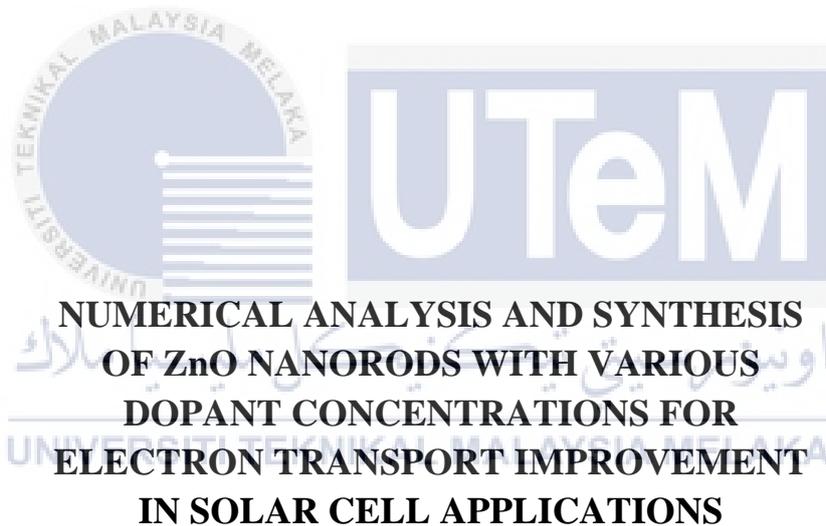




Faculty of Electronic and Computer Engineering



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Master of Science in Electronic Engineering

2023

**NUMERICAL ANALYSIS AND SYNTHESIS OF ZnO NANORODS WITH
VARIOUS DOPANT CONCENTRATIONS FOR ELECTRON TRANSPORT
IMPROVEMENT IN SOLAR CELL APPLICATIONS**

NUR SYAFIQAH NADIAH BINTI MOHD ALIAS

**A thesis submitted
in fulfillment of the requirements for the degree of Master of Science in Electronic
Engineering**



Faculty of Electronic and Computer Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2023

DECLARATION

I declare that this thesis entitled “Numerical Analysis and Synthesis of ZnO nanorods with various dopant concentrations for Electron Transport Improvement in Solar Cell Applications” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



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APPROVAL

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DEDICATION

Writing this thesis has never been an easy task as many parties are involved. First of all, I would like to thank Allah for always being there for me and guiding me throughout this long, tough, and traumatic journey of my study.

I would like to express my earnest gratitude to my supervisor, Ts. Dr. Faiz Bin Arith, who have been overwhelmingly supportive throughout my current circumstances. His reviews, comments, support, and encouragement were really important, impressive and were immensely felt throughout.

To my beloved parents, Mohd Alias Bin Kamaruddin and Salmah Binti Baharuddin, who has always comforted me with love and care throughout my education journey. I wouldn't have completed this work without their support and belief in me obtaining and finishing my master's degree. I am also grateful to my only brother, Muhammad Syazwan Bin Mohd Alias, who is always there for me when I feel unwillingness and also helps me with proofreading my journal paper and thesis writing. Last but not least, I want to thank all of my friends for their support and doa's.

ABSTRACT

Dye-sensitized solar cell (DSSC) and Perovskite Solar Cell (PSC) are categorized as the third generation in solar cell technology. Both solar cells are known for its low production cost, simple preparation methodology, low toxicity, substrate flexibility and suitability for indoor use. In the previous two decades, PSC has shown a very encouraging rate of improvement in performance, rising from single digits to double digits rapidly. The Electron Transport Layer (ETL) plays an important role in PSC through charge extraction. TiO₂ material has been used as an ETL conventionally, but the process of further improving the performance of PSC-based TiO₂ ETL is nearly saturated and deadlocked. In theory, the ZnO material possesses an energy band gap value similar to the TiO₂ material, but with superior electron mobility. This clearly shows the potential of ZnO material to replace TiO₂ material acting as photoanode and ETL for DSSC and PSC, respectively. However, previous articles have reported that pure ZnO is still insufficient in improving the performance of solar cells. Herein, small amounts of Al and Ni dopants are added into the ZnO layers, believed to passivate the widely known Zn²⁺ lattice defect in the ZnO bulk layer. In addition, the structural features of ZnO nanorods also imply providing a higher surface aspect ratio allowing a greater charge carrier reaction mechanism. Initially, this work started with the simulation of complete DSSC and PSC utilizing the ZnO layer as the photoanode and ETL, respectively using SCAPS software. The Al and Ni dopant concentrations are varied in enhancing cell performance. Power conversion efficiency (PCE) as high as 3.96% and 3.9% were obtained using concentrations of 3 mol% and 4 mol% for ZnO:Al and ZnO:Ni photoanodes in DSSC, respectively. Meanwhile, PCE values of PSC reaching 17.6% and 17.58% were recorded from dopant concentration of 1 mol% for both ZnO:Al ETL and ZnO:Ni ETL, respectively. Compatibility with other layers was also studied, suggesting the use of Cu₂O as the HTL and Pb-free CH₃NH₃SnI₃ perovskite material as the absorber layer. It has been discovered that the combination of Al-doped ZnO ETL with Cu₂O HTL and CH₃NH₃SnI₃ absorber layer in PSC has successfully produced considerable PCE values as high as 27.72% and 21.18% for ZnO:Al ETL and ZnO:Ni ETL, respectively. Based on simulations and experimental evidence, the combination of a small amount of dopant into the ZnO layer with appropriate inorganic HTL and Pb-free perovskite layers is shown to be promising in enhancing the performance of the PSC. This study clearly has an impact in providing guidance to researchers and industry before the full fabrication process of solar cells is carried out.

ANALISIS BERANGKA DAN SINTESIS ZnO NANOROD DENGAN PELBAGAI KEPEKATAN BAHAN DOP UNTUK PENAMBAHBAIKAN PENGANGKUTAN ELEKTRON DALAM APLIKASI SEL SURIA

ABSTRAK

Sel Surya Disensitasi Pewarna (DSSC) dan Sel Surya Perovskite (PSC) dikategorikan sebagai generasi ketiga dalam teknologi sel suria. Kedua-dua jenis sel suria ini terkenal dengan kos pengeluarannya yang rendah, metodologi penyediaan yang mudah, ketoksikan yang rendah, fleksibiliti substrat dan kesesuaian untuk kegunaan dalaman. Dalam dua dekad sebelum ini, PSC telah menunjukkan kadar peningkatan prestasi yang amat memberangsangkan, meningkat daripada satu digit kepada dua digit dengan pantas. Lapisan Pengangkutan Elektron (ETL) memainkan peranan penting dalam PSC melalui pengekstrakan cas. Bahan TiO₂ telah digunakan sebagai ETL secara konvensional, namun proses meningkatkan lagi prestasi PSC berasaskan TiO₂ ETL hampir tepu dan buntu. Secara teori, bahan ZnO memiliki nilai julat tenaga yang serupa dengan bahan TiO₂, namun dengan mobiliti elektron yang jauh lebih baik. Ini jelas menunjukkan potensi bahan ZnO untuk menggantikan bahan TiO₂ yang bertindak sebagai fotoanod dan ETL untuk DSSC dan PSC. Walau bagaimanapun, artikel sebelum ini telah melaporkan bahawa ZnO tulen masih tidak mencukupi dalam meningkatkan prestasi sel suria. Di sini, sejumlah kecil dopan Al dan Ni ditambah ke dalam lapisan ZnO, dipercayai memasifkan kecacatan kekisi Zn²⁺ yang diketahui secara umum dalam lapisan pukal ZnO. Di samping itu, ciri-ciri struktur nanorod ZnO juga menyifatkan dalam menyediakan nisbah aspek permukaan yang lebih tinggi yang membolehkan mekanisme tindak balas pembawa cas yang unggul. Pada mulanya, kerja ini bermula dengan simulasi DSSC dan PSC lengkap menggunakan lapisan ZnO sebagai fotoanod dan ETL, menggunakan perisian SCAPS. Kepekatan dopan Al dan Ni adalah berbeza-beza dalam meningkatkan prestasi sel. Kecekapan penukaran kuasa (PCE) setinggi 3.96% dan 3.9% diperolehi menggunakan kepekatan 3 mol% dan 4 mol% untuk fotoanod ZnO:Al dan ZnO:Ni dalam DSSC. Sementara itu, nilai PCE daripada PSC mencecah nilai 17.6% dan 17.58% direkodkan daripada kepekatan 1 mol% untuk kedua-dua ZnO:Al ETL dan ZnO:Ni ETL. Keserasian dengan lapisan lain juga dikaji, mencadangkan penggunaan Cu₂O sebagai HTL dan bahan Pb-bebas CH₃NH₃SnI₃ sebagai lapisan penyerap. Gabungan Al-didop ZnO ETL dengan lapisan penyerap Cu₂O HTL dan CH₃NH₃SnI₃ dalam PSC telah didapati berjaya menghasilkan PCE yang besar setinggi 27.72% dan 21.18% untuk ZnO:Al ETL dan ZnO:Ni ETL. Berdasarkan simulasi dan bukti eksperimen, gabungan sejumlah kecil dopan ke dalam lapisan ZnO dengan lapisan perovskite bebas Pb dan HTL bukan organik yang sesuai telah menunjukkan prestasi yang menjanjikan dalam PSC. Kajian ini jelas memberikan impak dalam memberi panduan kepada para penyelidik dan pihak industri sebelum proses fabrikasi penuh sel suria dijalankan.

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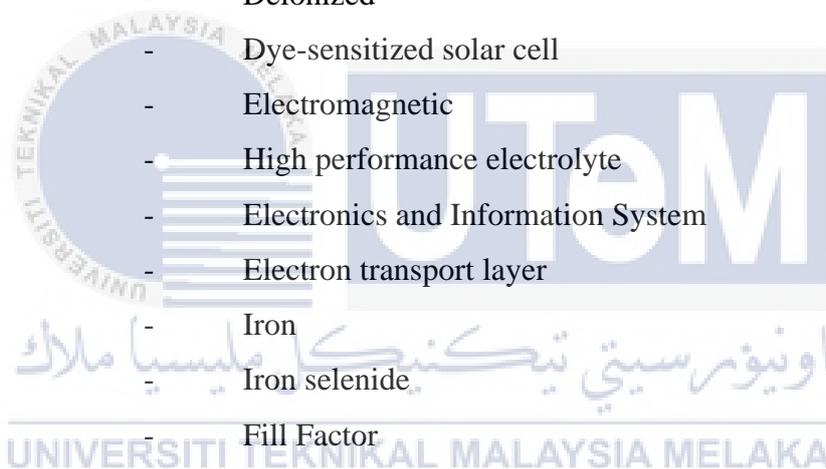
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LIST OF ABBREVIATIONS

AC	-	Alternating current
ACN	-	Acetonitrile
Al	-	Aluminium
Al ³⁺	-	Aluminium ion
AlCl ₃ H ₁₂ O ₆	-	Aluminium chloride hexahydrate
ALD	-	Atomic layer deposition
Al ₂ O ₃	-	Aluminium oxide
AR	-	Antireflective
As	-	Arsenic
Au	-	Gold
B	-	Boron
C – f	-	Capacitance - Frequency
C – V	-	Capacitance - Voltage
C	-	Carbon
CaTiO ₃	-	Calcium titanate
CB	-	Conduction band
CBD	-	Chemical bath deposition
Cd	-	Cadmium
CDCA	-	Chenodeoxycholic acid
CdTe	-	Cadmium tellurite
CE	-	Counter electrode
CH ₃ NH ₃ ⁺	-	Methyl-ammonium
CH ₃ NH ₃ PbBr ₃	-	Methylammonium Bromide
CH ₃ NH ₃ PbI ₃	-	Methylammonium lead iodide
CH ₃ NH ₃ SnI ₃	-	Methylammonium tin halide

CIGS	-	Copper indium gallium selenide
Co	-	Cobalt
CoNi _{0.25}	-	Nickel-modified cobalt phosphide
CoS	-	Carbonylsulfide
(CH ₂) ₆ N ₄	-	Hexamethylenetetramine
C ₂ H ₅ OH	-	Ethanol
C ₃ H ₆ O	-	Acetone
CuI	-	Copper (I) iodide
CuInSe ₂	-	Copper indium selenide
Cu ₂ O	-	Copper (I) oxide
CuSCN	-	Cuprous thiocyanate
DC	-	Direct current
DI	-	Deionized
DSSC	-	Dye-sensitized solar cell
EM	-	Electromagnetic
EL-HPE	-	High performance electrolyte
ELIS	-	Electronics and Information System
ETL	-	Electron transport layer
Fe	-	Iron
FeSe	-	Iron selenide
FF	-	Fill Factor
FTO	-	Fluorine-doped tin oxide
GaAs	-	Gallium arsenide
Ge	-	Germanium
GO	-	Graphite oxide
H ₂ O	-	Deionized water
HOMO	-	Highest occupied molecular orbital
HTL	-	Hole transporting layer
I – V	-	Current - Voltage
IL	-	Ionic liquid
In	-	Indium
I _{sc}	-	Short circuit current
ITO	-	Indium-doped tin oxide



J _{sc}	-	Lower cell photocurrent
La	-	Lanthanum
LUMO	-	Lowest unoccupied molecular orbital
MgO	-	Magnesium oxide
N _A	-	Acceptor doping
NaOH	-	Sodium hydroxide
Nb ₂ O ₅	-	Niobium (V) oxide
Ni	-	Nickel
Ni ²⁺	-	Nickel ion
NIR	-	Near infrared ranges
NMP	-	N-methylpyrrolidine
NR	-	Nanorods
Nit	-	Interface density of state
OHIP	-	Organic-inorganic hybrid-perovskite
P3HT	-	Poly(3-hexylthiophene-2,5-diyl)
P	-	Phosphorus
Pb ²⁺	-	Lead (II) ion
PCBM	-	Phenyl-C61-butyric acid methyl ester
PCE	-	Power conversion efficiency
PEDOT:PSS	-	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PSC	-	Perovskite solar cell
Pt	-	Platinum
c	-	Poly(triaryl amine)
PV	-	Photovoltaic
PVD	-	Physical vapor deposition
QE	-	Quantum efficiency
RF	-	Radio frequency
RH	-	Hall coefficient
Sb	-	Antimony
SCAPS	-	Solar cell capacitance simulator
SEM	-	Scanning electron microscope
Si	-	Multicrystalline Silicon
SnO ₂	-	Tin (IV) oxide

TBP	-	4-Tert-butylpyridine
TCO	-	Transparent conductive oxide
Te	-	Tellurium
TEL	-	Transport electrode layer
TiCl ₄	-	Titanium tetrachloride
TiO ₂	-	Titanium dioxide
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet-visible
VB	-	Valence band
V _{oc}	-	Open circuit voltage
WE	-	Working electrode
XRD	-	X-ray diffraction
ZnA	-	Zinc acetate dihydrate
ZnO	-	Zinc Oxide
Zn ²⁺	-	Zinc ion
ZnO:Al	-	Aluminium doped ZnO
Zn(CH ₃ CO ₂) ₂ ·2H ₂ O	-	Zinc Acetate Dihydrate
ZnO:Ni	-	Nickel doped ZnO
Zn(NO ₃) ₂ ·6H ₂ O	-	Zinc Nitrate Hexahydrate

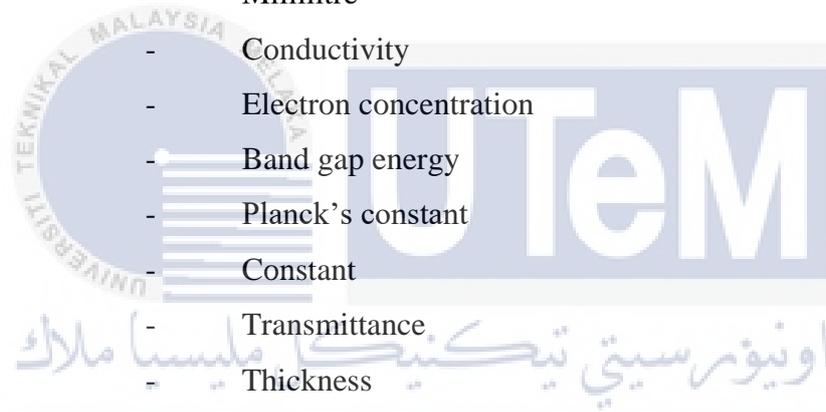


UNIVERSITI TEKNIKAL MALAYSIA MELAKA

LIST OF SYMBOLS

A	-	Organic cation
B	-	Metal cation
X	-	Halide anion
%	-	Percent
°C	-	Celsius
$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	-	Electron mobility
Å	-	Angstrom
η	-	Efficiency
Ω/cm^2	-	Volume resistivity
eV	-	Electronvolt
S ⁺ /S	-	Ground state
S ⁺ /S*	-	Excited state
h	-	Planck constant
ν	-	Frequency
$r_A, r_B,$ and r_X	-	Ionic radii
nm	-	Nanometer
2 θ	-	2-Theta
mol%	-	Percentage of the total moles compound
μH	-	Hall mobility
kg	-	Kilogram
MB	-	Megabyte
n	-	Free holes
p	-	Electrons
n_t	-	Trapped holes
p_t	-	Trapped electrons

ψ	-	Electrostatic potential
q	-	Electron charge
G	-	Generation rate
ξ	-	Permittivity
D	-	Diffusion coefficient
N_a^-	-	Ionised acceptor-like doping concentration
N_b^-	-	Ionised donor-like doping concentration
cm^{-3}	-	Doping density
K	-	Kelvin
cm^{-2}	-	Defect density
mM	-	millimolar
g/mol	-	Molecular mass
ml	-	Millilitre
σ	-	Conductivity
n	-	Electron concentration
E_g	-	Band gap energy
h	-	Planck's constant
A	-	Constant
T	-	Transmittance
d	-	Thickness



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