FIRST-PRINCIPLES CALCULATIONS ON SOL-GEL ZINC OXIDE NANOPARTICLES OPTOELECTRONIC PROPERTIES

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by

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LIST OF ABBREVIATIONS

Abbreviation	Description
CASTEP	Cambridge Serial Total Energy Package
CB	Conduction band
CBM	Conduction band minimum
DFT	Density functional density
DOS	Density of state
FESEM	Field emission scanning electron microscope
GGA	Generalized gradient approximation
GGA-PBE	Generalized gradient approximation with Perdew-Burke-Ernzerhof scheme
GGA-PBE+U	Generalized gradient approximation with Perdew-Burke-Ernzerhof and Hubbard-U correction scheme
GGA-PBESol	Generalized gradient approximation with Perdew-Burke-Ernzerhof scheme for solid
GGA-PBESol+U	Generalized gradient approximation with Perdew-Burke-Ernzerhof scheme for solid and Hubbard-U correction scheme
GOF	Goodness of fit
ICSD	Inorganic Crystal Structure Database
LDA	Local density approximation

LDA+U	Local density approximation with Hubbard-U correction scheme
PDOS	Partial density of state
PL	Photoluminescence
SGC	Sol-gel centrifuge
SGS	Sol-gel storage
SIC	Self-interaction correction
TGA	Thermal gravimetric analysis
TEM	Transmission electron microscope
UV	Ultra violet
UV-VIS	Ultra violet-visible
VB	Valence band
VBM	Valence band maximum
XC	Exchange-correlation
XRD	X-ray diffraction
3D	Three dimension

LIST OF SYMBOLS

Symbols

%	Percentage
°	Degree
°C	Degree Celcius
°C min^{-1}	Degree Celcius per minute
Ψ	Wavefunction
ε_1	Real part of dielectric function
ε_2	Imaginary part of dielectric function
ω	Photon frequency
∇	Gradient of electron density
λ	Wavelength
Å	Angstrom
α	Absorption coefficient
a	Lattice parameter in *x*-axis
c	Lattice parameter in *z*-axis
e	Charge of electron
e^{hom}	Homogenous electron gas
m	Mass of ion
n(r)	Particle density at point *r*
h	Planks's constant
h	Hour
j	Jam

r	Coordinates of electron
v	Frequency of light
E_g	Energy band gap
E_{HF}	Hartree-Fock energy
$\hat{H}$	Hamiltanion operator
M	Mass of electron
P_1	Momenta of ion
P_2	Momenta of electron
R	Coordinate of ion
R	Residual factor
R_{exp}	Expected profile residual
R_{wp}	Weighted profile residual
U	Coulomb repulsion energy
Z	Charge of ion
GPa	Giga Pascal
nm	Nano meter
eV	Electron Volt
meV	Mili electron Volt

LIST OF CHEMICAL FORMULA

CH_3OH	Methanol
H_2O	Water
NaOH	Sodium hydroxide
$Zn(CH_3COO)_2.2H_2O$	Zinc acetate dihydrate
$Zn(OH)_2$	Zinc hydroxide
$Zn(OH)_4^{2-}$	Zincate ion
OH^-	Hydroxide ion
Zn^{2+}	Zinc ion
O^{2-}	Oxygen ion
ZnO	Zinc oxide
TiO_2	Titanium oxide
CdS	Cadmium sulfide
CdSe	Cadmium selenide
SnO_2	Tin oxide

PENGIRAAN PRINSIP-PERTAMA TERHADAP CIRI-CIRI OPTOELEKTRONIK PARTIKEL NANO SOL-GEL ZINK OKSIDA

ABSTRAK

Diagnostik berkesan antara eksperimentasi dan pengiraan teori adalah perlu untuk memastikan sinergi antara kedua pendekatan. Kajian ini menggunakan input struktur daripada experimentasi ke dalam rangka kerja teori. Permulaannya, partikel nano ZnO telah disintesis melalui kaedah sol-gel pada waktu penuaan berbeza. Analisa fasa dan struktur mengesahkan penghasilan struktur ZnO wurtzit heksagon dengsn sampel dituakan selama 36 j menunjukkan penghabluran tertinggi dan memberikan visual tepat terbaik dalam analisa Rietveld. Pemerhatian morfologi menunjukkan penghasilan partikel nano sfera yang seragam pada masa penuaan melebihi 6 j manakala variasi yang kecil direkodkan pada jurang jalur tenaga antara 3.08 – 3.12 eV. Jalur kependarkilauan menunjukkan pelepasan hijau kerana kekosongan oksigen. Di dalam pengiraan prinsip pertama, sel unit ZnO dibina berdasarkan parameter struktur daripada analisa Rietveld bagi menghubungkan kajian eksperimental. Beberapa fungsi penukaran-korelasi termasuk LDA, GGA-PBE, GGA-PBESol, LDA+U, GGA-PBE+U dan GGA-PBESol+U. Fungsi GGA-PBE+U ($U_{d,Zn}$ = 10 eV dan $U_{p,O}$ = 6.1 eV) menunjukkan sisihan kekisi terendah dan berjaya mengulang jurang jalur tenaga eksperimentasi. Struktur ZnO super sel bersama kekosongan oksigen menunjukkan kedudukan kecacatan lebih nyah-setempat dan berada pada 1.90 eV dari atas jalur konduksi. Posisi ini menepati tenaga pembebasan foton (2.06 eV) seperti terlihat di spektrum kependarkilauan. Dapatan ini bermanfaat dalam rekabentuk anod sel solar bagi meningkatkan penyerapan cahaya nampak.

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ABSTRACT

An efficient diagnostic between experimental and theoretical calculation is essential to ensure the synergy between these two approaches. This study made attempt to use structural input from experimental in the theoretical framework. Initially, ZnO nanoparticles were synthesized by sol-gel method at different aging time. The phase and structural analyses confirmed the formation of hexagonal wurtzite ZnO structure at which sample aged at 36 h showed highest crystallinity and gave the best visual fit in Rietveld analysis. Morphological observation revealed spherical nanoparticles were formed at aging time higher than 6 h while only small variation in energy band gap recorded between 3.08 – 3.12 eV. The photoluminescence spectra revealed a green emission due to oxygen vacany. In first-principles calculation, the ZnO unit cell was built based on structural parameter from Rietveld analysis in order to provide a bridge with experimental study. Several exchange-correlation functional including LDA, GGA-PBE, GGA-PBESol, LDA+U, GGA-PBE+U and GGA-PBESol+U were tested. The GGA-PBE+U ($U_{d,Zn}$ = 10 eV and $U_{p,O}$ = 6.1 eV) showed lowest lattice deviation and successfully reproduced the experimental band gap. ZnO supercell structure with oxygen vacancy showed that defect state were more delocalized and appeared at 1.90 eV from top of conduction band. This position was close to the photon energy released due to recombination of electron (2.06 eV) as observed in luminescence spectra. The results are beneficial in designing photoanode material in solar cell that will enhance visible light absorption.

CHAPTER ONE

INTRODUCTION

1.1 Study background

The 21st century has marked a tremendous research work focusing on potential clean and renewable energy technology. The new generation of solar cell known as dye-sensitize solar cell (DSSC) is an example of energy device that actively studied. In DSSC, the photoanode consist of a metal oxide semiconductor plays important role that contributes to overall efficiency. It serves as a scaffold that supports the dye molecules and transferring electrons [1]. Zinc oxide (ZnO) has become a potential photoanode material pertaining to its unique and comparable properties from its former counterpart.

ZnO is a II-VI semiconductor with a wide energy band gap (3.3 eV) and high electron mobility with magnitude larger than anatase TiO_2 (μ_{TiO2} = 0.1-4 cm^2 Vs^{-1}, μ_{ZnO} = 200-300 cm^2 Vs^{-1}) [2]. To date, issue on the incapability of ZnO to fully utilize visible light due to its wide band gap has limited its potential use especially in solar cell. Several attempts have been conducted such as the introduction of a doping element and monitoring the native defects [3, 4]. These work in return involved number of experiments before the ideal properties can be achieved.

Pure ZnO nanoparticles can be obtained through several synthesis routes such as solid state reaction [5], hydrothermal [6] and sol-gel methods [7-9]. Notably, the sol–gel method has been favoured for the synthesis of ZnO because it can take place at a

lower temperature (<100℃), involves simple starting materials, and produces ZnO with excellent chemical homogeneity. The synthesis condition including solution pH [8, 10], type of starting materials [11], and pre- and post-heat treatment [12] are found to give impact on properties of sol-gel derived ZnO.

Meanwhile, the current practice used first-principles calculations based on the density functional theory (DFT) to study the properties of ZnO. DFT has become the preferred computational method due to the simplicity of the software and its ability to calculate the ground state properties with predictive accuracy. The principles of DFT are based on two theorems pioneered by Hohenberg-Kohn [13] and Kohn-Sham [14] that simplify the complexity of the many-body Schrodinger equation. By considering the electron density instead of many-body wave function, DFT has made the computational work much easier to be solved [15].

A number of theoretical studies have been conducted to simulate the optoelectronic properties ZnO [16-19]. Based on this method, fast and accurate results have been achieved, along with reduced trial and error, as often happens in experimental work. However, calculations based on the DFT are sensitive as the varying of unnecessary parameters may lead to unphysical and misinterpreted results.

1.2 Problem Statement

Previous studies have shown that intensive investigations on the properties of ZnO have been carried out by means of experimental and theoretical methods. Hence, it is necessary to verify these two approaches to ensure the synergy of each

work and in return leading to a significant improvement. One intriguing approach is to integrate the theoretical calculation with the input from the experimental result.

This approach used lattice parameters and atomic coordination obtained from experimentation to build the ZnO crystal structure in theoretical framework. However, the reported studies had used lattice inputs from random literature during the structure modelling stage [20, 21]. This strategy successfully created a ZnO model, but it did not offer a close representation of experimentally-grown ZnO. As a result, no bridging is attained and the calculated optoelectronic properties are merely belong another system.

To obtain an exact crystal structure is a challenging task. The refined diffracted profile from X-ray diffraction analysis offered structural information that is close representation to the synthesized version. Therefore, a well synthesized ZnO must be produced with a controlled parameter and carefully characterized.

In the sol-gel method, several processes involved such as hydrolysis, condensation, nucleation and aging. The growth of ZnO mainly occurred during aging [22] and if the gel is freely aged over time, the formation of ZnO nanoparticles could be investigated. Previous literature has noted that stabilized ZnO can be obtained after short-time aging lasting 0–36 h [23], 48 h [7, 8], and even after a month [24]. The range of aging time is rather very wide and may lead to difficulties when the optimum aging is to be chosen for practical consideration. Hence, aging time must be carefully examined to allow complete formation of ZnO.