

**PROPERTIES OF 4-FLUOROBENZOIC ACID MODIFIED ZINC  
OXIDE NANOPARTICLES BY SOL-GEL METHOD**

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NANOPARTICLES BY SOL-GEL METHOD

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Dedicated to my beloved family, my wife, my little brother (Raman)

and best friend who has always believed in me.

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## ABSTRACT

Metal oxide semiconductor has been widely studied due to its varied properties and application. Among metal oxides, ZnO semiconductor is of great interest due to its wide bandgap (3.2-3.4 eV) with hexagonal wurtzite structure. This study involves preparing ZnO by sol-gel method and the comparison of optical properties of ZnO nanoparticles at (350 and 450°C) before and after modifying with 4-fluorobenzoic acid (4-FBA). The optical properties were studied using UV-Vis-NIR scanning spectrophotometer. FESEM image shows that the irregular spherical shape and there is variation in the surface morphology of modified and unmodified ZnO nanoparticles. The grain size increased with increasing temperature, but with addition of modifier the particle size didn't change. The bandgap decreased with increasing temperature but recorded no changes after applying modifier. The XRD patterns of these samples are in close agreement with the JCPDS standard (No. 36-1451). It was observed that all samples were polycrystalline with hexagonal wurtzite structure with diffraction peaks oriented along the (100), (002), (101), (102), (110) and (103) planes. Fourier transform infrared spectroscopy (FTIR) showed a band of 400-600  $\text{cm}^{-1}$  corresponding to the Zn-O vibration mode.

## ABSTRAK

Kajian ke atas logam oksida semikonduktor telah dilakukan secara meluas dan kajian menunjukkan logam ini mempunyai sifat yang berbeza serta pelbagai kegunaan. Antara kumpulan oksida logam, kajian tertumpu pada ZnO semikonduktor kerana mempunyai sifat jurang jalur lebar (3.2-3.4 eV) dengan struktur wurtzite heksagon. Kajian ini tertumpu kepada penyediaan ZnO dengan kaedah sol-gel bagi membandingkan sifat optik ZnO nano zarah (350 dan 450°C) sebelum dan selepas pengubahsuaian dengan 4-fluoro asid benzoik (4-FBA). Ciri-ciri optik telah dikaji menggunakan UV-Vis-NIR spektroskopi. Imej FESEM menunjukkan bahawa bentuk sfera yang tidak teratur dan terdapat variasi dalam morfologi permukaan nanoparticle ZnO yang telah diubahsuai dan tidak diubahsuai. Saiz meningkat dengan pertambahan suhu, tetapi dengan tambahan pengubahsuaian ke atas logam, saiz zarah tidak berubah. Jurang jalur menurun dengan peningkatan suhu mencatatkan tetapi tiada sebarang perubahan selepas pengubahsuaian. Corak XRD sampel adalah sama dengan standard JCPDS (No. 36-1451). Dalam kajian ini, semua sampel adalah polihablur dengan struktur wurtzite heksagon dengan pembelauan puncak berorientasikan (100), (002), (101), (102), (110) dan (103). Fourier mengubah spektroskopi inframerah (FTIR) menunjukkan jalur 400-600  $\text{cm}^{-1}$  yang sepadan dengan mod getaran Zn-O.

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**LIST OF SYMBOLS**

eV	-	Electron volt
°C	-	Degree celsius
μm	-	Micrometer
nm	-	Nanometer
Å	-	Angstrom
g mol <sup>-1</sup>	-	Gram per mole
mol/L	-	Mole per liter
cm	-	Centimeter
K	-	Kelvin
min	-	Minute
Θ	-	Angle theta
%	-	Percentage
g	-	Gram
mL	-	Milliliter
M	-	Molarity
mW	-	Milliwatt
meV	-	Mega volt
Gpa	-	Giga pascal
kV	-	Kilo volt
mA	-	milliampere

**LIST OF ABBREVIATIONS**

4-FBA	-	4-fluorobenzoic acid
FESEM	-	Field emission scanning electron microscope
M.wt	-	Molecular weight
XRD	-	X- Ray diffraction
Zn <sub>i</sub>	-	Interstitial zinc atoms
V <sub>O</sub>	-	Oxygen vacancies
TG	-	Thermogravimetric
FTIR	-	Fourier transform infrared spectroscopy
E <sub>g</sub>	-	Bandgap energy
FWHM	-	Full width at half maximum
Rpm	-	Revolution per minute

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## CHAPTER ONE

### INTRODUCTION

#### 1.1 Nanotechnology

Richard Feynman in 1959 "*The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom*". Therefore, Feynman's could be understood as beginning stages of nanotechnology. Eric Drexler, in the early 1980's invented the word nanotechnology. The world of nanotechnology is developed very fast in the present decades. In order to Royal Society & the Royal Academy of Engineering's recent definition of nanoscience and nanotechnology, Nanoscience deals with study of phenomena and doctrinaire of materials at atomic, macromolecular and molecular scales whereas at larger scales, properties were quite differ. Generally nanotechnology is the styling, characterization, production and applications of structures, controlling shape and size of the nanometer scale due to devices and systems. Basically, the taken nanorange is about (1-100) nm for convention as per National Nanotechnology Initiative in the US.

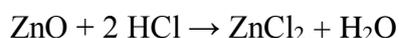
Nanotechnology is also the study of manipulation of the matter on the molecular level which has a significant influence in many different domains. In solar energy transformation (Matt *et al.*, 2005) and In medicine, may lead to mend drug delivery systems (Sahoo *et al.*, 2007) and imaging techniques (Chan and Nie, 1998) It is also expected to provide the desire energy from solutions and cause more efficient lighting (Balke *et al.*, 2009). Zinc oxide widely used recently because of a

wide-range application, for that it does deem important for many applications including fuel cells, photovoltaic, catalysis, and sensor applications (Han *et al.*, 2010).

## 1.2 Zinc oxide (ZnO)

Semiconductors with dimensions in the nanometer realm are important because their optical, electrical and chemical properties can be set by changing the size of particles. Optical properties have great interest for application in optoelectronics, photovoltaic and biological sensing. Numerous chemical synthetic methods have been developed to prepare such nanoparticles (Aneesh *et al.*, 2007).

Zinc oxide is a white powder and has amphoteric property (Degen and Kosec, 2000). It is nearly not dissolve in water, but it is soluble in most acids, in case of hydrochloric acid:



Bases also can dissolve the solid to give soluble zincates:

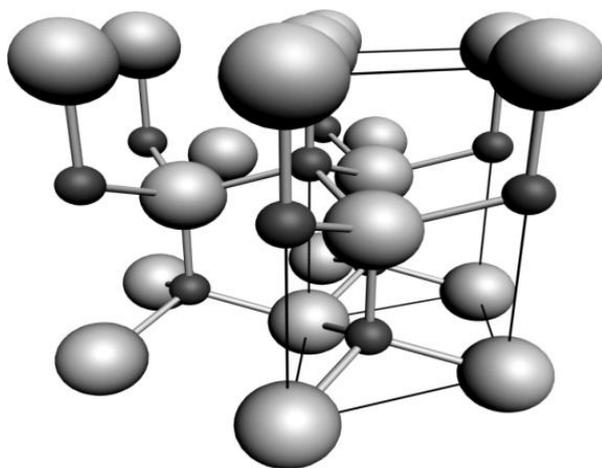


High surface area porous materials have shown advantages in fuel cells, catalysis and sensor applications. Synthesis of these high surface area materials can be done using sol-gel chemistry, hard templating and soft templating approaches (Han *et al.*, 2011). Although many useful semiconductors have been prepared by these methods, synthesis of zinc oxide (ZnO) with high surface area has somewhat limited.

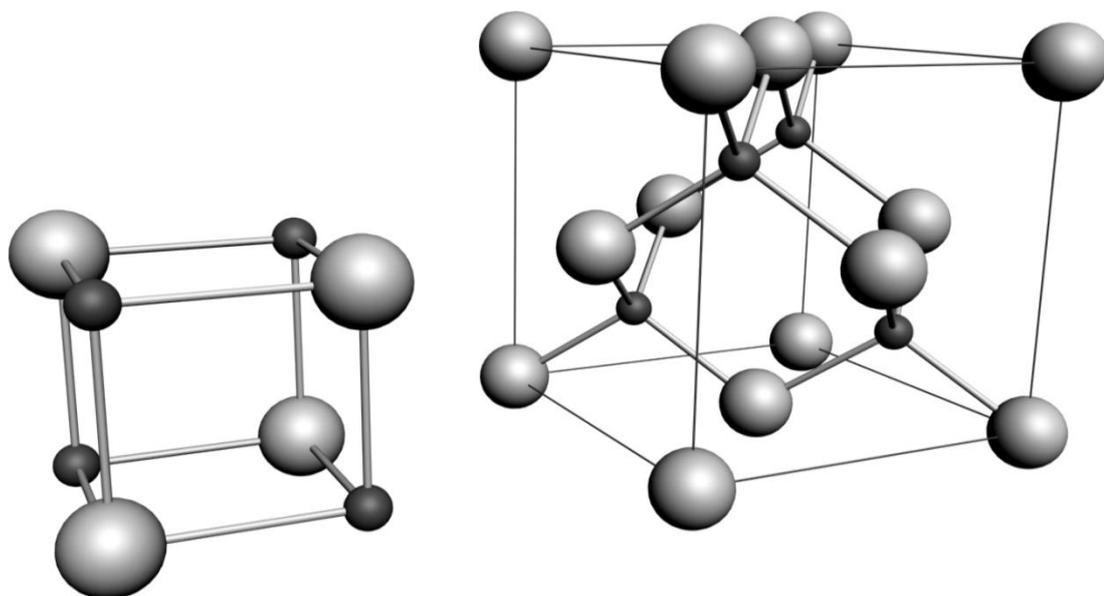
Zinc oxide (ZnO) is one of an important inorganic compound II–VI, n-type semiconductor material with a wide bandgap 3.37 eV and high exciton-binding energy of 60 meV (Han *et al.*, 2010). It also possesses good optical properties (i.e. transparent conducting film) as well as piezoelectric properties. These interesting properties of ZnO have led to applications in catalysis, UV-light emitting diodes, gas, lasers and bio-sensors (Han *et al.*, 2011).

Another interesting application of ZnO is its use in photovoltaic solar cells. Previously (Law *et al.*, 2005) and (Zhang *et al.*, 2008) have successfully employed aggregated nanowires and nanocrystallites of ZnO respectively, to produce efficient dye-sensitized solar cells. Although these examples proved the usefulness of ZnO in such application, in both systems the low surface areas were limited the conversion efficiency of solar energy to electrical energy. Many attempts at achieving high surface area ZnO have been made, such as surfactant template methods (Wang *et al.*, 2002). Although surfactant driven synthesis of ZnO has been successful in synthesizing nano structured ZnO, and because of the presence of the structure directing agents the internal surface areas were not attainable.

Zinc oxide has three sorts of crystallization, which are hexagonal wurtzite, cubic zinc blende, and the rarely observed cubic rocksalt. The wurtzite structure among them is the most stable structure as shown in figure 1.1. The zinc blende structure as shown in figure 1.2 can be stabilized by growing ZnO on substrates with cubic lattice structure (Özgül *et al.*, 2005). In both cases, the zinc and oxide are tetrahedral. The rocksalt NaCl-type structure as shown in figure 1.2 can be observed only at relatively high pressures ~10 GPa (Özgül *et al.*, 2005). Wurtzite is characterized by two sublattices of  $\text{Zn}^{2+}$  and  $\text{O}^{2-}$  interconnecting, from structure each Zn ion is surrounded by tetrahedra of O ions, and vice-versa. The typical bond of this tetrahedral coordination is  $\text{sp}^3$  covalent bond, but also these materials have a substantial ionic character. This tetrahedral coordination responsible of polar symmetry along the hexagonal axis, and a reason for a number of the properties of ZnO, such as its piezoelectricity and spontaneous polarization, and is also a key factor in etching, crystal growth and defect generation (Bunn, 1935).



**Figure 1.1:** The hexagonal wurtzite structure of ZnO. O atoms are shown as large white spheres, Zn atoms as smaller black spheres. One unit cell is outlined for clarity.



**Figure 1.2:** The rock salt (left) and zinc blende (right) phases of ZnO. O atoms are shown as white spheres, Zn atoms as black spheres. Only one unit cell is illustrated for intelligibility.

**Table 1.1:** Physical properties of wurtzite ZnO (Pearnton *et al.*, 2005).

Properties	Values
Lattice constant	
$a_0$	0.34296 nm
$b_0$	0.52096 nm
Density	5.6 g / cm <sup>3</sup>
Melting point	2248 K
Relative dielectric constant	8.66
Gap energy	3.4 eV, direct
Intrinsic carrier concentration	<10 <sup>6</sup> cm <sup>-3</sup>
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron mobility	200 cm <sup>2</sup> / V.s
Hole effective mass	0.59
Hole mobility	5-50 cm <sup>2</sup> / V.s

### 1.3 Electronic and optical properties of ZnO

#### 1.3.1 Electronic properties

N-type conductivity are usually present in growing ZnO, the main faster responsible of this n-type conductivity is intrinsic defects such as zinc interstitials ( $Zn_i$ ) or oxygen vacancies ( $V_O$ ). However, the contribution of oxygen vacancies to conductivity has been controversial. Theoretical calculations proved that oxygen vacancies are deep donors instead of shallow donors (Janotti and Van de Walle, 2007). Easily n-type conductivity of ZnO can be increased by doping with Al (Kim *et al.*, 1997), Ga (Alivov *et al.*, 2003), or In (Caglar *et al.*, 2007). Moreover hydrogen can also contribute as a shallow donor to increase n-type conductivity in bulk ZnO (Thomas and Lander, 1956).

The surface properties and sample ambient have important roles in the electronic behavior of ZnO. In terms of a surface conductive channel that exists in vacuum, it's explained that under vacuum the semiconducting sample can be changed into a conductive state, but it's not stable which destroy after introducing to the air due to the elimination of conductive layer in the surface bonds (Hliang, 2007).

### 1.3.2 Optical properties

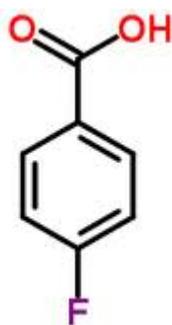
ZnO is one of the attractive materials for optoelectronic applications due to its high efficiency of luminescence in the UV to visible regions of the spectrum. Fusing free electrons in the conduction band into the holes in the valence band raises near-bandgap emission. A broadband emission within the visible region, due to transitions involving defect states, is a common photoluminescence advantage of bulk ZnO (Meyer *et al.*, 2004). Visible emission can be contributed by impurity atoms such as green luminescence from Cu acceptors in ZnO (Garces *et al.*, 2002).

The n-type nanoparticles that made by electron transfer doping exhibited strong mid-IR absorption due to intra-band transitions of electrons in the conduction band. Large surface area of nanoparticles, gives the adsorbed oxygen an important role which traps the photo generated electron and influences the visible emission process on the emission properties of ZnO nanoparticles (Van Dijken *et al.*, 2001).

## 1.4 4-fluorobenzoic acid

Fluorinated benzoic acids are the most widely employed tracers in campaigns aimed at the description of oil reservoirs, and Fluorinated benzoic acids are nonvolatile and polar compounds (Serres *et al.*, 2011). 4-fluorobenzoic acid or para-fluoro benzoic acid is a white solid organic compound with the formula  $C_7H_5O_2F$

and molar mass  $140.11 \text{ g mol}^{-1}$ . It is a synthetic intermediate. 4-fluorobenzoic acid is used as an intermediate for the production of pharmaceuticals and pesticides. The structure of the starting material was reported in 1992 with a carboxylic acid dimer as the main supramolecular synthon (Kubota and Ohba, 1992) as shown in figure 1.3.



**Figure 1.3** Molecular structure of 4-fluorobenzoic acid.

This structure contains a halogen bond,  $\text{F}\cdots\text{O-H}$ , of  $3.246 \text{ \AA}$  which connects the linear carboxylic acid dimers. 4-fluorobenzoic acid dimer is held together by a relatively strong halogen bond,  $\text{F}\cdots\text{F}$ , of distance  $2.618 \text{ \AA}$ . 4-FBA have low-lying unfilled  $\pi^*$  orbital's, which can readily act as electron acceptors. In order to being polar and existing flour on the ring that has a high electronegativity, which can pull the rings electron density and making it active compound to make interactions. Furthermore, the substituent on the ring is known to provide a strong and stable adsorption to semiconductors, ensuring proximity to the semiconductor surface (Sun and Zhao, 2007).

## 1.5 Background of the study

Recently, it has magnetized considerable interest in the photoluminescence properties of many metal oxides such as  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{In}_2\text{O}_3$  and  $\text{WO}_3$ . For example they can be used as nanoscopic optical storage elements or as probes in systems

alive. Zinc oxide nanoparticle is an important class of technologically with a wide ability for applications in transparent conductive electrodes and transistors. Applications of ZnO have recently been the extended to solar cells because of the optical conductivity of ZnO nanoparticles (Zhang *et al.*, 2008).

The sol-gel is a widely employed method to prepare many famous semiconducting metal oxide nanoparticles because it is simple, cost effective and free of pollution. The sol-gel method has several special advantages over other technique due to its lower crystallization temperature, ability to adjust microstructure via sol-gel chemistry, ability of conformal deposition, compositional control and large surface area coating capability (Shane *et al.*, 2007), offers admirable homogeneity, using both inorganic and organic precursors and above all, environmental friendly (Muthuvinayagama *et al.*, 2011).

There are many factors affect the properties of sol-gel based ZnO nanoparticles, which they are, the chemistry of the sol-gel method, post heat treatment and the interaction between the nanoparticles with the modifier during the process. All these factors have a distinct effect on the nanoparticles. However, heating temperature and heating time were the principal parameters of interest.

Lately, surface modified ZnO particles received much attention because of enhanced dispersability in fluids. Well dispersable ZnO particles can be used in ointments, cosmetic creams and lotions formulations (Gudkova *et al.*, 2005). In addition, modifiers has many other advantages including, increasing surface area of nanoparticles with enhancing size and morphology and low degree of aggregation for nanoparticles (Veriansyah *et al.*, 2010).

## 1.6 Statement of problem

Semiconductor nanocrystals are new materials oriented between the molecular and solid state regime, with the unique properties of controlled size and shape. None the less, as the wave functions of electrons and holes were seized by physical dimensions of the nanocrystals, the resulting optical and electrical properties and the structure of electronic levels are the robustly enhanced. When size reducing occurs of the semiconductor nanocrystals regime, a characteristic blue shift of the bandgap appears, and the discrete level structure develops because of quantum size effect in these quantum structures (Millo *et al.*, 2001).

These above proclaimed phenomena provide and rich grounds of basic scientific research, that has and persists to attract attention, Because of the amaze optical and electrical properties, which able nanocrystals to act as a key role in the emerging field of nanotechnology in new applications ranging from lasers and other optoelectronic devices, to biological fluorescence tagging, sensing and solar cell (Bruchez *et al.*, 1998). However, from characterizations, these properties are not monotone with the calcinations temperature. In particular, at 450°C calcined materials are attractive because of their higher defective, which is an important feature for fast charge-exchange processes (Silvia *et al.*, 2009).

In many applications, a key factor that influences the performance of ZnO is its nonstoichiometry (i.e. crystal defects), which measures the semi-conductive property and further semiconductor related properties (Dutta *et al.*, 2009). For example, in Cu/ZnO catalyst for methanol synthesis, it is the metallic Zn (Zn interstitial) produced by H<sub>2</sub> annealing to produce the active sites rather than morphology change (Choi *et al.*, 2001). Some researchers also assumed that the relatively higher gas response of ZnO might be attributed to more content of oxygen vacancy (Gao and Wang, 2005), but the proof is nevertheless not enough (Han *et al.*, 2010).

By modifying and using different annealing temperature the surface of ZnO nanoparticles can enhance many properties of it such as size, morphology, surface

area, and dispersion stability (Veriansyah *et al.*, 2010). In spite of many decades of research, some of the basic properties of ZnO still remain extremely unknown. Such as the nature of the residual n-type conductivity in unmodified ZnO, whether being due to impurities of some native defect or defects, is still under some degree of doubt. Some authors referring it to residual background to intrinsic defects; oxygen vacancies  $V_O$  or interstitial zinc atoms  $Zn_i$ , and others to noncontrollable introduced hydrogen impurities during growth. The renowned green band in ZnO luminescence broad spectra, observed nearly in all samples regardless of growth conditions, is referred to singly ionized oxygen vacancies by some and to residual copper impurities by others (Özgür *et al.*, 2005).

Zinc oxide (ZnO) is a wide bandgap semiconductor (about 3.37 eV), which presents high transparency in the visible (above 90%) and high reflectivity in the infrared. The wide bandgap makes ZnO an attractive matrix for electrically activated emission, since wide bandgap semiconductors have higher excitation ionization energy. Besides, the wide gap decreases the luminescence quenching effects. Recently observed that the size of particle depends on hydrolysis time (Hossain *et al.*, 2005), small ZnO nanoparticle has many defects such as oxygen the vacancies because of a large area. Therefore, lead to increases the trap of emission in the visible region. In the case of nanoparticles, these ideal surfaces do not exist, or increasing the number of unreconstructed surfaces, surface vacancies, and dangling bonds that induce acceptor or donor levels at the grain surface (Raul, 2002).

The sol-gel method is preferred due to its lower crystallization temperature, ability to tune microstructure via sol-gel chemistry, compositional control, conformal deposition ability and large surface area coating capability. The two main drawbacks of the colloidal process is an active control of the crystallographic structure and pore sizes of the inorganic phase is difficult which resulting in electron traps and resistance to the electron percolation. Besides that heat treatment limit the substrate choice to heat resistant materials, thus excluding temperature sensitive materials such as polymers. Annealing temperature is sol-gel techniques own problem when too high temperature may lead to overgrown dopant precipitates, while annealing at too low temperature would lead to insufficient pyrolysis, crystallization thus poor

nanoparticle properties. The present studies are deals with the studies of zinc oxide nanoparticles with (4-fluorobenzoic acid) organic compound as a modifier. Note, it is not studied before for this interaction by any researcher, therefore, will be study the effect of temperature on zinc oxide nanoparticle and modified ZnO by 4-FBA via characterization.

### **1.7 Research objectives**

1. To prepare ZnO nanoparticles using sol-gel method.
2. To investigate the interaction between ZnO and 4-fluorobenzoic acid.
3. To characterize the modified ZnO for structural, thermal, and optical properties.

### **1.8 Scope of study**

In order to achieve this above mentioned objectives, this study begins with the preparation of zinc sol precursor. Zinc sol precursor was prepared by sol-gel method. Zinc sol was prepared by using zinc acetate dehydrate solution and mixing it with sodium hydroxide solution as starting materials then increasing appropriate amount of ammonium bicarbonate under vigorous stirring at room temperature, the obtained colloid centrifuged and dried. The precursor calcinated at 350°C and 450°C then washed by de-ionized water and anhydrous alcohol and dried to obtain sample of ZnO nanoparticle. To investigate the interaction between ZnO and 4-fluorobenzoic acid, (FTIR) analysis absorption spectra was employed that shows what type of chemical bonds are present in the sample. Therefore, it will be studying the effect of change of the size of the zinc oxide nanoparticle before and after modifying with 4-FBA. Characterizations including XRD patterns to study the structure and the size of particles via Debye-Scherrer's equation, field emission scanning electron microscope (FESEM) for imaging the morphology of the surface, and UV-Vis-NIR scanning spectrophotometer for studying optical properties.

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