SYNTHESIS AND CHARACTERIZATION OF TIN BASED HYBRID NANOFIBERS AND NANOFLOWERS AS PHOTOELECTRODE IN DYE-SENSITIZED SOLAR CELLS

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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DEDICATION

This thesis is dedicated to my beloved parents, husband, brothers, sisters, and kids.

Without whom none of my success would be possible

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Zinab H. Bakr

ABSTRAK

Fotoanod memainkan peranan penting dalam operasi sel suria peka-pewarna kerana pelbagai fungsi termasuk: (1) menyediakan permukaan untuk penjerapan bahan pewarna dan (2) menerima elektron yang teruja dari pewarna melalui suntikan sinaran cahaya, seterusnya mengalirkannya ke litar luar untuk menghasilkan arus elektrik. Penyelidikan yang terkandung dalam tesis ini menerangkan sintesis komposit struktur nano oksida logam serta binari oksida logam tulen serta penilaian kesesuaian bahan sebagai fotanod dalam sel solar peka-pewarna. Oleh kerana sifat-sifat seperti tahap konduksi yang baik dalam TiO_2/ZnO, mobiliti elektron yang tinggi (150 cm^2 V^{-1} s^{-1} untuk kristal nano) dan kelebihan kekonduksian elektrik SnO_2; oksida logam komposit dalam sistem SnO_2-TiO_2 dan SnO_2-ZnO dipilih untuk dikaji dalam kerja semasa. Kaedah elektrospinning digunakan untuk mensintesis komposit nano pelbagai morfologi disebabkan keupayaannya untuk pembangunan dan penghasilan bahan nano yang berskala besar. Penghasilan komposit telah ditentusahkan oleh pembelauan sinar-X, penyebaran tenaga X-ray dan analisis dari spektroskopi X-ray foto elektron. Morfologi pula diuji oleh mikroskop pengimbas emisi elektron dan mikroskop transmisi dengan serakan elektron di kawasan terpilih. Kajian morfologi menunjukkan bahawa SnO_2-TiO_2 terbentuk dalam dua struktur, fiber nano dan nanoflowers apabila kepekatan prekursor diselaraskan manakala SnO_2-ZnO memberikan morfologi fiber nano. Sinergi dalam sifat optik, elektronik dan komposit elektrik fiber nano ditunjukkan oleh voltametri siklik, Mott Schottky, dan spektroskopi penyerapan. Voltan-arus, kemerosotan voltan litar terbuka dan pengukuran impedans elektrokimia menunjukkan bahawa struktur nano komposit mempunyai sifat-sifat yang beerti apabila digunakan sebagai fotoanod dalam sel suria peka-pewarna disebabkan oleh kecekapan pengubahan cahaya (PCE ~5.65% untuk fiber nano komposit SnO_2-ZnO, 7.4% untuk komposit nanoflowers SnO_2-TiO_2 dan ~ 8.5% untuk fiber nano komposit SnO_2-TiO_2) berbanding dengan logam oksida tulen SnO_2 (~3.90%), ZnO (~1.38%) dan TiO_2 fiber nano (~5.1%). Hasil kajian ini menunjukkan kaedah ringkas dan berskala ringkas mampu untuk menghasilkan reka bentuk komposit elektrod bagi meningkatkan prestasi fungsi peranti akhir.

ABSTRACT

Photoanode plays a crucial role in the operation of dye-sensitized solar cells due to its many functions: (1) provide a surface for the adsorption of the dye and (2) accepts photoinjected electrons from the excited dye and conducts them to the external circuit to produce an electric current. The research embodied in this thesis describes the synthesis of composite metal oxides nanostructure as well as pure binary metal oxides and evaluate their suitability as a photoanode in the dye-sensitized solar cells. Due to the advantageous properties such as favorable conduction band level of TiO_2/ZnO, high electron mobility (150 $cm^2 V^{-1} s^{-1}$ for nanocrystals) and high electrical conductivity of SnO_2, attention is devoted to these three materials. Composite metal oxides in the SnO_2-TiO_2 and SnO_2-ZnO nanostructures are chosen for the current work to overcome the limitation of the single metal oxide; such as low conduction band edge of SnO_2, low charge mobility of TiO_2 and lack of stability of ZnO based photoanode in dye-sensitized solar cells. Electrospinning method is adopted for the synthesis of composite nanostructures morphologies due to the feasibility of this method for developing nanoscale materials in large scales. The composites formation is confirmed by X-ray diffraction, energy dispersive X-ray and X-ray photoelectron spectroscopy analyses. The morphology is examined by field emission scanning electron microscopy and transmission electron microscopy with selected area electron diffraction. Morphological studies show that SnO_2-TiO_2 formed in two structures, nanofibers and nanoflowers by adjusting the precursor's concentration whereas SnO_2-ZnO gave nanofibers morphology. Synergy in the optical, electronic and electrical properties of the composite nanofibers is demonstrated by cyclic voltammetry, Mott-Schottky, and absorption spectroscopy. Current-voltage, Open-circuit voltage decay and electrochemical impedance measurements revealed that the composite nanostructures offering valuable properties when utilized as a photoanode in dye-sensitized solar cells in terms of photoconversion efficiency (PCE ~5.65% for SnO_2-ZnO composite nanofibers, 7.40% for SnO_2-TiO_2 composite nanoflowers and ~8.50% for SnO_2-TiO_2 composite nanofibers) compared to its binary counterparts SnO_2 (~3.90%), ZnO (~1.38%) and TiO_2 nanofibers (~5.10%). Results of this research revealed a facile and scalable method to fabricate a simple composite electrode design for enhancing the functional performances of the final device.

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LIST OF SYMBOLS AND UNITS

A	Absorption
k_B	Boltzmann constant
N_D	Charge density
cP	Centipoise
J	Current density
cm	Centimeter
η_{cc}	Charge collection efficiency
ε_m	Dielectric constant of the semiconductor
L_n	Electron diffuse length
n	Electron density
D_n	Electron diffuse coefficient
τ_n	Electron lifetime
τ_d	Electron transit time
μ_e	Electron mobility
E_g	Energy gap
F	Farad
V_{fb}	Flat-band potential
∇E_F	Gradient in Fermi levels of a materials interface
Z''	Imaginary impedance
k	Kilo
I_{max}	Maximum current
f_{max}	Maximum frequency
P_{max}	Maximum power
V_{max}	Maximum voltage
μ	Micro
ms	Millisecond
mV	Millivolt
ε	Molar extinction coefficient
V_{OC}	Open circuit voltage
Ω	Ohm
d	Photoelectrode thickness

Z'	Real impedance
R_{Rec}	Recombination resistance
R	Reflectance
C_{μ}	Photoanode chemical capacitance
C	Space charge capacitance
J_{SC}	Short circuit current density
R_t	Transport resistance
R_s	Series resistance
R_{Sh}	Shunt resistance
T	Transmittance
T	Temperature
λ	Wavelength
ε_0	Vacuum permittivity

LIST OF ABBREVIATIONS

ALD	Atomic layer deposition
AM	Air mass
ACG	Aqueous chemical growth
BET	Brunauer-Emmett-Teller
CB	Conduction band
CBD	Chemical bath deposition
CPM	Chemical precipitation method
CV	Cyclic voltammetry
CE	Counter electrode
CPE	Constant phase element
CdTe	Cadmium telluride
CIGS	Copper indium gallium diselenide
DCTP	Direct current thermal plasma
DSSCs	Dye-sensitized solar cells
EM	Electrochemical method
EIS	Electrochemical impedance spectroscopy
EDX	Energy dispersive X-ray spectroscopy
EDM	Electrodeposited method
ES	Electrospun method
FSP	Flame spray pyrolysis.
FESEM	Field emission scanning electron microscopy
FF	Fill factor
FTO	Fluorine-doped tin oxide
HTM	Hydrothermal method
HOMO	Highest occupied molecular orbitals
HRTEM	High-resolution transmission electron microscopy
H	Hydrolysis
ITO	Indium-tin-oxide
pI	Isoelectric point
LSV	Linear sweep voltammetry
LPD	liquid-phase deposition

LUMO	Lowest unoccupied molecular orbitals
MOS	Metal oxide semiconductor
MS	Mott–Schottky
NFs	Nanofibers
NPs	Nanoparticle
NRs	Nanorods
NTs	Nanotubes
NWs	Nanowires
1D	One dimensional
OCVD	Open circuit voltage decay
PSCs	Perovskite solar cells
PV	Photovoltaic
PCE	Power conversion efficiency
Pt	Platinum
PCE	Polyethylene naphthalate
SAED	Selected area electron diffraction
S	Sputtering
SC	Spin coating
STM	Solvothermal method
TL	Transmission line
TE	Thermal evaporation
3D	Three-dimensional materials
2D	Two-dimensional materials
TPM	Two probe method
TEM	Transmission electron microscopy
TCO	Transparent conductive oxide
TGA	Thermogravimetric analysis
UV-Vis-NIR	Ultraviolet-visible near-infra-red
VB	Valance band
WE	Working electrode
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

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