₂ nanotube arrays and FeNi-MOF anodized TiO₂ nanotube arrays in the first hour was quite stable (Figure 3.6(B)). However, they noticed that after 2 hours of measurement, the photocurrent of FeNi-MOF/anodized TiO₂ nanotube arrays is higher than that of FeNi/ anodized TiO₂ nanotube arrays, as shown in Figure 3.6(C). It was seen that the photocurrent of FeNi/ anodized TiO₂ nanotube arrays decreased to 1.1 mA/cm₂ after 180 min of operation. The

one for FeNi-MOF/ anodized TiO₂ nanotube arrays maintained to be 1.3 mA/cm² during the measurement.

3.4.5. Current–voltage

A current–voltage characteristic or I–V curve (current–voltage curve) is used to measure the electric current in a circuit, device, or material, and its corresponding voltage, or potential difference across it in order to characterize photovoltaic (PV) devices. I–V curves are required for characterisation of PV cell, by providing the electrical parameters that describe the operation of the device under test. There are at least six different techniques (Variable Resistor, Capacitive Load, Electronic Load, Bipolar Power, Amplifier, 4-Quadrant Power Supply and DC-DC Converter) used to perform this I–V task and Duran and co-workers [124] comprehensively reviewed them. The authors compared the flexibility, modularity, fidelity, fast response, direct display and cost of each method. I–V curve analysis is normally an invasive technique to detect the deterioration of PV cells that consists of applying a variable load on the module terminals to obtain their current and voltage response. As a result, the analysis of the cell response curves provides us with a direct information on the electrical "state" of the cell. For example, Ramasubbu and co-workers [125] investigated the impact of MOF doped on the TiO₂ nanomaterial for the enhancement of TiO₂ nanomaterial properties such as the photocurrent density, photovoltage, and power conversion efficiency (PCE) in the presence of a dye using the I-V curve, as shown in Figure 3.6(D). They revealed that the fabricated cells based on pure TiO₂ aerogel and the nanocomposite aerogels with the various MOF loadings which were labelled as quasi-solid dye-sensitized solar cells (QSDSC)-0, QSDSC-0.25, QSDSC-0.50, and QSDSC-0.75 possessed the good performance with high PCE between 7-9 %. In a different study, Puah and co-workers [126] used I–V curves to deduce the resistance of the sol-gel spin coated TiO₂ nanoparticles and correlate with the sensitivity measurement. I-V curves were also used to evaluate the solar cell performance characteristics of TiO₂/Au/Si composite and it was noted that the presence of TiO₂ enhances the open circuit voltage and short-circuit current density [90]. As a result, the

composite is considered capable to harvest photon energy by utilizing the double Schottky barriers.

3.5. CONCLUSION

This review chosen to concentrate on the role of different techniques for the characterization in titanium dioxide composites. Different conventional analytical techniques can be used for the characterisation of some features of titanium dioxide composites due to its good physical and chemical properties of TiO_2 . Therefore, in this comprehensive work, the application of different analytical techniques (spectroscopic, microscopic, physical and electrochemical) are demonstrated, emphasising on their application principle and review on the corresponding results obtained from characterisation of titanium dioxide composites. Therefore, we finally hope that a careful reading of this review will help to identify which valuable techniques which are suitable to study the behaviour of titanium dioxide composites. Structural characterisations using FTIR, Raman, and UV-vis spectroscopy are discussed and showed that the optical properties can also be revealed for semi-conductor and electrocatalytic applications as well as showing the different functional groups obtained during synthesis of titanium dioxide composites. The other structural characterisation method which can reveal the phase properties of titanium dioxide composites which is the XRD, is useful to calculate the crystalline sizes of the nanomaterials from the Debye-Sherer equations. It was also seen that the morphological and elemental analysis of titanium dioxide composites can be revealed using microscopic techniques coupled with EDS detectors. The TGA and DSC (thermal methods) showed to be beneficial to understand the thermal stabilities of TiO_2 composites. Lastly, electrochemical methods can into the picture as analytical techniques to study the redox properties of the TiO_2 composites as well as to evaluate photovoltaic applications.

AVAILABILITY OF SUPPORTING DATA

Not applicable.

COMPETING INTERESTS

The authors declare no competing interests.

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AUTHOR'S CONTRIBUTION

Conceptualization, K.D.M. and P.S.R.; writing—original draft preparation, P.S.R.; writing—review and editing, T.R.S. and E.M.; visualization, M.S.M.; supervision, M.J.H.; project administration, K.M.; funding acquisition, K.D.M. All authors have read and agreed to the published version of the manuscript.

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CHAPTER 4:

FABRICATION, CHARACTERIZATION, AND PHOTOVOLTAIC PERFORMANCE OF TITANIUM DIOXIDE/METAL-ORGANIC FRAMEWORK COMPOSITE

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Abstract

The titanium dioxide-metal-organic framework (TiO₂-MOF) composite was prepared using the sol-gel method for photovoltaic applications. Raman analyses showed the presence of MOF clusters in the TiO₂ sol-gel network. Using the Brunauer-Emmett-Teller method, the resultant composite material exhibited a surface area of 111.10 m² g⁻¹ as compared to the surface area values of 262.90 and 464.76 m² g⁻¹ for TiO₂ and MOF, respectively. The small optical band gap values of 2.63 for direct electronic transition and 2.70 eV for indirect allowed electronic transition in TiO₂/MOF composite were observed using ultraviolet-visible supported by cyclic voltammetry (CV). The chronoamperometry (CA) results showed the current drop of 0.21 mA observed at 0.025 s for TiO₂ and the current drop of 1.00 mA for MOF and 1.4 mA for TiO₂-MOF composite at 0.3 s. The stability of the composite was achieved through the synergistic effect of MOF on TiO₂ which resulted in a high current density. Electrochemical impedance spectroscopy showed a fast electron transfer as well as high ionic conductivity. The overall power conversion efficiency of 0.722% along with a photocurrent density of 0.46 mA cm⁻² was achieved for the composite. The approach proposed in this work is facile and can be used for the large-scale fabrication of efficient and flexible photoanode electrodes for photovoltaic applications.

Keywords: Electrochemistry, metal-organic frameworks, composite, titanium dioxide, photovoltaic studies.

4.1. INTRODUCTION

Globally, there has been a dynamic change in the energy outlook over the years due to the negative environmental impact associated with the use of fossil fuels and the exponential growth in technologies (i.e., optoelectronic applications such as touch screens, solar modules, and photodetectors and electric vehicles). These factors have fostered the development of clean, diversified, sustainable, and low-cost renewable energy systems (i.e., photovoltaic solar cells, wind turbines, etc.) to become valuable for energy provision and technological sustainability [1, 2]. The use of solar power to produce clean energy is made possible through the *R&D* of smart materials to be fabricated into photovoltaic (PV) devices. Photovoltaic devices harness the sun's radiation directly into electricity using the photovoltaic effect [3]. There are several types of solar cells which include perovskite solar cells, organic solar cells, inorganic solar cells, silicon solar cells, dye-sensitized solar cells (DSSC) [4-10], etc. Among these types of solar cells, DSSC is regarded as a potential alternative technology [4], due to its low cost, easy fabrication, and relatively high efficiency. The first work concerning PVs was first reported by Gratzel and O'regan in 1991, which employed the use of DSSC in the production of electric energy from the energy package of light [5]. The effective operation and efficiency of DSSC depend on the type of semiconductors employed. The semiconductors should possess a smaller energy bandgap to facilitate the photo-excited electrons arising from moderate or low energy photons efficaciously for power energy conversion (PEC) [8-10]. For a while, titanium dioxide, TiO_2 has been employed as a photoanode used in the DSSCs due to some of its favorable properties in photovoltaic studies such as high chemical and optical stability, non-toxicity, low cost, and corrosion resistance [11-14].

TiO₂ materials can be prepared in several methods such as physical vapour deposition, chemical vapour deposition, hydrothermal, solvothermal and sol-gel methods [12-17]. Among these methods, sol-gel method is more convenient and it produces TiO₂ materials with high purity, homogeneity, felicity, and flexibility [15,17]. There are three commonly known phases of TiO₂ (i.e., rutile, brookite, and anatase) found in nature. Amongst the three, anatase was found to be the most stable form of TiO₂ in the nano-sized particles, even though rutile is the most thermodynamically stable form [11]. Qin *et al.* [13] reported that porous pure anatase possesses a high surface-to-volume ratio, which is coupled with the surface charge density and has an n-type junction. This has made pure TiO₂ (with its several features) a good candidate for photovoltaic applications with a power conversion efficiency (PCE) of 5.5% [15]. Nonetheless, TiO₂ has high electron recombination of photo-excited electrons and weakly absorbs in the visible regions of the spectra [16]. It has been shown that coating the surface of titanium particles with a nanoscale-thick layer of metal-organic frameworks (MOFs) results in a substantial increase in open-circuit voltage due to inhibited interfacial charge recombination in dye-sensitized solar cells [17-20]. In particular, MOFs have emerged as next-generation materials for various applications (including DSSC) due to their tailorable porosity, large specific surface area, rich redox metal centers, and tunable chemistry (organic linker or metal centers). MOFs are sponge-like crystalline materials made by combining the organic groups through strong bonding components known as organic linkers [19]. Molecular engineering and advancing synthetic technologies have permitted the development of novel MOFs with unique compositions, topologies, and/or architectures, which has resulted in the overwhelming interest in the synthesis of MOFs [20]. Some of the reported synthetic

methods include (i) electrochemical synthesis (which was firstly reported in 2005 by researchers at BASF) [20]; (ii) microwave-assisted method (which involves an introduction of energy using microwave irradiation depending on the interaction between electromagnetic waves and electric charges) [21]; (iii) sonochemical synthesis (which uses a high-energy ultrasound to the reaction mixture) [22]; (iv) mechanochemical method (which employs mechanical energy in a chemical reaction) [22]; and (v) solvo/hydrothermal synthesis (which is a commonly known method to prepare MOFs via conventional electric heating in a reactor) [21,22]. It was seen that the quality of the crystals obtained by the solvothermal method is similar to those produced by the regular microwave-assisted method [21]. MOFs have been extensively studied for various applications such as heterogeneous catalysis, drug delivery, gas sensing, separation, and storage [23-36]. This is because of their ultra-high surface area, porosity, and tunable functionality [28-32]. Therefore, $\text{TiO}_2/\text{Cu-MOF}$ composite sol-gel possesses synergetic properties of both TiO_2 and Cu-MOF materials, resulting in a better photovoltaic device. Lee et al. [25] demonstrated the use of a Cu-based MOF decorated with TiO_2 sol-gel ($\text{TiO}_2\text{-Cu-MOF}$ composite) which achieved the highest PCE of 0.26%. They also showed that the increased power conversion efficiency of $\text{TiO}_2/\text{Cu-MOF}$ was 0.46% with the addition of carbon nanotubes (CNTs). In another study, the $\text{TiO}_2/\text{Ru-MOF}$ composite exhibited a power conversion efficiency of 1.22% [26]. Moloto et al. [27] reported that $\text{TiO}_2\text{-Zn-MOF}$ with current-potential curves and photocurrent density of 1.01 mA cm^{-2} as well as photo-efficiency of 0.67%. It is noteworthy to investigate the feasibility of Cu-based MOF on a TiO_2 surface in a solar cell. Previous studies demonstrated the thin film of ruthenium-based MOFs is synthesized using a layer-by-layer technique in a TiO_2 -based

liquid junction solar cell [26]. Herein, we report on the synthesis of a TiO₂-Cu-MOF composite prepared using the sol-gel method and used for the first time as a photoanode which demonstrated an enhanced efficiency when fabricated into a photovoltaic device. The weight percentage of the MOF loading was 10 wt. % of the titanium precursor. The interaction between TiO₂ sol-gel and Cu-MOF was confirmed through X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential thermal analysis (DTA), Raman spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) method. It was discovered that the overall optical absorption was improved using TiO₂-MOF composites. Furthermore, the effects of combining Cu-MOF and TiO₂ sol-gel on photovoltaic performance were investigated via photocurrent response density measurements and electrochemical impedance spectroscopy (EIS). The fabricated solar cells achieved a maximum PCE of 0.722%, which was due to the synergistic effects of increased photocurrent density, faster electron transport, and reduced charge recombination.

4.2. EXPERIMENTAL SECTION

4.2.1. Materials

Copper nitrate trihydrate (CuH₆N₂O₉) (≥ 99% unadulterated), titanium (IV) tetraisopropoxide (TTIP) (≥ 99% unadulterated), trimesic acid (H₃BTC, ≥ 98%), sodium hydroxide (NaOH), acetic acid (glacial), 1-methyl-2-pyrrolidinone, nickel foam substrate, 0.5 mol L⁻¹ lithium iodide, copper nitrate, and chloroplatinic acid hydrate (H₂PtCl₆) were purchased from Sigma Aldrich, South Africa. Acetonitrile, dimethylformamide (DMF),

ethylene glycol, 2-propanol, and 1-octanol were purchased from Merck, South Africa. The parafilm plastic film was obtained from Bemis, South Africa. Acetic acid, acetyl acetate, ethanol (EtOH), and methanol were purchased from Rochelle Chemicals, South Africa.

4.2.2. Synthesis of TiO₂/MOF composite

A copper-based MOF was synthesized by following the reported hydrothermal procedure of Ramohlola *et al.* [32]. Concisely, 4.5 mmol of Cu (NO₃)₂·3H₂O in hot distilled water was mixed with 2.5 mmol of H₃BTC (1, 3, 5 tricarboxylic acid benzene/trimesic acid) in hot ethanol. The subsequent mixture was placed in an autoclave and then subjected to a heating treatment for 36 hrs in an oven at 120 °C. The TiO₂ and TiO₂-MOF composite were prepared using a sol-gel synthetic procedure [15, 17, 27] with some modifications. Titanium isopropoxide (TTIP) was stabilized using glacial acetic acid and subjected to hydrolysis with deionized water. The titanium solution was stirred vigorously for 1 hr. In the case of TiO₂-MOF composite, about 10 wt.% of MOF to TIP was added to the titanium sol and the mixture was stirred for 2 hrs and adjusted to pH 5 using a 25% ammonia solution to initiate the condensation process. The solution was then left for 24 hrs at 50 °C and after cooling, the solution was filtered and dried at room temperature for 24 hrs to yield 8.54 g of the desired product.

4.2.3. Electrode preparation

The photovoltaic cells were fabricated according to literature methods [38] with minor modifications. The Ni foam as the substrate was cut into 1 cm × 1 cm dimensions and pasted with a slurry prepared from the photoanode materials (i.e., TiO₂, MOF, and TiO₂-MOF composite). The slurry was prepared by mixing and grinding 1.00 g of TiO₂, MOF, or TiO₂-MOF composite with 0.0005 g of polyvinylidene fluoride (PVDF) and 0.30 mL of

1-methyl-2-pyrrolidinone (NMP) in a quartz pestle and mortar [39]. The electrochemical evaluation (CV, EIS, and CA) of the prepared electrodes was done in a three-electrode cell configuration (0.1 M Na₂SO₄ as electrolyte) using the Biologic instrument (VMP300, EC-lab software) in a temperature-controlled environment at 25 °C. The photocurrent density (I–V curves) was measured at a potential range of 0.3–1.0 V under light conditions at a scan rate of 0.10 Vs⁻¹ using a solar simulator equipped with a halogen lamp (potential=12 V, power=20 W, power density=64 mW m⁻², Germany, to determine the photocurrent response of the photoanode materials). The EIS was performed at a frequency range from 0.1 Hz to 100 kHz with an open circuit potential (the Z-fit tool was used for EIS data fitting analysis), and CA analysis was measured at a current density of 2.0 A g⁻¹.

4.2.4. Characterization Technique

Electronic absorption spectra of the materials were documented using a wavelength range of 300 nm to 900 nm over a single front lens at moderate temperatures of around 25 °C utilizing a UV-vis spectrophotometer under ethanol. Structural studies of TiO₂-MOF composite and its precursors were carried out using XRD, Phillips 1830 fitted out with a fine focus lens with a wavelength (λ) peak position of 1.54 angstrom, for both qualitative and quantitative analysis. The crystallography information files (CIF) of TiO₂ and MOF were used in order to plot the XRD simulated pattern. The CIF files were introduced to MAUD software and the powder diffraction analyses were taken. An Agilent Cary 600 Series FTIR spectrometer was used for the identification of functional groups to validate the synthesized TiO₂, MOF, and TiO₂-MOF composite. The FTIR spectra were obtained at room temperature in the wavenumber range between 400 and 4000 cm⁻¹. The surface

morphology was studied using scanning electron microscopy (SEM on an FEI Nova 600 instrument) performed at 30 kV. To avoid charging the samples, all the samples were carbon-taped and attached onto aluminum and gold/palladium. A Raman analysis (micro-Raman mod; Jobin-Yvon T64000, wavelength = 532 nm) was done at a focal plane of 1.5 μm in diameter. The BET surface area and pore diameter of the synthesized materials were determined using Micromeritics Tristar 300, outgassing the samples at 150 °C for 4 hrs, and gas sorption using liquid nitrogen (-195 °C). The thermal stability of the materials was conducted using a TGA (Perkin Elmer 6000). Prior to the analysis, the sample (10 mg) was heated in an alumina cup at a temperature starting from a range of 35 °C up to a maximum of 800 °C at a constant heating rate of 10° C min⁻¹.

4.3. RESULTS AND DISCUSSIONS

4.3.1. Structural characterization

Figure 4.1 shows the XRD patterns for TiO₂, MOF, and TiO₂-MOF composite. The patterns in Figure 4.1(a) for TiO₂ show the diffraction peaks at $2\theta = 25.0^\circ$, 38.3° , 48.0° , 54.0° , and 62.0° , as an indication of the presence of the anatase TiO₂ phases for the hkl indexes of (101), (004), (200), (105) and (204) corresponding to the simulated pattern (JCPDS no: 21-1272), respectively. The findings are similar to the work reported by Alwin *et al.* [17] and Devi *et al.* [40]. It means that the TiO₂ particles are favorably crystallized in the anatase phase. It was seen that the broad diffraction peaks are owing to the nanosized anatase crystals from the TiO₂ sol-gel network [17]. This was supported by the crystallite size of 16.12 nm for TiO₂ material calculated using the Debye–Scherrer formula from (101) plane using Equation 4.1 [36, 37].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4.1)$$

where β represents the full-width at half-maximum (FWHM) measured in radians, λ for the X-ray wavelength of Cu-K α radiation, which is 1.5406 Å, and θ stands for the Bragg's angle. In addition, the calculated d-spacing ($2d \sin \theta = n\lambda$) for 101 hkl value was 3.48 Å for TiO₂.

It is noticeable that MOF has an octahedral crystal structure similar to the simulated one from crystal structure information data (CSID) (Figure 4.1(b)). This shows that the structural phases of MOF known as HKUST-1 were well-maintained with high purity [28-32]. Furthermore, MOF showed well-defined sharp peaks as an indication of a highly crystalline compound [33-35]. The intense patterns were indexed at $2\theta = 6.9, 9.2, 11.50, 13.27$ and 18.85° for (200), (220), (222), (400) and (440) planes [33-35], respectively. It was seen at lower 2θ that the intense peaks were characteristics of a microporous material, which had several tiny pores or cavities [28-35]. This was also supported by the crystallite size of 99.76 nm for MOF material calculated using the Debye–Scherrer formula from (222) plane and d-spacing of 7.69 Å. On the other hand, the diffraction peaks emanating from the TiO₂ spectrum were noticed in the TiO₂-MOF composite as shown in Figure 1(c) by a simulated TiO₂ pattern. The TiO₂MOF composite phases were shown by the most crystalline peak at $2\theta = 25.0^\circ$ for the 101 hkl index of the TiO₂ phase [17]. Moreover, the peaks originated from MOF in the pattern of TiO₂-MOF composite (Figure 4.1(d)) were also simulated and indexed at $2\theta = 6.9, 9.2, 11.62,$ and 13.27° for (200), (220), (222), and (400) [33-35]. It was seen that the MOF has not affected the anatase phase formation of TiO₂ crystals during synthesis [15, 17]. The crystallite size of the TiO₂-

MOF composite was found to be 123.41 nm with a d-spacing of 3.52 Å, which is consistent with the reported TiO₂ sol-gel composites [17, 27]. The amount of MOF crystallinity in the TiO₂-MOF composite was estimated from its phase intensity by applying Vegard's law and found to be 9.031wt. %.

In XRD, the lattice strain ($\epsilon = \beta \cos \theta / 4$) and dislocation density ($\rho = 1/D^2$) of the TiO₂, MOF, and TiO₂-MOF composite can be determined from full-width at half-maximum, and crystallite size. The lattice strain in TiO₂, MOF, and TiO₂-MOF composite was found to be 21.5×10^{-4} , 3.47×10^{-4} , and 2.81×10^{-4} , respectively. This indicates a reduction of lattice strain upon composite formation. The ρ values were estimated to be 38.46×10^{14} lines m⁻² for TiO₂ and with a reduction dislocation density of 0.6646×10^{14} lines m⁻² for composite and 1.0146×10^{14} lines m⁻² for MOF. The lower ρ value of TiO₂-MOF indicates that the composite has a high degree of crystallinity as compared to TiO₂ due to the presence of MOF as an indication of a suitable material for photovoltaic solar cells

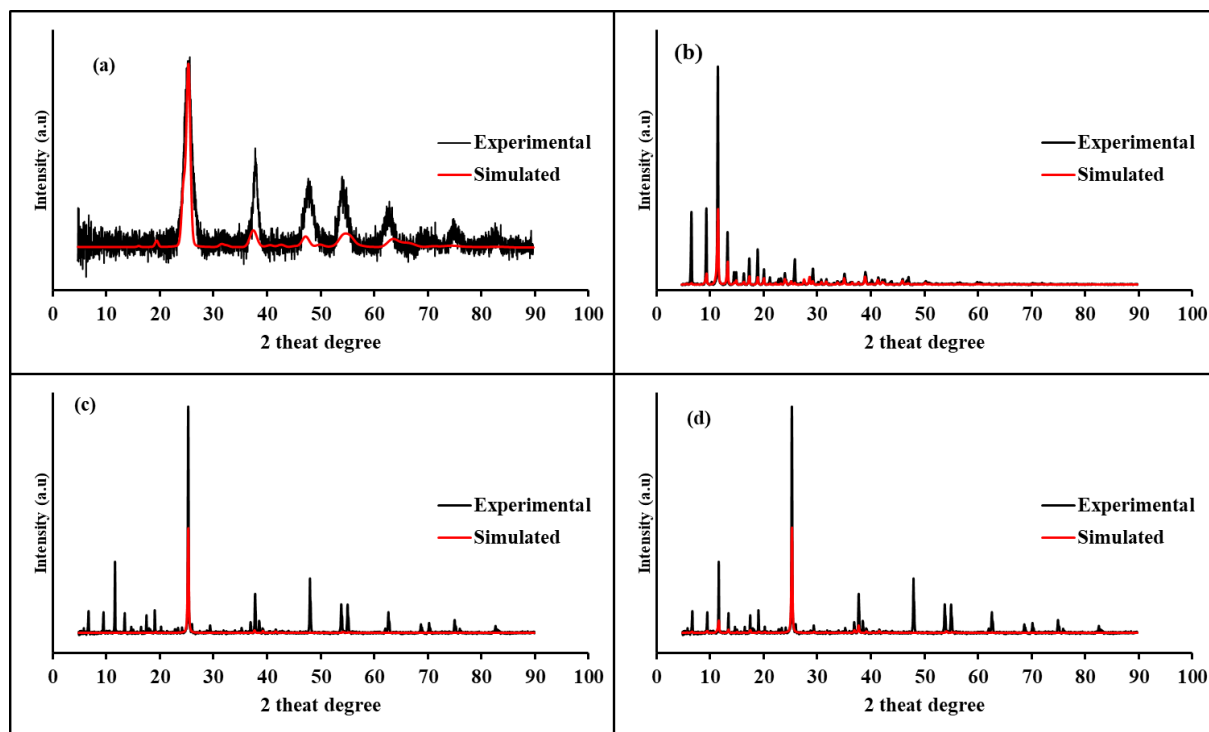


Figure 4.1: Experimental and simulated XRD patterns for (a) TiO_2 and (b) MOF. XRD patterns of TiO_2 -MOF experimental and simulated with TiO_2 (c) and MOF (d) patterns.

The BET results for surface area and porous structure obtained from nitrogen adsorption measurements were evaluated at 77 K are listed in Table 4.1 and given in Figure 4.2(a). The specific surface area of the TiO_2 -MOF composite was found to be $111.10 \text{ m}^2 \text{ g}^{-1}$, which was lower than the one of TiO_2 ($262.90 \text{ m}^2 \text{ g}^{-1}$) and MOF ($464.76 \text{ m}^2 \text{ g}^{-1}$). The addition of 10% MOF has a substantial change in the surface area of the composite due to the formation of agglomerates [34, 35] and MOF occupying the pores of the TiO_2 network [17]. It was demonstrated that the MOF clusters may be attached to the surface of the sol-gel network and either increase the surface area or be left unchanged depending on the surface area of the MOF [17]. However, the pore width in the composite was observed to be a bit higher as compared to TiO_2 due to the introduction of MOF. The

surface area and pore width observed in the TiO₂-MOF composite indicates that the composite can have an influence on a carrier transport in solar cells.

Figure 4.2(b) shows the FTIR spectra for TiO₂, MOF, and TiO₂-MOF composite. In the spectrum of TiO₂, the characteristic anatase TiO₂ is confirmed by the peaks at 627 cm⁻¹ and 1404 cm⁻¹, which are ascribed to the Ti-O stretching vibration and Ti-O-Ti stretching vibrations, respectively. The FTIR spectrum of MOF shows two small peaks at 731 and 761 cm⁻¹ that corresponds to in-plane and out-of-plane C-H bending modes on the benzene ring in MOF [28-30]. The strong peak at 1371 cm⁻¹ is due to the vibrational mode of the R-C-O stretch of Cu-MOF [33]. The peaks at 1489 and 1550 cm⁻¹ are assigned to the symmetry and asymmetry vibrational modes of C=O of carboxylate groups in both MOF and composite [34, 35]. The peak at 1645 cm⁻¹ attributed to the C=C vibrational of the benzene ring in MOF was observed [31, 32]. After the formation of the TiO₂-MOF composite, a broad peak in the region of 400 - 1000 cm⁻¹ is due to the vibrational mode of the Ti-O stretching bond [40]. The weak peaks at 2200 and 2400 cm⁻¹ are attributed to TiO₂ asymmetric in both TiO₂ and composite [40, 41]. The broad peaks in the region of 3000 and 3400 cm⁻¹ are assigned to the vibrational modes of Ti-OH of TiO₂ and OH that show the existence of hydrated Cu-MOF [41, 28]. Both TiO₂ and MOF vibrational modes were observed in the TiO₂-MOF composite spectrum as an indicative of composite formation. Figure 4.2 (c)-(f) shows the TGA and differential thermal analysis (DTA) for TiO₂, MOF, and TiO₂-MOF composite. In Figure 2(c), the TGA curve of TiO₂ shows one small degradation step that is due to the loss of moisture and this suggests the stability of TiO₂ while the DTA curve shows one small exothermic peak of TiO₂. This is in contrast with Zoccal *et al* [42], where they observed two degradation steps which are due to the

loss of water and pyrolysis. Figure 4.2 (d) shows the TGA curve with the two main degradation steps of MOF. The first degradation step corresponds to the loss of water and ethanol, and the second degradation step corresponds to the loss of organic linker and the product remains with CuO. The DTA curve in Figure 4.2(d) agrees with the TGA and shows the two main exothermic peaks [32]. Figure 4.2(e) shows two small degradation steps, which correspond to the loss of water and organic linker of MOF in the composite. This indicates the presence of MOF in the TiO₂-MOF composite. In addition, the DTA curve in Figure 4.2(e) shows the two small exothermic peaks. Therefore, the TGA curves in Figure 4.2(f) suggest the improvement in the thermal stability of the TiO₂-MOF composite as compared to MOF.

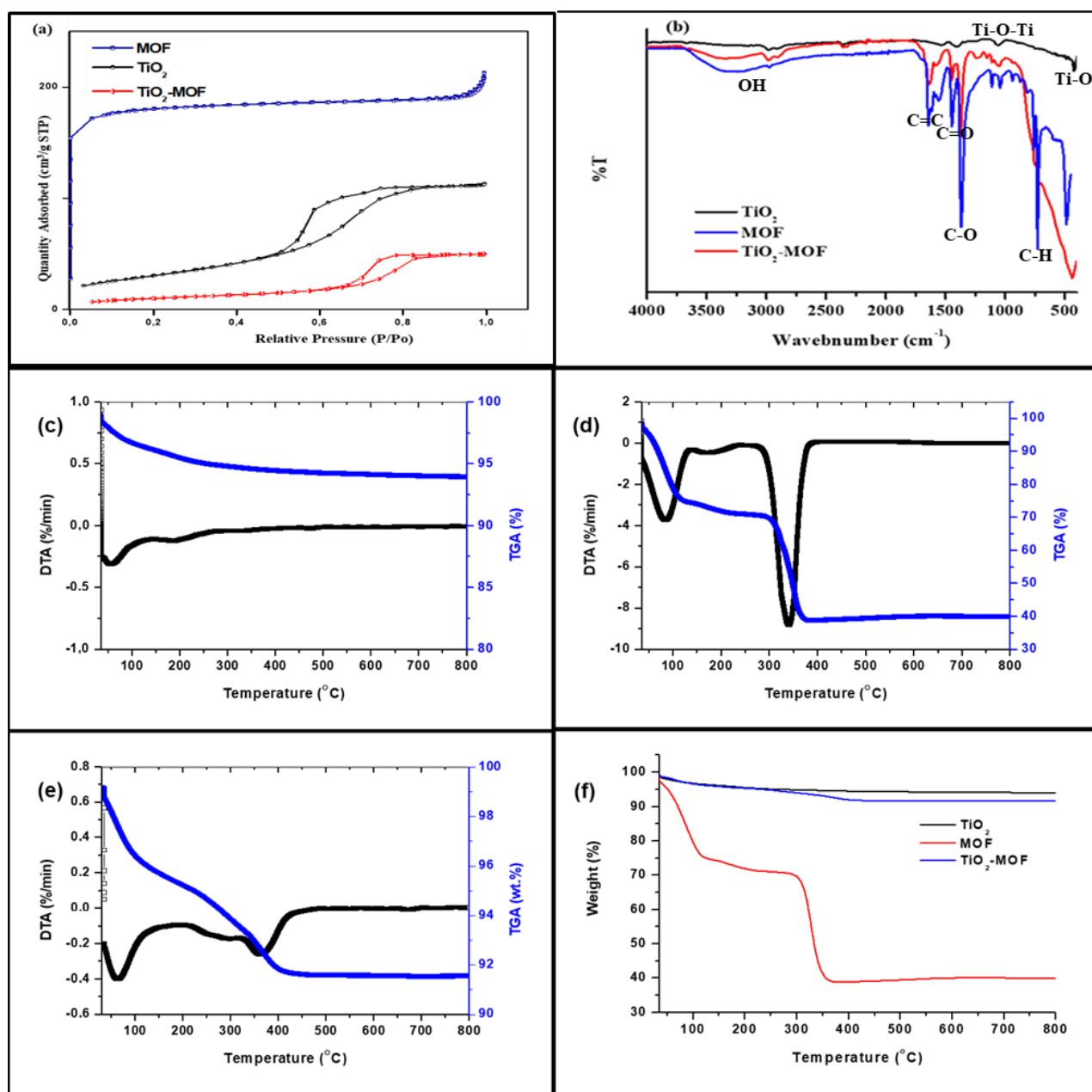


Figure 4.2: (a) BET plots and (b) FTIR of TiO₂, MOF, and TiO₂-MOF composite; (c) DTA-TGA curves of TiO₂; (d) DTA-TGA curves of MOF; (e) DTA-TGA curves of TiO₂-MOF; and (f) TGA of TiO₂, MOF and TiO₂-MOF composite.

This was further confirmed by Raman's analysis of the TiO₂-MOF composite as represented in Figure 4.3 which shows the Raman images (a and d) and spectra (c) of

the TiO₂-MOF composite. The strong vibrational mode in the composite around 140 cm⁻¹ is assigned to the symmetric stretching vibration of a single crystal (E_g) for O-Ti-O in TiO₂ [41]. Three weak vibration modes at a wavenumber of 399 cm⁻¹ (B_{1g}), 513 cm⁻¹(A_{1g}), and 639 cm⁻¹ (E_g) are caused by the antisymmetric bending vibration of O-Ti-O [40, 41]. The vibrational modes at 193- 172 cm⁻¹ for MOF in the composite were observed due to the presence of Cu-O and Cu-Cu stretching modes [43] The vibrational mode in the region of 790-810 cm⁻¹ for composites is attributed to the C-H of the aromatic ring stretching mode of the MOF component [32]. Furthermore, the 1450-1510 cm⁻¹ region in the composite shows the presence of C=O attached to the aromatic ring in MOF [32].

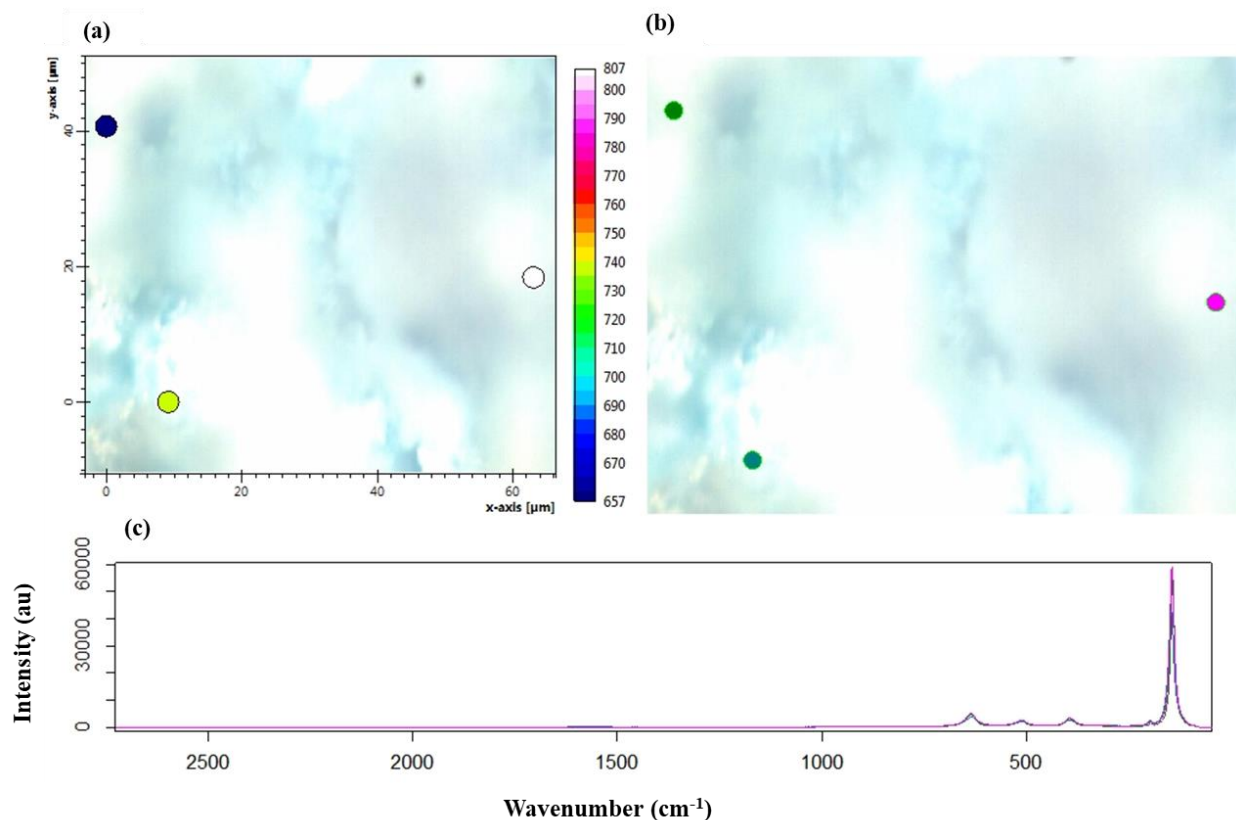


Figure 4.3: Raman images (a) and (b) and spectra (c) of TiO₂/MOF composite.

Figure 4.4(a) shows a pure TiO_2 smooth granule shape [40]. As shown in Figure 4.4(b), MOF displays usual irregular crystals which possess octahedral shapes with smooth surfaces [28]. The intervention of TiO_2 and MOF is shown in Figure 4.4(c), which shows uniformly arranged particles with an irregularly shaped aggregate on the surface. The particles are well interconnected with each other and form a continuous network structure. The appearance was similar to the TiO_2 -Zn-MOF reported by Alwin *et al.* [17]. It is noteworthy to indicate that the network structure of the TiO_2 -MOF composite is highly porous and the porous morphology is visible from the SEM image (Figure 4.4(c)). It is also well-known from the image that the microporous MOF clusters are attached to the surface of the TiO_2 network [17].

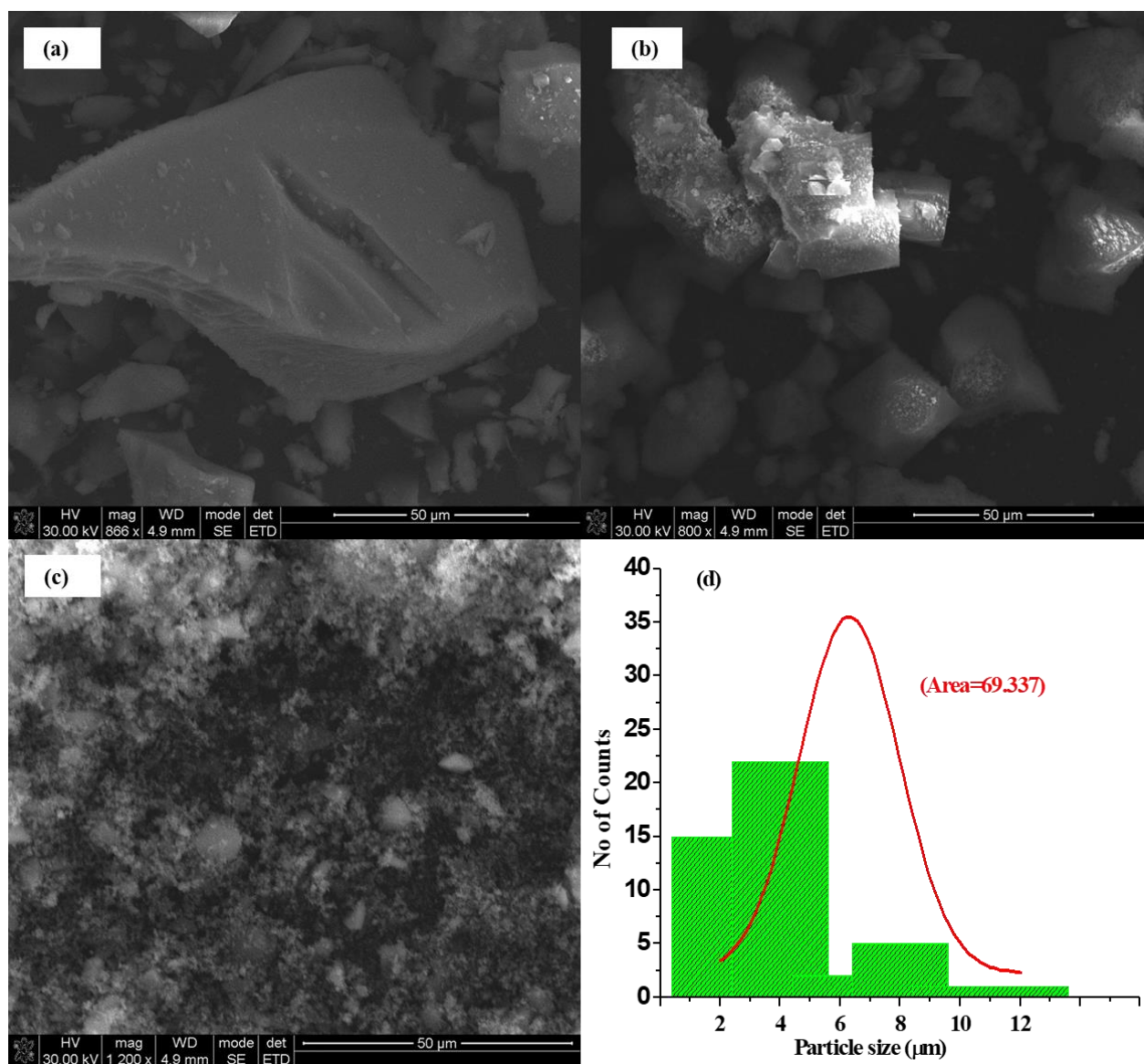


Figure 4.4: SEM images of (a) TiO₂, (b) MOF, and (c) TiO₂/MOF; and (d) particle size distribution of TiO₂/MOF.

In addition, it was seen that the continuous arrangement of the pore-solid network was also evident from the SEM image with major particle sizes ranging between 4-6 μm (Figure 4.4(d)). The fitted surface area from particle size distribution was found to be 69.337 m² g⁻¹ which was supported by the BET analysis above.

Table 4.1: BET parameters, optical and electrochemical properties of TiO₂, MOF and TiO₂/MOF nanocomposite.

Material	BET	Pore width	Optical	E _{1/2} ^{ox}	E _{1/2} ^{red}	E _{HOMO}	E _{LUMO}
	Surface	(nm)	Bandgap	(V)	(V)	(eV)	(eV)
	area (m ² g ⁻¹)		(eV) ^a				
Ni foam	-	-	-	0.40	0.35	-5.1	-4.35
TiO ₂	262.90	2.66	3.15	0.41	0.33	-5.08	-4.34
MOF	464.76	2.56	2.96	0.63	0.50	-5.25	-4.12
TiO ₂ -MOF	111.10	3.40	2.63	0.47	0.24	-4.99	-4.28

a= optical bandgap using direct allowed transition

4.3.2. Optical characterization

The UV-visible spectra of TiO₂, MOF, and TiO₂-MOF composite are presented in Figure 4.5(a). The TiO₂ shows an absorption maxima at 342 nm which corresponds to the d-d transition of TiO₂ [17]. The MOF has an absorption band at 357 nm, which is attributed to the ligand-to-metal charge transfer [43]. Remarkably, different metal ions and ligands in MOF have varied interactions and distinct optical absorption, which make them suitable photocatalysts [43, 44]. The introduction of MOF on the TiO₂ surface resulted in a redshift of the d-d transition of TiO₂ due to light-harvesting of MOF [44]. It was reported that the absorption of a photon with energy equal to or greater than the bandgap results in the excitation of an electron from the valence to the conduction band, leaving a hole in the valence band [45]. The generation of an electron-hole pair within the same molecule corresponds to the optical bandgap energy [45]. Based on the UV-vis spectra (Figure 4.5(a)), the optical bandgap energies were determined using the Tauc plot by Equation 4.2 [36, 37, 38]:

$$\alpha h\nu(\nu) = \beta(h\nu - E_g)^n \quad (4.2)$$

The absorptivity coefficient is represented as α ; frequency of light as ν ; and β for the bandgap tailing parameter. The plank constant and optical band gap energy is represented as h and E_g , respectively. The n symbol in Equation 4.2 represents the transition probability index for direct and indirect allowed electronic transitions with n values of 1/2 and 2, respectively. The E_g values were presented in Figure 4.5(b, c) and (d) for direct and indirect allowed electronic transition of TiO₂, MOF, and TiO₂/MOF composite. The composite has been shown to have a small bandgap of 2.63 and 2.70 eV for direct and indirect allowed electronic transitions (Figure 4.5(d) and Table 4.1). The smaller bandgap energy of TiO₂/MOF material indicates that there are some new electronic states between the valence and conduction bands of TiO₂ [17]. It was also

shown the smaller bandgap increases the photoactivity of the material in a wider range of solar spectrum which is favorable to achieving better performance in a photovoltaic cell.

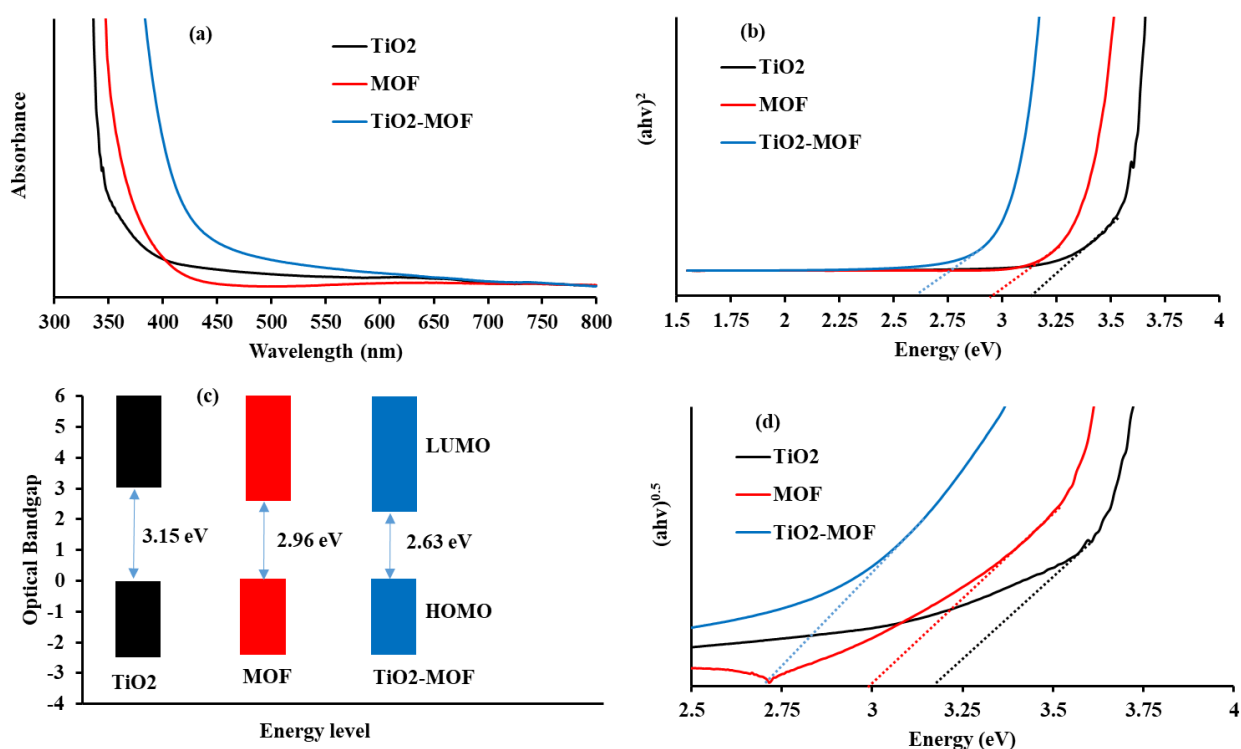


Figure 4.5: (a) UV-vis spectra of TiO₂, MOF and TiO₂/MOF nanocomposite; and (b) their respective optical energy band gap using the (c) direct and (d) indirect allowed electronic transitions.

4.3.3. Electrochemical characterization

It is well known that the electron injection into a neutral molecule (first reduction process) and electron extraction from a neutral molecule (first oxidation process) are electrochemically determined using CV [45]. Figure 4.6(a) shows the overlaid cyclic voltammograms of bare Ni foam (blank), TiO₂, MOF, and TiO₂-MOF composite. The potential for the first ring oxidation and reduction, $E_{1/2(ox)}$ and $E_{1/2(red)}$, respectively are

listed in Table 4.1. From these values, the highest occupied molecular orbital (E_{HOMO}) energy levels were calculated according to Data *et al.* [46] using Equation 3:

$$E_{\text{HOMO}} = -(E_{1/2(\text{red})} + 4.75) \text{ eV} \quad (4.3)$$

The E_{HOMO} values were found to be -5.10, -5.08, -5.25, and -4.99 eV for bare Ni foam, TiO_2 , MOF, and TiO_2 -MOF nanocomposite, respectively. A significant lowering of E_{HOMO} was observed due to an increase in the electronic properties of the composite caused by the addition of MOF. On the other hand, the lowest unoccupied molecular orbital (E_{LUMO}) values are determined using Equation 4.4 [46,47]. In this work, the E_{LUMO} values were calculated using Equation 4 and found to be -4.35, -4.34, -4.12, and -4.28 eV for bare Ni foam, TiO_2 , MOF, and TiO_2 -MOF composite, respectively.

$$E_{\text{LUMO}} = -(-E_{1/2(\text{ox})} + 4.75) \text{ eV} \quad (4.4)$$

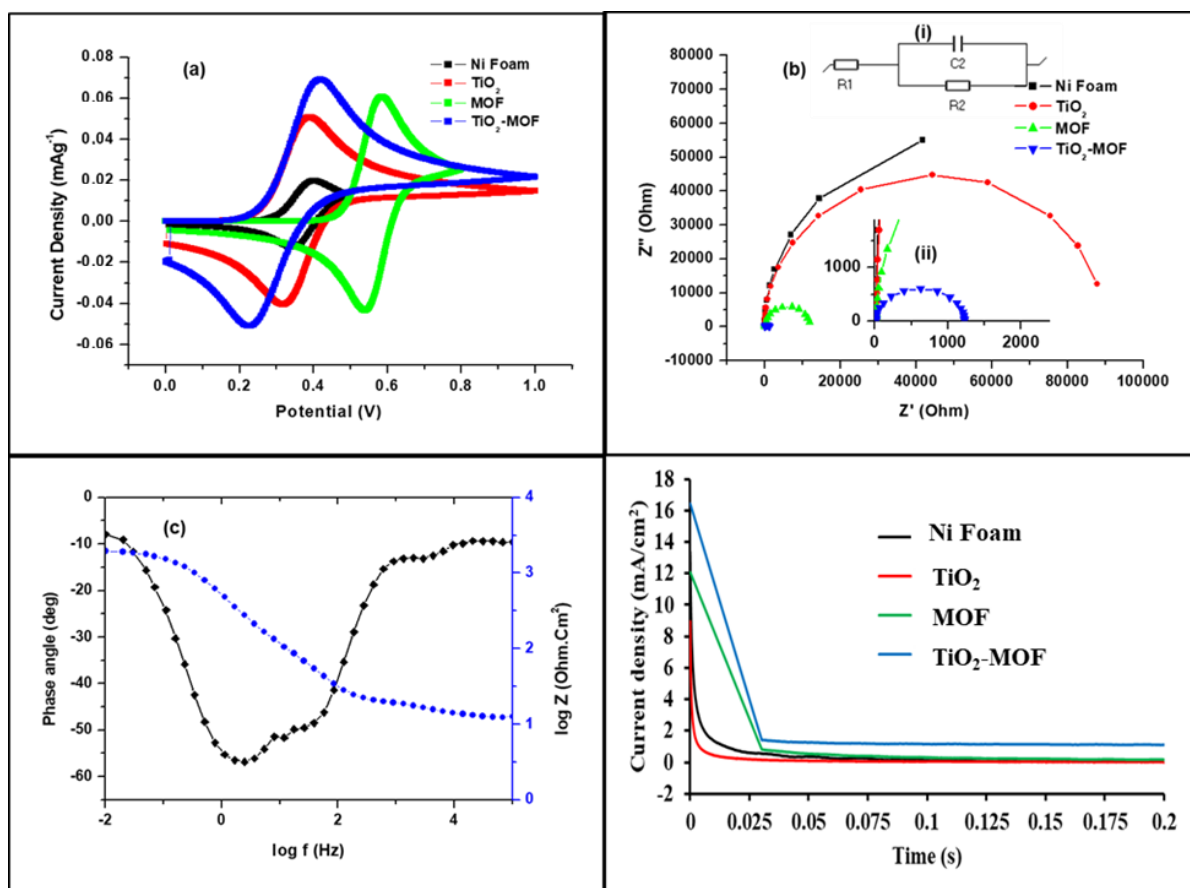


Figure 4.6: (a) Cyclic voltammograms (at scan rate 0.10 V s⁻¹) and (b) Nyquist plots, of bare Ni foam, TiO₂, MOF, and TiO₂-MOF composite (Inset: (i) equivalent circuit and (ii) enlargement area); (c) Bode plot of TiO₂-MOF composite; and (d) chronoamperometry curves of bare Ni foam, TiO₂, MOF and TiO₂-MOF, in 0.1M Na₂SO₄ electrolyte.

The EIS is usually used to examine the dynamics of electron transport and recombination across interfaces [33]. Figure 4.6(b) shows the Nyquist plots of the bare Ni foam, TiO₂, MOF, and TiO₂-MOF composite, the experimental data were fitted using the Z-fit software according to the electrical equivalent circuit. It comprises Voigt RC elements, involving a solution/electrolyte resistance (Rs denoted as R1), charge-transfer resistance (Rct denoted as R2), and constant phase elements (CPE or Q denoted as C2) as shown by inset (i) in Figure 4.6(b). The diameter of the semicircle

from the Nyquist curve provides information about the R_{ct} . As seen in Figure 4.6(b), the semicircle of TiO_2 -MOF composite (inset (ii)) is smaller than the one of TiO_2 material, which suggests the reason for enhanced electrochemical properties caused by MOF. The values of the fitted EIS parameters are summarized in Table 4.2. The R_s value decreased with the introduction of MOF content as compared to TiO_2 material from 23.32 Ω to 15.3 Ω in the composite. This indicates that the composite provides better contact with the Ni foam substrate which results in improved electronic performance than pristine TiO_2 [17]. The total ionic conductivity (δ) is estimated from the charge-transfer resistance (R_{ct}) using the thickness (t) and the cross-sectional area (A) by the following relation in Equation 4.5.

$$\delta = t/(R_{ct} A) \quad (4.5)$$

The total ionic conductivity of Ni foam, TiO_2 , MOF, and TiO_2 -MOF nanocomposite was found to be 0.9, 1.1, 8.4, and 82.6 $\mu S/cm$, respectively. The lower value of ionic conductivity observed in bare Ni foam and TiO_2 was due to high charge-transfer resistance, because it limits the total ionic conductivity in the materials. It was seen that the introduction of MOF increased the ionic conductivity. The comparison of the results obtained in this work with the previous reports in the literature is presented in Table 2, which shows that the ionic conductivity obtained in this work is in good agreement with the values reported previously [33]. In addition, a logarithmic of impedance and phase angle are both plotted as a function of logarithmic frequency to give a Bode plot. The phase angle vs log frequency curve of the TiO_2 -MOF composite (Figure 4.6(c)) shows a broad peak and the peak height is proportional to the charge-transfer resistance response. The lower charge-transfer resistance values occurring at the higher frequency indicate that the TiO_2 -MOF composite possesses a high ionic conductivity as observed in the Nyquist plot. The lifetime (τ) of the composite was

estimated from a maximum peak frequency ($f_{\max}$) of 57.5° using Equation 4.6 [48] and it was found to be 2.77 ms.

$$\tau = 1/(2\pi f_{\max}) \quad (4.6)$$

Furthermore, the chronoamperometric method was used to investigate the electrochemical stability of bare Ni foam, TiO₂, MOF, and TiO₂-MOF composite which involves measuring current as a function of time and controlling the voltage. The chronoamperometric current time response curves are presented in Figure 4.6(d). A well-defined chronoamperometric response was seen on the curve for all materials with a high current at the initial stage. A current drop in the chronoamperometry curve of 0.50 mA was observed at 0.025 s for Ni foam and a fast drop in TiO₂ of 0.21 mA. The current drops of 1.00 and 1.40 mA were observed at 0.3 s for MOF and TiO₂/MOF composite, respectively. It was seen that the introduction of MOF resulted in a high current density of 1.4 mA which denotes the stability of the electrode surface [10]. It was seen in this work that the tested current remained constant for such a long time to indicate the better stability of the composite.

Table 4.2: Fitted circuit parameters of EIS of Ni foam, TiO₂, MOF and TiO/MOF composite and calculate ionic conductivity

Material	Electrolyte	Rs (Ω)	CPE (μF)	Rct (kΩ)	Conductivity (μS/cm)
Ni foam	0.1 Na ₂ SO ₄	M 19.7	184	114	0.9

TiO₂	0.1	M	23.3	25.7	89.6	1.1
	Na ₂ SO ₄					
MOF	0.1	M	21.3	153	11.9	8.4
	Na ₂ SO ₄					
TiO₂-MOF	0.1	M	15.3	172	1.21	82.6
	Na ₂ SO ₄					

The photocurrent densities of the prepared Ni Foam, TiO₂, MOF, and TiO₂-MOF composite were obtained from the cathodic cyclic voltammetry scan conducted on the photoanodes in simulated light (64 mW m⁻² intensity), and the results are given in Figure 4.7(a). It was shown that Ni foam, TiO₂ and MOF materials possessed photocurrent densities of 0.02 (at 0.38V), 0.39 (at 0.31 V) and 0.19 (at 0.66 V) mA cm⁻². The low photocurrent is ascribed to the poor light absorption resulting from the compact nature of the nanoparticles at the material's surface, which caused poor charge separation and reduced photocatalytic efficiency [49]. The maximum photocurrent density of 0.46 mA cm⁻² at 0.44 V was obtained in TiO₂-MOF materials. The highest photocurrent density attained for the composite was well within the many photoresponses that have been reported for the material under illumination conditions [50-53]. Table 4.3 compares the maximum photocurrent attained by the Ni, TiO₂, MOF, and TiO₂-MOF materials in this work with other reported values in the literature. The enhanced photocurrent obtained for the TiO₂-MOF composite is largely related to the porous nature of the material's surface, which created a larger area and increased active sites for the electron transfer mechanism, thus enhancing the photocurrent. The power conversion efficiency (η) of the Ni foam, TiO₂, MOF, and TiO₂-MOF composites, was calculated using Equation 4.7 [27]:

$$\eta = ((E_{\text{rev}}^0 - E_{\text{mea}}) \times I) / P_{\text{in}} \quad (4.7)$$

where I (mA cm^{-2}) is the measured photocurrent density, E_{mea} is the electrode potential of the working electrode whose photocurrent was tested under irradiation, E_{rev}^0 is the standard state-reversible potential (1.43 V Ag/AgCl) of the working electrode, and P_{in} (mW cm^{-2}) is the input power of the simulated light intensity.

The η values estimated for the Ni foam, TiO_2 , MOF, and TiO_2 -MOF composites are given in Figure 4.7(b). The highest and lowest η values were 0.722 and 0.066 % for the TiO_2 -MOF composite and Ni foam, respectively. The conversion efficiencies of TiO_2 and MOF were 0.617 and 0.255%, respectively. The η values reported in Table 4.3 for TiO_2 -MOF composite are higher than those reported in the literature at 0.26% using $\text{TiO}_2/\text{Cu-MOF}$ [25], 0.67% using $\text{TiO}_2/\text{Zn-MOF}$ [27], and 0.46% for $\text{TiO}_2\text{-Cu-MOF/CNT}$ [25], whereas its efficiency value was less than that of 1.22% using $\text{TiO}_2\text{-Ru-MOF}$ [26]. However, the results are comparable showing that the Cu-based MOF has the potential to be used to improve TiO_2 properties. The overall power conversion efficiency of 0.722% and photocurrent density of 0.46 mA cm^{-2} for TiO_2 -MOF composite were attributed to the increase in the electronic properties of the composite material [17]. It is shown that Cu-BTC MOFs are the best candidates to be employed as stabilizing materials for TiO_2 photoanodes in solar cells. This is due to their simple synthetic route and environmental friendliness as compared to other MOFs. The heterojunction between TiO_2 and Cu-based MOF also improved the thermal stability of the MOFs as shown above. In addition, the TiO_2 -MOF composite showed higher performance as compared to zinc oxide doped with copper (Cu-ZnO) film [53] in the same electrolyte of 0.1 M Na_2SO_4 solution.

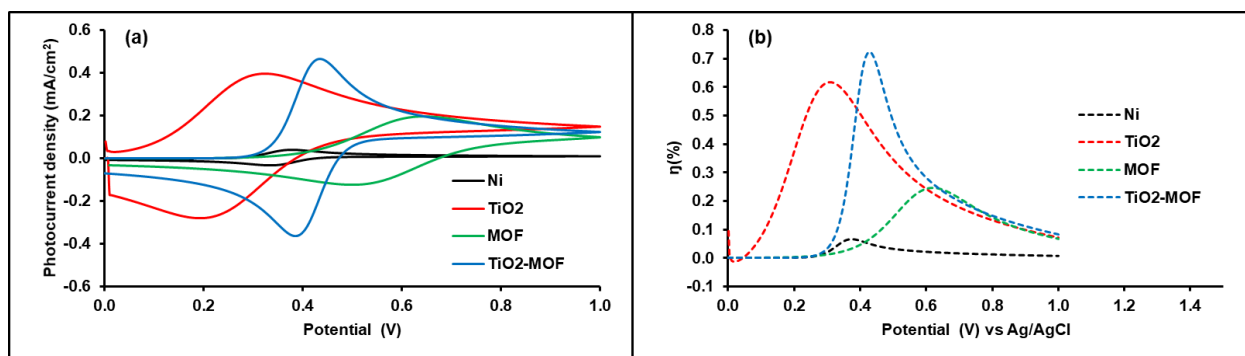


Figure 4.7: (a) Photocurrent response and (b) power conversion efficiency of Ni foam, TiO₂, MOF, and TiO₂-MOF composite.

Table 4.3: Comparison of the photocurrent density obtained for Ni foam, TiO₂, MOF, and TiO₂-MOF composites in this study with the literature values prepared using various methods.

Material	Electrolyte	Photocurrent (mA/cm ²)	Efficiency (%)	Ref
Ni foam	0.1 M Na ₂ SO ₄	0.02	0.066	In this work
TiO ₂	0.1 M Na ₂ SO ₄	0.39	0.617	In this work
MOF	0.1 M Na ₂ SO ₄	0.19	0.255	In this work
TiO ₂ -MOF	0.1 M Na ₂ SO ₄	0.46	0.722	In this work
TiO ₂ -Cu-MOF	I ₃ /I ⁻ redox	-	0.26	[25]
TiO ₂ -Cu-MOF/CNT	I ₃ /I ⁻ redox	-	0.46	[25]

TiO₂-Ru-MOF	I ₃ /I ⁻ redox	-	1.22	[26]
TiO₂-Zn-MOF	ACN, LiI, I ₂ & LiClO ₄	1.04	0.67	[27]
Cu-ZnO	0.1 M Na ₂ SO ₄	-	0.062%	[53]

4.4. CONCLUSION

A new class of TiO₂/Cu-based MOF composite was prepared by the sol-gel method and confirmed by XRD, FTIR, Raman, SEM, and BET. The synthesized materials were employed as photoanode materials for photovoltaic solar cells. The XRD pattern of the materials confirmed the phase of the pure MOF and TiO₂ in the TiO₂-MOF composite. Raman and FTIR spectra revealed the vibrations of benzene rings of MOF and Ti-O stretches, further confirming the high purity of the nanocomposite produced. It was found that the thermogravimetric analysis showed an improvement in the thermal stability of the composite. The optical band gap values ranged between 3.15 and 2.63 eV from UV-Vis; and the HOMO-LUMO values using CV were estimated for the TiO₂, MOF, and TiO₂-MOF composites. On the other hand, the EIS showed that the TiO₂-MOF composite possessed high conductivity. These parameters make TiO₂-MOF composite a suitable candidate for photovoltaic solar cell applications. A maximum photocurrent and power efficiency of 0.46 mA cm⁻² and 0.722% were recorded for the TiO₂-MOF composite under a simulated light source, respectively. The TiO₂-MOF composite was more porous compared to the other films, as revealed by SEM studies, allowing for easier charge separation of photogenerated charge carriers and leading to the improved photocurrent observed. Notwithstanding, the sol-gel method for preparing TiO₂-MOF composite used in this study showed promising photocurrent

response and could also be employed for making TiO₂-MOF composite for photovoltaic applications.

Acknowledgements

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CHAPTER 5
EFFECTS OF PHTHALOCYANINE DYE ON TITANIUM DIOXIDE-METAL
ORGANIC FRAMEWORK COMPOSITE FOR THE FABRICATION OF DYE-
SENSITIZED SOLAR CELLS

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ABSTRACT

In order to enhance the photovoltaic performance of dye-sensitized solar cells (DSSCs), titanium oxide based metal-organic frameworks (TiO₂-MOFs) composite and copper phthalocyanine (CuPc) molecules were prepared and used as an efficient material and sensitizing dye, respectively. The structural and morphological studies of the prepared CuPc dye and TiO₂-MOF/CuPc were characterized using various analytical techniques. The optical studies revealed the absorption of CuPc by the TiO₂-MOF composite. Raman and Fourier transform infrared spectroscopies showed the presence of the N-Cu-N and O-Cu-O vibrational modes in CuPc and MOF, as well as the symmetrical and antisymmetric vibration modes of O-Ti-O of TiO₂ in TiO₂-MOF/CuPc. The scanning electron microscopy images of the final TiO₂-MOF/CuPc showed the rod-like structure of CuPc, the agglomerated structure of TiO₂ upon the introduction of MOF, and the octahedral structure of MOF. The Tauc plot of TiO₂-MOF/CuPc showed a bandgap of 2.7 eV followed by interrogation of its electrochemical properties using electrochemical methods. It was seen that the TiO₂-MOF/CuPc composite achieved a maximum power conversion efficiency of 1.63 % owing to the synergistic effects of increased photocurrent density, faster electron transport, and reduced charge recombination.

Keywords: dye-sensitized solar cells, copper phthalocyanine, metal-organic frameworks, titanium dioxide, photovoltaics.

5.1. INTRODUCTION

Rapid growth of the world's population leads to greater energy consumption, resulting in a need for new and effective methods for energy production from renewable energy resources [1-4]. Contrarily, sources of energy are being used up rapidly to supply energy to the world. Organisations such as the Energy Information Administration, the International Energy Agency, and the European Environmental Agency, revealed that from 2001–2017, oil and coal have been the rapidly growing sources of energy in the whole world [5 –7]. Dealing with the above concern, several technologies are being employed to find ways of producing energy through the use of renewable energy resources [8 – 9].

Solar cells have gained great attention for the potential production of renewable energy. Their operation uses the photovoltaic (PV) technology which involves the conversion of light energy (photons) into electric energy by making use of light-sensitive semiconductor materials that are capable of ejecting photo-excited electrons at a certain frequency [10]. Amongst the semiconductor materials, TiO_2 has been identified as a suitable material owing to its high thermal and chemical stabilities, low cost, and corrosion resistance [11–2]. However, TiO_2 has the problem of requiring high energy light for it to produce photocurrent or it needs to be coated with expensive dyes for it to function efficiently [11]. Over the years, researchers have been improving the PV performance of SC by using photosensitive materials such as dyes [10-12]. In a dye-sensitized solar cell (DSSC) a photosensitive material which is effective in cloudy weather conditions adsorbs on the surface of the semiconducting material to reduce the band gap. [12-14]. Often, suitable secondary organic materials for incorporation into the semiconductors are metal organic frameworks (MOFs) [15-22]. MOFs were found to be light-sensitive materials [16–17]. MOFs are spongy-like

materials composed of organic linkers and metal clusters. They possess high surface areas and also have tunable properties for different applications [18]. MOFs are photosensitive materials, and there are various straightforward procedures that can be used in their synthesis. Nevertheless, MOFs were found to have steady electron transport when employed in the photovoltaics [19]. According to recent research, there are several synthesised MOFs that absorb light in the visible region, and the organic linkers are responsible for light capturing in the solar cells [20]. The technique of coating TiO_2 with MOF through enhancement of the solar cell showed an energy conversion efficiency of around 4.5%, hence increasing the power output of the PVs [21]. Consequently, the findings for coating MOF can also be used as a sensitizer on the surface of TiO_2 as reported by Young Ahn *et al.* [22], giving a maximum energy conversion efficiency of 2.1 %, which surpasses that of MOF alone.

On the other hand, some studies show that the introduction of metal phthalocyanines (MPcs) with the TiO_2 material as the dyes due to their chemical stability, and they strongly absorb in the blue to green area of spectra [23–25]. MPcs are used as the functionalizing medium in fields such as hydrogen production [23], corrosion [24], nonlinear optics [25], energy [26] and gas sensing [27]. Recent studies of copper phthalocyanine (CuPc) as an organometallic dye in TiO_2 composites show that it can delay electron recombination of photo-excited electrons [28]. CuPc can help to lower the band gap of the composite by absorption of energy package of light in the visible radiation [28]. For example, Mekprasart *et al.* [1] synthesized TiO_2 composite with 0.05 wt .% CuPc through homogenization and ball milling process and their composite showed the energy conversion efficiency of 1.24 %. The composite of TiO_2/CuPc was also studied for more than a decade, and reports show more

desirable photocatalytic features resulting in enhanced energy effectiveness of DSSCs [1, 15, 28].

Hence, in this study we report on the synthesis of novel TiO₂-MOF/CuPc consisting of TiO₂, MOF, and CuPc used as a photo-anode, which demonstrates an improved photovoltaic efficiency. The amount of the MOF loading was 10 weight % of the titanium precursor and CuPc dye was loaded via adsorption technology. The effects of CuPc dye on the photovoltaic performance were carried out through current response density measurements using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The overall power conversion efficiency (PCE) of 1.63% as well as photocurrent density of 1.80 mA cm⁻² were achieved by the TiO₂-MOF/CuPc composite as an indication of a promising material in DSSC applications.

5.2. EXPERIMENTAL SECTION

5.2.1. Materials

Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) (≥99% unadulterated), titanium (IV) tetraisopropoxide (TTIP) (≥ 99% unadulterated), trimesic acid (H₃BTC, ≥ 98 %), sodium hydroxide (NaOH), acetic acid (glacial), 1-methyl-2-pyrrolidinone, polyvinylidene fluoride (PVDF) nickel foam substrates, sulphuric acid and sodium sulphate (Na₂SO₄) were purchased from Sigma Aldrich, South Africa. Acetonitrile, dimethyl formamide (DMF), phthalimide, excess urea, ammonium molybdate and nitrobenzene were purchase from Merck, South Africa. Parafilm plastic film was from Bemis, South Africa. Acetic acid, acetyl acetate, ethanol (EtOH), 2-propanol and methanol were purchased from Rochelle chemicals, South Africa.

5.2.2. Synthesis of titanium dioxide-metal organic framework/copper phthalocyanine composite.

CuPc was synthesized from phthalimide using the refluxing method outlined in the literature [29]. Briefly, a combination of 5.8 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.02 mmol of phthalimide were dissolved in nitrobenzene and approximately, 0.05 mmol excess urea and 0.06 mmol of ammonium molybdate were added to the solution and refluxed for 5 hours at 180°C to produce a dark blue CuPc.

Copper-based MOF preparation was achieved following a reported hydrothermal procedure by Ramohlola *et al.* [30–33]. In brief, a solution of 2.5 mmol trimesic acid (H_3BTC) in hot ethanol and with 4.5 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in hot distilled water were mixed. The subsequent mixture was placed in an autoclave and then subjected to heating treatment for 36 hours in an oven at 120°C .

TiO_2 and TiO_2 -MOF composites were prepared using a sol-gel synthetic procedure [20, 34–35] with some modification. Titanium isopropoxide (TIP) was stabilised using glacial acetic acid and subjected to hydrolysis with deionised water. The titanium solution was stirred vigorously for 1 hour. In the case of the TiO_2 -MOF composite, approximately 10 weight % of MOF in relation to TIP was added to the titanium solution. In order for the solution to initiate the condensation processes, the resulting solution was stirred for 2 hours and adjusted to pH 5 using a 25 % ammonia solution. The gel was allowed to age at 50°C for 24 hours in deionized water. The solvent exchange processes was introduced by addition of 2-propanol on the gel repeatedly at 50°C in order to remove water from the gel network. Finally, the gel network was dried at room temperature for 24 hour.

The copper phthalocyanine dye adsorption was prepared by 0.1g of dried TiO₂-MOF and CuPc (0.12 mol/L) dissolved in 12 mL of N N-Dimethylformamide, then the two solutions mixed together and stirred at 50 °C for 24 hours, and UV-vis was used to monitor the adsorption process. The final product was filtered, and rinsed with ethanol, and stored at 50 °C overnight.

5.2.3. Photoanode material

The photovoltaic cells were prepared as reported in the literature [36] with minor modifications. The Ni foam as the substrate was cut into 1 cm × 1 cm dimensions and pasted with a slurry prepared from the photoanode materials (i.e. TiO₂, MOF, and TiO₂-MOF composite). The slurry was prepared by mixing and grinding 1.00 g of CuPc, TiO₂, MOF, or TiO₂-MOF/CuPc composite with 0.0005 g of polyvinylidene fluoride (PVDF) and 0.30 mL of 1-methyl-2-pyrrolidinone (NMP) in a quartz pestle and mortar [20]. The electrochemical evaluation (CV and EIS) of the prepared electrodes was done in a three-electrode cell configuration (0.1 M Na₂SO₄ as electrolyte) using the Biologic instrument (VMP300, EC-lab software) in a temperature-controlled environment at 25 °C. The photocurrent density (I–V curves) was measured at a potential range of 0.3 -1.0 V under light conditions at a scan rate of 0.10 V/s using a solar simulator equipped with a halogen lamp (potential=12 V, power=20 W, power density=64 mW m⁻², Germany) to determine the photocurrent response of the photoanode materials [37–39]. The EIS was performed at a frequency range from 0.1 Hz to 100 kHz with an open circuit potential (the Z-fit tool was used for EIS data fitting analysis).

5.2.4. Characterization Technique

Electronic absorption spectra of the materials were investigated using wavelength range 200 nm to 900 nm over single frond lens at moderate temperatures of around 25 °C utilizing UV-vis spectrophotometer under H₂SO₄. Structural studies of materials were carried out using X-Ray Diffraction (XRD) Phillips 1830 fitted out with fine focus lens with wavelength (λ) peak position 1.54 angstrom, for both qualitative and quantitative analysis. Agilent Cary 600 Series Fourier transform infrared spectroscopy (FTIR) was used for functional group identification to validate the synthesized, CuPc, TiO₂, MOF, and TiO₂-MOF/CuPc composite, wavenumber extent from 400 cm⁻¹ to 4000 cm⁻¹ also at controlled temperature of around 25 °C. The surface morphology was studied using Scanning electron microscopy (SEM), FEI Nova 600 instrument at 30 kV. Raman analysis (micro-Raman mod; Jobin-Yvon T64000, wavelength = 532 nm) was done at the focal plane of 1.5 μ m in diameter. The Brunauer–Emmett–Teller (BET) surface area and pore diameter of the synthesized materials were determined using Micromeritics Tristar 300, outgassing the samples at 150 °C for 4 hrs, and gas sorption using liquid nitrogen (-195 °C). The thermal stability of the materials were conducted using Thermogravimetric analysis (TGA), Perkin Elmer 6000. Prior to the analysis, the sample (10 mg) was heated in an alumina cup at a temperature starting from range of 35 °C up to a maximum of 900 °C for 90 minutes per analysis.

5.3. RESULTS AND DISCUSSIONS

5.3.1. Dye characterization

The Raman images and spectra for the CuPc molecule at different regions are shown in Figure 5. 1. The Raman images (Figure 5.1(a) and (b)) show a rod-like appearance

of CuPc. The selected regions possess similar Raman spectra (Figure 1(c) with Raman bands between 1600 and 1000 cm^{-1} as a result of the C=C stretching vibrations of the aromatic ring in CuPc [40]. The vibrations between 1000 and 500 cm^{-1} are mainly composed of the dihedral plane deformations involving the aromatic CH groups and ring radial vibrations of the isoindole moieties [41].

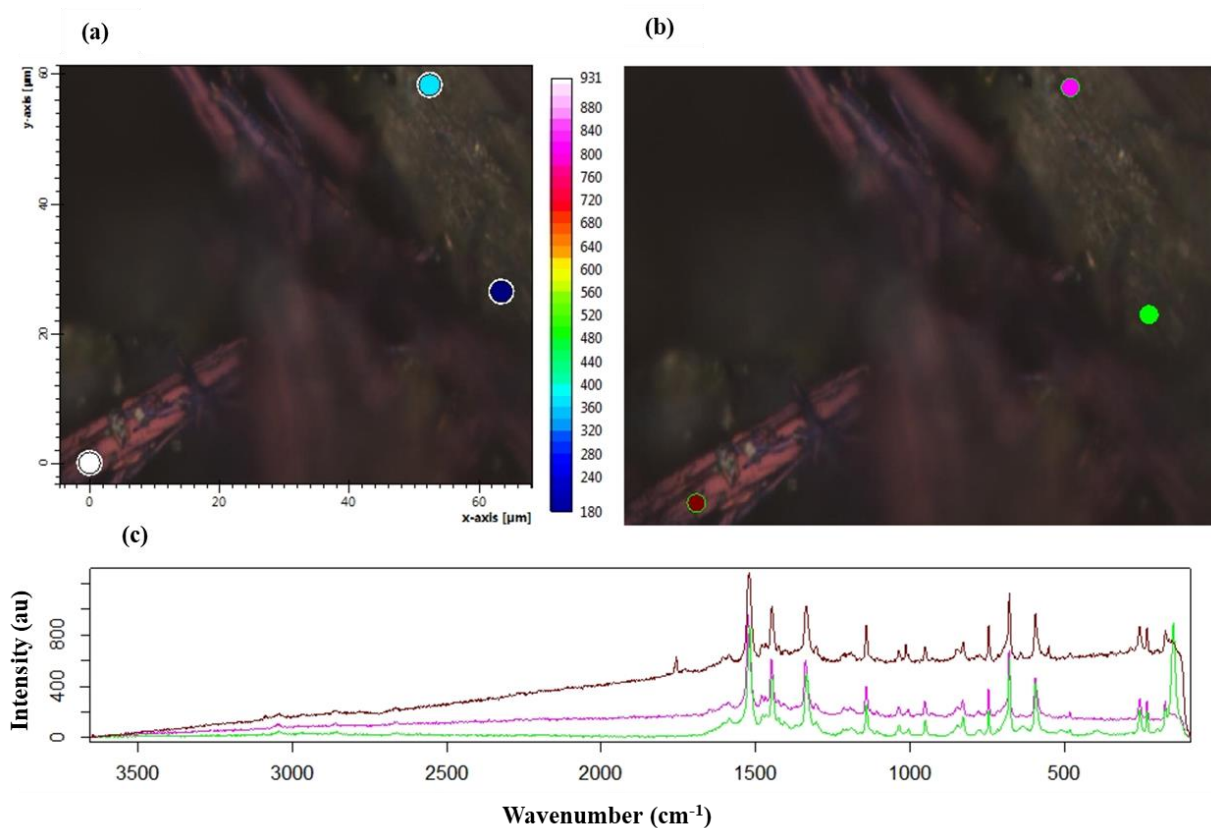


Figure 5.1: Raman images (a and b) and spectra (c) of CuPc molecule.

The SEM image of CuPc (Figure 5.2(a)) shows the occurrence of rod-like structure with 200 μm in length and 5 μm diameter. This result in this work is in agreement with the SEM images of phthalocyanine illustrated by Monama et al. [23, 29]. The XRD patterns of the synthesized CuPc (Figure 5.2(d)) are similar to the ones reported in the

literature, suggesting a cub structure of phthalocyanine [42–43]. Note that Cu-Pc has different crystal phases: α -, β -, and χ -phases [44–45]. The α -phase is metastable and undergoes a polymorphic transition to the stable β -phase when heated and when stored in certain organic solvents. The XRD patterns of CuPc exhibit sharp peaks at 2θ equal to 7.11° and 9.30° , which correspond respectively to the (100) and (102) β -CuPc phase diffraction planes [46].

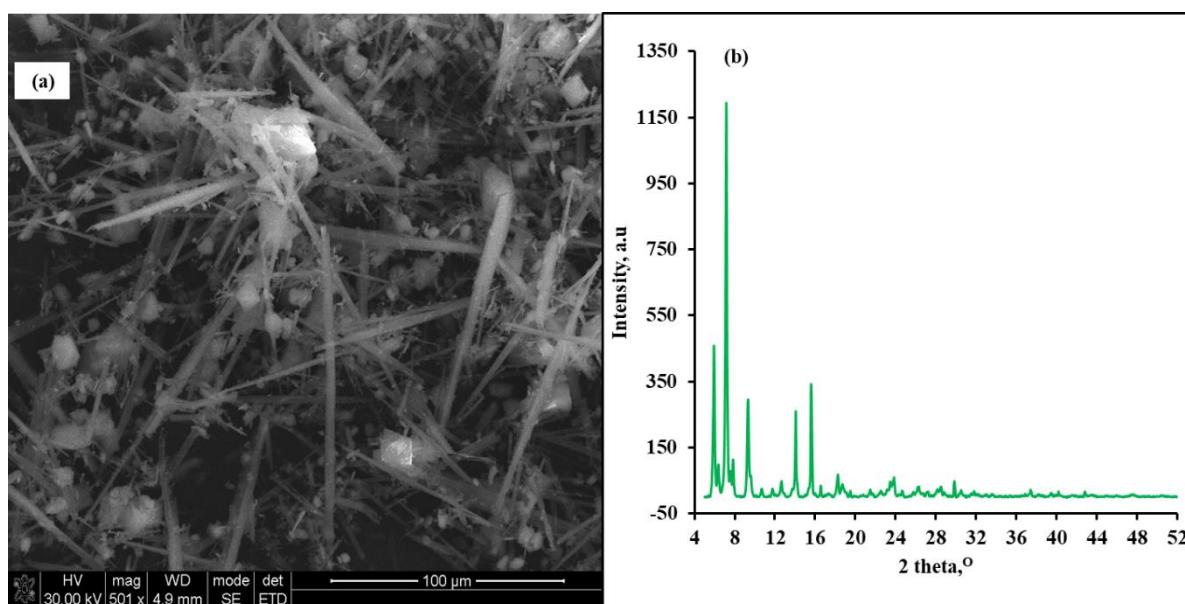


Figure 5.2: (a) SEM image and XRD patterns of CuPc molecule.

The amount of CuPc dye adsorbed by the materials was determined using UV-vis spectroscopy (Figure 5.3). The UV-Vis spectrum of CuPc in H_2SO_4 exhibited a characteristic B-band (Soret band), vibronic band, and Q-band in the 240–440 nm, 700 nm, and 790 nm regions, respectively, of the phthalocyanine ring [29]. The B-band shows absorbance in the UV-region due to the $S_0 \rightarrow S_2$ transition, whereas the Q-band arises due to the $S_0 \rightarrow S_1$ with $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the visible region [47]. The inset in Figure 5.3(a) shows the effect of concentration on the absorbance of CuPc. Due to the Beer-Lambert law [48], it was discovered that

absorbance increases with increasing concentrations. Furthermore, the increase in concentration does not shift the position of the absorption peaks; hence, the conduction band on the composite did not change [48]. The absorption of CuPc dye by TiO₂-MOF was monitored in comparison with the UV-vis of TiO₂ and MOF (Figure 5.3(b)). The TiO₂ exhibits absorption between 250 and 350 nm, which corresponds to the d-d transition of TiO₂ [17]. On the other hand, MOF shows an intense peak at 350 nm, which is attributed to the ligand-to-metal charge transfer [43]. Following dye absorption, the appearance of peaks corresponding to both components, i.e., TiO₂ and CuPc, confirmed the successful immobilisation of CuPc units onto the TiO₂-MOF support (Figure 5.3(b)). A small decrease in the Q-band indicated the presence of nonaggregated CuPc moieties in the composites and the concentration of the absorbed dye was determined to be 25 ppm. The optical bandgap energies were determined using the Tauc plot based on the UV-vis spectra (Figure 5.3(b)) in accordance with Equation 5.1 [48–49].

$$\alpha h\nu(\nu) = \beta(h\nu - E_g)^n \quad (5.1)$$

where α represents the absorptivity coefficient; ν represents the frequency of light; and β shows band gap tailing parameter. The plank constant and optical band gap energy are shown as h and E_g , respectively. Then the symbol in Equation 5.2 represents the transition probability index for direct and indirect allowed electronic transitions with n values of 1/2 and 2, respectively. Figure 5.3(c) and (d) present the Tauc plots using direct and indirect allowed electronic transitions, respectively, for TiO₂, MOF, and TiO₂-MOF/CuPc. The CuPc plot revealed three distinct $\pi \rightarrow \pi^*$, metal to ligand charge transfer (MLCT), and $S_0 \rightarrow S_2$ transitions with energy gaps of 1.37, 2.28, and 2.99 eV (Figure 5.3(c) and Table 5.1). For TiO₂ and MOF, the obtained band gaps were 3.38 and 3.60 eV. However, the absorption of the CuPc moieties on the TiO₂-MOF support

led to a notable reduction in the band gap to 3.10 eV and with a new emerging band gap of 1.46 eV due to the characteristic $\pi \rightarrow \pi^*$ of the phthalocyanine [47]. It has been shown from Table 5.1, it shows the surface area for TiO₂-MOF/CuPc to be 100.91 m²/g due to adsorption of CuPc nanoparticles, which is expected to transfer electrons faster and reduce the band gap [50–51].

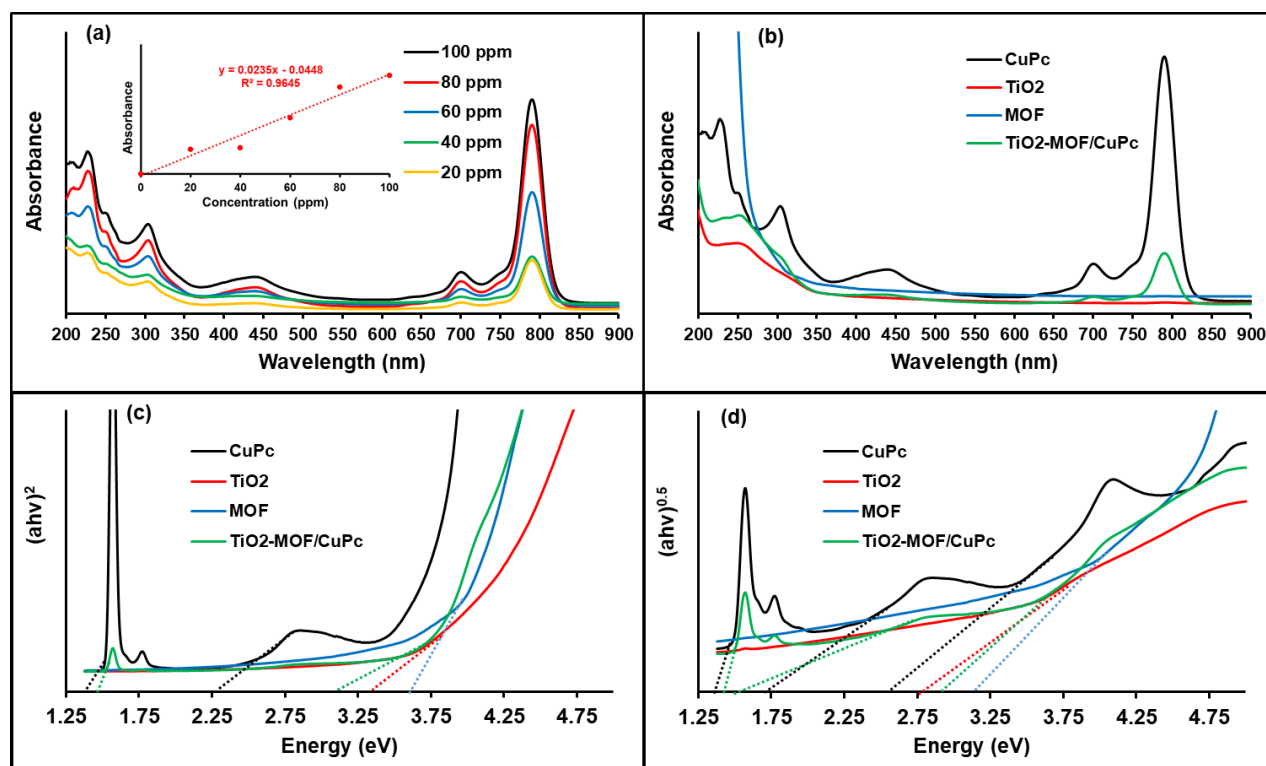


Figure 5.3: (a) UV-vis spectra of 20–100 ppm CuPc at 20 ppm intervals in H₂SO₄ (Inset: absorbance as a function of concentration); (b) UV-vis spectra of CuPc, TiO₂, MOF and TiO₂-MOF/CuPc at 100 ppm in H₂SO₄; and Tauc plots of CuPc, TiO₂, MOF and TiO₂-MOF/CuPc for direct allowed electronic transition (c) and in direct allowed electronic transition (d).

Table 5.1: BET parameters, optical and electrochemical properties of CuPc, TiO₂, MOF and TiO₂-MOF/CuPc nanocomposite.

Material	BET	Pore width	Optical	$E_{1/2}^{ox}$	$E_{1/2}^{red}$	E_{HOMO}	E_{LUMO}
	Surface	(nm)	Bandgap	(V)	(V)	(eV)	(eV)
	area (m ² g ⁻¹)		(eV) ^a				
Ni foam	-	-	-	0.40	0.35	-5.1	-4.35
CuPc	12.69	4.91	1.37; 2.28; 2.99	0.43	0.17	-4.92	-4.32
TiO ₂	262.90	2.66	3.38	0.41	0.33	-5.08	-4.34
MOF	464.76	2.56	3.60	0.63	0.50	-5.25	-4.12
TiO ₂ - MOF/CuPc	100.91	2.77	1.46; 3.10	0.88	0.40	-5.15	-3.87

a= optical band gap using direct allowed transition

5.3.2. Structural characterization of the composite after dye adsorption.

Figure 5.4 (a) shows the XRD patterns for TiO₂, MOF, and TiO₂/MOF-CuPc. The patterns of TiO₂, which show the diffraction peaks at $2\theta = 38.3^\circ$, 48.0° , 54.0° and 62.0° , indicate the anatase TiO₂ phases that correspond to the crystal plane of (101), (004), (200), (105), and (204) [20, 50]. The patterns of TiO₂-MOF/CuPc show the CuPc phases at $2\theta = 8.0^\circ$, 9.1° , 10.2° , 16.0° and 25.0° [52]. The TiO₂ and MOF phases have been shown by the most crystalline peak at $2\theta = 25.0^\circ$ and the other small peaks from $2\theta = 5.0^\circ$ to 20.0° are due to the TiO₂ [53] and MOF phases [54]. This is in agreement with the crystallite size of 2.05 nm for TiO₂ material determined using the Debye–Scherrer formula from (101) plane using Equation 5. 2 [53–54].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (5.2)$$

The symbol β represents the full-width at half-maximum (FWHM) measured in radians, λ for the X-ray wavelength of Cu-K α radiation, which is 1.5406 Å, and θ stands for the Bragg's angle. The crystallite size of TiO₂-MOF/CuPc was found to be 4.03 nm, which is consistent with the reported TiO₂ aerogel composites [50]. In order to confirm the formation of TiO₂-MOF/CuPc, the functional groups were observed using FTIR and Raman analysis. Figure 5. 4 (b) shows the FTIR spectra for TiO₂ nanoparticles, MOF, and TiO₂-MOF/CuPc. A broad peak in the region of 40–1000 cm⁻¹ observed is due to the vibrational mode of Ti-O stretching bond [57]. In MOF, the two minor peaks at 731 and 761 cm⁻¹ correspond to in-plane and out-of-plane C-H bending modes on the benzene ring [58]. The vibrational modes in TiO₂ and MOF were observed in TiO₂-MOF/CuPc. The small peak that appears at 900 cm⁻¹ shows the existence of CuPc in TiO₂-MOF/CuPc [59]. In the region of 1400 and 1800 cm⁻¹, the peaks attributed to C-C and C=C vibrational of the benzene ring [52] in MOF and CuPc were observed.

Weak peaks that appeared at 1272 cm^{-1} were due to the vibrational mode of the RC-O stretch of Cu-MOF [20]. The strong peaks at 1371 in MOF and $\text{TiO}_2\text{-MOF/CuPc}$ materials were assigned to the symmetry and asymmetry vibrational modes of C=O of carboxylate groups in MOF [60]. Furthermore, weak peaks at 2200 and 2400 cm^{-1} in both TiO_2 and $\text{TiO}_2\text{-MOF/CuPc}$ materials were attributed to hydroxyl groups attached to TiO_2 asymmetric [61]. The broad peaks in the region of 3000 and 3400 cm^{-1} are assigned to the vibrational mode of $4\text{Ti}^{4+}\text{-OH}$ of TiO_2 [62] and OH that shows the existence of hydrated MOF [63].

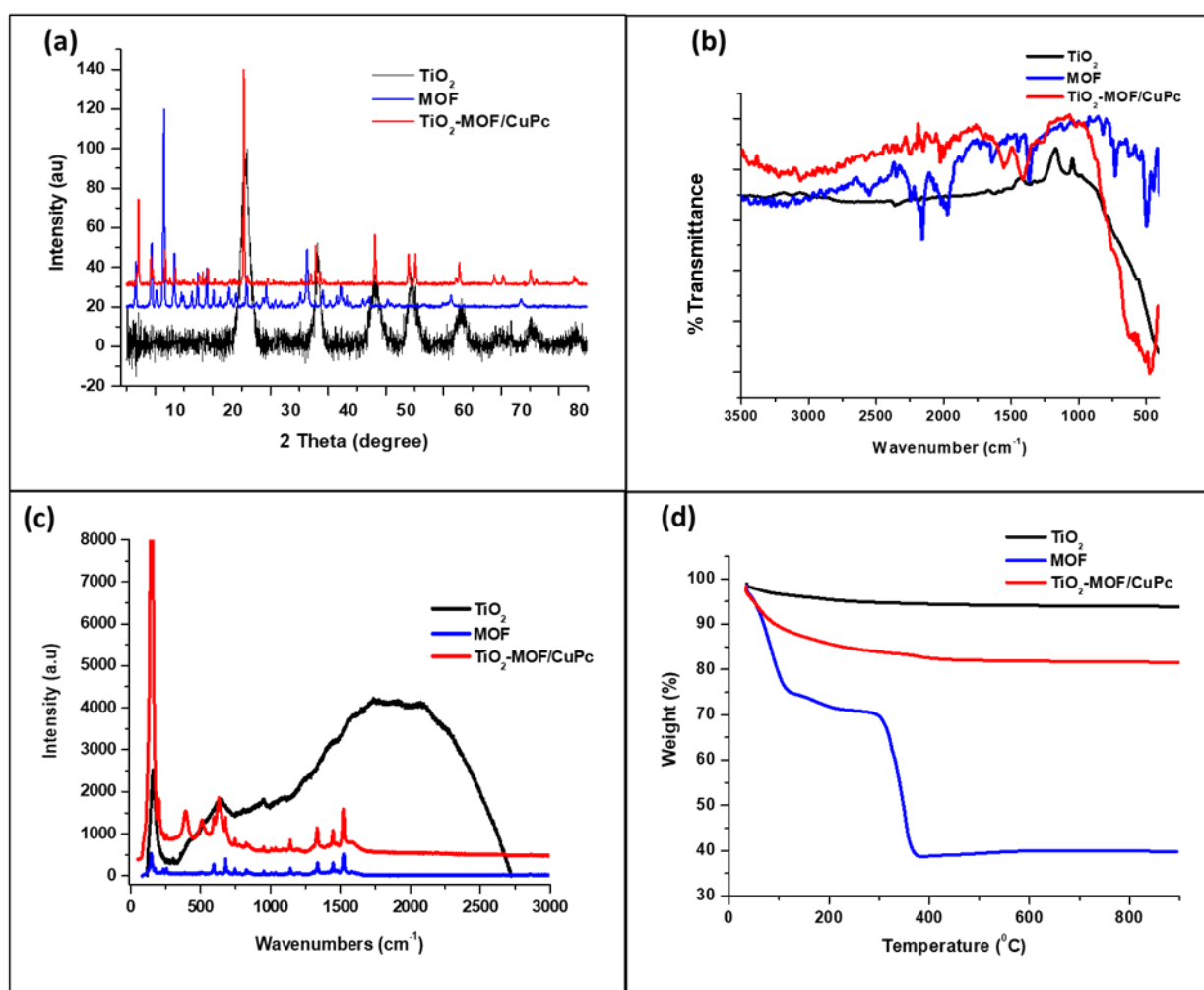


Figure 5.4: (a) XRD patterns, (b) FTIR, (c) Raman spectra and (d) TGA of TiO_2 , MOF and $\text{TiO}_2\text{/MOF-CuPc}$.

In addition, Figure 5.4(c) shows the Raman spectra of TiO₂, MOF, and TiO₂/MOF-CuPc materials. A strong vibration was observed at 140 cm⁻¹ in TiO₂ and TiO₂/MOF-CuPc due to the symmetric stretching vibration of a single crystal (Eg) for O-Ti-O [64, 65]. Three weak vibration modes at 399 cm⁻¹ (B1g), 513 cm⁻¹ (A1g) and 639 cm⁻¹ (Eg) were caused by the antisymmetric bending vibration of O-Ti-O [66, 67]. This was further confirmed by Raman analysis of the TiO₂-MOF/CuPc as represented in Figure 5.5, which shows the Raman images (a and d) and overlaid Raman spectra (c). The Raman images showed some dark blue spots due to the presence of adsorbed CuPc by the composite. Figure 5.5(c) shows that the vibration modes at 1481 and 1610 cm⁻¹ in TiO₂/MOF-CuPc material were caused by CuPc structure C-N-C and C-C stretching [68, 69]. The vibration stretches at 1592, 1341, and 1309 cm⁻¹ were due to pyrrole deformations of the phthalocyanine ring [69] in TiO₂/MOF-CuPc material. The vibrational modes at 193 –172 cm⁻¹ that are assigned to the Cu-O and Cu-Cu stretching modes of CuPc were observed in MOF and TiO₂/MOF-CuPc materials. Furthermore, the spectrum of TiO₂/MOF-CuPc material shows peaks in the region of 790–810 cm⁻¹ and 1600 cm⁻¹, which were attributed to C-H and C=C of aromatic ring stretching modes of MOF [70, 71]. The spectra of MOF and TiO₂/MOF-CuPc materials display the presence of O=C=O attached to the aromatic ring in MOF [70]. Furthermore, Figure 5.4(d) depicts the thermal gravimetric (TGA) results for TiO₂, MOF, and TiO₂-MOF/CuPc composite, demonstrating one small degradation step for TiO₂ due to moisture loss. Whereas MOF thermogram showed the first degradation step corresponds to the loss of water and ethanol, and the second degradation step corresponds to the loss of organic linker, the product remains with CuO [33]. Upon adsorption of CuPc, there was a degradation step, which corresponded to the loss of

water, suggesting improvement in the thermal stability of the TiO₂-MOF/CuPc composite as compared to MOF.

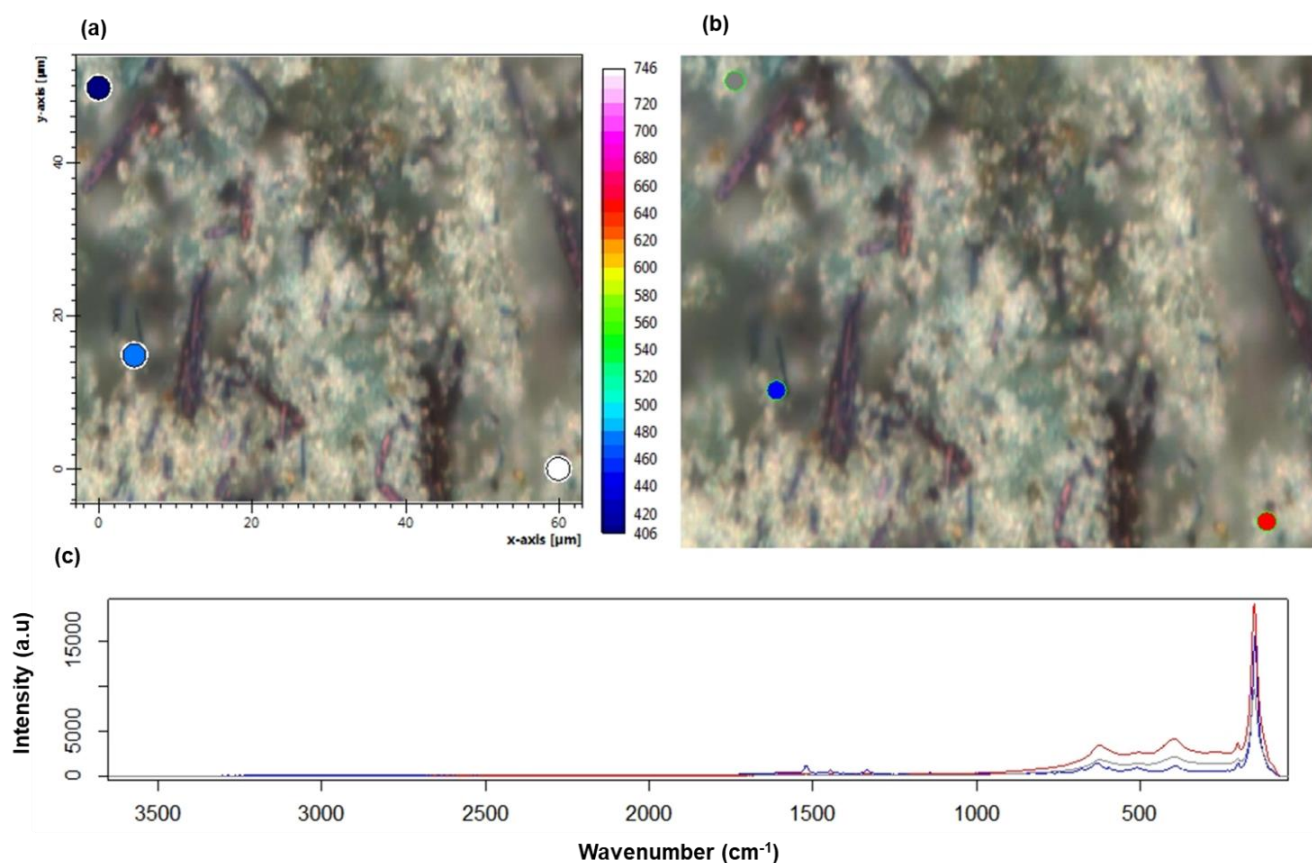


Figure 5.5: Raman images (a and b) and spectra (c) of TiO₂-MOF/CuPc molecule.

Figure 5. 6 presents the SEM images of (a) TiO₂, (b) MOF, and (c) low and (d) high magnification for TiO₂-MOF/CuPc composites. In nature, however, pulverized TiO₂ has spherical shapes [72] with large particles estimated to be around 100 μm in size using particle size distribution approach. Figure 5.6(b) shows an SEM image of an octahedral MOF [73] with particles ranging in size from 10 to 25 μm . Figure 5.6(c) depicts the intervention of TiO₂, MOF, and CuPc by the pyramidal shape of MOF and the transition from granules to an agglomerated structure of TiO₂. It is clear that the

distribution of all materials and the spherical shapes of both TiO_2 and the rod like structure of CuPc [74] together with the octahedral shape of MOF are observed in the composite, which shows successful formation of the composite with all the morphological structure of each material being observed. In addition, the surface area of TiO_2 , MOF, CuPc and TiO_2 -MOF/CuPc composite was determined using nitrogen adsorption measurements and their results are presented in Figure 5.7 and Table 5.1. The specific surface area of TiO_2 -MOF/CuPc composite is $100.91 \text{ m}^2 \text{ g}^{-1}$, which is comparable with the surface area of CuPc ($12.69 \text{ m}^2 \text{ g}^{-1}$) TiO_2 ($262.90 \text{ m}^2 \text{ g}^{-1}$) and MOF ($464.76 \text{ m}^2 \text{ g}^{-1}$). The addition of 10% MOF and followed by CuPc dye adsorption has changed the surface area substantially due to agglomerates MOF [15] and CuPc occupying the pores of the TiO_2 network [19].

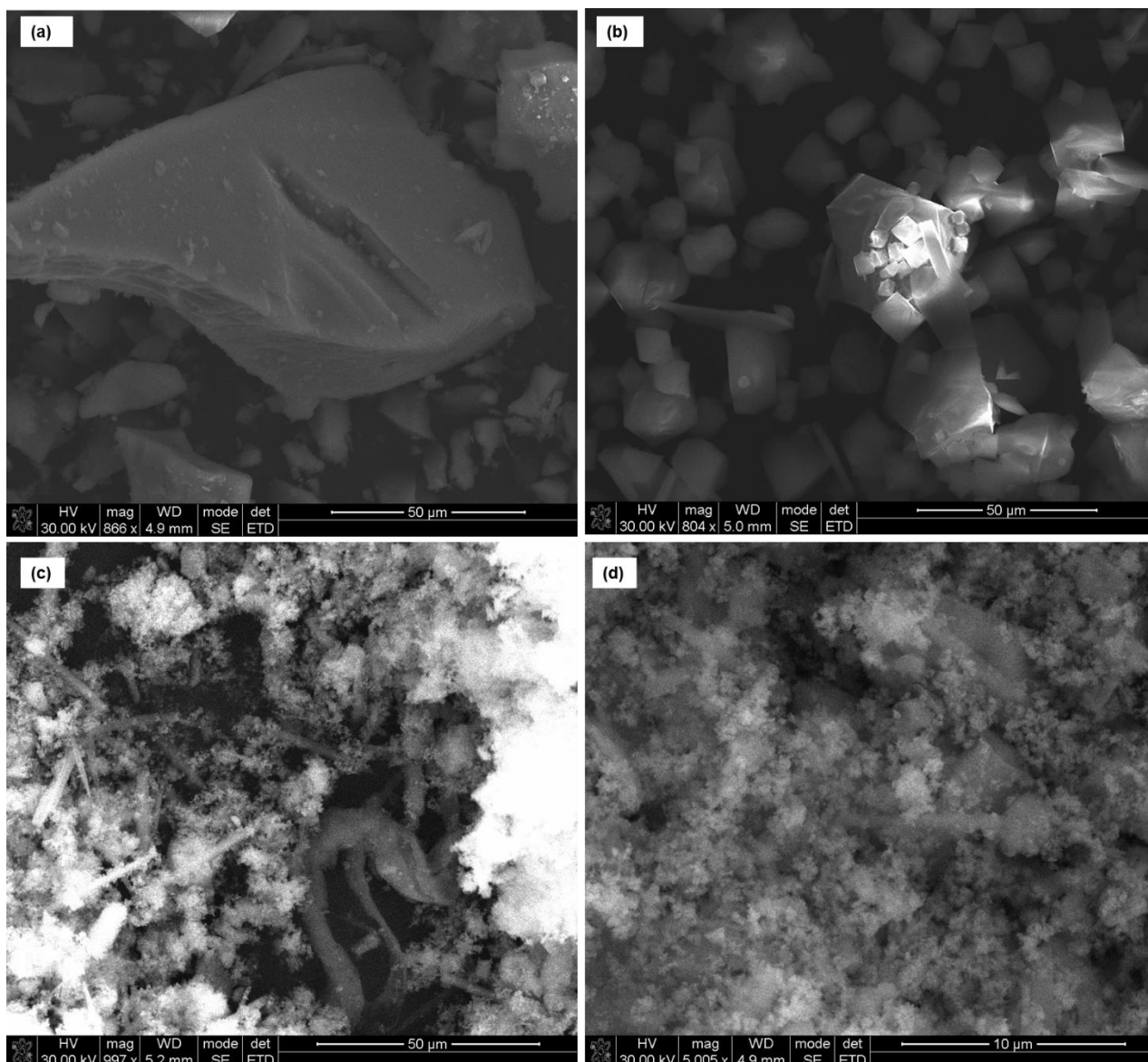


Figure 5.6: SEM images of TiO_2 (a), MOF (b), and $\text{TiO}_2\text{-MOF/CuPc}$ at (c) low and (d) high magnification.

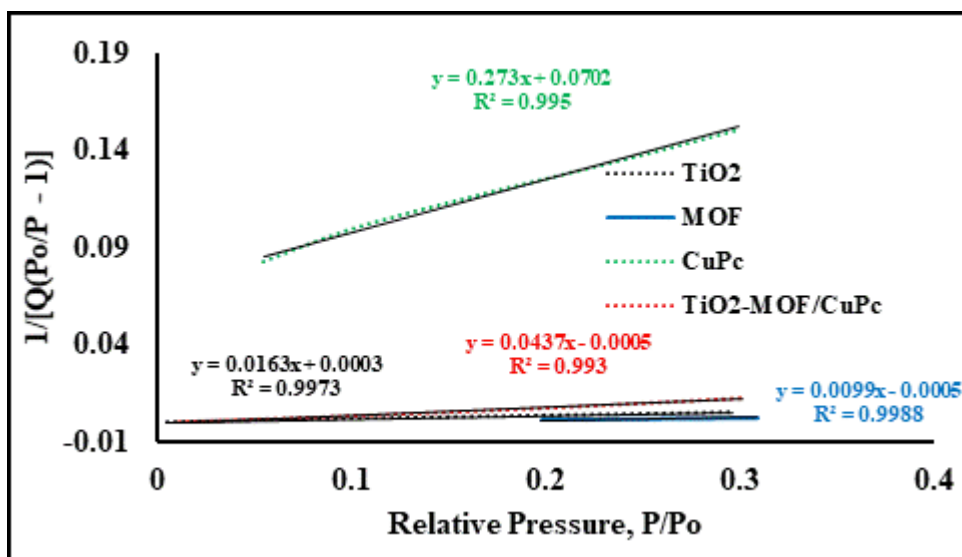


Figure 5.7: BET surface area plot of TiO₂, MOF, CuPc and TiO₂-MOF/CuPc composite.

5.3.3. Electrochemical characterizations

The nanocomposite photoanode materials were investigated by means of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Both electrochemical characterizations were performed at a scan rate of 100 mV/s for platinum (Pt) counter electrode in 0.1 M disodium sulphate (Na₂SO₄) alkaline, as well as the reference electrode of Ag/AgCl for dye-sensitised solar cell applications. Figure 5.8(a) shows the CV for Ni Foam, TiO₂, MOF, and TiO₂-MOF/CuPc. It was observed that the TiO₂-MOF/CuPc composite exhibited good reversibility similar to the parent materials. The voltammograms display capacitive behaviour without notable peaks due to the influence of intrinsic trap state kinetics in the 3D framework of the nanocomposite [75]. When the voltammetry scan was performed in the cathodic direction, the Fermi level shifted up, and the electrons occupied the trap states while the conduction band was completely occupied at a higher cathodic voltage [75]. It is

noticed that the cathodic and anodic peaks were observed in both scan directions. It was realized that the electron transfer travelled through the conduction band and valence band, resulting in a cathodic and an anodic peaks, respectively [76-78]. Furthermore, the potential for the first ring oxidation and reduction, $E_{1/2}^{ox}$ and $E_{1/2}^{red}$, respectively, is listed in Table 5.1 for Ni foam, TiO_2 , MOF and TiO_2 -MOF/CuPc composite. From these values, the highest occupied molecular orbital (E_{HOMO}) energy levels were determined according to Data *et al.* [79] using Equation 5.3:

$$E_{HOMO} = -(E_{1/2}^{red} + 4.75) \text{ eV} \quad (5.3)$$

The E_{HOMO} values were found to be -5.10, -5.08, -5.25, and -5.15 eV for Ni foam, TiO_2 , MOF, and TiO_2 -MOF/CuPc nanocomposite, respectively. The one of CuPc dye alone was seen to be -4.92 eV (Table 1). On the other hand, the lowest unoccupied molecular orbital (E_{LUMO}) values are calculated using Equation 5.4 [46, 47]. In this work, the E_{LUMO} values were found to be -4.35, -4.34, -4.12, and -3.87 eV for Ni foam, TiO_2 , MOF, and TiO_2 -MOF/CuPc composite, respectively, as compared to -4.32 eV for CuPc dye alone.

$$E_{LUMO} = -(-E_{1/2}^{ox} + 4.75) \text{ eV} \quad (5.4)$$

Impedance spectroscopy, which measures conductivity over a wide frequency range ranging from mHz to kHz, provides valuable information on the different conductive species and pathways, which is important in understanding and controlling the system's conduction mechanism [42, 43]. The circular arc radius of the Nyquist plots in Figure 5.8(b) provides information on facilitated charge transport properties. At the electrode/electrolyte interface, the TiO_2 -MOF composite coated with CuPc dye (Figure 5.8(b)) is expected to have the lowest charge transfer resistance (R_2/R_{ct}).

The values of the fitted EIS parameters are summarized in Table 5.2. There was a decrease in Rs value TiO₂-MOF/CuPc as compared to TiO₂ material from 20.35 Ω to 19.69 Ω in the nanocomposite. This indicates that the composite provides better contact with the Ni foam substrate than pristine TiO₂ aerogel [4]. The total ionic conductivity (δ) is estimated from the charge-transfer resistance (Rct) using the thickness (t) and the cross sectional area (A) by the following relation in Equation 5.5.

$$\delta = t/(R_{ct} A) \quad (5.5)$$

The total ionic conductivity of Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPc composite was found to be 0.9, 1.1, 8.4, and 172 $\mu\text{S}/\text{cm}$, respectively. The ionic conductivity values determined in this work were similar to the one reported in the literature [4]. In addition, a logarithmic of impedance and phase angle are both plotted as a function of logarithmic frequency to give a Bode plot. The phase angle vs log frequency curve of the TiO₂-MOF/CuPc composite (Figure 5.8c) possessed a broad peak and the peak height is proportional to the charge-transfer resistance response. The lower charge-transfer resistance values occurring at the higher frequency indicated that the TiO₂-MOF/CuPc composite possesses a high ionic conductivity as observed in the Nyquist plot. The lifetime (τ) of the TiO₂-MOF/CuPc composite was estimated from its maximum peak frequency (f_{max}) of 47.5° using Equation 5.6 [81] and it was found to be 3.34 ms.

$$\tau = 1/(2\pi f_{\text{max}}) \quad (5.6)$$

Furthermore, a constant phase element (C₂/CPE) is chosen to accommodate double layer capacitance for the porous nature of the electrode material. This is expected to greatly enhance the interaction at the electrode/electrolyte interface in the intended

solar cell applications. The proposed mechanism for photovoltaic studies is shown in Figure 5.8(d).

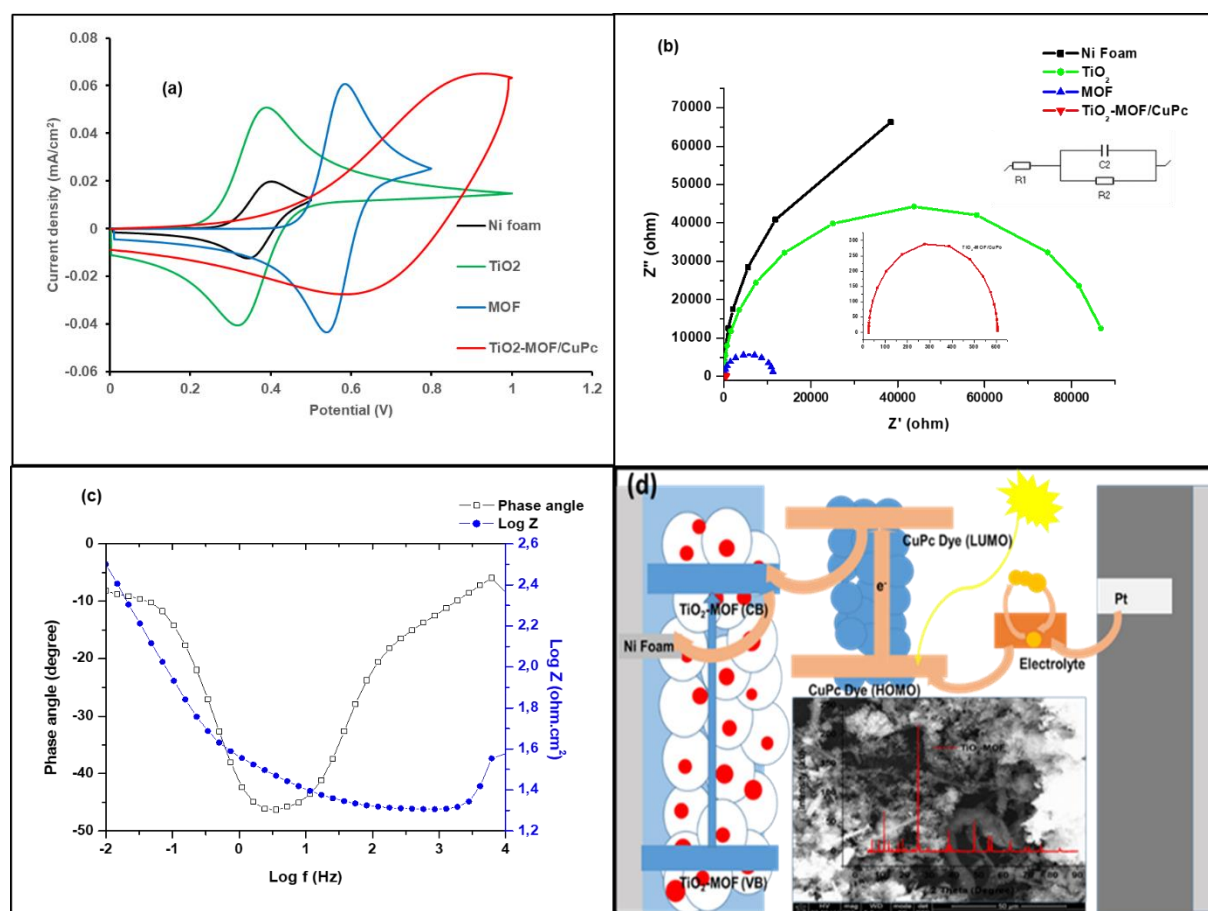


Figure 5.8: (a) Cyclic voltammetry and (b) Electrochemical Impedance spectroscopy for Ni Foam, TiO₂, MOF and TiO₂-MOF composite in Copper phthalocyanine dye; (c) Bode impedance for TiO₂-MOF/CuPc composite; (d) Geometry of DSSCs and scheme of the electron transport process using a band diagram for TiO₂-MOF/CuPc.

Table 5. 2: Fitted circuit parameters of EIS of Ni foam, TiO₂, MOF and TiO₂-MOF/CuPc composite and calculate ionic conductivity.

Material	Electrolyte	Rs	CPE	Rct	Conductivity
		(Ω)	(μF)	(kΩ)	y
					(μS/cm)

Ni foam	0.1 M Na ₂ SO ₄	19.7	184	114	0.9
TiO₂	0.1 M Na ₂ SO ₄	23.3	25.7	89.6	1.1
MOF	0.1 M Na ₂ SO ₄	21.3	153	11.9	8.4
TiO₂- MOF/CuPc	0.1 M Na ₂ SO ₄	24.19	284	0.582	172

The photocurrent densities of the prepared Ni Foam, TiO₂, MOF, and TiO₂-MOF/CuPc materials were determined using a cyclic voltammetry scan in simulated light (64 mW m⁻² intensity), as shown in Figure 5.9(a). It was shown that Ni foam, TiO₂ and MOF materials possessed photocurrent densities of 0.02 (0.38 V), 0.39 (0.31 V) and 0.19 (0.66 V) mA cm⁻². The low photocurrent is attributed the poor light absorption by the material's surface. This results in poor charge separation and hence, reduction of photocatalytic efficiency [82]. Approximately, 0.98 mA.m⁻² photocurrent density at 0.89 V was obtained in TiO₂-MOF/CuPc materials. The highest photocurrent density attained for the composite was well within the many photo-responses that have been reported for the material under illumination conditions [83]. Table 5.3 compares the maximum photocurrent attained by the Ni, TiO₂, MOF, and TiO₂-MOF/CuPc materials in this work with other reported values in the literature [83-85]. The enhanced photocurrent obtained for the TiO₂-MOF/CuPc material is largely related to the presence of CuPc, which increases active sites for electron transfer mechanisms, thus enhancing the photocurrent [38].

The power conversion efficiency (η) of the Ni foam, TiO₂, MOF, and TiO₂-MOF composites, was calculated using Equation 5.7 [85]:

$$\eta = ((E_{\text{rev}}^0 - E_{\text{mea}}) \times I) / P_{\text{in}} \quad (5.7)$$

where I (mA/cm²) is the represents photocurrent density, E_{mea} stands for the working electrode potential o, E_{rev}^0 represents 1.43 V Ag/AgCl for the standard of the reversible potential, and P_{in} (mW/cm²) is the input power of the simulated light intensity.

The η values estimated for the Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPc composites are represented in Figure 5.9(b). The highest η value was 1.63% for the TiO₂-MOF/CuPc, whereas the lowest was 0.066 % for the Ni foam. The η values of TiO₂ and MOF were 0.617 and 0.255%, respectively. The η values reported in Table 5.3 for the TiO₂-MOF/CuPc composite are better than the one reported in the literature. The values of η are 0.26% for TiO₂/Cu-MOF [41] 0.17% for TiO₂/Zn-MOF [85], but less than the value 1.22% for TiO₂/Ru-MOF [86]. Whereas its efficiency value was less than the one of 2.34% using TiO₂/Zn-MOF in the presence of N719 dye [20]. Therefore, the results shows that CuPc dye may be used to enhance TiO₂-MOF properties. The overall power conversion efficiency of 1.63% acquired from the photocurrent density of 1.80 mA cm⁻² are due to the TiO₂-MOF/CuPc composite, this was attributed to the increase in the electronic properties of the composite material [85].

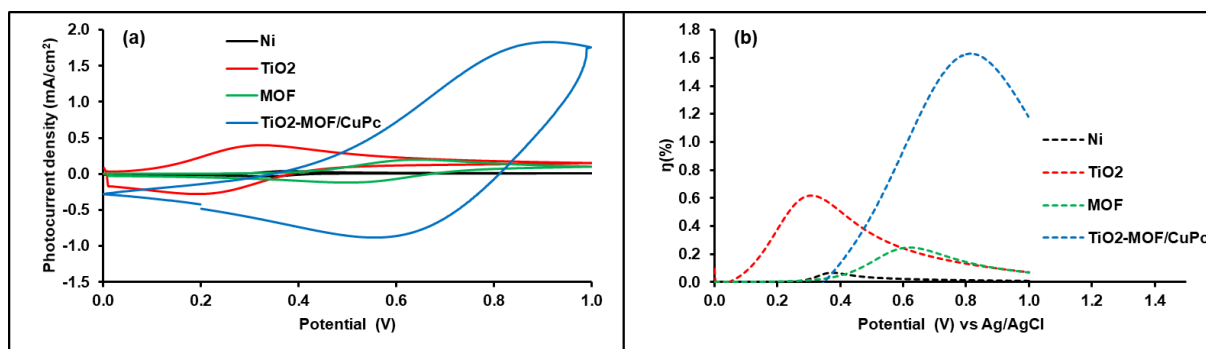


Figure 5.9: (a) Photocurrent response and (b) power conversion efficiency of Ni foam, TiO₂, MOF and TiO₂-MOF/CuPc photoanode nanocomposites.

Table 5.3: Comparison of the photocurrent density obtained for Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPc composites in this study with the literature values prepared using various methods.

Material	Electrolyte	Photocurrent (mA/cm ²)	Efficiency (%)	Ref
Ni foam	0.1 M Na ₂ SO ₄	0.02	0.066	In this work
TiO ₂	0.1 M Na ₂ SO ₄	0.39	0.617	In this work
MOF	0.1 M Na ₂ SO ₄	0.19	0.255	In this work
TiO ₂ -MOF/CuPc	0.1 M Na ₂ SO ₄	1.80	1.63	In this work
TiO ₂ -Cu-MOF	I ₃ /I ⁻ redox	-	0.26	[41]

TiO₂-Ru-MOF	I ₃ /I ⁻ redox	-	1.22	[86]
TiO₂-Zn-MOF	ACN, LiI, I ₂ & 1.04 LiClO ₄		0.67	[85]
TiO₂/Zn-MOF/N719	PEGOPEG/NaI/I ₂ / EMITFMSI/AN		2.34	[20]

N719=Di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II); AN=acetonitrile;
PEGOPEG=poly(ethylene oxide)-poly(ethylene glycol); and EMITFMSI= 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide

5.4. CONCLUSION

A new class of porous materials based on TiO₂-MOF together with CuPc dye was prepared by the sol-gel method followed by dye adsorption technology. The CuPc dye was prepared through the reflux of phthalimide. The synthesized materials were characterized using XRD, FTIR, Raman spectroscopy, SEM, TGA/DTA, TEM/SAED, and BET. The XRD pattern of the CuPc, TiO₂ and MOF in the final composite confirmed successful preparation of our target materials. Raman spectroscopy and FTIR revealed the vibrations for benzene rings, C-N and Ti-O stretches of MOF, CuPc, and TiO₂, respectively, as an indication of high purity of the composite produced. It was also seen in the gravimetric studies that the thermal stability of the composite was improved. The optical band gap values ranged between 3.10 and 1.46 eV from UV-Vis; and the HOMO-LUMO values using CV were estimated for the TiO₂-MOF/CuPc with reference to TiO₂ and MOF photoanode materials. On the other hand, the EIS showed that the TiO₂-MOF/CuPc photoanode composite possessed high conductivity as compared to the parent materials. These parameters make the TiO₂-MOF/CuPc composite a good candidate for dye-sensitized solar cell applications. The maximum

photocurrent and power efficiency for TiO₂-MOF/CuPc composite under simulated light source were 1.80 mA.cm⁻² and 1.63%, respectively. The morphological studies revealed that the TiO₂-MOF/CuPc composite was more porous as compared to others, resulting in facilitator of photogenerated electron and leading to the improved photocurrent as the case here. Notwithstanding, the sol-gel and adsorption methods for preparing TiO₂-MOF/CuPc composites used in this work showed the promising photocurrent responses and could also be used for preparation of TiO₂-MOF/CuPc composites for DSSC applications.

Acknowledgements

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CHAPTER 6:

INFLUENCE OF PHTHALOCYANINE NANOWIRE DYE ON THE PERFORMANCE OF TITANIUM DIOXIDE-METAL ORGANIC FRAMEWORK NANOCOMPOSITE FOR DYE-SENSITIZED SOLAR CELLS

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ABSTRACT

In clean energy, dye-sensitized solar cells (DSSCs) have become a key tool for the photovoltaic effect. Copper phthalocyanine nanowire (CuPcNW) dyes can be used in DSSCs to generate low-cost devices, light-harvesting, fast electron transfer materials, and prevent recombination processes, as well as improve conductivity. This study investigates the effect of CuPcNW dye on TiO_2 , MOF, and TiO_2 -MOF in photovoltaic performance. Electrochemical characterizations such as cyclic voltammetry and electrochemical impedance spectroscopy (EIS) have also revealed the half-wave peak potentials of the ternary nanocomposite with values of 0.44 and 0.35 V for the oxidation and reduction reversible reactions. The EIS behavior revealed the improved conductivity of the nanocomposite with a value of 244 $\mu\text{S}/\text{cm}$. It was seen that the TiO_2 -MOF/CuPcNW nanocomposite achieved a maximum power conversion efficiency of 6.467 % owing to the presence of CuPcNW, which improved the photocurrent density, faster electron transport, and reduced charge recombination in the nanocomposite.

Keywords: phthalocyanine nanowire, titanium dioxide, metal-organic framework, nanocomposite, dye-sensitized solar cells

6.1. INTRODUCTION

Titanium dioxide (TiO_2) is a transition metal dioxide which is widely used owing to its well-known properties such as extensive optical band gap (~ 3.2 eV) [1-5]. Because of its outstanding properties, TiO_2 is applied in different applications, including photodegradation of organic pollutants in the water treatment process [6-8], photo-carrier collector [9], and electron transport layer in dye-sensitized solar cells (DSSC) [10-12]. Hitherto, its major setbacks are the high recombination of electron-hole pairs and a poor absorption in the visible region [13–14]. In this case, numerous methods have been proposed for surface modification of TiO_2 to solve these inferiorities by converting TiO_2 into nanostructures including thin film structures, nanoparticles, nanorods, nanosheets, and nanotubes to improve its performance [15–18]. Currently, it is also seen that TiO_2 combined with suitable semiconductors in the form of composite materials can overcome its disadvantages [19–22]. Ko et al. [19] prepared TiO_2 doped with aluminum and tungsten, which displayed an increase in short-circuit current as well as open-circuit voltage in DSSC. Hou et al. [20] investigated the use of a $\text{SnO}_2/\text{TiO}_2$ nanotube composite for the decrease of recombination of electron-hole pairs in photoreactivity. Xiaodan et al. [21] also reported on the enhancement of the visible light absorption of TiO_2 using ZnS/TiO_2 nanocomposite. Wang and Wang [22] reported on the increase of photoelectric conversion in the solar cell using PPV/TiO_2 nanocomposite.

The notion of improvement of photovoltaic performance using TiO_2 in the form of an organometallic hybrid composite is one of the promising techniques. It was discovered that coating the surface of titanium oxide with metal-organic frameworks (MOFs) resulted in improved photo-conversion efficiency (PCE) [23-26]. MOFs are made of a metal core connected through organic linkers, and they have gained much attention

due to their interesting properties such as high surface area, porosity, and tunable functionality [25-41]. They have also been extensively studied for various applications, such as photovoltaic solar cells [27–30], gas sensing [31–32], and hydrogen production [33–41]. Vinogradov *et al.* [28] reported on single-step hydrothermal synthesis of the TiO₂-MOF composite, which was applied for the first time to produce a monolithic perovskite/TiO₂-MOF heterojunction solar cell with 6.4% PCE. Ramasubbu *et al.* [30] reported on highly interconnected porous TiO₂-Ni-MOF composite aerogel photoanodes in quasi-solid dye-sensitized solar cells with 8.846% PCE.

On the other hand, the addition of dye compounds in the TiO₂ composite, such as metal phthalocyanines (MPcs), results in improved photovoltaic performance. MPcs are documented to have great resistance to chemical degradation, intense absorption in the visible region, and excellent thermal stability [42–43]. They have been used as functional materials in many applications, including diodes, transistors, gas sensors, and photovoltaic devices [44-48]. Mekprasart *et al.* [49] reported the preparation of TiO₂/copper-phthalocyanine (CuPc) nanocomposites as modified working electrode materials in dye-sensitized solar cells with a PCE of 1.24% and a fill factor of 0.45. Other studies showed a high open-circuit voltage using Schottky diode solar cells having a CuPc of low concentration due to a small exciton diffusion length of a few nm [50 – 51]. As the photovoltaic properties are dependent on the interface, it is necessary to control the structure and morphology of the electrode material. It was shown that nanowire cell designs provide a way out of this serious disadvantage as a path to high-efficiency solar cells [51]. The CuPc nanowires may display better performance because the morphologies of the nanowires can be tailored through different synthesis routes [52]. Xu *et al.* [52] fabricated CuPc nanowire arrays in porous anodized

aluminum oxide templates and used a double-layer photoreceptor to demonstrate enhanced photosensitivity.

In this work, we report for the first time the effect of copper phthalocyanine nanowires adsorbed on the TiO₂-MOF nanocomposite surface as a photoanode for DSSCs. The presence of CuPc nanowires had the ability to enhance the photovoltaic properties of TiO₂-MOF by CuPc nanowire dispersion in the TiO₂ matrix and the homogeneity in the ternary nanocomposite (TiO₂-MOF/CuPcNW). Their fundamental structural, physical, and electrochemical properties were thoroughly investigated by x-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The TiO₂-MOF/CuPcNW ternary nanocomposite was applied to modify working electrode materials in DSSC and investigated through photocurrent response density measurements. The overall power conversion efficiency of 6.467% along with a photocurrent density of 4.07 mA cm⁻² was achieved by the TiO₂-MOF/CuPcNW nanocomposite.

6.2. MATERIALS AND METHOD

6.2.1. Materials

Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) (≥99% unadulterated), titanium (IV) tetraisopropoxide (TTIP) (≥ 99% unadulterated), trimesic acid (H₃BTC, ≥ 98 %), sodium hydroxide (NaOH), acetic acid (glacial), 1-methyl-2-pyrrolidinone, polyvinylidene fluoride (PVDF), nickel foam (NF) substrates, sulphuric acid and sodium sulphate (Na₂SO₄) were procured from Sigma Aldrich, South Africa. Acetonitrile, dimethyl formamide (DMF), trifluoro acetic acid, phthalimide, excess urea,

ammonium molybdate, and nitrobenzene were acquired from Merck, South Africa. The Parafilm film was purchased from Bemis, South Africa. Acetic acid, acetyl acetate, ethanol (EtOH), 2-propanol, and methanol were bought from Rochelle chemicals, South Africa.

6.2.2. Synthesis of titanium dioxide-metal organic framework/copper phthalocyanine nanowire composite.

MOF was prepared according to a reported hydrothermal procedure in the literature [33–41]. TiO₂ and TiO₂-MOF were synthesized using a sol-gel synthetic procedure [33]. Copper phthalocyanine (CuPc) was synthesized according to a previous method reported elsewhere [39–41]. Copper phthalocyanine nanowires (CuPcNW) dye-sensitized were prepared by dispersion of CuPc powder (1×10^{-4} mol L⁻¹) in chloroform (CHCl₃) solution and ultrasonicated for 10 min. The trifluoroacetic acid (CF₃COOH) (1.8×10^{-4} mol L⁻¹) was added and mixed with the solution by using a magnetic stirrer for 5 h. The CuPc molecules were chemically self-assembled into the form of CuPc nanowires that were filtered and dried for 24 h [52].

The TiO₂-MOF/CuPcNW was prepared using adsorption technology. 0.1 g of dried TiO₂-MOF and CuPcNW (0.1 g) were dissolved in 12 mL of DMF, then the solution was mixed together and stirred at 50 °C for 24 h for the adsorption process. The resultant ternary nanocomposite was filtered, rinsed with ethanol, and dried overnight at 50 °C. UV-vis was used to monitor the adsorption process.

6.2.3. Photoanode material

The photoanode electrodes were prepared as reported in the literature [33, 53-57]. The electrochemical characterization (CV and EIS) of the prepared electrodes was achieved in a three-electrode cell configuration (0.1 mol L⁻¹ Na₂SO₄ as electrolyte)

using the Biologic instrument (VMP300, EC-lab software) in a temperature-controlled environment at 25 °C. The photocurrent density (I–V curves) was measured according to Ramaripa et al. [33]. The EIS was measured at a 0.1 Hz to 100 kHz frequency with an open circuit potential and the Z-fit model was used to fit the EIS data).

6.2.4. Characterization Technique

Lambda 365 UV/Vis (ultraviolet-visible) Spectrophotometer operated at a wavelength of 300-900 nm under H₂SO₄ was used to evaluate electronic properties of the prepared materials. X-ray diffraction (XRD) on Phillips 1830 with a focus lens at 1.54 angstroms was used to determine phases and crystallite size. The functional group was identified using Agilent Cary 600 Series Fourier transform infrared spectroscopy (FTIR) from 400 cm⁻¹ to 4000 cm⁻¹ at 25 °C. Scanning electron microscopy (SEM) of FEI Nova 600 instrument was used for morphological imaging at 30 kV. Micro-Raman mod; Jobin-Yvon T64000 at wavelength of 532 nm was also used for functional group analysis at a focal plane of 1.5 µm in diameter. FEI Tecnai G2 20 field emission gun (FEG) transmission electron micrographs (TEM) was also used for morphological image utilizing in bright field mode with an accelerating voltage of 200 kV. Micromeritics Tristar 300 was employed for Brunauer–Emmett–Teller (BET) surface area and pore diameter, outgassing the samples at 150 °C for 4 h, and gas sorption using liquid nitrogen (-195 °C). Perkin Elmer 6000 thermogravimetric analysis (TGA) was used for thermal stability of the materials.

6.3. RESULTS AND DISCUSSION

6.3.1. Dye characterization

The blue clusters of CuPc nanowires (NW) was found inside the tube during the growth process of the CuPc molecule, and then these nanowires placed inside the tube were

collected into a bottle. It was seen that CuPcNW of 1.0 cm length, was grown. The results showed that using self-assembly through strong π - π stacking for organic molecules to fabricate CuPcNW, a one-dimensional nanostructured material, provides an effective and low-cost processing approach [58]. The Raman images and spectra of CuPc nanowires are represented in Figure 6.1. The Raman images (a and b) show an agglomeration of particles that appear to be CuPcNW. The selected regions possessed similar Raman spectra (Figure 6.1(c)) of CuPcNW. The wavenumber less than 200 cm^{-1} showed the phthalocyanine lattice vibrations and crystal symmetry [59]. The wavenumber higher than 200 cm^{-1} attributed to the intra-molecular modes for CuPc (D_{4h}) [60]. It was shown that the Raman peaks this region are also related to the intermolecular vibration [61]. CuPcNW showed to possess the vibrational modes of the A_{1g} , B_{1g} , and B_{2g} for in-plane vibrations, and the E_g for out-of-plane vibration mode [61]. It is well known that the fingerprint for intra-molecular vibrations is observed 1300 and 1600 cm^{-1} due to the presence of typical phthalocyanine [62]. Three prevailing Raman peaks were seen at around 1340 and 1450 cm^{-1} , owing to B_{1g} mode and B_{2g} mode, respectively, from C-C and C-N in-plane vibrations [63].

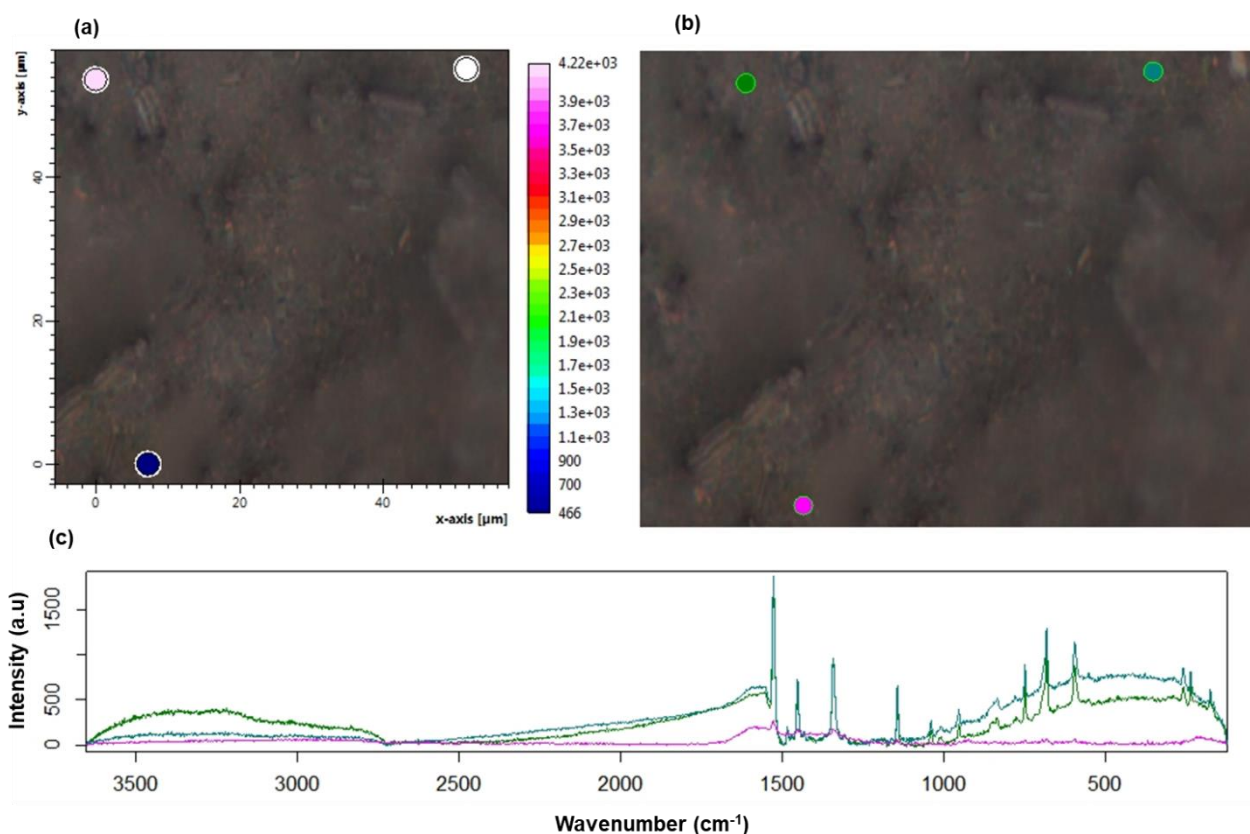


Figure 6.1: Raman images (a and b) and spectra (c) of CuPc nanowires.

Figure 6.2 shows the TEM, HRTEM, and SAED images and the XRD pattern of the CuPcNW. The TEM image (Figure 6.2(a)) showed the branches encompass bundles of nanowires that have growth directions. Figure 2(b) shows the HRTEM image of the CuPc nanowires with the diameter of the self-assembled CuPc nanowires being 70 nm, and the results were similar to those reported in the literature [52]. The interlayer d-space of the CuPcNW was estimated to be ~ 1.2 nm as shown in Figure 6.2(c) from the SAED image. This shows an increase in the crystallinity of the CuPc after the conversion to nanowires. This was further confirmed by the XRD analysis in Figure 6.2(d). The pattern shows characteristic XRD peaks at $2\theta = 7.13^\circ$ and 9.35° for β -CuPc phases [64]. This was supported by the determination of crystallite size for CuPc nanowires using the Debye–Scherrer formula from (100) and (102) planes using Equation 6.1 [65].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (6.1)$$

The symbol β signifies the full-width at half-maximum (FWHM) in radians, λ stands for the 1.5406 Å wavelength of Cu-K α radiation and θ is the Bragg's angle. The D values of CuPcNW were found to be 12.39Å and 9.45Å for (100) and (102), respectively.

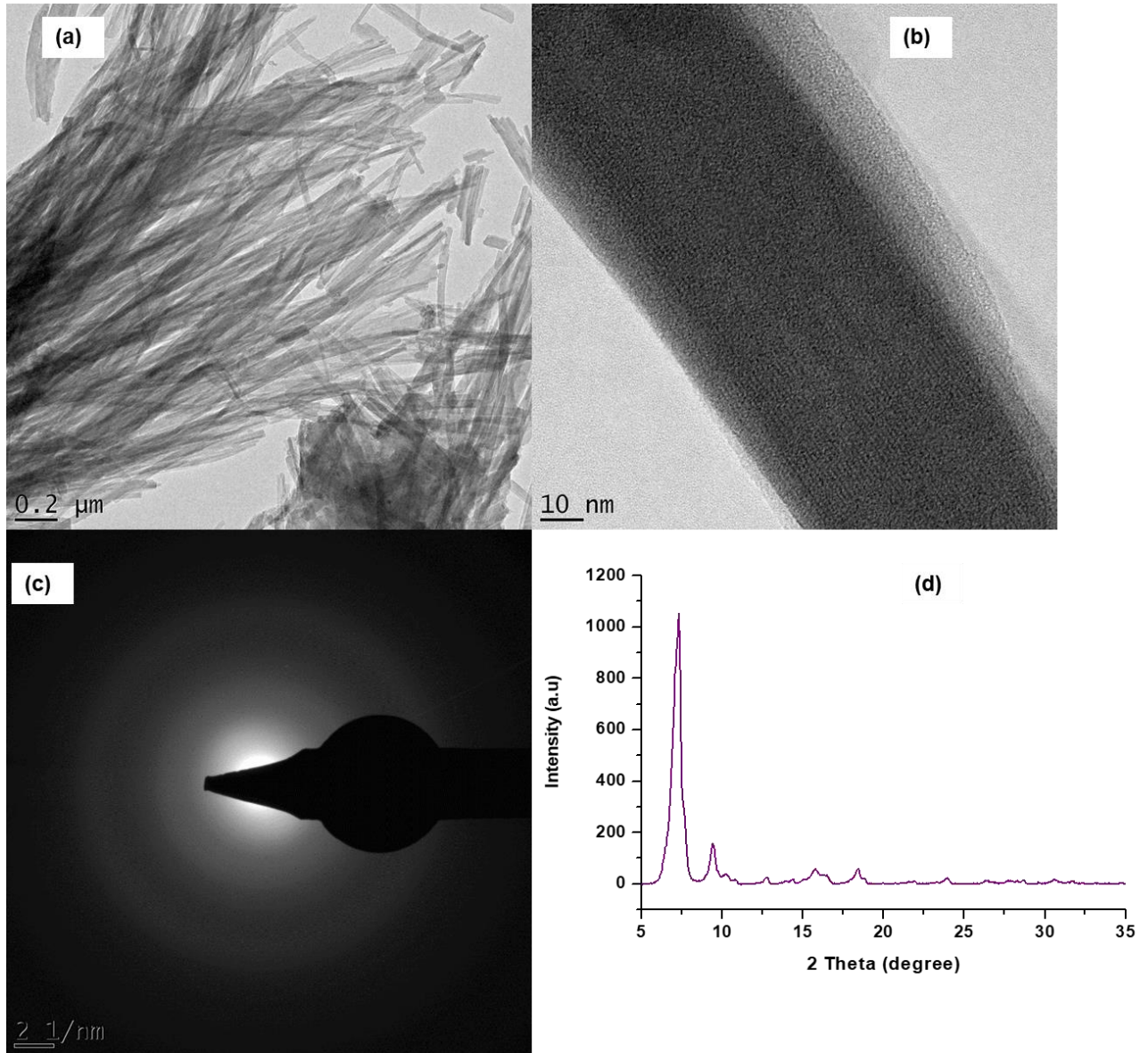


Figure 6.2: An illustration of (a) TEM, (b) HRTEM, (c) SAED images and (d) XRD of CuPc nanowire.

6.3.2. Dye Adsorption

UV-Vis spectrometer was employed to determine the amount of CuPcNW absorbed by TiO₂, MOF, and TiO₂-MOF (Figure 6.3). The UV-Vis spectra of CuPcNW in H₂SO₄ with different concentrations are presented in Figure 6.3(a). The spectra showed intense absorption peaks due to the transitions between the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital of phthalocyanines [66]. The intense absorption peaks were characteristic of the B-band (Soret band), vibronic band, and Q-band in the 240-440, 700, and 791 nm regions of the phthalocyanine ring [38-40]. The B- and Q-bands were due to the HOMO-LUMO of S₀ → S₂ and S₀ → S₁ with $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the visible region [67]. Those B and Q bands that appear in the spectra of CuPc nanowires exist because of the dependence of their molecules on the angle between the planes of molecules [68]. The inset in Figure 6.3(a) shows the effect of concentration on the absorbance of CuPcNW obeying the Beer-Lambert law [31]. Furthermore, the increase in concentration does not shift the position of the absorption peaks; hence, the conduction band in the composite did not change [32]. The absorption of CuPcNW dye by TiO₂ and TiO₂-MOF was monitored in comparison with the UV-vis of TiO₂ and MOF (Figure 6.3(b)). TiO₂ showed an absorption between 250 and 350 nm due to the d-d transition [69]. Moreover, the UV-vis spectrum of MOF exhibited an intense peak at 350 nm owing to the ligand-to-metal charge transfer [35-37]. The appearance of absorption bands matching to TiO₂, and CuPcNW after dye absorption in the resultant composite (TiO₂-MOF/CuPcNW) confirmed the successful immobilization of CuPcNW units onto the TiO₂ and TiO₂-MOF support (Figure 6.3(b)). The reduction in the Q-band indicated the presence of non-aggregated CuPcNW moieties in the nanocomposite, and the concentration of the absorbed nanowire dye was determined to be 2.61 and 2.35 ppm in TiO₂/CuPcNW

and TiO₂-MOF/CuPcNW, respectively. The optical band gap energies were determined from the UV-vis spectra (Figure 6.3(b)) using the Tauc plot and Equation 6.2 [31–32]:

$$\alpha h\nu(\nu) = \beta(h\nu - E_g)^n \quad (6.2)$$

where α represents absorptivity coefficient; β designates the band gap tailing parameter and ν stands for the frequency of light. The h and E_g symbols represent plank constant and optical band gap energy, respectively. The n symbol stands for the transition probability index for direct and indirect allowed electronic transitions, $n = 1/2$ and 2, respectively.

Figure 6.3(c) and (d) present the Tauc plots using direct and indirect allowed electronic transitions, respectively, for CuPcNW, TiO₂, MOF, TiO₂-CuPcNW, and TiO₂-MOF/CuPcNW. The CuPcNW plot revealed three characteristic $\pi \rightarrow \pi^*$, metal to ligand charge transfer (MLCT) and S₀ $\rightarrow$ S₂ transitions which revealed energy gaps of 1.46, 1.70, and 3.20 eV, respectively (Figure 6.3(d) and Table 6.1) using indirect allowed electronic transition. Figure 6.3(d) shows that the energy gaps for TiO₂ and MOF, the obtained band gaps, were found to be 2.88 and 3.11 eV, respectively. However, the absorption of the CuPcNW moieties on the TiO₂ and TiO₂-MOF supports led to a notable reduction in the band gap to 2.79 eV in TiO₂-CuPcNW and 2.58 eV in TiO₂-MOF/CuPcNW and with a new emerging band gap of 1.45 and 1.44 eV, respectively, as a result of the characteristic $\pi \rightarrow \pi^*$ of the phthalocyanine [70]. The smaller band gap of the TiO₂-MOF/CuPcNW showed the improvement of optical properties and suitable material for photovoltaic application.

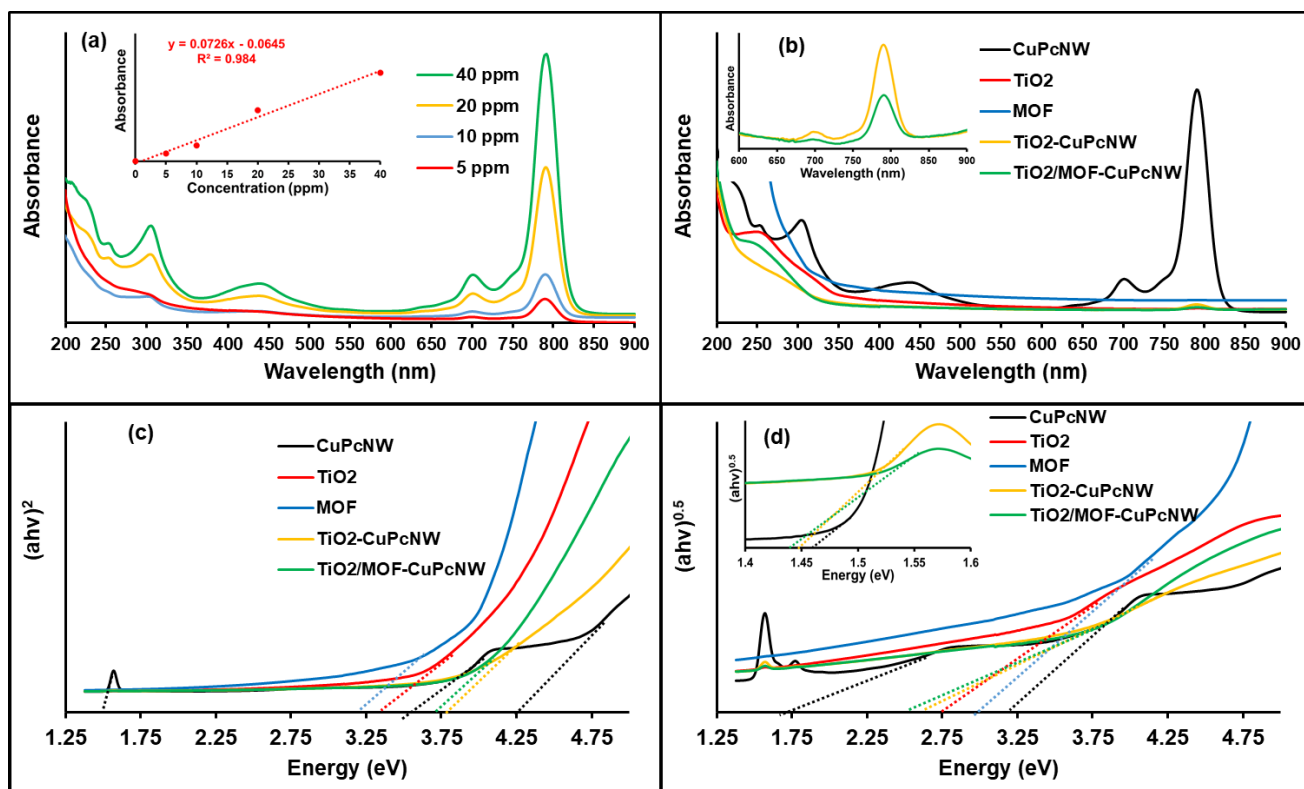


Figure 6.3: An illustration of (a) UV-vis spectra of 5–40 ppm CuPcNW in H_2SO_4 (Inset: absorbance as a function of concentration); (b) UV-vis spectra of CuPcNW, TiO_2 , MOF, TiO_2 -CuPcNW and TiO_2 -MOF/CuPcNW in H_2SO_4 (Inset: Enlargement at 600 to 900 nm); and Tauc plots of CuPcNW, TiO_2 , MOF, TiO_2 -CuPcNW and TiO_2 -MOF/CuPcNW for direct allowed electronic transition (c) and indirect allowed electronic transition (d, Inset: Tauc plots enlargement for CuPcNW, TiO_2 -CuPcNW and TiO_2 -MOF/CuPcNW).

Table 6.1: Electronic and electrochemical properties of MOF, TiO_2 , and TiO_2 -MOF/CuPcNW nanocomposite.

Material	Optical Bandgap (eV) ^a	$E_{1/2}^{\text{ox}}$ (V)	$E_{1/2}^{\text{red}}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
Ni foam	-	0.40	0.35	-5.10	-4.35
TiO_2	3.38	0.41	0.333	-5.08	-4.34
MOF	3.60	0.63	0.50	-5.25	-4.12

TiO₂-MOF/CuPcNW	1.75	0.44	0.35	-5.1	-4.31

a= optical band gap using direct allowed transition

6.3.2. Structural characterization of the nanocomposite after dye adsorption.

Figure 6.4(a) shows the XRD pattern of the TiO₂-MOF/CuPcNW nanocomposite as compared to the ones of TiO₂ and MOF. The pattern of the ternary nanocomposite reveals a shift in major peaks as compared to TiO₂ and MOF precursors due to structural changes. As the CuPcNW was adsorbed by TiO₂-MOF, there was a shift in XRD patterns and the crystallite size was found to be 42.15 nm using the Debye–Scherrer formula from the (101) plane in Equation 6.1. The shift in patterns was due to the incorporation of CuPcNW and MOF into the TiO₂ structure [71].

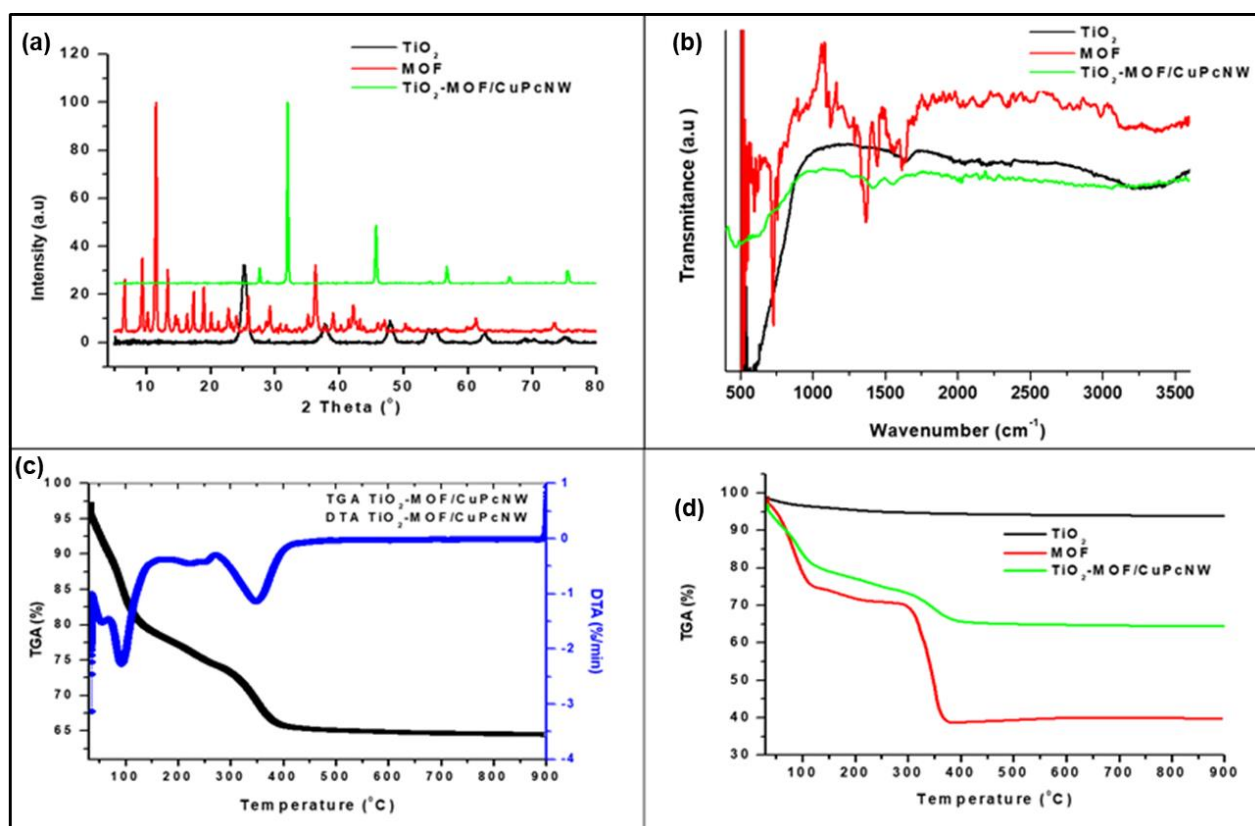


Figure 6.4: (a) XRD patterns, (b) FTIR spectra, (c) TGA of TiO₂, MOF and TiO₂/MOF-CuPcNW and (d) TGA/DTA of TiO₂/MOF-CuPcNW.

The FTIR spectra of TiO₂-MOF/CuPcNW showed the vibrations of CuPcNW group at 1166 and 1287 cm⁻¹ owing to the vibration mode of Cu-N bonding and the C=N-C at bridge sites (see Figure 6.4(b)) [52]. A broad band at 500 cm⁻¹ was observed due to vibrational mode of the Ti-O stretching bond [72]. The in-plane and out-plane C-H bending modes are observed as small peaks at 731 and 761 cm⁻¹ due to the presence of benzene rings in MOF [35-37]. In the region of 1500 and 1700 cm⁻¹, the peaks attributed to the C-C and C=C vibrationals of the benzene ring [36] in MOF and CuPcNW were observed in the dye adsorbed nanocomposite. The peaks at 1371 cm⁻¹ in MOF and TiO₂-MOF/CuPcNW materials were assigned to the symmetry and asymmetry vibrational modes of the C-O carboxylate groups in MOF [73]. TGA and DTA measurements provide information about the phase-transition properties as shown in Figure 6.4. The TGA curve in Figure 6.4(c) indicates that TiO₂ has good thermal stability with a 6% weight loss due to the loss of water and organic species present [74]. The TGA curve of MOF in Figure 6.4(c) shows two degradation steps at 95 and 340 °C due to water loss and organic linker degradation [35, 73]. The thermogram (Figure 6.4 (c) and (d)) of TiO₂-MOF/CuPcNW reveals the improvement of the thermal stability with 35% weight loss due to water loss and degradation of organic compounds [37].

The morphological properties of the prepared TiO₂-MOF/CuPcNW in comparison with TiO₂, MOF, and TiO₂-CuPcNW were studied using TEM. Figure 6.5 shows that the TEM image of TiO₂ exhibited a semispherical morphology with a particle size of 58–83 nm and a relatively narrow size dispersion of the sol-gel method [75], whereas the MOF image shows a disordered meso-structured framework with three-dimensional connectivity and a large particle size of around 450 nm and partially crumpled layer separation [76]. The TiO₂-CuPcNW image indicates the adsorption of dye with the

addition of agglomeration and a large particle size of 200 nm. The agglomeration was observed to decrease in $\text{TiO}_2\text{-MOF/CuPcNW}$, which can be ascribed to the Van der Waals attractive or electrostatic repulsion forces [77]. However, the repulsion forces outweighed the attractive forces in $\text{TiO}_2\text{-MOF/CuPcNW}$, resulting in less agglomerated particles with a size of between 42 and 150 nm.

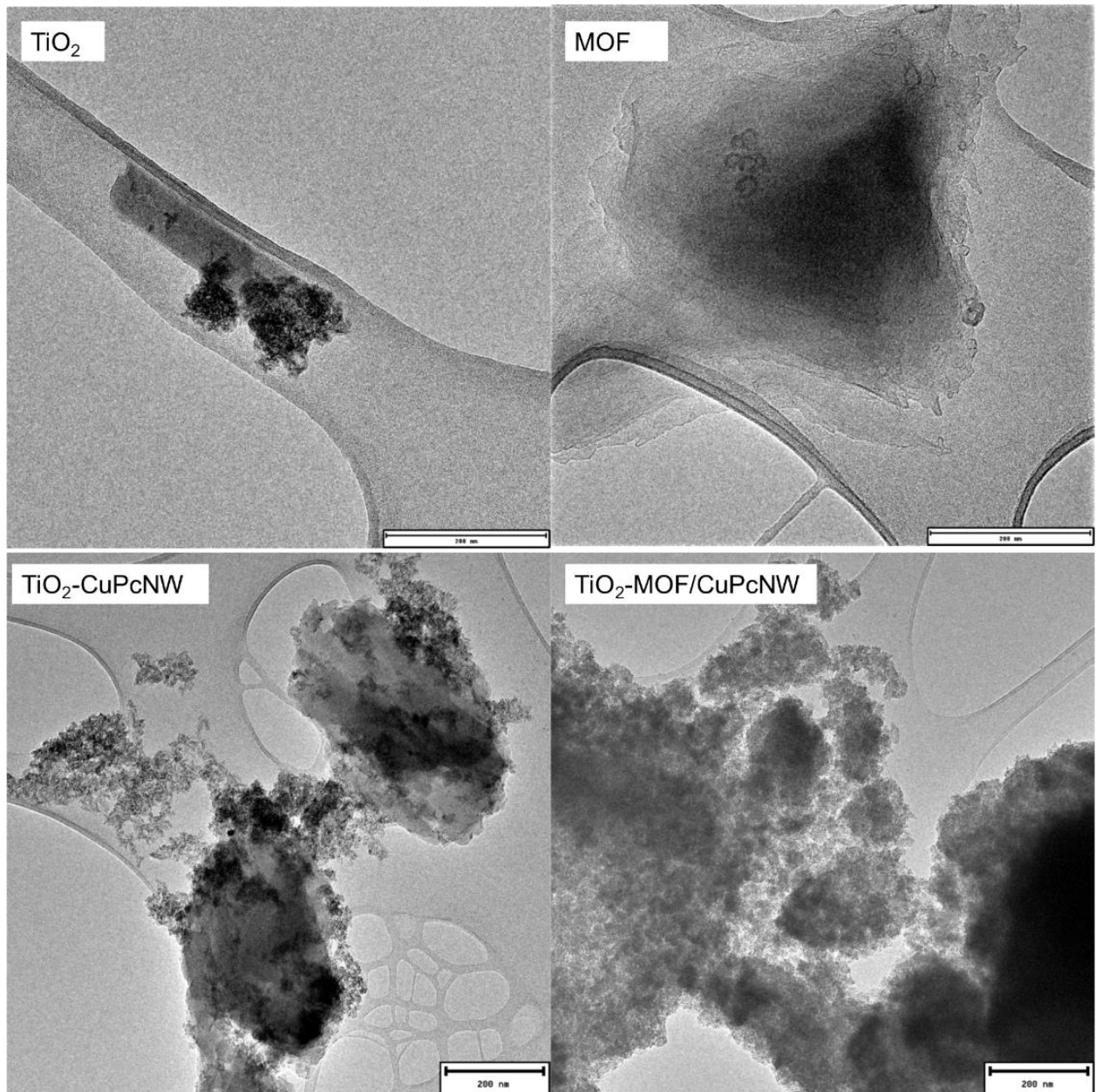


Figure 6.5: TEM images of $\text{TiO}_2\text{-MOF/CuPcNW}$ in comparison with the one of TiO_2 , MOF, and $\text{TiO}_2\text{-CuPcNW}$.

6.3.3. Electrochemical characterizations

Figure 6.6 presents the electrochemical behaviors of blank Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW. At room temperature, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in a 0.1 M Na₂SO₄ solution using TiO₂, MOF, and TiO₂-MOF/CuPcNW as working electrodes, platinum wire as counter electrode, and Ag/AgCl as reference electrode. CV in Figure 6.6 (a) shows the initial potential of 0.0 V to the final potential of 1.0 V for all materials. The figure shows one anodic reduction peak in the forward scan and one cathodic oxidation peak in the reverse scan for TiO₂, MOF, and TiO₂-MOF/CuPcNW anodes. These CVs were employed to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for TiO₂, MOF, and TiO₂-MOF/CuPcNW. The half-wave peak potential ($E_{1/2}$) for the first ring reduction and oxidation, respectively, is listed in Table 6.1. The E_{HOMO} and E_{LUMO} were calculated using Equations 6.3 and 6.4 [78], respectively:

$$E_{HOMO} = - (E_{1/2}^{red} + 4.75) \text{ eV} \quad (6.3)$$

$$E_{LUMO} = - (-E_{1/2}^{ox} + 4.75) \text{ eV} \quad (6.4)$$

The E_{HOMO} values were found to be -5.1, -5.08, -5.25, and -5.1 eV for Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW, respectively. On the other hand, the E_{LUMO} values were obtained to be -4.35, -4.34, -4.12, and -4.31 eV for Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW, respectively. The HOMO-LUMO values were within the reported values in the literature [78].

Electrochemical impedance in Figure 6.6(b) shows the Nyquist plot used to determine the conductivity of TiO₂, MOF, and TiO₂-MOF/CuPcNW nanocomposites. It is clear from the Bode plots and the corresponding phase angle measurements (Figure 6.6(c))

that the pure nickel foam is at least one order of magnitude higher in resistance than both TiO₂-coated substrates. The values of the conductivity were obtained using Equation 6.5 [79]:

$$\sigma = t/R_{ct}.A \quad (6.5)$$

where t is the thickness of an electrode, R_{ct} is the charge transfer resistance and A is the area of the substrate.

The conductivity of Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW nanocomposites (Table 6.2) was found to be 0.9, 1.1, 8.4, and 244 $\mu\text{S}/\text{cm}$, respectively. This reveals an enhancement of conductivity on the electrodes using TiO₂-MOF/CuPcNW. High conductivity is one of the requirements for charge transfer in dye-sensitized solar cells. The lifetime (τ) of the TiO₂-MOF/CuPcNW nanocomposite was estimated from its maximum peak frequency (f_{max}) of 47.5° using Equation 6.6 [80], and it was found to be 3.35 ms.

$$\tau = 1/(2\pi f_{\text{max}}) \quad (6.6)$$

Moreover, a constant phase element (C_2/CPE) is chosen to accommodate double-layer capacitance for the porous nature of the surface of the electrode material. This is expected to greatly enhance the interaction at the electrode/electrolyte interface in the intended solar cell applications. The proposed mechanism for photovoltaic studies is shown in Figure 6.6(d).

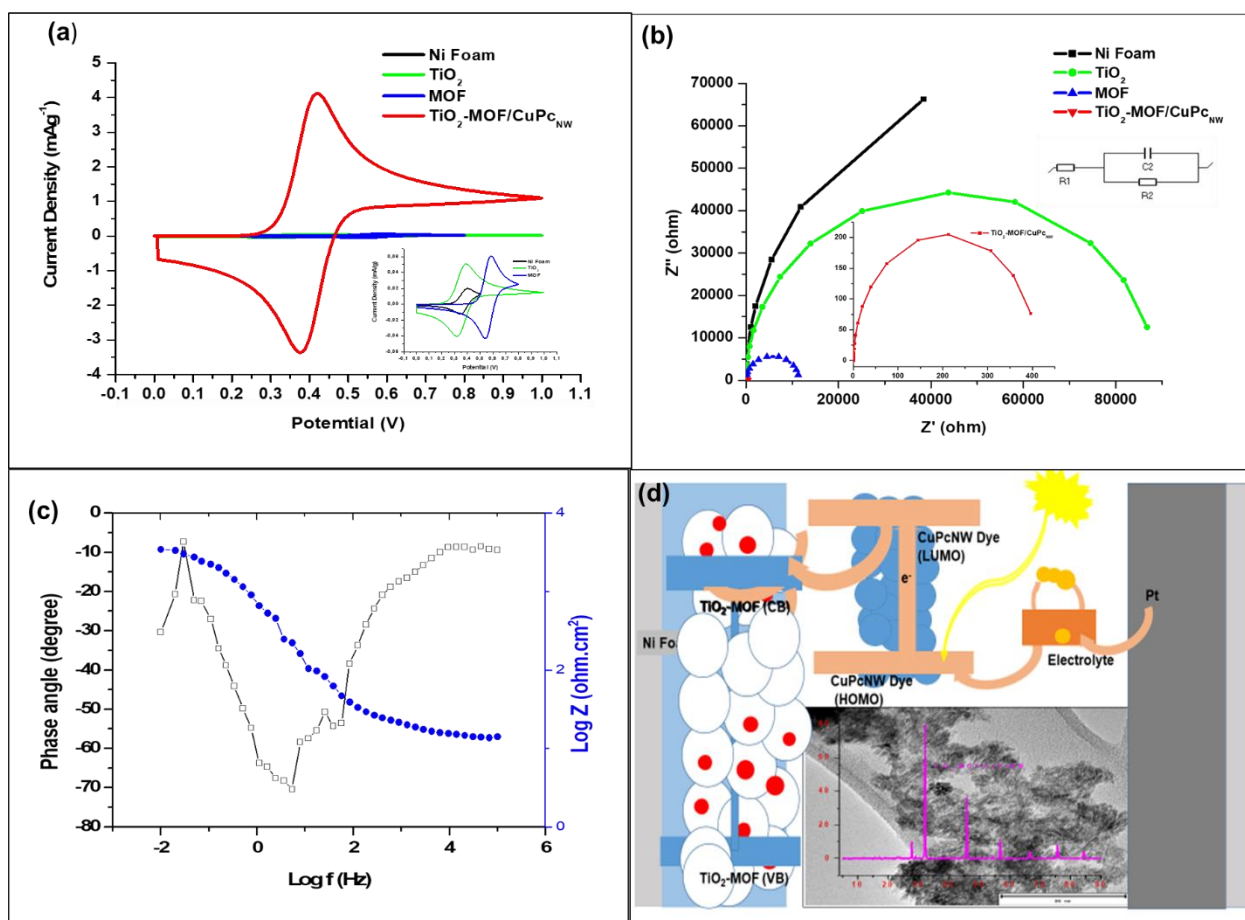


Figure 6.6: (a) Cyclic voltammetry and (b) Electrochemical Impedance spectroscopy for Ni foam, TiO_2 , MOF, and $\text{TiO}_2\text{-MOF/CuPcNW}$ nanocomposite; (c) Bode impedance for $\text{TiO}_2\text{-MOF/CuPcNW}$ composite; (d) Geometry of DSSCs and scheme of the electron transport process using a band diagram for $\text{TiO}_2\text{-MOF/CuPcNW}$.

Table 6.2: Fitted circuit parameters of EIS of Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW nanocomposite in 0.1 M Na₂SO₄ and calculated ionic conductivity.

Material	Rs (Ω)	CPE (μF)	R_{ct} ($\text{k}\Omega$)	Conductivity ($\mu\text{S/cm}$)
Ni foam	19.7	184	114	0.9
TiO ₂	23.3	25.7	89.6	1.1
MOF	21.3	153	11.9	8.4
TiO ₂ -MOF/CuPcNW	0.8767	7.53	0.410	244

6.3.4. Photovoltaic performance.

The photocurrent densities of the prepared Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW nanocomposite were measured using a CV scan in simulated light (64 mW m⁻² intensity) in Figure 6.7(a). It was found that the Ni foam, TiO₂, and MOF materials have photocurrent densities of 0.02 (0.38 V), 0.39 (0.31 V), and 0.19 (0.66 V) mA cm⁻², respectively. The low photocurrent is attributed to the poor light absorption by the material's surface. This results in poor charge separation and, hence, a reduction in photocatalytic efficiency [81]. Approximately 4.067 mA m⁻² photocurrent density at 0.430 V was obtained in the TiO₂-MOF/CuPcNW nanocomposite. The highest photocurrent density attained by the nanocomposite was well within the many photo-responses that have been reported for the material under illumination conditions [82]. Table 6.3 compares the maximum photocurrent attained by the Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW nanocomposite obtained in this work with other reported values in the literature [82–84]. The enhanced photocurrent obtained for the TiO₂-MOF/CuPcNW nanocomposite is largely related to the presence of CuPcNW, which increases active sites for electron transfer mechanisms, thus enhancing the

photocurrent [78]. This was confirmed by the addition of CuPcNW to Ni foam, TiO₂, and MOF, which improved photocurrent but had 50% lower photocurrent densities than the nanocomposite (Figure 6.7(b)). The power conversion efficiency (η) of the Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW nanocomposite was calculated using Equation 6.7 [85]:

$$\eta = ((E_{\text{rev}}^0 - E_{\text{mea}}) \times I) / P_{\text{in}} \quad (6.7)$$

where I (mA cm²) is for photocurrent density, E_{mea} represents the working electrode potential, E_{rev}^0 represents 1.43 V Ag/AgCl for the standard of the reversible potential, and P_{in} (mW/cm²) stands for the input power of the simulated light intensity.

The η values determined for the Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNW nanocomposite are represented in Figure 6.7(c). The highest η value was 6.47% for the TiO₂-MOF/CuPcNW nanocomposite, whereas the lowest was 0.066 % for the Ni foam. The η values of TiO₂ and MOF were found to be 0.617 and 0.255%, respectively. The η values reported in Table 6.3 for the TiO₂-MOF/CuPcNW nanocomposite are better than the ones reported in the literature [20, 41, 85, 86]. The values of η are 0.26% for TiO₂/Cu-MOF [41] 0.17% for TiO₂/Zn-MOF [85], 1.22% for TiO₂/Ru-MOF [86] and 2.34% using TiO₂/Zn-MOF in the presence of N719 dye [20]. The enhanced η values obtained for the TiO₂-MOF/CuPcNW nanocomposite were also related to the presence of CuPcNW. This was further confirmed by the adsorption of CuPcNW by Ni foam, TiO₂, and MOF, and the resultant dye composite showed an improvement of η values. Their η values, however, were 50% lower than those of one of the nanocomposites (Figure 6.7(d)). Hence, the results show that CuPcNW dye may be used to enhance the photovoltaic performance of TiO₂-MOF properties [87]. The overall power conversion efficiency of 6.47%, acquired from the photocurrent density

of 4.067 mA cm^{-2} at 0.430 V , was due to the $\text{TiO}_2\text{-MOF/CuPcNW}$ ternary nanocomposite as a result of an increment in the electronic properties [84].

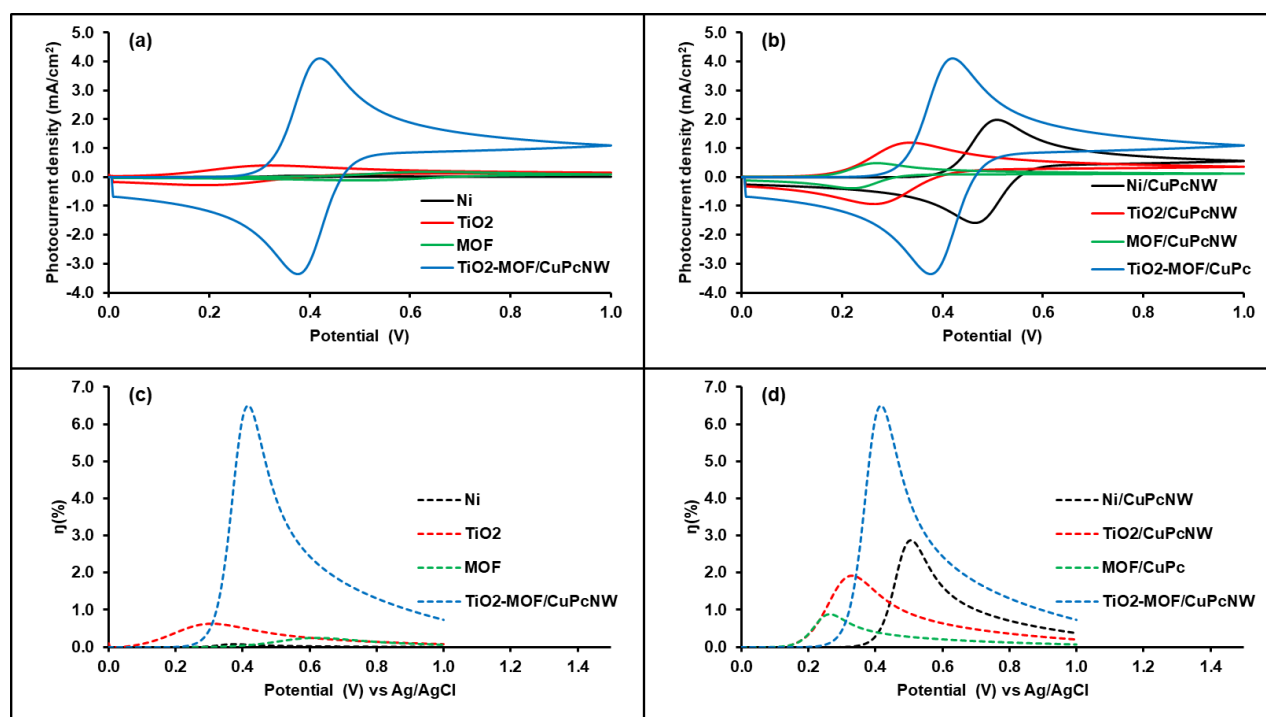


Figure 6.7: (a) Photocurrent response and (c) power conversion efficiency of Ni foam, TiO_2 , MOF, and $\text{TiO}_2\text{-MOF/CuPcNW}$ nanocomposite; and (c) photocurrent response and (d) power conversion efficiency of Ni foam/ CuPcNW , $\text{TiO}_2/\text{CuPcNW}$, MOF/CuPcNW , and $\text{TiO}_2\text{-MOF/CuPcNW}$ nanocomposite.

Table 6.3: Comparison of the photocurrent density obtained for Ni foam, TiO_2 , MOF, and $\text{TiO}_2\text{-MOF/CuPcNW}$ nanocomposites in this study with the literature values prepared using various methods.

Material	Electrolyte	Photocurrent (mA/cm²)	Efficiency (%)	Ref
Ni foam	0.1 M Na_2SO_4	0.02	0.066	In this work
TiO_2	0.1 M Na_2SO_4	0.39	0.617	In this work
MOF	0.1 M Na_2SO_4	0.19	0.255	In this work

Ni/CuPcNW	0.1 M Na ₂ SO ₄	1.984	2.786	In this work
TiO₂/CuPcNW	0.1 M Na ₂ SO ₄	1.042	1.773	In this work
MOF/CuPcNW	0.1 M Na ₂ SO ₄	0.479	0.832	In this work
TiO₂-MOF/CuPcNW	0.1 M Na ₂ SO ₄	4.067	6.467	In this work
TiO₂-Cu-MOF	I ₃ /I ⁻ redox	-	0.26	[41]
TiO₂-Ru-MOF	I ₃ /I ⁻ redox	-	1.22	[86]
TiO₂-Zn-MOF	ACN, LiI, I ₂ & LiClO ₄	1.04	0.67	[85]
TiO₂/Zn-MOF/N719	PEGOPEG/NaI/I ₂ /EMITFMSI/AN		2.34	[20]

N719=Di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-

dicarboxylato)ruthenium(II); AN=acetonitrile; PEGOPEG=poly(ethylene oxide)–poly(ethylene glycol); and EMITFMSI= 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide

6.4. CONCLUSION

A new class of porous materials based on TiO₂-MOF together with a nanoribbon-like CuPc nanowire dye was prepared by the sol–gel method followed by dye adsorption technology. The CuPc nanowire dye was created by dissolving copper phthalocyanine powder in chloroform and adding an aqueous tetrafluoroacetic acid solution. Ultraviolet-visible spectroscopy revealed that the resultant ternary nanocomposite has a small band gap of 1.75 eV at an absorption wavelength of 798 nm. The x-ray diffraction patterns, Fourier transform infrared and Raman spectra showed that the TiO₂, MOF, TiO₂-MOF, and CuPcNW phases, and functional groups in the TiO₂-MOF/CuPcNW nanocomposite, respectively. It was also seen in the gravimetric

studies that the thermal stability of the composite had been improved. The calculated HOMO and LUMO energies of the nanocomposite were calculated from CV and found to be -5.1 and -4.31 eV, respectively. On the other hand, the EIS showed that the TiO₂-MOF/CuPcNW photoanode composite possessed a high conductivity of 244 $\mu\text{S}/\text{cm}$ as compared to the parent materials. These parameters make the TiO₂-MOF/CuPcNW composite an excellent candidate for dye-sensitized solar cell applications. The maximum photocurrent and power efficiency of the TiO₂-MOF/CuPcNW composite were 4.067 mA cm⁻² at 0.430 V and 6.47%, respectively, under a simulated light source. The morphological studies revealed that the TiO₂-MOF/CuPcNW nanocomposite was more ribbon-like as compared to others, resulting in easier charge separation of photogenerated charge carriers and leading to improved photocurrent as the case here. Notwithstanding, the sol-gel and adsorption methods for preparing TiO₂-MOF/CuPcNW ternary nanocomposite used in this study showed promising photocurrent responses and power conversion efficiency, could also be employed for making TiO₂-MOF/CuPcNW ternary nanocomposite for DSSC applications.

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CHAPTER 7:

**IMPACT OF COPPER PHTHALOCYANINE NANOTUBE DYE ON
PHOTOVOLTAIC PERFORMANCE OF TITANIUM OXIDE-METAL ORGANIC
FRAMEWORK NANOCOMPOSITE**

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ABSTRACT

Copper phthalocyanine nanotube (CuPcNT) dye was prepared and used in TiO₂ based composite Dye synthesized solar cells (DSSCs) This work investigates the impact of CuPcNT dye on TiO₂, MOF and TiO₂-MOF materials in photovoltaic performance. The formation of ternary nanocomposite was confirmed by Ultraviolet visible spectroscopy revealing the absorption at 798 nm wavelength with a bandgap energy of 2.62 eV. X-ray diffraction patterns, and Raman spectroscopy showed the TiO₂, MOF and CuPcNT phases, and functional groups in the TiO₂-MOF/CuPcNT ternary nanocomposite. Cyclic voltammetry and electrochemical impedance spectroscopy showed the half wave peak potentials of the TiO₂-MOF/CuPcNT composite with the HOMO and LUMO values -4.85 and -4.37 eV. The EIS behaviour showed the improvement of conductivity of the ternary nanocomposite with the value 172 $\mu\text{S}/\text{cm}$. The overall power conversion efficiency of 11.69%, acquired from the photocurrent density of 7.02 mA cm^{-2} at lower potential of 0.35 V, was observed in the TiO₂-MOF/CuPcNT ternary nanocomposite. This shows that CuPcNT dye may be used to enhance the photovoltaic performance of TiO₂-MOF composite in the DSSCs.

Keywords: Composites, copper phthalocyanine nanotube, dye synthesized solar cells, metal organic framework, titanium dioxide

7.1. INTRODUCTION

An increase in energy demand has led to energy crisis worldwide, support economic growth and reduction of greenhouse effect caused by the fossil fuel product combustion [1 7] . In order to overcome those problems, there is a need to develop an alternative clean energy technology. More than the decades, dye sensitized solar cells

(DSSCs) have been considered as an excellent alternative clean energy technology [8-17]. DSSCs have the advantages of cost effective, easy to manufacture and pollution-free [18-22]. In DSSCs technology, the photons from sunlight are absorbed and converted into electricity by the processes of photovoltaic effect [23-27] whereby electron from the dye become excited, and then injected to the metal oxide semiconductor surface [28-31]. The photoanode employed in the DSSCs is typically constructed using the thick film ($\sim 10\ \mu\text{m}$) especially TiO_2 , ZnO or SnO nanoparticles. Amongst metal oxides, TiO_2 film is largely considered due to its large inherent absorptive surface area for the light scattering [31-32]. Furthermore, TiO_2 has its outstanding properties, which are utilized in different applications including photodegradation of organic pollutants in the water treatment process [33-35]. However, its obstacles are the high recombination of photo-generated electron-hole pairs and the weak absorption in the visible region [36, 37]. Researchers developed a way in which the surface area of TiO_2 nanoparticle could be modified in order to solve these inferiorities. They converted TiO_2 into nanostructures including thin film structure, nanoparticle, nanorod, nanosheet, and nanotube to improve its performance [38, 22-24]. Nowadays, the issue of combining TiO_2 with the suitable semiconductors in the form of composite material can overcome its disadvantages [25-27, 39]. Ko et al. [26] studied the TiO_2 material doped with aluminum and tungsten metals which revealed an increase in open-circuit voltage and short circuit current in DSSC. Hou et al. [27] prepared the $\text{SnO}_2/\text{TiO}_2$ nanotube composite and used it for the reduction of recombination of electron-hole pairs in photoreactivity. Xiaodan et al. [39] also reported on the enhancement of visible light absorption of TiO_2 using ZnS/TiO_2 nanocomposite. Wang and Wang [40] reported on the increase of photoelectric conversion in the solar cell using PPV/TiO_2 nanocomposite.

The room for an improvement of the photovoltaic performance using a TiO_2 in form of an organometallic hybrid composite is one of the promising techniques. It was seen that coating the surface of titanium oxide with metal-organic frameworks (MOFs) resulted in the improvement of photo-conversion efficiency (PCE) [41-44]. MOFs are crystalline material made up of a metal core connected through organic linkers and they have gained much attention due to their interesting properties [43]. MOF is another photoanode that is extensively employed in the photovoltaic studies owing to its high surface area in order to absorb more photons from the light [44-47], gas sensing [48, 9], and hydrogen production [49-57]. Vinogradov *et al.* [46] reported on single-step hydrothermal synthesis of the TiO_2 -MOF composite which was applied for the first time to produce a monolithic perovskite/ TiO_2 -MOFs heterojunction solar cell with 6.4% PCE. Ramasubbu *et al.* [48] reported on highly interconnected porous TiO_2 -Ni-MOF composite aerogel photoanodes in quasi-solid dye-sensitized solar cells with 8.846% PCE. However, MOF has a drawback of slow electron transfer.

On the other hand, the addition of dye compounds in the TiO_2 composite such as metal phthalocyanines (MPcs) results in improved photovoltaic performance. MPcs are documented to have great resistance to chemical degradation, intense absorption in the visible region, and excellent thermal stability [9, 49]. They have been used as functional materials in many applications including diodes, transistors, gas sensors, and photovoltaic devices [59-64]. Mekprasart *et al.* [65] studied the preparation of TiO_2 /copper-phthalocyanine (CuPc) nanocomposites as modified working electrode materials in dye-sensitized solar cells with PCE of 1.24% and fill factor of 0.45. Whereas, the researchers discovered a high open-circuit voltage by using Schottky diode solar cells having CuPc of low concentration due to a small exciton diffusion length of a few nm [65-68]. The phthalocyanine derivative dye such as copper

phthalocyanine nanotubes (CuPcNT) is a suitable inorganic dye for the DSSCs applications and it absorbs at the visible and ultraviolet regions [51]. CuPcNT is a 2D aromatic molecule, hollow tubular rectangular nanotube prepared from the ribbon-like structure CuPc nanowire. Due to its outstanding properties including the ability to self-assemble into stacker through π - π supra-molecule interaction and relatively high charge-carrier mobilities in electronic devices [5, 65]. In addition, CuPcNT micro molecule possesses the outstanding electrical and optical properties and makes the perfect materials for the molecular electronics [52]. This owes to the additional properties such as high thermal and chemical stability as well as outstanding electronic properties [53]. The preparation of TiO₂-MOF incorporated with CuPcNT dye, is seen to be promising nanocomposite that could enhance the performance in DSSCs application. In this work, we report for the first time the impact of copper phthalocyanine nanotubes adsorbed on the surface of the TiO₂-MOF nanocomposite as a photoanode in the DSSCs application. The presence of CuPc nanotubes had the ability to enhance the photovoltaic properties of TiO₂-MOF by CuPc nanotubes dispersion in the TiO₂ matrix and the homogeneity in ternary nanocomposite (TiO₂-MOF/CuPcNT). Their fundamental structural, physical, and electrochemical properties were thoroughly investigated. The TiO₂-MOF/CuPcNT ternary nanocomposite was applied to modify working electrode materials in DSSC and investigated through photocurrent response density measurements.

7.2. EXPERIMENTAL

7.2.1. Materials

Copper nitrate trihydrate, titanium (IV) tetraisopropoxide, trimesic acid, sodium hydroxide, acetic acid, 1-methyl-2-pyrrolidinone, polyvinylidene fluoride, nickel foam substrates, sulphuric acid and sodium sulphate (Na₂SO₄) were procured from Sigma

Aldrich, South Africa. Acetonitrile, chloroform, dimethyl formamide (DMF), trifluoro acetic acid, phthalimide, excess urea, ammonium molybdate and nitrobenzene were acquired from Merck, South Africa. The parafilm plastic film was from Bemis, South Africa. Acetic acid, acetyl acetate, ethanol (EtOH), 2-propanol and methanol were obtained from Rochelle Chemicals, South Africa.

7.2.2. Synthesis of titanium dioxide-metal organic framework/copper phthalocyanine nanotube composite.

A copper benzenetricarboxylate MOF was synthesized following a reported hydrothermal procedure in the scientific literature [35, 54].

TiO₂ and TiO₂-MOF composite were synthesized using sol -gel method [5, 40]

Copper phthalocyanine nanotube (CuPcNT) was prepared by mixing 0.02 mol of phthalimide and 0.05 mol of excess urea, 0.06 of ammonium molybdate, in 5.8 mmol of copper nitrate in nitrobenzene as an solvent of high boiling point, was refluxed for 5 h to produce a dark blue of copper phthalocyanine [55-57]. The resultant dark blue was placed in chloroform solution to make 1×10^{-4} mol/L and the solution was stirred for 10 min. The trifluoro acetic acid (CF₃COOH) (1.8×10^{-4} mol/L) was added and stirred with the solution for 5 h. The dark blue CuPc was chemically self-assembled into a form of CuPc nanowires (NW) that was filtered and dried for 24 h [58]. Therefore, 0.1 g CuPcNW in 25 ml EtOH placed in a hydrothermal stainless-steel autoclave and heated at 180 °C for 24 h. The resulting nanotube [59] was filtered and left on the surface in order to allow it to be dry.

The TiO₂-MOF/CuPcNT was prepared using an adsorption technology. Briefly, 0.1g of dried TiO₂-MOF and CuPcNT (0.1 g) dissolved in 12 mL of DMF, then the solution was

mixed and stirred at 50 °C for 24 h for the adsorption process. The resultant ternary nanocomposite was filtered and rinsed with EtOH and overnight at 50 °C. UV-vis was used to monitor adsorption process.

7.2.3. Photoanode material

The photoanode electrodes were prepared as reported in the literature [33, 60-63]. The electrochemical characterization (CV and EIS) of the prepared electrodes was achieved in a three-electrode cell configuration (0.1 mol L⁻¹ Na₂SO₄ as electrolyte) using the Biologic instrument (VMP300, EC-lab software) in a temperature-controlled environment at 25 °C. The photocurrent density (I–V curves) was measured according to Ramaripa et al. [33]. The EIS was measured at a 0.1 Hz to 100 kHz frequency with an open circuit potential and the Z-fit model was used to fit the EIS data).

7.2.4. Characterization Technique

Lambda 365 UV/Vis (ultraviolet-visible) Spectrophotometer operated at a wavelength of 300-900 nm under H₂SO₄ was used to evaluate electronic properties of the prepared materials. X-ray diffraction (XRD) on Phillips 1830 with a focus lens at 1.54 angstroms was used to determine phases and crystallite size. The functional group was identified using Agilent Cary 600 Series Fourier transform infrared spectroscopy (FTIR) from 400 cm⁻¹ to 4000 cm⁻¹ at 25 °C. Scanning electron microscopy (SEM) of FEI Nova 600 instrument was used for morphological imaging at 30 kV. Micro-Raman mod; Jobin-Yvon T64000 at wavelength of 532 nm was also used for functional group analysis at a focal plane of 1.5 μm in diameter. FEI Tecnai G2 20 field emission gun (FEG) transmission electron micrographs (TEM) coupled with selected area electron diffraction (SAED) was also used for morphological image utilizing in bright field mode

with an accelerating voltage of 200 kV. Perkin Elmer 6000 thermogravimetric analysis (TGA) was used for thermal stability of the materials.

7.3. RESULTS AND DISCUSSION

7.3.1. Dye characterization

The rectangular CuPc nanotube (NT) were found inside the tube during transformation process [64] and was confirmed by various analytical techniques. Figure 7.1 (a)-(d) shows TEM and SAED images; and XRD patterns of CuPcNT. Figure 7.1 (a) shows the hollow tubular CuPcNT with the diameter of 0.267 μm respectively. Figure 7.1(b) clearly shows the smooth high resolution transmission electron microscopy (HRTEM) morphology of CuPcNT that displayed the hollow rectangular nanotube and the single wall thickness of nanotube that ranges from 18.3 nm similar to the literature [65]. Figure 7.1 (c) shows the SAED for the CuPcNT with the d-spacing of 0.476 nm. Figure 7.1(d) shows a typical XRD pattern of the CuPcNT material. It can be seen that there are two strong peaks at $2\theta = 7.08$ and 9.25° with the crystallite size estimated to be 265.0 and 353.0 nm, respectively, using the Debye–Scherrer formula in Equation 7.1.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (7.1)$$

The β stands for the full-width at half-maximum measured in radians, λ represents the x-ray wavelength of Cu-K α radiation and θ is for the Bragg's angle. In addition, the interlayer d-spacing was estimated from XRD pattern and found to be 0.952 nm. The two strong peaks indicates the formation of β phases of CuPc nanotubes. This is in good agreement and corresponds with standard JCPDS data card (number: 39-1881).

The absence of other strong diffraction peaks conclusively confirm formation of pure phase CuPcNT crystal [66].

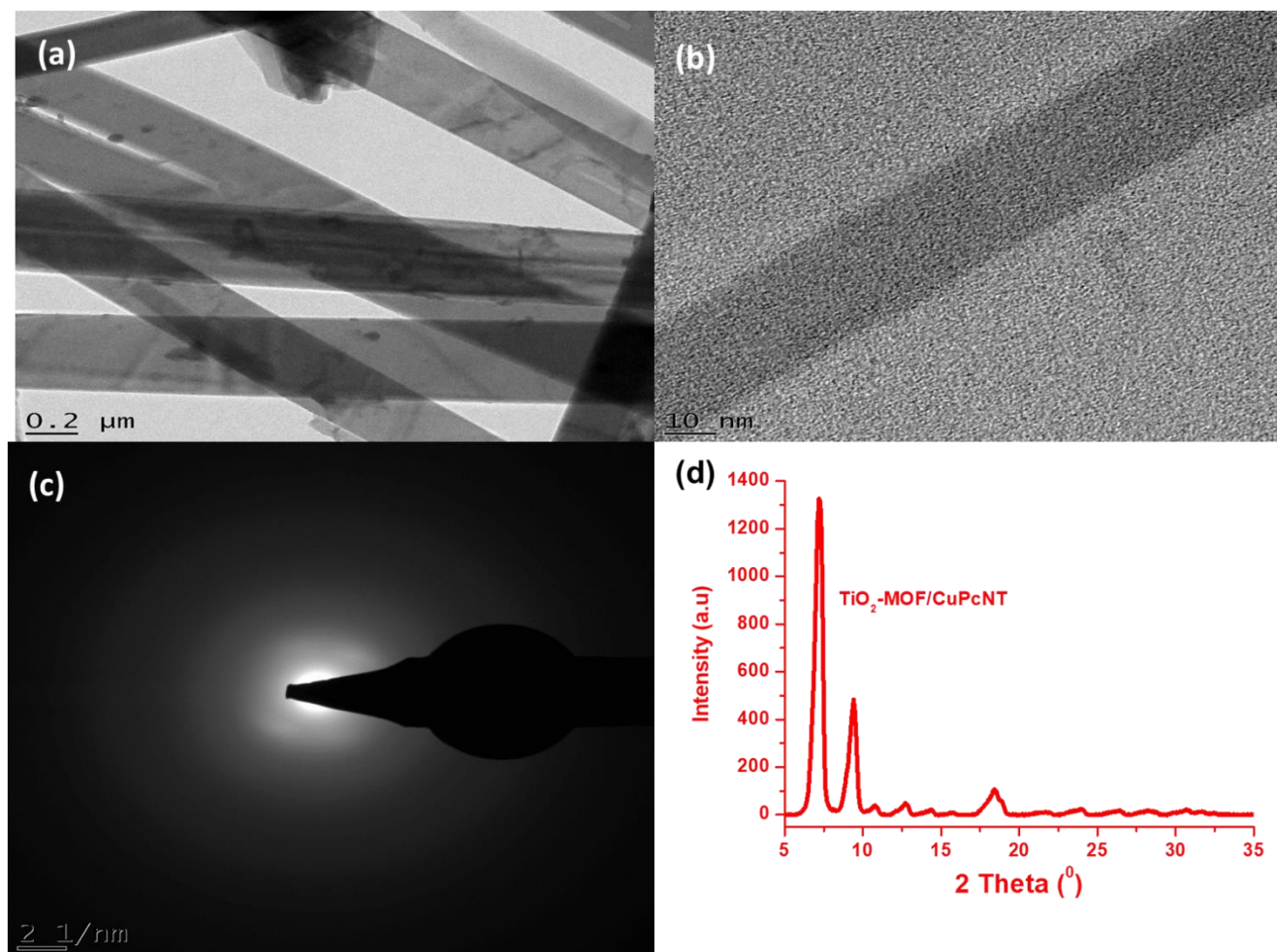


Figure 7.1: (a) TEM, (b) HRTEM, (c) SAED images and (d) XRD of CuPcNT.

7.3.2. Dye Adsorption

The electronic properties of CuPcNT was investigated using UV-vis spectroscopy. The UV-Vis spectra of CuPcNT in H₂SO₄ are presented in Figure 7.2 (a) and they possess a characteristic B-band (Soret band), vibronic band and Q-band at 240– 440, 700 and 790 nm, respectively, typical for phthalocyanine molecule [67-69]. There was little bathochromic shift of absorbance during the formation of CuPc nanotube as compared

to CuPc molecule [33, 70]. The observed band broadening and maximum shift in the B- and Q-bands in the absorption spectra of CuPcNT was due to the planes of the phthalocyanine molecules in the structure [70]. The inset in Figure 7.2(a) demonstrates the effect of concentration on the absorbance of CuPcNT which showed a trend with in absorbance obeying the Beer-Lambert law [9]. The absorption of CuPcNT dye by TiO_2 and TiO_2 -MOF was monitored using UV-vis spectroscopy as given in Figure 7.2(b). The UV-vis spectrum of TiO_2 possessed an absorption band at around 275 nm due to the 3d-2p transition of Ti and O elements in TiO_2 [71]. The spectrum of MOF showed an intense peak at 350 nm owing to the ligand-to-metal charge transfer [26]. After dye CuPcNT absorption, the resultant nanocomposites (TiO_2 -CuPcNT and TiO_2 -MOF/CuPcNT) possessed the appearance of peaks corresponding to both components, i.e., TiO_2 and CuPcNT [72]. This confirmed the successful adsorption of CuPcNT units onto the TiO_2 -MOF support (Figure 7.2(b)). The inset in Figure 7.2(b) shows a small Q-band as an indication of the presence for non-aggregated CuPc moieties in the composite [55, 72]. The concentration of the absorbed CuPcNT dye was determined to be 16.34 and 13.49 ppm for TiO_2 -CuPcNT and TiO_2 -MOF/CuPcNT, respectively.

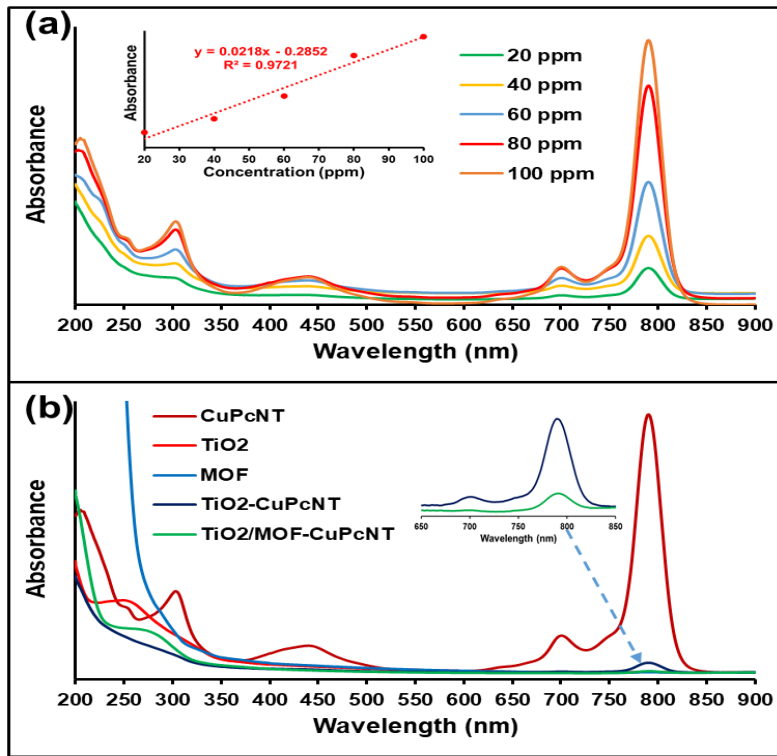


Figure 7.2: (a) UV-vis spectra of 20–100 ppm CuPcNT at 20 ppm intervals in H₂SO₄ (Inset: absorbance as a function of concentration); and (b) UV-vis spectra of CuPcNT, TiO₂, MOF, TiO₂-CuPcNT and TiO₂-MOF/CuPcNT at 100 ppm in H₂SO₄ (Inset: Enlargement absorption spectra of TiO₂-CuPcNT and TiO₂-MOF/CuPcNT).

The band gaps can be determined through UV-Vis spectroscopy using Tauc plot in accordance with Equation 7.2 [7-9, 73]. .

$$\alpha h\nu(\nu) = \beta(h\nu - E_g)^n \quad (7.2)$$

where α , ν , β , h , E_g , and n represent assumturity coefficient; frequency of light; band gap tailing parameter, plank constant, optical band gap energy, and transition probability index, respectively. The transition probability index values of 1/2 and 2 are known to be direct and indirect allowed electronic transitions, respectively. Figure 7.3(a) and (b) show the Tauc plots using direct (DAET) and indirect (IAET) allowed electronic transitions, respectively, for CuPcNT, TiO₂, MOF, TiO₂-CuPcNT and TiO₂-

MOF/CuPcNT. The DAET plot of CuPcNT revealed two characteristic $\pi \rightarrow \pi^*$, metal to ligand charge transfer (MLCT) and $S_0 \rightarrow S_2$ transitions which revealed energy gaps of 2.07 and 3.22 eV [74](Figure 7.3(a) and Table 7.1). However, this is in contrast with the work of Samanta et al. [75] where they observed only one characteristic $\pi \rightarrow \pi^*$ metal to ligand charge transfer with $S_0 \rightarrow S_2$ transitions which revealed energy gaps of 2.27 eV. For TiO_2 and MOF, the obtained band gaps were 3.04 and 2.84 eV using DAET method, respectively. The absorption of the CuPcNT moieties on the TiO_2 support results with a band gap of 3.71 eV. However, the presence of MOF on TiO_2 -MOF/CuPcNT led to the notable reduction in the band gap to 3.48 eV due to characteristic $\pi \rightarrow \pi^*$ of the phthalocyanine [54]. The IAET plot of CuPcNT showed three characteristic bands for phthalocyanine compounds [65] with lower energy gaps of 1.99 and 2.94 eV than DAET method, (Figure 7.3(b) and Table 7.1). The IAET band gap values for TiO_2 was found to be 2.75 eV and for MOF was 2.98 eV. TiO_2 -CuPcNT material showed to have an IAET band gap of 3.16 eV, but there were reduction of band gap to 2.62 eV in TiO_2 -MOF/CuPcNT.

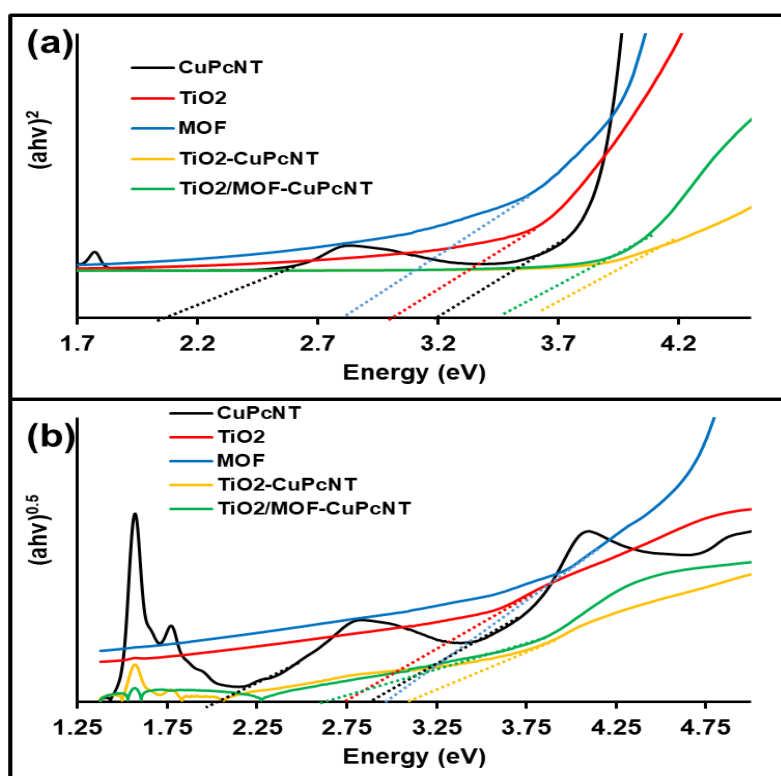


Figure 7.3: Tauc plots of CuPcNT, TiO₂, MOF, TiO₂-CuPcNT and TiO₂-MOF/CuPcNT at 100 ppm in H₂SO₄ for direct allowed electronic transition (a) and in indirect allowed electronic transition (b).

Table 7.1: Electronic and electrochemical properties of TiO₂, MOF, and TiO₂-MOF/CuPcNT ternary nanocomposite.

Material	Optical Bandgap (eV) ^a	$E_{1/2}^{ox}$ (V)	$E_{1/2}^{red}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
Ni foam	-	0.40	0.35	-5.10	-4.35
TiO ₂	2.75	0.41	0.333	-5.08	-4.34
MOF	2.98	0.63	0.50	-5.25	-4.12
TiO ₂ -MOF/CuPcNT	2.62	0.38	0.10	-4.85	-4.37

^a= optical band gap using indirect allowed transition

7.3.3. Structural characterization of the nanocomposite after dye adsorption.

Figure 7.4(a) shows the XRD pattern of TiO₂-MOF/CuPcNT nanocomposite as compared to the ones of TiO₂ and MOF. The pattern of the ternary nanocomposite revealed a shift in major peaks as compared to TiO₂ and MOF precursors due to structural changes. As the CuPcNT was adsorbed by TiO₂-MOF, there was a shift in XRD patterns and also the crystallite size was found to be 42.15 nm using Debye–Scherrer formula from the (101) plane in Equation 7.1. The shift in patterns was due to the incorporation of CuPcNT and MOF on the TiO₂ structure [76-79].

The FTIR spectrum of TiO₂-MOF/CuPcNT shows the peaks of CuPcNT groups at 1165, 1287 and 1334 cm⁻¹, which were due to the vibration mode of Cu-N bonding and the π -bridge C=N-C moiety [33]. The spectra shows the pyrrole in-plane mode that are attributed as sharp peaks at 899, 1067 and 1120 cm⁻¹, whereas the out-plane modes were shown at 877 cm⁻¹ due to the phthalocyanine skeletal structure [33]. Furthermore, the vibrational mode of the pyrrole ring were observed at 1420, 1508 and 1609 cm⁻¹ [65, 77], as compared to TiO₂ and MOF (see, Figure 7.4(b)) [67]. A vibration for TiO₂ was observed as a broad peak at 500 cm⁻¹ for Ti-O stretching bond [80]. The presence of MOF was observed by the appearance of in-plane and out-plane C-H bending modes at 731 and 761 cm⁻¹ due to the benzene ring in MOF [51-53].

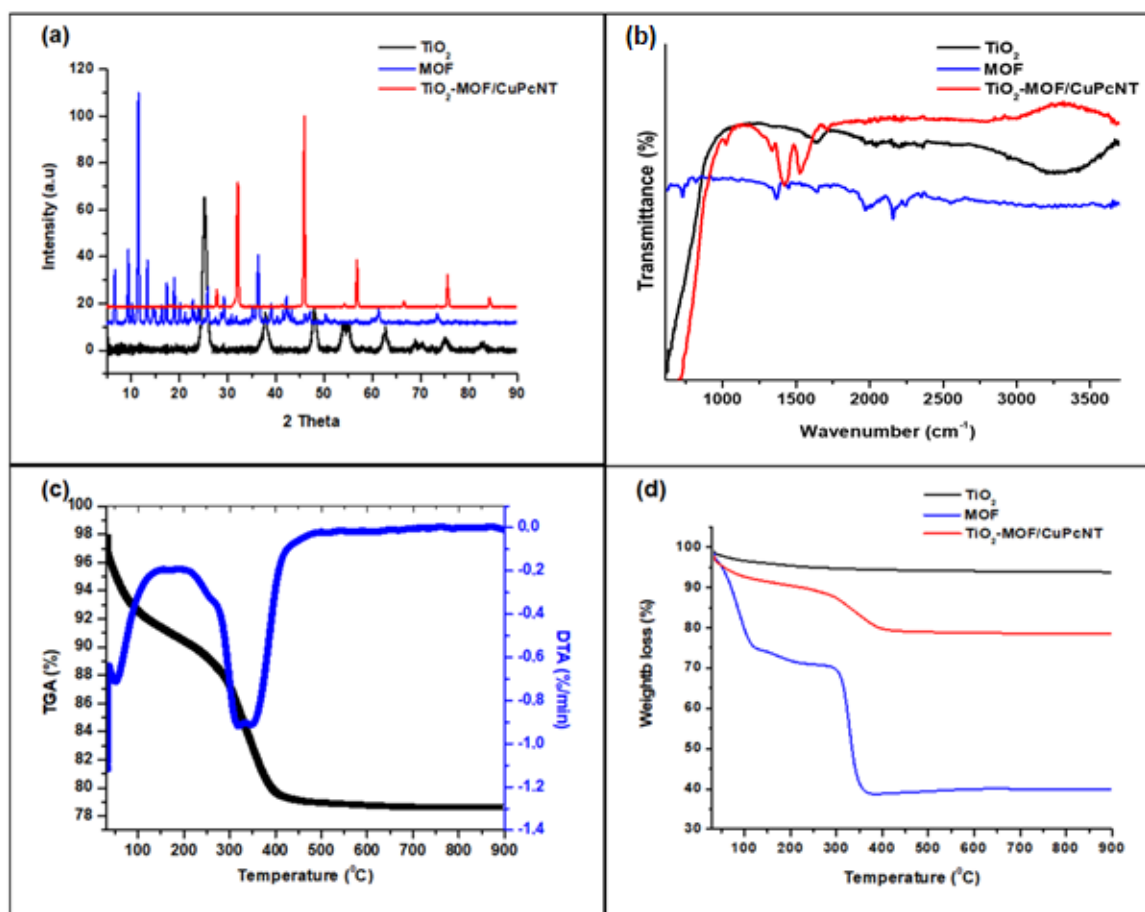


Figure 7.4: (a) XRD patterns, (b) FTIR, (c) TGA/DTA of a nanocomposite and TGA for TiO_2 , MOF and $\text{TiO}_2\text{-MOF/CuPcNT}$ composite.

The peaks at 1371 cm^{-1} in MOF and $\text{TiO}_2\text{-MOF/CuPcNT}$ materials were assigned to symmetry and asymmetry vibrational mode of C-O of carboxylate groups in MOF [81]. TGA and DTA measurements provide information about the thermal stability as shown in Figure 7.4(c and d). TGA curve in Figure 7.4(d) indicates that TiO_2 has good thermal stability with a 6% weight loss due to the loss of water and organic species present [82]. TGA curve of MOF in Figure 7.4(d) shows the two degradation steps at 95 and 340 $^{\circ}\text{C}$ owing to water loss and degradation of organic linkers [51, 81]. The thermogram (Figure 7.4(c) and (d)) of $\text{TiO}_2\text{-MOF/CuPcNT}$ reveals the improvement of the thermal stability with 35% weight loss due to water loss and degradation of organic compounds [53].

The morphological properties of the prepared $\text{TiO}_2\text{-MOF/CuPcNT}$ in comparison with TiO_2 , MOF, and $\text{TiO}_2\text{-CuPcNT}$ were studied using TEM. Figure 7.5 shows that the TEM image of TiO_2 exhibited a semispherical morphology with a particle size of 58-83 nm and a relatively narrow size dispersion of the sol-gel method [83]. Whereas the MOF image shows a disordered meso-structured framework with three-dimensional connectivity and large particle size of around 450 nm and partially crumpled layer separation [84]. The $\text{TiO}_2\text{-CuPcNT}$ image indicates the adsorption of dye with the addition of agglomeration and the large particle size of 200 nm. The agglomeration was observed to decrease in $\text{TiO}_2\text{-MOF/CuPcNT}$, which can be ascribed to the Van der Waals attractive or electrostatic repulsion forces [85]. However, the repulsion forces outweighed the attractive forces in $\text{TiO}_2\text{-MOF/CuPcNT}$ resulting in less agglomerated particles with average particle size between 3 to 10 nm (Figure 7.5(d)).

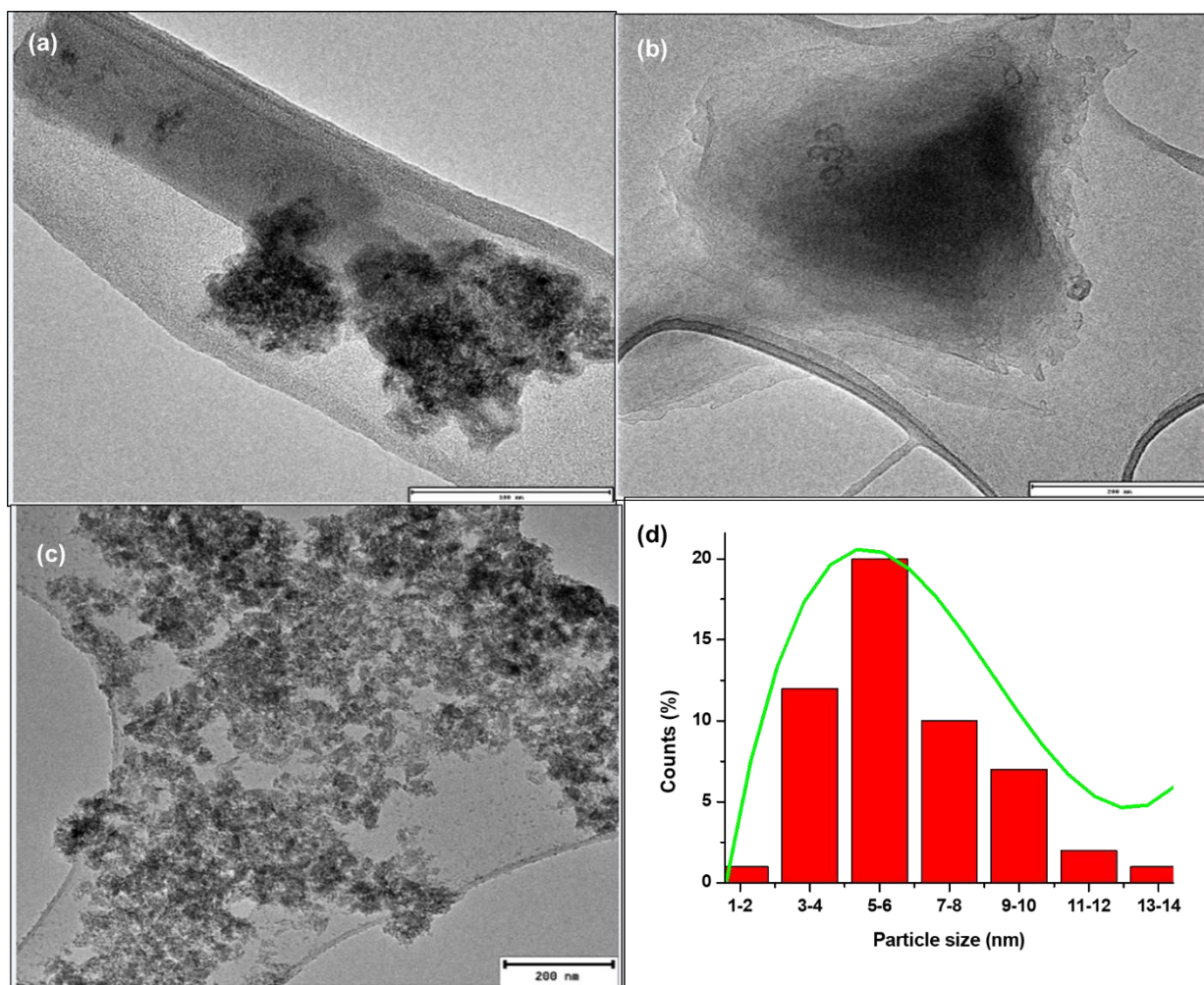


Figure 7.5:a)-(c), TEM for TiO₂, MOF and TiO₂-MOF/CuPcNT ternary nanocomposite and (d) the particle size distribution for TiO₂-MOF/CuPcNT.

7.3.4. Electrochemical characterizations.

Electrochemical behaviours of blank Ni Foam, TiO₂, MOF and TiO₂-MOF/CuPcNT are presented in Figure 7.6(a-d). Figure 7.6 (a) illustrates the cyclic voltammetry for the photoanode materials. The voltammetry responses showed the presence of a chemical reaction at the more negative potential and the decomposition of the reduce species [79]. In this case, the reduction couple i.e anodic peak of the redox processes get chemically irreversible even in the lower scan rate of 10 mVs⁻¹. The value of

potential difference between the reduction and the oxidation processes ($\Delta E_{1/2}$) was determined from CV and represents the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the photoanode [80]. The half wave peak potential ($E_{1/2}$) for the first ring reduction and oxidation are listed in Table 7.1. The E_{HOMO} and E_{LUMO} were calculated using Equation 7.3 and 7.4 [81], respectively:

$$E_{\text{HOMO}} = - (E_{1/2}^{\text{red}} + 4.75) \text{ eV} \quad (7.3)$$

$$E_{\text{LUMO}} = - (-E_{1/2}^{\text{ox}} + 4.75) \text{ eV} \quad (7.4)$$

The E_{HOMO} values were found to be -5.1, -5.08, -5.25 and -4.85 eV for Ni foam, TiO_2 , MOF and TiO_2 -MOF/CuPcNT, respectively. The E_{LUMO} values were obtained to be -4.35, -4.34, -4.12 and -4.37 eV for Ni foam, TiO_2 , MOF and TiO_2 -MOF/CuPcNT, respectively. The HOMO and LUMO values were within the reported values in the literature [81]. In addition, the voltammograms of the prepared materials showed that there was no higher barrier present to resist electron mobility [82]. The electron mobility of the TiO_2 , MOF and TiO_2 -MOF/CuPcNT was further determined using electrochemical impedance spectroscopy (EIS) in Figure 7.6(b). Surprisingly, MOF photoanode possessed a smaller semicircle as compared to TiO_2 material. There was an improvement of electron mobility in the ternary nanocomposite as compared to TiO_2 . Furthermore, the Nyquist plot was used to determine the conductivity of TiO_2 , MOF and TiO_2 -MOF/CuPcNT nanocomposites. It is clear from the Bode plots and the corresponding phase angle measurements (Figure 7.6(c)) that the pure nickel foam is at least one order of magnitude higher in resistance than both TiO_2 -coated substrates. The values of the conductivity were obtained using Equation 7.5 [83]:

$$\sigma = t/R_{ct}.A \quad (7.5)$$

where t , R_{ct} , and A represent the thickness of an electrode, charge transfer resistance and area of the substrate, respectively. The conductivity of Ni Foam, TiO_2 , MOF and TiO_2 -MOF/CuPcNT ternary nanocomposites (Table 4.2), were found to be 0.9, 1.1, 8.4, and 1.39 $\mu\text{S}/\text{cm}$, respectively. This reveals an enhancement of conductivity on the electrodes using TiO_2 -MOF/CuPcNT. The high conductivity is one of the requirements for charge transfer in dye sensitizer solar cells. The lifetime (τ) of the TiO_2 -MOF/CuPcNT nanocomposite was also estimated from its maximum peak frequency (f_{max}) of -82.0° using Equation 7. 6 [84] and it was found to be 1.94 ms.

$$\tau = 1/(2\pi f_{\text{max}}) \quad (7.6)$$

Moreover, a constant phase element (C_2/CPE) is chosen to accommodate double layer capacitance for the porous nature of the surface of the electrode material. This is expected to greatly enhance the interaction at the electrode/electrolyte interface in the intended solar cell applications. The proposed mechanism for photovoltaic studies is shown in Figure 7.6(d). This findings are in agreement with the results revealed by the optical band gap.

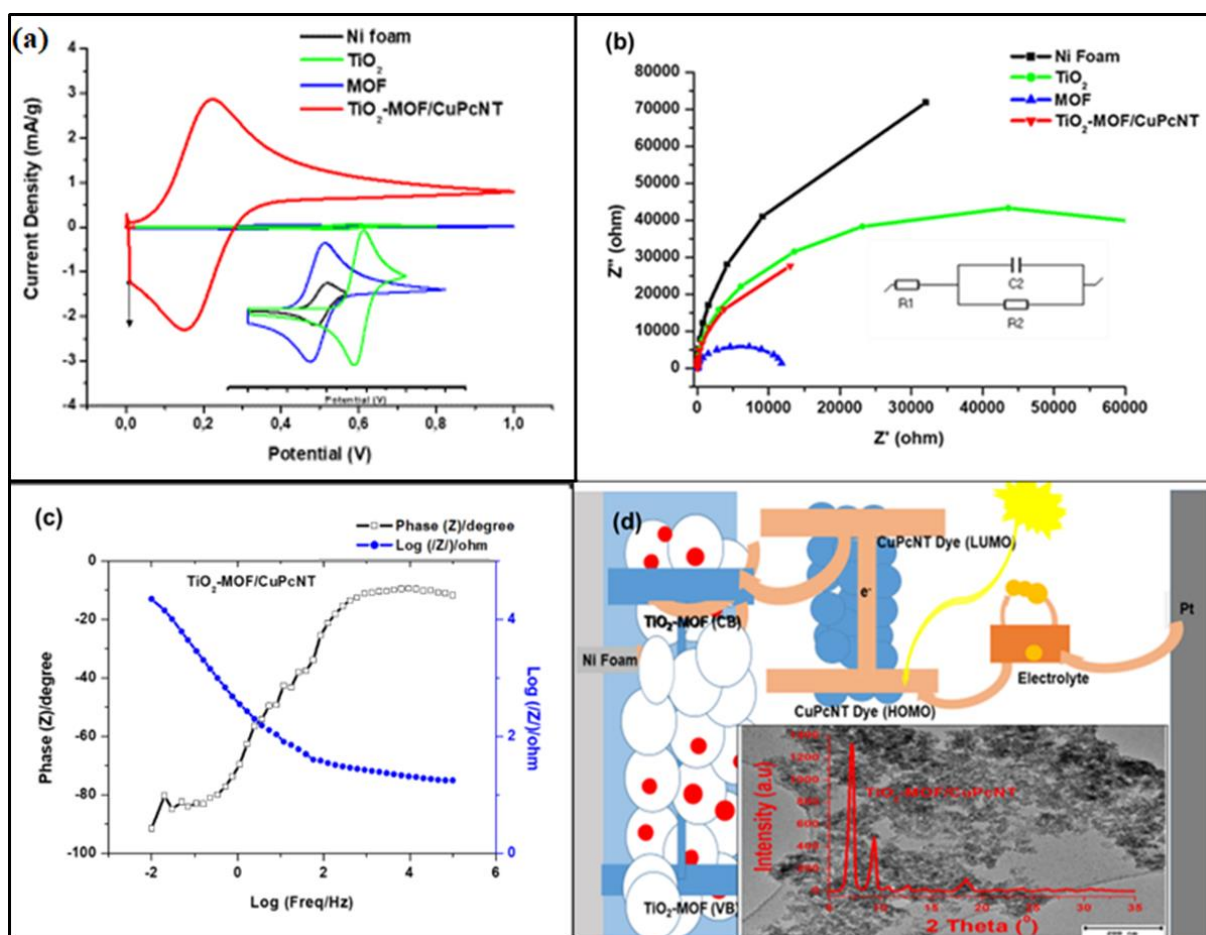


Figure 7.6: (a) Cyclic voltammetry and (b) Electrochemical impedance spectroscopy of Ni Foam, TiO₂, MOF and TiO₂-MOF/CuPcNT, (c) and (d) Bode impedance in phase degree and log of the absolute value of Z for TiO₂-MOF/CuPcNT nanocomposite.

Table 7.2: Fitted circuit parameters of EIS of Ni foam, TiO₂, MOF and TiO₂-MOF/CuPc nanocomposite and calculate ionic conductivity.

Material	Electrolyte	Rs	CPE	Rct	Conductivity
		(Ω)	(μF)	(kΩ)	y
					(μS/cm)
Ni foam	0.1	M 19.7	184	114	0.9
	Na ₂ SO ₄				

TiO₂	0.1	M	23.3	25.7	89.6	1.1
	Na ₂ SO ₄					
MOF	0.1	M	21.3	153	11.9	8.4
	Na ₂ SO ₄					
TiO₂-	0.1	M	24.19	472	71.8	1.39
MOF/CuPcNT	Na ₂ SO ₄					

7.3.4. Photovoltaic performance

The photovoltaic performance of the synthesized Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNT ternary nanocomposite was investigated using a CV scan in simulated light (64 mW m⁻² intensity). Their photocurrent densities are presented in Figure 7.7(a). The Ni foam has a photocurrent density of 0.02 mA cm⁻² at 0.38 V. The photocurrent density of 0.39 mA cm⁻² at 0.31 V was observed in TiO₂ material. The one for MOF was 0.19 mA.cm⁻² at 0.66 V. The low densities are ascribed to the poor light absorption which resulted in poor charge separation [86]. The TiO₂-MOF/CuPcNT ternary nanocomposite showed an improvement of photocurrent density of 7.02 mA.cm⁻² at 0.35 V. The highest photocurrent density obtained by the ternary nanocomposite was well within the many photo-responses that have been reported for the material under illumination conditions [87]. Table 7.3 compares the maximum photocurrent attained by the Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNT ternary nanocomposite obtained in this work with other reported values in the literature [87–89]. The increase photocurrent obtained for the TiO₂-MOF/CuPcNT nanocomposite is largely related to the presence of CuPcNT, which increases active sites for electron transfer mechanisms, thus enhancing the photocurrent [33]. The power conversion efficiency

(η) of the Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNT ternary nanocomposite was calculated using Equation 7.7 [90]:

$$\eta = ((E^0_{\text{rev}} - E_{\text{mea}}) \times I) / P_{\text{in}} \quad (7.7)$$

where I (mA cm²) stands for photocurrent density, E_{mea} is the working electrode potential, E^0_{rev} denotes 1.43 V Ag/AgCl for the standard of the reversible potential, and P_{in} (mW/cm²) signifies for the input power of the simulated light intensity.

The η values calculated for the Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNT nanocomposite are represented in Figure 7.8(b). The highest η value was 11.69 % for the TiO₂-MOF/CuPcNT ternary nanocomposite, whereas the lowest was 0.066 % for the Ni foam. The η values of TiO₂ and MOF were determined to be 0.617 and 0.255%, respectively. The η values reported in Table 7.3 for the TiO₂-MOF/CuPcNT nanocomposite are better than those reported in the literature [26, 41, 90, 91]. The values of η are 0.26% for TiO₂/Cu-MOF [41] 0.17% for TiO₂/Zn-MOF [90], 1.22% for TiO₂/Ru-MOF [91] and 2.34% using TiO₂/Zn-MOF in the presence of N719 dye [26]. The increased in η values for the TiO₂-MOF/CuPcNT ternary nanocomposite were also related to the presence of nanotubes. Therefore, the results show that CuPcNT dye may be used to enhance the photovoltaic performance of TiO₂-MOF properties [92]. The overall power conversion efficiency of 11.69%, acquired from the photocurrent density of 7.02 mA cm⁻² at lower potential of 0.35 V, was due to the TiO₂-MOF/CuPcNT ternary nanocomposite as a result of an increment in the electronic properties [89].

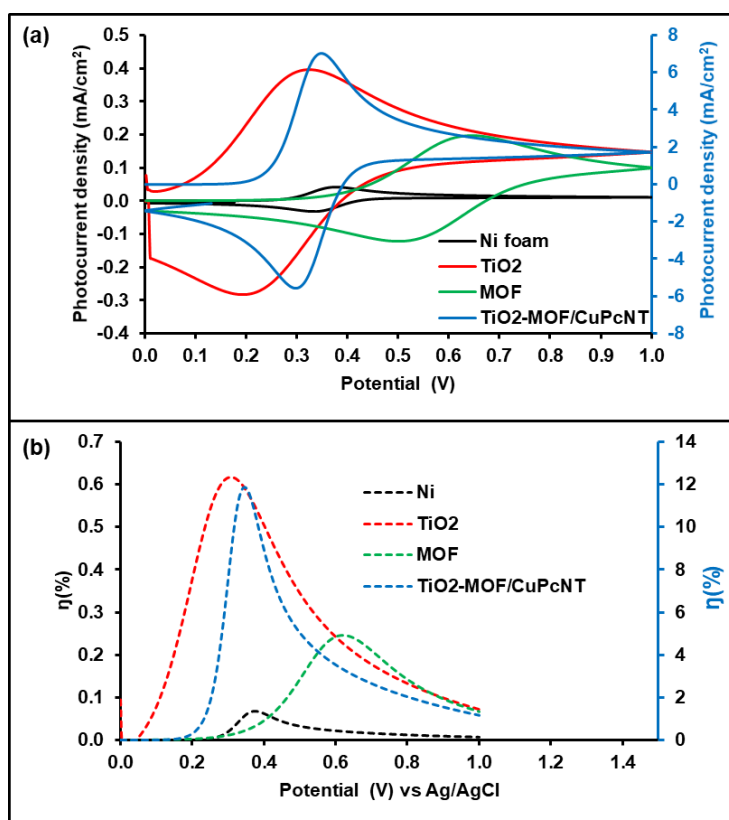


Figure 7.7: (a) Photocurrent response and (b) power conversion efficiency of Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNT ternary nanocomposite.

Table 7.3: Comparison of the photocurrent density obtained for Ni foam, TiO₂, MOF, and TiO₂-MOF/CuPcNT ternary nanocomposites in this study with the literature values prepared using various methods.

Material	Electrolyte	Photocurrent (mA/cm ²)	Efficiency (%)	Ref
Ni foam	0.1 M Na ₂ SO ₄	0.02	0.066	In this work
TiO ₂	0.1 M Na ₂ SO ₄	0.39	0.617	In this work
MOF	0.1 M Na ₂ SO ₄	0.19	0.255	In this work
TiO ₂ -MOF/CuPcNT	0.1 M Na ₂ SO ₄	7.02	11.69	In this work
TiO ₂ -Cu-MOF	I ₃ /I ⁻ redox	-	0.26	[41]
TiO ₂ -Ru-MOF	I ₃ /I ⁻ redox	-	1.22	[91]

TiO₂-Zn-MOF	ACN, Lil, I ₂ & 1.04 LiClO ₄	0.67	[90]
TiO₂/Zn-MOF/N719	PEGOPEG/NaI/I ₂ /EMITFMSI/AN	2.34	[26]

N719=Di-tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II); AN=acetonitrile; PEGOPEG=poly(ethylene oxide)–poly(ethylene glycol); and EMITFMSI= 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)imide

7.4. CONCLUSION

The CuPc nanotube dye was developed using hydrothermal technology at 180 °C for 24 hrs. The TiO₂-MOF/CuPcNT ternary nanocomposite was prepared by immersing TiO₂-MOF in a blue CuPcNW dye solution for adsorption process. Ultraviolet-visible spectroscopy revealed that the resultant ternary nanocomposite has a small band gap of 2.62 eV at an absorption wavelength of 798 nm. The structural characterization showed that the TiO₂, MOF, and CuPcNT phases, functional groups, and the improved thermal stability of the TiO₂-MOF/CuPcNT ternary nanocomposite. The morphological studies revealed that the TiO₂-MOF/CuPcNT ternary nanocomposite was more hollowed tubular rectangular. The HOMO and LUMO energies of the ternary nanocomposite were calculated from CV and found to be -4.85 and -4.37 eV, respectively. The EIS showed that the TiO₂-MOF/CuPcNT ternary nanocomposite possessed a high conductivity of 1.39 μS/cm with a lifetime of 1.94 ms as compared to the parent TiO₂ materials. The maximum photocurrent and power conversion efficiency of the TiO₂-MOF/CuPcNT composite were 7.02 mA cm⁻² and 11.69 % at lower potential of 0.35 V under a simulated light source, respectively. These

parameters make the TiO₂-MOF/CuPcNT composite an excellent candidate for dye-sensitized solar cell applications.

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7.5. REFERENCES.

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CHAPTER 8:

GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

8.1. GENERAL DISCUSSION AND CONCLUSIONS

This chapter deals with discussion and conclusion of the thesis and make further recommendations for future photovoltaic solar cells research. This study focuses towards the preparations of titanium dioxide (TiO_2), copper-metal-organic framework (MOF), copper phthalocyanine (CuPc) and its derivatives copper phthalocyanine nanowire (CuPcNW and copper phthalocyanine nanotubes (CuPcNT). The overall goal of this thesis was to prepare the most optimal, efficient and viable novel photo-anodes nanocomposite in order to increase the scope of these materials for application in different areas such as; photovoltaic solar cells, fuel batteries, super-capacitors and in the development of dye sensitized solar cell devices in the future. The photo-anodes and the copper phthalocyanine dye materials studied were identified and chosen based on the excellent properties they offer. For example, titanium dioxide exhibits electronic properties of semiconductors in photovoltaic process, whilst retaining attractive thermal and mechanical properties Its photovoltaic performance can be further improved by rational design of the material as nanostructure with special surface and structural properties. On the other hand, MOF and CuPc reveal favourable electrochemical redox properties such as being able to undergo electron transfer reactions at potentials that are accessible. They offer remarkable photo-physical, electrical and optical spectroscopic properties, due to their exceptional properties such as high surface area, fast electron transfer, reduction of electron recombination and their porous structure. The work is outlined into eight chapters.

Chapter one serves to introduce the subject of the research. For any research to be meaningful, it has to serve a purpose and for that reason the first part of this chapter deals with the purpose of the study. It gives the background of photovoltaic solar cells against which the research takes place and justifies the research based upon an identified problem of TiO_2 composites in solar cells. The problem statement and motivation/rationale of the study were outline. It was seen that TiO_2 semiconductor

was extensively studied due to its advantage of the high chemical and optical stability, nontoxicity and inexpensive. But, TiO_2 has the larger energy band gap of 3.2 eV which results in low power conversion efficiency (PCE). Therefore, it is a paramount important to introduce secondary compound in titanium dioxide structure to form TiO_2 composite in order to reduce its bandgap. The TiO_2 -MOF composite has a slow electron transfer and this also results in lowering of PEC. Hence a TiO_2 based composites that can lower the energy band gap and also improve the power conversion efficiency of the system are needed. In this study, the effects of nanosized copper phthalocyanine were identified as alternative novel methods to improve PCE of TiO_2 -MOF composite.

Chapter two (literature review) is based on the background of photovoltaic on titanium dioxide and metal organic framework. The background on energy was provided and solar cells showed to be an alternative source of energy for different applications such as mobile commerce, building integrated photovoltaics, and vehicles. It was seen that in TiO_2 hybrid materials, photovoltaic cells were prepared by taking the advantages of organic or inorganic properties, however they still produce low power conversion efficiencies. The addition of 3-dimensional nanostructures, such as nanotubes, nanowires, composite films with metal, or metal organic frameworks was identified as alternative strategy to improve TiO_2 material. The MOFs in TiO_2 photovoltaic cells showed to improve the power conversion efficiency due to high larger surface areas for the sensitizer adsorption. It was reported that MOFs suffer from poor electrical properties owing to its insulator characteristics of organic linkers. The alternative method of achieving the better light harvesting ability is to look at other dye molecules such as phthalocyanine and its derivatives that can be adsorbed on the cavities of 3-dimensional MOF structure and TiO_2 .

Chapter three involves the literature survey on characterisation techniques of TiO_2 composite. The chapter identified the analytical techniques such as spectroscopic, microscopic, physical and electrochemical which are used for the characterisation of some features of titanium dioxide composites due to its good physical and chemical properties. The structural characterisations using FTIR, Raman, and UV-vis spectroscopy showed to be useful techniques to reveal the presence of the functional groups and optical properties. The XRD was also discussed to be a suitable instrument to reveal the phase properties of titanium dioxide composites and also to determine the crystallite size of the nanomaterials. It was also discussed in the chapter that the

morphological and elemental analysis of titanium dioxide composites can be evaluated using SEM/TEM coupled with EDS detectors. The particle distribution size of the TiO₂ composite can also be determine from the SEM/TEM images. It was further seen that TGA and DSC techniques can be used to reveal the thermal stability and confirmation of TiO₂ composites. The electrochemical methods such a CV, LSV and EIS are used to reveal electrochemical band gap from HOMO and LUMO, photocurrent response, conductivity, life time, and power conversion efficiency as one of photovoltaic parameters in solar cells.

Chapter four involves the synthesis, fabrication, characterization and photovoltaic solar cells of TiO₂. MOF and TiO₂-MOF photo-anode materials. Formation of anatase TiO₂ sol-gel was obtained through stabilisation, hydrolysis and condensation processes in the presence of glacial acetic acid, water and 25 % ammonium solution. MOF was prepared by mixing the hot solutions of trimesic acid in ethanol and copper (ii) nitrate tetra hydrate in water and using hydrothermal method to obtain highly-crystalline material. TiO₂-MOF composite was also prepared using sol-gel method with 10 % by weight of MOF. Fabrication of the photo-anodes such as TiO₂, MOF and TiO₂-MOF nanocomposite materials was conducted on Ni Foam substrate using a doctor Blades method. Structural and morphological characterisations using FTIR, Raman, XRD, SEM and TEM confirmed the successful preparation of TiO₂, MOF and TiO₂-MOF and showed that MOF is incorporated into TiO₂ network. Photovoltaic studies was evaluated using electrochemical characterization such as CV, CA and EIS. The reaction took place in 0.1 M Na₂SO₄ solution as an electrolyte in the three-electrode system. TiO₂, MOF and TiO₂-MOF were treated as working electrodes, 0.1 M Ag/AgCl was regarded as a reference electrode and platinum wire was acting as a counter electrode. The intense cathodic and anodic peaks in fitted CV was observed. It showed that TiO₂-MOF hybrid composite has great potential to be used in photovoltaic process as it can easily generate and adsorb light through straight forward electrochemical process under simulated light source. Therefore, a maximum photocurrent and power efficiency of 0.46 mA cm⁻² and 0.722% at 0.44 V were achieved byTiO₂/MOF composite. The PCE values was higher than the one of MOF which was 0.255% at 0.66 V and the one of TiO₂ was 0.617% at 0.31 V.

It has been demonstrated that the TiO₂-MOF nanocomposite is not only robust and stable but also effective on the unfavourable conditions. Remarkably, the observed

photovoltaic is dictated by the identity of electricity source, which opens the new avenues for multi analyte investigation.

Chapter five is based on a copper phthalocyanine dye absorbed on the surface of titanium dioxide-metal organic framework to form $\text{TiO}_2\text{-MOF/CuPc}$ ternary composite in order to developed a device towards the photovoltaic solar cells for the production of electricity.

Raman spectroscopy and FTIR showed the vibrations for the presence of organic linker, phthalocyanine skeletal structure, and Ti-O stretches of MOF, CuPc, and TiO_2 , respectively, as an indicative for formation of $\text{TiO}_2\text{-MOF/CuPc}$ ternary composite. This was supported by the gravimetric studies that the thermal stability of the ternary composite was improved. The UV-vis spectra revealed the optical band gap values which ranged between 3.10 and 1.46 eV in the case of the ternary composite. The HOMO-LUMO values using CV were estimated for the $\text{TiO}_2\text{-MOF/CuPc}$ photoanode materials and showed improved in electrochemical band gap. The $\text{TiO}_2\text{-MOF/CuPc}$ ternary composite can significantly increase the performance of the photo-anode and enhance the exchange current density, as such reduce the electrochemical reaction resistance. The electrochemical activity shows that $\text{TiO}_2\text{-MOF/CuPc}$ ternary composite with phthalocyanine The PCE value of $\text{TiO}_2\text{-MOF/CuPc}$ ternary composite under simulated light source was 1.63% which was higher than 0.722% of $\text{TiO}_2\text{-MOF}$ composite.

Chapter six deals with the use of CuPc nanowire dye that was prepared by dissolving copper phthalocyanine powder in chloroform together with tetrafluoroacetic acid solution. The UV-vis spectrum confirmed the formation of highly soluble CuPcNW with appearance of the Q- and B- bands typical for phthlocyanine compound. The formation of ternary nanocomposite was achieved through adsorption technology on the surface of the $\text{TiO}_2\text{-MOF}$ composite. The resultant ternary nanocomposite showed to have a small band gap of 1.75 eV at an absorption wavelength of 798 nm. The structural characterisation revealed the presence of functional groups, and phases of MOF, CuPcNW and TiO_2 as well as improved thermal stability in the $\text{TiO}_2\text{-MOF/CuPcNW}$ ternary nanocomposite. The morphological studies revealed that the $\text{TiO}_2\text{-MOF/CuPcNW}$ ternary nanocomposite possessed a ribbon-like structure. The HOMO and LUMO energies of $\text{TiO}_2\text{-MOF/CuPcNW}$ ternary nanocomposite were determined from CV and found to be -5.1 and -4.31 eV, respectively. Furthermore, the EIS revealed a high ionic conductivity in the ternary nanocomposite of 244 $\mu\text{S/cm}$ as

compared to the 82.6 $\mu\text{S}/\text{cm}$ of TiO_2 -MOF composite and 172 $\mu\text{S}/\text{cm}$ of TiO_2 -MOF/CuPc ternary composite. These parameters make the TiO_2 -MOF/CuPcNW composite an excellent candidate for dye-sensitized solar cell applications. The maximum photocurrent and power efficiency of the TiO_2 -MOF/CuPcNW ternary nanocomposite were 4.067 mA cm^{-2} at 0.430 V and 6.47%, respectively, under a simulated light source better than the one observed in TiO_2 , MOF, TiO_2 -MOF and TiO_2 -MOF/CuPc.

Chapter seven is based on the preparation of copper phthalocyanine nanotube and its ternary nanocomposite from TiO_2 -MOF through adsorption technology. The resultant TiO_2 -MOF/CuPcNT ternary nanocomposite showed to have a bandgap of 2.62 eV using indirect allowed electronic transition. The XRD, FTIR and Raman spectra as well as thermal gravimetric analysis showed that the TiO_2 , MOF, and CuPcNT phases, functional groups, and the improved thermal stability of the TiO_2 -MOF/CuPcNT ternary nanocomposite, respectively. The hollowed rectangular image was observed for TiO_2 - MOF/CuPcNT nanocomposite using TEM/HRTEM. The HOMO and LUMO energies of the nanocomposite were determined from CV and found to be -4.85 and -4.37 eV, respectively. The EIS showed that TiO_2 -MOF/CuPcNT ternary nanocomposite possessed a high conductivity of 172 $\mu\text{S}/\text{cm}$ with a lifetime of 1.94 ms as compared to the parent materials. A maximum power efficiency of 11.69 % at 0.35 V were recorded for TiO_2 - MOF/CuPcNT ternary nanocomposite under simulated light source which was higher than the one observed for TiO_2 -MOF/CuPcNW ternary nanocomposite. Notwithstanding, the sol-gel and adsorption method for preparing TiO_2 - MOF/CuPcNT nanocomposite used in this study showed promising photocurrent response and could also be employed for making TiO_2 -MOF/CuPcNT nanocomposite for DSSC applications.

8.2. RECOMMENDATIONS FOR FUTURE WORK

Further improvement of the photoanode materials will aid towards an increase dye sensitized solar cells and efficiency. An important milestone in the work was to develop other alternative TiO_2 and MOF, which are to TiO_2 -MOF photoanodes in DSSCs. The dye plays the centralized role in dye-sensitized solar cells (DSSCs) by ejecting the

electrons on irradiation and initiating the mechanism. The basic components of DSSCs primarily consist of transparent conducting oxide (TCO) film-coated glass substrates, dye, photoanode, electrolytes, and counter electrode.

It was clear from the work that the DSSCs responses obtained using Ni Foam as a substrate and sodium sulphate electrolyte was not that good enough for DSSCs application, it is recommended that Fluorine Tin doped glass substrate and I/I_3^{-1} electrolyte be used in the DSSCs applications. Furthermore, since the CuPc, CuPcNW and CuPcNT dyes in the conventional solvents such ethanol and ethanol:DMF showed to be insoluble and partially soluble, respectively. Thus, it would be useful to consider DMF solvents alone with an increase in temperature to 90 °C the same time overnight that can be used for homogeneous DSSC applications. In addition, DSSCs disadvantage stems from the fact that the liquid electrolyte used in DSSCs is sensitive to very high and very low temperatures. At low temperatures, the electrolyte can freeze, and at high temperatures, the liquid electrolyte expands making the solar cell unusable. Therefore, the use of conductive hydrogel electrolyte may overcome this stability.

Moreover, low DSSC responses of TiO_2 -MOF, TiO_2 -MOF/CuPc, TiO_2 -MOF/CuPcNW and TiO_2 -MOF/CuPcNT of less than 12.3 % PCE for cobalt (II/III)-based redox electrolytes and Pt-based counter electrodes by M. Grätzel et al. [ref] was observed. To improve the efficiency of DSSCs, light absorption properties of organic dye rather than CuPc, CuPcNW and CuPcNT must be used to have a maximum response throughout visible and near infra-red spectrum.

To investigate the solar cell current–voltage (I–V) measurement is one of the requirement to determine the following parameters photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill-factor (FF).

The photovoltaic characteristics of the DSSCs under AM 1.5 illumination (equivalent to one sun) is encouraged. The fabrication of solar panel for real commercialization step is needed.

DSSC presented here showed to generate PCE in the daytime than in the dark. Therefore, the fabrication long persistence phosphors with mesoscopic TiO_2 -MOF/CuPcNT photoanodes will be help to make the material to produce PCE in the dark.

To gain insight on the electronic structure and optical properties of the TiO₂-based dyes, density functional theory (DFT) and time dependent DFT calculations are required.

APPENDIX

APPENDIX 1

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Photovoltaic Performance of Titanium Oxide/Metal-Organic Framework Nan

[5] M. S. Organic Frameworks: Nanocomposites (Ph.D. thesis, Chapter 1, available at: <https://www.tdx.cat/handle/10810/5780429346262/metal-organic-framework-nanocomposites-el-estudio-de-sus-propiedades-fotofisico-quimicas>).

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Chapter



Photovoltaic Performance of Titanium Oxide/Metal-Organic Framework Nanocomposite

By Phuti S. Rametse, Kiriang M. Molapo, Thehang R. Somo, Mafesile G. Tefu, Mphahlele J. Wato, Mafesile S. Mafesile-Nkomo, Katiago Molapo, Emmanuel I. Avouha, Rivena G. Modibane

Book: [Metal-Organic Framework Nanocomposites](https://www.taylorfrancis.com/books/mono/10.1201/9780429346262/metal-organic-framework-nanocomposites-el-estudio-de-sus-propiedades-fotofisico-quimicas) (<https://www.taylorfrancis.com/books/mono/10.1201/9780429346262/metal-organic-framework-nanocomposites-el-estudio-de-sus-propiedades-fotofisico-quimicas>).

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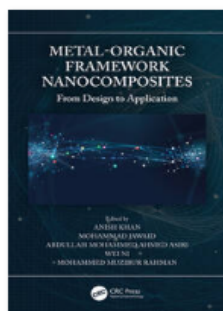
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By Phuti S. Ramaripa, Kerileng M. Molapo, Thabang R. Somo, Malesela D. Teffu, Mpitloane J. Hato, Manoko S. Maubane-Nkadimeng, Katlego Makgopa, Emmanuel I. Iwouha, Kwena D. Modibane

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APPENDIX 2

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Mini Review

Recent Applications of Analytical Techniques and Electrochemical Methods in Characterizations of the Titanium Dioxide Composites

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This work reports on the characterisation techniques of titanium dioxide (TiO_2) and its composites for photovoltaic studies. TiO_2 is good semiconductor material owing to its low-cost, superior thermal and chemical stability. The synthesised TiO_2 material needs to be analysed and characterised to check if they are suitable for the entire applications. As such, there is a need to study their structural, optical, morphology, thermal and electrochemical properties. Titanium dioxide (TiO_2) composites are regarded as photo-anodes in the dye sensitized solar cells application. As such, they have received a great interest in energy applications due to its exceptional properties such as stability, high surface area, conductivity, and catalytic activities. TiO_2 photo-anode has the drawback of high band gap of ~ 3.2 eV. To decrease the band gap of TiO_2 photo-anode, metal organic framework (MOF) nanomaterials are incorporated TiO_2 to form a TiO_2 -MOF composite that enhances the TiO_2 photo-anode property. Herein, we report literature survey on characterization techniques used to analyse TiO_2 nanomaterials and TiO_2 - composites. Hence, this review will comprehensively discuss detailed literature survey on analytical techniques that can be used to study the chemical, physical and surface properties of TiO_2 and its composites, namely ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray diffraction, scanning and transmission electron microscopies energy dispersive X-ray spectroscopy, thermogravimetric analysis, differential scanning calorimetry and electroanalytical methods which include linear sweep voltammetry, cyclic voltammetry voltammetry, chronoamperometry, electrochemical impedance spectroscopy and current-voltage measurement.

Keywords: Analytical techniques, composites, titanium dioxide, photoanode, photovoltaic. (<http://creativecommons.org/licenses/by/4.0/>).



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Fabrication, characterization, and photovoltaic performance of titanium dioxide/metal-organic framework composite

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ABSTRACT

The titanium dioxide-metal-organic framework (TiO₂-MOF) composite was prepared using the sol-gel method for photovoltaic applications. Raman analysis showed the presence of MOF clusters in the TiO₂ sol-gel network. Using the Brunauer-Emmett-Teller method, the resultant composite material exhibited a surface area of 111.10 m² g⁻¹ as compared to the surface area values of 262.90 and 464.76 m² g⁻¹ for TiO₂ and MOF, respectively. The small optical band gap values of 2.60 for direct electronic transition and 2.70 eV for indirect allowed electronic transition in TiO₂/MOF composite were observed using ultraviolet-visible spectroscopy by cyclic voltammetry (CV). The chronoamperometry (CA) results showed the current drop of 0.21 mA observed at 0.025 s for TiO₂ and the current drop of 1.00 mA for MOF and 1.4 mA for TiO₂-MOF composite at 0.3 s. The stability of the composite was achieved through the synergistic effect of MOF on TiO₂ which resulted in a high current density. Electrochemical Impedance Spectroscopy showed a fast electron transfer as well as high ionic conductivity. The overall power conversion efficiency of 0.722% along with a photocurrent density of 0.46 mA cm⁻² was achieved for the composite. The approach proposed in this work is facile and can be used for the large-scale fabrication of efficient and flexible photovoltaic electrodes for photovoltaic applications.

1. Introduction

Globally, there has been a dynamic change in the energy outlook over the years due to the negative environmental impact associated with the use of fossil fuels and the exponential growth in technologies (i.e., optoelectronic applications such as touch screens, solar modules, and photodetectors and electric vehicles). These factors have fostered the development of clean, diversified, sustainable, and low-cost renewable energy systems (i.e., photovoltaic solar cells, wind turbines, etc.) to become valuable for energy provision and technological sustainability [1, 2]. The use of solar power to produce clean energy is made possible through the R&D of smart materials to be fabricated into photovoltaic (PV) devices. Photovoltaic devices harness the sun's radiation directly

into electricity using the photovoltaic effect [3]. There are several types of solar cells which include perovskite solar cells, organic solar cells, inorganic solar cells, silicon solar cells, dye-sensitized solar cells (DSSC) [4–10], etc. Among these types of solar cells, DSSC is regarded as a potential alternative technology [4], due to its low cost, easy fabrication, and relatively high efficiency. The first work concerning PVs was first reported by Gratzel and O'Regan in 1991, which employed the use of DSSC in the production of electric energy from the energy package of light [8]. The effective operation and efficiency of DSSC depend on the type of semiconductor employed. The semiconductor should possess a smaller energy bandgap to facilitate the photo-excited electrons arising from moderate or low energy photons efficaciously for power energy conversion (PEC) [8–10]. For a while, titanium dioxide, TiO₂ has been

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APPENDIX 4

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Title: Effects of phthalocyanine dye on titanium dioxide/metal organic framework composite for the fabrication of dye-sensitized solar cells

Corresponding Author: Dr Sadanand Pandey

Co-Authors: Phuti S Ramaripa, M.Sc; Kwena D Modibane, PhD; Katlego Makgopa, PhD; Mpho S. Ratsoma, B.Tec;

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M.Sc; Edwin Makhado, PhD; Deepanshu Balakrishnan, PhD

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Journal: Chemical Engineering Journal Advances
Title: Influence of phthalocyanine nanowire dye on the performance of titanium dioxide-metal organic framework nanocomposites for dye-sensitized solar cells
Corresponding Author: Prof Kwena Desmond Desmond Modibane
Co-Authors: Phuti S Ramaripa, MSc; Kadogo Makgopa, PhD; Ostar A Seerane, BSc; Manoko S Maubane-Nkadimang, PhD; Edwin Makhado, PhD
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Journal name: Applied Sciences

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Type of manuscript: Article

Title: Impact of copper phthalocyanine nanotube dye on photovoltaic performance of titanium oxide/metal organic framework nanocomposite

Authors: Phuti S Ramaripa, Kwena Desmond Modibane *, Katlego Makgopa, Kabelo E Ramohlola, Manoko Maubane-Nkadimeng, Edwin Makhado

Received: 29 September 2022

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APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT

[Section 30 (1)-Regulation 22]

The granting of a patent is hereby requested by the undermentioned applicant on the basis of the present application.

Official Application No.		Applicant's or Agent's Reference
21	01	2022/10097
		ABOMJZ

71	Full Name(s) of Applicant(s)
Prof Kwena Desmond Modibane	
Department of Chemistry, University of Limpopo, Polokwane, 0727, South Africa	

54	Title of Invention
PHthalocyanine nanowire decorated titanium dioxide/metal organic framework ternary nanocomposite photovoltaic system	

The applicant has claimed priority (if any) as set out in the abovementioned international application	

This application is for a patent of addition to patent application No-	
21	01

This application is a fresh application in terms of section 37 and based on Application No-	
21	01

This application is accompanied by:	
X	1. A single copy of a provisional specification of 23 pages.
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