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**QUANTUM DOTS FOR CLEAN ENERGY
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**(TITIK KUANTUM UNTUK TEKNOLOGI
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Dedicated to the root of our strength – family and friends

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In the name of Allah, the Most Gracious and Most Merciful. Praise be to Allah; the Lord of the universe. Peace and blessings be upon Prophet Muhammad (Peace be Upon Him) and people who walks on the path of His guidance until the judgement day.

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ABSTRACT

Solar cells are in focus for decades due to their capability to convert solar energy into electrical energy. Quantum dots sensitized solar cell (QDSC), in which the photovoltaic (PV) effect occurs at the interface between a quantum dot (QD) conjugated wide band gap metal oxide semiconductor (MOS) and a redox electrolyte, gained much consideration due to their relatively simpler device structure and similarity to dye sensitized solar cell (DSSC), in which dye molecules replace QDs. The QDs are potentially having larger absorption cross-section, tuneable band edges, and atomic-like energy levels. These salient features make QDs capable of delivering more than one electron per single absorbed photon of sufficient energy, a phenomenon known as multi-exciton generation (MEG). The MEG effect makes QDSCs capable of achieving PV conversion efficiency (PCE) as high as 60%. Despite the remarkable feature of QDs as a light absorber, QDSCs deliver much inferior practical PCE (~8.6 %). Besides, they show inferior PCE compared to DSSCs (~13%). Therefore, this doctoral research aims to establish the structure-property correlation in QDSCs. A combination of experimental results and quantum chemical calculations under the framework of density functional theory (DFT) was employed for this purpose. In this approach, firstly CdSe QDs were synthesized using chemical methods and studied their structure and properties. Secondly realistic cluster models were empirically developed using DFT and experimental results. The structure-property correlation was established by comparing the experimental and theoretical results. The calculated absorption cross-section, band edges, band gaps, and emitting states of QDs with and without surface ligands were compared with that of $\text{RuL}_2(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$; $L = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid (N3) dye in order to correlate the capability of light absorption of QDs or dye molecules on the overall performance of device. This procedure was adopted to (i) understand the fundamental differences of electronic states in the bare QDs and the dye structures and (ii) evaluate electron channelling in QDs-ligand conjugate thus correlating with electron injection efficiency from QDs to MOS. Five parameters were concluded to have distinct effects on the PV properties of QDSCs. They are (i) emitting states of QDs, (ii) ligand usage, (iii) QDs size distribution, (iv) absorption cross-section, and (v) redox potential of electrolyte. The QDs-MOS conjugates were chemically developed and spectroscopically demonstrated efficient electron injection from QDs to MOS. However, such structures raised serious concerns on long term stability under operating conditions. This research finally propose future possible methodologies for stable and efficient QDSCs.

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ABSTRAK

Sel suria menjadi focus semenjak beberapa dekad kerana keupayaannya untuk menukar tenaga suria kepada tenaga elektrik. Sel suria terpeka titik kuantum (QDSC), yang mana kesan fotovoltaiik (PV) berlaku di antara permukaan konjugat titik kuantum (QD)–semikonduktor logam oksida berjurang tenaga lebar (MOS) dan elektrolit, menerima pertimbangan yang sewajarnya berikutan struktur peranti yang mudah dan persamaan dengan sel suria terpeka pewarna (DSSC), yang mana molekul pewarna menggantikan titik kuantum (QD). QD berpotensi untuk mempunyai keratan rentas spektrum serapan yang luas, mengubah jurang tenaga and ciri tahap tenaga seperti atom. Ciri-ciri penting ini menjadikan QD mampu mengujakan lebih dari satu elektron dengan setiap penyerapan satu foton dengan tenaga yang mencukupi. Fenomena tersebut dinamakan *multi-exciton generation* (MEG) yang menjadikan QDSC mampu mencapai kecekapan penukaran tenaga foto (PCE) sehingga 60 %. Namun, walaupun dengan adanya ciri-ciri luar biasa ini, penggunaan QD sebagai penyerap cahaya peranti QDSC hanya mampu menghasilkan PCE yang rendah secara praktikal (~8.6 %). Tambahan pula, kecekapan tersebut lebih rendah berbanding dengan kecekapan DSSC (~13%). Oleh itu, kajian peringkat kedoktoran ini menyasarkan pembuktian korelasi di antara struktur komponen dan ciri fotovoltaiik QDSC. Gabungan keputusan ujikaji dan pengiraan peringkat kimia kuantum menggunakan *density functional theory* (DFT) telah digunakan untuk tujuan ini. Melalui pendekatan ini, pertama sekali QD CdSe telah disintesis menggunakan kaedah kimia dan struktur serta ciri-cirinya dikaji. Kedua, model kluster realistik dibangunkan secara empirik menggunakan DFT dan keputusan ujikaji. Korelasi struktur-ciri dibuktikan dengan melakukan perbandingan di antara keputusan ujikaji dan pengiraan teori. Ciri-ciri QD dan konjugat QD–ligan seperti keratan rentas spektrum penyerapan, aras tenaga, jurang tenaga dan keadaan teruja telah dibandingkan dengan ciri-ciri milik $\text{RuL}_2(\text{NCS})_2 \cdot 2\text{H}_2\text{O}$; $L = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid (pewarna N3) untuk pembuktian korelasi di antara keupayaan penyerapan cahaya oleh QD dan molekul pewarna dengan prestasi keseluruhan peranti. Prosedur ini dijalankan untuk (i) memahami perbezaan keadaan elektronik kluster-kluster QD dan molekul pewarna secara asas dan (ii) menilai kecekapan penyaluran elektron di dalam konjugat QD–ligan yang berkait rapat dengan kecekapan suntikan elektron dari QD kepada MOS. Lima parameter telah disimpulkan mempunyai kesan kepada ciri PV QDSC iaitu, (i) keadaan tersinar QD, (ii) penggunaan ligan, (iii) taburan saiz QD, (iv) luas keratan rentas spektrum penyerapan dan (v) potensi redoks elektrolit. Konjugat QD-MOS telah dihasilkan secara kimia dan menunjukkan kecekapan suntikan elektron dari QD ke MOS secara spektroskopik. Walaubagaimanapun, struktur-struktur ini telah menimbulkan kebimbangan terhadap kestabilan jangka panjang pengoperasian peranti. Kajian ini mencadangkan metodologi yang mungkin boleh digunakan untuk menghasilkan QDSC yang stabil dan cekap.

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LIST OF SYMBOLS

J_x	Current density
$\mu(x)$	1-D electron mobility
$\nabla F_n(x)$	Gradient in Fermi levels of the materials across which the electrons flow
V_{OC}	Maximum photovoltage
J_{SC}	Short circuit current density
c -Si	Monocrystalline silicon
a -Si:H	Amorphous silicon
p -Si	Polysilicon
mc -Si	Multi-crystalline silicon
E_g	Bandgap energy
$E_{kinetic}$	Kinetic energy
η	Power conversion efficiency
α_A	Absorption cross-section
wt%	Weight percentage
w/o	Water in oil
o/w	Oil in water
ε	Extinction coefficient
λ	Wavelength
λ_{exc}	Excitation wavelength
λ_{em}	Emission wavelength
I_o	Intensity of illuminated light
I	Intensity of transmitted light
T	Transmittance

A	Absorbance
\hat{H}	Hamiltonian operator
$\hat{T}(x)$	Kinetic energy
$\hat{V}(x,t)$	Potential energy
Ψ	Wavefunction
$\rho(r)$	Electron density
$1S_{3/2} - 1S_e$	HOMO-0 – LUMO+0 transition
$1S_{1/2} - 1S_e$	HOMO-0 – LUMO+1 transition
$1P_{3/2} - 1S_e$	HOMO-0 – LUMO+2 transition
$2S_{1/2} - 1S_e$	HOMO-0 – LUMO+3 transition
\hbar	Planck constant (6.58×10^{-16} eV.s)
m_e	Effective mass of electron (i.e., $0.13 m_o$)
m_h	Effective mass of hole (i.e., $0.45 m_o$)
m_o	Electron rest mass (9.10×10^{-31} kg)
e	Charge of an electron
ϵ	Dielectric constant
σ	Surface tension
ζ	Zeta represents the exponent of an Slater Type Orbital basis function
-SH	Thiol functional group
-COOH	Carboxylic functional group
Φ_{IN}	Electron injection efficiency
σ_{TR}	Electron transport efficiency through MOS
σ_{DR}	Fluorophore regeneration efficiency
f	Oscillator strength

E_{ads}	Adsorption energy
$E_{QD-ligand}$	Energy of QDs–ligand conjugate
E_{QD}	Energy of QDs
E_{ligand}	Energy of ligand
E°	Redox potential energy
ΔG_{OX}	Free energy difference between anion and neutral state of electrolyte
F	Faraday constant (23.06 kcal/mol.V)
G_{II}	Absolute free energy of neutral state of electrolyte
G_I	Absolute free energy of redox species of electrolyte
$E_{SCF I}$	Computed self-consistent field energies from optimized structures of redox species
SCF	Self-consistent field
$E_{SCF II}$	Computed self-consistent field energies from optimized structures of neutral state
G_{corr}	Thermal correction to Gibbs free energy
\emptyset	Diameter

LIST OF ABBREVIATIONS

AM1.5 G	Standard Terrestrial Spectra of Air Mass 1.5 Global Illumination
BA	4-butylamine
BHJ	Bulk heterojunction
BSE	Backscattered electrons
B3LYP	Becke's three parameter hybrid method with the Lee, Yang and Parr gradient corrected correlation functional
CBD	Chemical bath deposition
CIGS	CuInGaSe ₂
CVD	Chemical vapour deposition
DA	Direct attachment
DFT	Density functional theory
DoS	Density of states
DSSC	Dye sensitized solar cell
EMA	Effective mass approximation
FCC	Face centered cubic
FEG	Field emission gun
FESEM	Field emission scanning electron microscope
FT-IR	Fourier Transform InfraRed
FTO	Fluorine doped tin oxide
FWHM	Full-width half-maximum
GuNCS	Guanidiniumisothiocyanate
HCP	Hexagonal close pack
HOMO	Highest occupied molecular orbital
HRTEM	High resolution transmission electron microscope

HTM	Hole transporting material
HTS	Hierarchical TiO ₂ spheres
IPCE	Incident photon to charge carrier efficiency
IR	Infrared
JCPDS-ICDD	Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data
LA	Ligand assistance
LEI	Lower detector
LUMO	Lowest unoccupied molecular orbital
MAA	Mercaptoacetic acid
MBA	Mercaptobenzoic acid
MDA	Mercaptododecanoic acid
MEA	Mercaptoethanol
MEG	Multi-exciton generation
MOS	Metal oxide semiconductor
MPA	Mercaptopropionic acid
MPTMS	(3-mercaptopropyl) trimethoxysilane
MSA	Mercaptosuccinic acid
NP	Nanoparticle
NREL	National Renewable Energy Laboratory
NW	Nanowire
OMO	Occupied molecular orbital
OSC	Organic solar cells
OTE	Optically Transparent Electrode
PCBM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester

PCE	Photovoltaic conversion efficiency
PL	Photoluminescence
PV	Photovoltaic
P3HT	Polythiophenes
QD	Quantum dot
QDSC	Quantum dots solar cell
QW	Quantum well
SAED	Selected area electron diffraction
SCCNT	Stacked cup carbon nanotube
SE	Secondary electrons
SEI	Upper secondary electron detector
SEM	Scanning electron microscope
SILAR	Successive ionic liquid adsorption and reaction
SWCNT	Single wall carbon nanotube
TAA	Thioacetic acid
TBP	Tert-butylpyridine
TDDFT	Time dependent density functional theory
TEM	Transmission electron microscope
TNRs	TiO ₂ nanorods
TOP	Trioctylphosphine
UMO	Unoccupied molecular orbital
UV-Vis	UV-Visible
VACNT	Vertically aligned carbon nanotube
XRD	X-ray diffractometer

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The quantum dots (QDs), the semiconducting nanocrystals of size less than their exciton Bohr radius with size-dependent opto-electronic properties, have been fascinating materials to scientists and engineers for nearly two decades. This fascination stems from two reasons: firstly, QDs are midway between molecules and crystals thereby giving opportunities to understand the evolution of properties of bulk materials compared to their molecules. Secondly, their size dependent opto-electronic properties make them promising candidates for a diverse range of applications. Figure 1.1 shows that when a bulk semiconductor is reduced to the size of QDs, one can observe that the density of states (DoS) of QDs is very similar to that of atoms, which enable them to be called artificial atoms (Alivisatos, 1996a).

Applications of QDs, where semiconductor physics meets nanotechnology, are now envisaged in diverse areas such as opto-electronics (Su et al., 2013), healthcare (Li et al., 2013), computation (Dietl et al., 2000), PVs (Rühle et al., 2010), and advanced electronics (Hai et al., 2013). The principle attraction in the use of QDs for PVs is related to the thermodynamic limit of the energy conversion efficiency of solar cells. Shockley and Queisser calculated the thermodynamic limit of conversion efficiency for solar cells to be 32% (Shockley et al., 1961). This limit arises from the difference between the energy absorbed by the photoactive semiconductor and its bandgap. As the electron injection or separation occurs only from the bottom of the conduction band, the above difference in energy is lost as heat through excitation of the lattice vibrations, otherwise called phonon relaxation (see Figure 1.2.a). In other words, the electrons are “cooled” by transferring the difference in energy to the lattice.