Synthesis and Characterization of ZnO Nanoparticles

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Declaration

I hereby declare that the work portrayed in this thesis was carried by me under the supervision of Dr. Chin Suk Fun at the Department of Chemistry, Faculty of Resource Science and Technology, Universiti Malaysia Sarawak and no portion of this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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Table of Content

List of Abbreviations

Adipic acid	$C_6H_{10}O_4$
Angstrom	Å
Atmospheric	atm
Carboxyl group	C=O
Carboxymethyl cellulose	CMC
Degree Celcius	℃
Electron volt	eV
Ethanol	C_2H_5OH
Fourier Transform Infrared Spectroscopy	FTIR
Hydroxyl group	-OH
Lithium hydroxide	LiOH
Mili electron volt	meV
Mili mole	mmol
Nanometer	nm/ 10^{-9} m
Polypyrrole	PPy
Polyvinyl alcohol	PVA
Polyvinylpyrrollidone	PVP
Potassium hydroxide	KOH
Scanning Electron Microscopy	SEM
Sodium carbonate	Na_2CO_3
Sodium chloride	NaCl
Sodium hydroxide	NaOH
Succinic acid	$C_4H_6O_4$
Transmission Electron Microscopy	TEM
Water	H_2O

Weight per volume	w/v
X-Ray Diffraction	XRD
Zinc (II) ion	Zn^{2+}
Zinc acetate dihydrate	$Zn(CH_3COO)_2 \cdot 2\ H_2O$
Zinc chloride	$ZnCl_2$
Zinc hydroxide	$Zn(OH)_2$
Zinc nitrate hydrate	$Zn(NO_3)_2 \cdot H_2O$
Zinc oxide	ZnO

List of Figures

Figures **Page**

List of Schemes

Schemes **Page**

List of Tables

Tables **Page**

Synthesis and Characterization of Zinc Oxide Nanoparticles

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ABSTRACT

ZnO nanoparticles have drawn a widespread attention recently due to their novel properties which contribute to various applications especially in optoelectronic devices. In this research project, the spherical ZnO nanoparticles with average size of less than 50 nm were successfully synthesized and their optical properties were measured. In order to maximize its efficiency, surface modification with surfactants is vital as ZnO nanoparticles easily agglomerate. In this study, precipitation method was applied where surfactants such as succinic acid, carboxymethyl cellulose, and adipic acid were used for enhanced properties. The addition of surfactants controlled the particle size and reduced the formation of agglomerates and at the same time helped to produce more homogenous and uniformly dispersed particles.

Keywords: zinc oxide, nanoparticles, surfactants, precipitation

ABSTRAK

Baru-baru ini, nanopartikel ZnO telah menarik perhatian ramai kerana ciri-ciri novel mereka yang menyumbang kepada pelbagai aplikasi terutamanya dalam optoelektronik peranti. Dalam projek penyelidikan ini, ZnO nanopartikel yang berbentuk sfera dengan saiz purata kurang daripada 50 nm telah berjaya disintesis dan ciri-ciri optik mereka diukur. Bagi memaksimumkan kecekapan, pengubahsuaian permukaan dengan surfaktan adalah penting kerana nanopartikel ZnO boleh menyebabkan penggumpalan. Dalam kajian ini, kaedah pemendakan telah digunakan di mana surfaktan seperti asid succinic, selulosa carboxymethyl, dan asid adipic telah digunakan untuk meningkatkan kecekapannya. Penambahan surfaktan memang membantu dalam kawalan saiz zarah dengan mengurangkan pembentukan gumpalan dan pada masa yang sama menghasilkan partikel yang lebih homogenus dan tersebar secara seragam.

Kata kunci: zink oxida, nanopartikel, surfaktan, pemendakan

1.0 Introduction

The idea and concept of nanotechnology was first introduced in a talk in 1959, “There’s Plenty of Room at the Bottom”. Nanotechnology can be described as the use of considerably enhanced nanosized structures ranging from 1 to 100 nm for the production of materials, devices or systems (Samal *et al*., 2010). The synthesis of nanostructure compound has been an extensively important research area in accordance to the development of nanotechnology field and the exhibition of novel properties in nanoscale materials.

Zinc oxide (ZnO) nanoparticles are hydrophobic inorganic compound existing in white powder form. Three types of crystalline structures of ZnO nanoparticles include hexagonal wurtzite, cubic zincblende and cubic rocksalt. Wurtzite is the most stable structure among all. It is hexagonal and symmetrical in shape with the absence of symmetrical center. This structure contributes to the high piezoelectricity property. ZnO nanoparticles are categorized as II-VI semiconductor as zinc and oxygen are from the 2^{nd} and 6^{th} group in periodic table, respectively. They also display features like high reflection rate, high photoelectric and non-linear optical coefficient (Chang & Tsai, 2008). The emerging novel optical and electronic properties of ZnO semiconductor have been a focusing issue among researchers due to the great prospective in optoelectronic applications. Bulk ZnO possesses wide band gap of 3.37 eV at room temperature which can be employed in the short wavelength range, information storage and sensors. In addition, its large excitation binding energy of 60 meV is responsible for excitonic transitions. Thus, it allows spontaneous emission with high radiative recombination efficiency and at the same time acts as laser emission due to its low threshold voltage (Kumbhakar *et al*., 2008).

Some modifications were implemented to enhance the applications of ZnO nanoparticles, for instance controlling nanoparticle size, addition of surfactant, and doping with magnetic ions. According to Moghaddam *et al.,* (2009), the ability of ZnO to form various nanostructures is a plus point to be advanced in photodetectors, surface acoustic wave devices, ultravioletnanolaser, varistors, solar cells, gas sensors, biosensors, ceramics, field emission, and nanogenerator.

Surfactant is a surface active agent which tends to reduce the surface tension of liquid and act as dispersant. Basically, it is an amphiphilic organic compound whereby it possesses both hydrophilic and hydrophobic characteristics. Indeed, it is proven that addition of surfactants is essential to prevent agglomeration. The presence of water molecules in ZnO nanoparticles lead to the formation of hard agglomerates. In order to setback this condition, surface modification with addition of surfactants were emphasized to increase their dispersability. Hence, the applications of ZnO nanoparticles will not be obstructed (Kang *et al*., 2011).

There were a few methods in conducting the synthesis of ZnO nanoparticles. The proposed techniques included direct precipitation (Kang *et al*., 2011), gas condensation method (Chang & Tsai, 2008), electrochemical method (Nyffenegger *et al*., 1998), sol-gel synthesis (Kundu *et al*., 2011), spray pyrolysis, thermal decomposition, molecular beam epitaxy, chemical vapour deposition, laser ablation, and chemical synthesis (Ashtaputre *et al*., 2005).

In this project, ZnO nanoparticles were synthesized *via* precipitation method. Zinc acetate, sodium hydroxide, and ethanol were employed for the preparation of ZnO nanoparticles. Aliphatic dicarboxylic acid functional group surfactants which are succinic acid **(Figure 1)** and adipic acid **(Figure 2)** were taken into account for surface modification of ZnO

nanoparticles. These surfactants were proposed as shorter aliphatic chain and the presence of two carboxyl groups in the compounds may enhance their surface activity and solubility in water. In that point of view, the properties of ZnO nanoparticles were optimized for advanced applications. In addition, carboxymethyl cellulose **(Figure 3)** was also used to test its efficiency as surfactant. Parameter such as concentration of surfactants was applied as variable to optimize the size and shape of the ZnO nanoparticles. Here, FTIR spectroscopy, TEM, SEM, and UV-Vis spectrophotometer were utilised to determine the physical, chemical, and optical properties of ZnO nanoparticles.

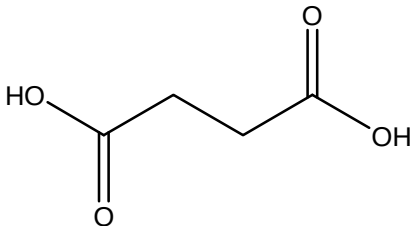


Figure 1: Structure of succinic acid

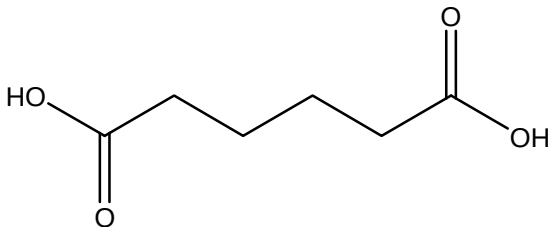
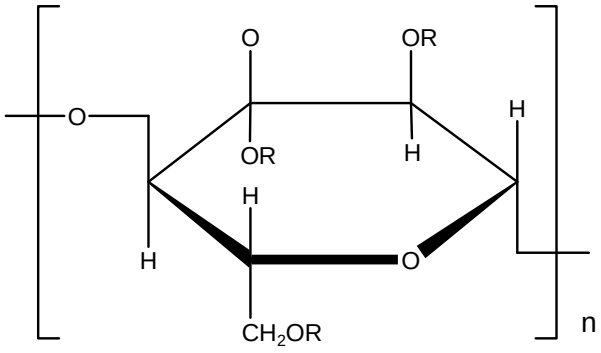


Figure 2: Structure of adipic acid



where R = CH_2COONa

Figure 3: Structure of carboxymethyl cellulose

1.1 Objectives

1. To synthesize ZnO nanoparticles.
2. To synthesize a surface-modified ZnO nanoparticles by using different types of surfactants.
3. To determine the synthesis parameters that will affect the morphology, size and optical properties of the synthesized ZnO nanoparticles.

2.0 Literature Review

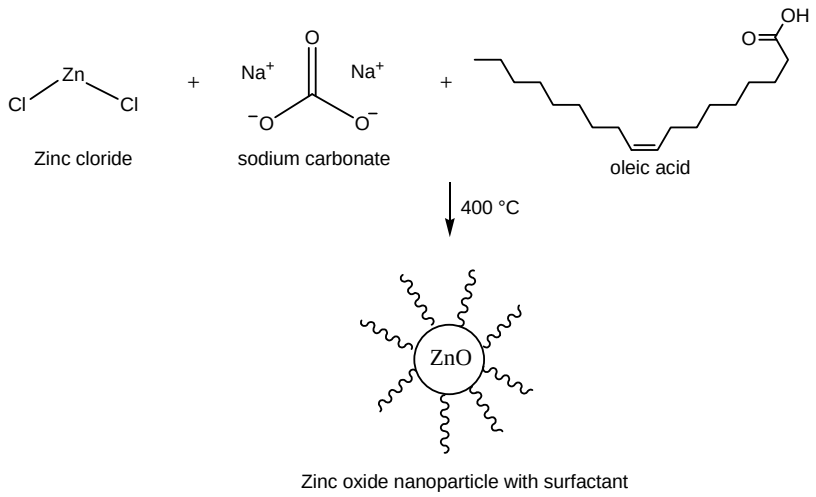
2.1 Synthesis of ZnO nanoparticles

ZnO nanoparticles have remarkable attention on the ongoing research study due to its unique properties. No doubt, their applications especially in optoelectronic appliances can be further advanced in size and shape dependant variation. As semiconductor nanoparticles, their significance has encountered the economic demand in various fields and hence becoming scientifically important materials. ZnO nanoparticles exhibit wide band gap energy (3.37 eV) and high exciton binding energy (60 meV) at room temperature. Valued for their novel characteristics, ZnO nanoparticles demonstrate vital applications in the short wavelength range, which means they can be activated in the green, blue and ultraviolet regions. Also, their ability in excitonic transitions under room temperature allows spontaneous and laser emission (Kumbhakar *et al*., 2008). For optimal functions, large intrinsic gap and nanostructure compound were applied. This implied that ZnO nanoparticles can considerably enhanced the emission activity if compared to bulk ZnO as tremendously small size particles lead to quantum confinement of the photo-generated electron-hole pair. Morphologically, the thermal stability, irradiation resistance, and flexibility of ZnO to form different nanostructures are the key to photoacoustic applications. Moreover, the stable wurtzite structure of ZnO contributes to photoluminescence effect with the presence of oxygen vacancies and zinc interstitials (Moghaddam *et al*., 2009).

Previous research study sought out a few alternatives in synthesising ZnO nanoparticles which include precipitation, gas condensation, electrochemical method, sol-gel synthesis, solvothermal method, and wet chemistry methods. These experimental procedures were carried out under various conditions.

2.1.1 Precipitation method

Kang *et al*., (2011) practiced direct precipitation in their recent project on surface-modified ZnO nanoparticles. In their experimental procedures, $ZnCl_2$ and Na_2CO_3 solution with surfactant were used for the synthesis of ZnO nanoparticles *via* precipitation process as shown in **Scheme 1**. ZnO nanoparticles were finally obtained after calcinations at 400 °C. They also verified that agglomeration may occur due to the presence of water molecules in ZnO nanoparticles. In order to prevent this phenomenon, they suggested surface modification of ZnO nanoparticles with oleic acid. In this case study, relatively small size nanoparticles of approximately 29 nm were reported. The reaction occurred between the active oxygen ions of ZnO nanoparticles and the carboxyl group of oleic acid resulted in the formation of covalent bond between the organic layer and the inorganic nuclei. This permitted high and stable dispersability and at the same time reduced water moiety due to steric hinderance of the extending aliphatic carbon chain in non polar solvent.



Scheme 1: Synthesis of ZnO nanoparticles with oleic acid surfactant *via* precipitation method

Liquid precipitation as stated by Hsieh (2007) effectively synthesized uniform and spherical ZnO nanoparticles. Zinc acetate dihydrate was used as precursor and ZnO nanoparticles were prepared in a water-ethanol mixture solution without heating under

high temperature condition. Triethanolamine **(Figure 4)** and n-propylamine **(Figure 5)** were used as surfactants to reduce aggregation and control the size of particles produced. The flow chart of liquid precipitation process is briefly described in **Scheme 2** (Hsieh, 2007).

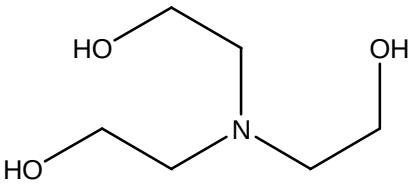


Figure 4: Structure of triethanolamine

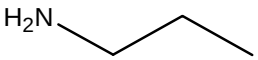
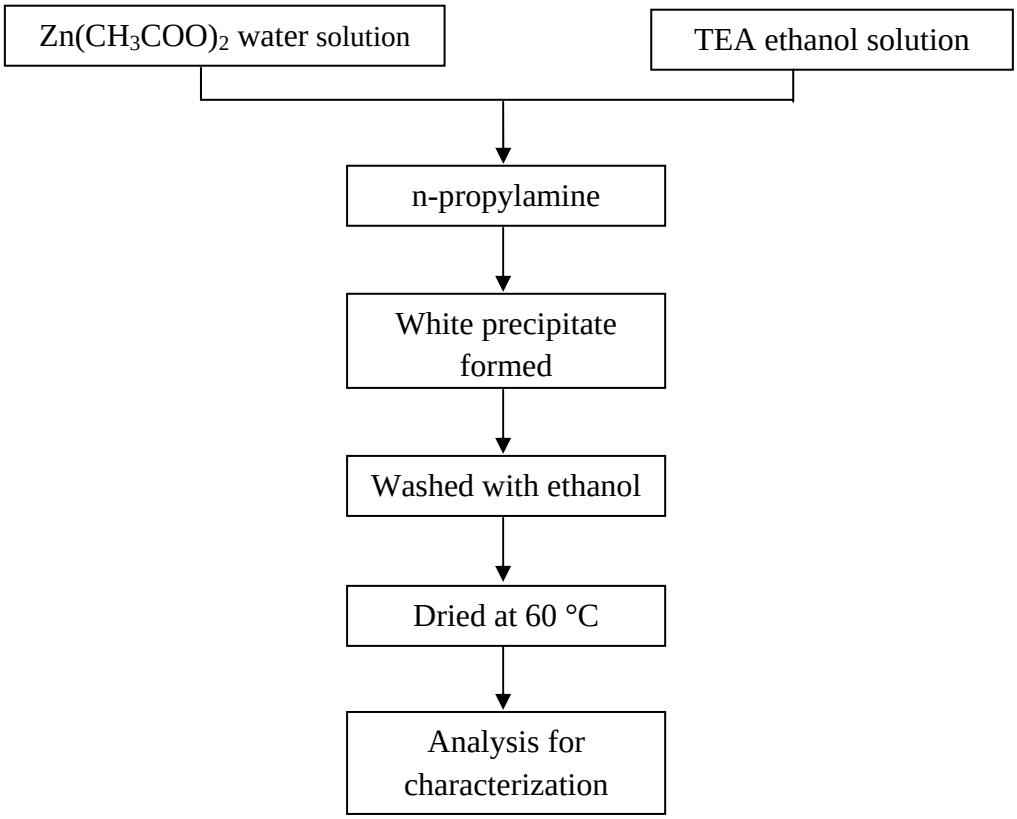


Figure 5: Structure of n-propylamine



Scheme 2: Flow chart of the synthesis of ZnO nanoparticles by liquid precipitation

The chemical routes with different capping agent under various synthesis conditions were explained by Ashtaputre *et al*., (2005), Kumbhakar *et al*., (2008), and Moghaddam *et al*.,

(2009). They discussed precipitation method in their experiments but without calcinations at high temperature to obtain monodispersed ZnO nanoparticles.

As specified by Ashtaputre *et al*., (2005), ZnO nanoparticles were formed by evaporating methanol present in the precipitate at room temperature and these particles were capped with thioglycerol **(Figure 6)** in alcoholic media to slow down and control the development of ZnO nanoparticles. Zinc chloride was used as precursor. This method is size-selective where size of particles formed can be controlled by varying the concentration of thioglycerol. For increment in size of nanoparticles, water was added. Here, they successfully synthesized less than 5.0 nm monodispersed nanoparticles and attained stability by thiol capping.

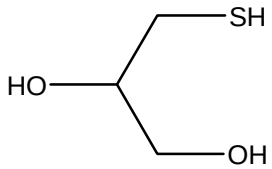


Figure 6: Structure of thioglycerol

On the other hand, Kumbhakar *et al*., (2008) prepared ZnO nanoparticles in double distilled water via chemical method. $Zn(NO_3)_2 \cdot H_2O$ and KOH were dissolved in distilled water under alkaline condition and PVP **(Figure 7)** was used as capping agent to prevent aggregation. The precipitate deposited was centrifuged and dried at room temperature for 30 hours to obtain the ZnO nanoparticles. These steps resulted in the formation of ZnO nanoparticles with average size of 1.9 nm.

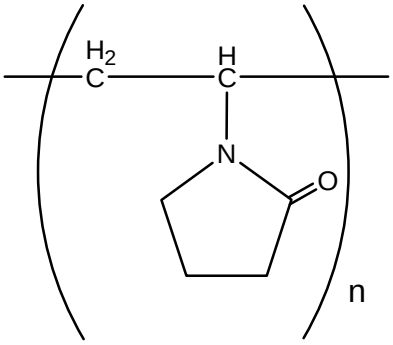


Figure 7: Structure of polyvinylpyrrolidone (PVP)

Alternatively, Moghaddam *et al*., (2009) investigated a more simple and efficient chemical method in synthesizing ZnO nanoparticles. ZnO nanoparticles were synthesized in zinc nitrate aqueous solution without the need of calcinations stage. The precipitated ZnO nanoparticles were dried at approximately 60 °C under atmospheric condition. They also synthesized PPy/ZnO nanoparticles via electropolymerization to determine and compare their differences in term of morphology and properties whereby PPy **(Figure 8)** acted as capping agent.

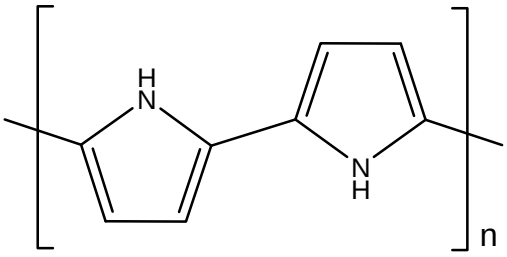


Figure 8: Structure of polypyrrole (PPy)

Hu *et al*., (2003) clarified the synthesis of ZnO nanoparticles by precipitation from zinc acetate in different solvent. They proved that diffusion-limited coarsening caused nucleation and growth to increase rapidly with time. As temperature and alcohol chain length increased, coarsening rate speeded up whereby the volume of particles was enlarged.

Solvent viscosity, surface energy, and bulk solubility of ZnO are the three parameters that affect the rate of coarsening. This indicated that solvent plays crucial role in controlling the size of particles formed.

Certainly, alcoholic solvents lead to the formation of more stable nanoparticles if compared to those in aqueous solution. Different solvent possesses different characteristics which influence the rate of nucleation and growth, as well as, coarsening and aggregation. Basically, water has dipolar, amphiprotic, and high dielectric constant properties whereas dielectric constant and viscosity of alcohol are based on the length of their chains. Apparently, salts have higher solubility in water than alcohols (Hu *et al.,* 2003).

2.1.2 Gas condensation method

Apart from that, gas condensation is also one of the most common methods in the preparation of ZnO nanoparticles which is reported by Chang and Tsai (2008). This method utilized sophisticated technology in the production of nanoparticles. The system consists of vacuum system, temperature control system, cold trap system, and nanoparticles automatic collection system in which energy was obtained from high frequency induction method to heat and vaporize the zinc metal in vacuum condition. As designated, high frequency induction method implied the employment of high temperature to heat a compound to produce nanoparticles. This step gave stable temperature in metal solution, maintained the balance of alloy material in the solution, and showed stable fabrication. However, it required a longer operation period. During vaporization process, the pressure inside the vacuum chamber was kept constant. At this stage, inert gas was inserted into the system. This enabled momentum exchange between the vaporized zinc and the inert gas to take place. When the vaporized zinc approaches the cold trap system, it consequently condensed to form nanoparticles due to the extremely low temperature. They

established the formation of hexagonal prism shape of ZnO nanoparticles with consistent size of 20 nm in diameter. Furthermore, they also generated even distribution and massive amount of nanoparticles in the end of the process. Nevertheless, the collection speed of nanoparticles was inconsistent during the initial vaporization route (Chang & Tsai, 2008).

2.1.3 Electrochemical method

In addition, Nyffenegger *et al*., (1998) demonstrated hybrid electrochemical/chemical (E/C) method in synthesizing ZnO nanoparticles as control of average particle size by means of deposition time is impossible via direct electrochemical route. As reported, there were two stages drawn in this approach. Size-selective deposition of zinc metal onto graphite-based surface occurred in the first place and then followed by spontaneous oxidation and dehydration of the deposited zinc which eventually formed ZnO wurtzite structure. They also synthesized ZnO nanoparticles via direct electrochemical procedure under three different conditions for comparison purposes. Nyffenegger and colleagues (1998) accounted narrow distribution of nanoparticles due to the instantaneous nucleation of zinc on graphite surface. The E/C method is not only simple and straightforward but it can be used to synthesis size-selective ZnO nanoparticles with diameters ranging from 15 to 100 Å. Sajanlal *et al*., (2011) denoted that the application of electrochemical method requires low processing temperature, modest and cheap equipments yet generates high-quality products.

2.1.4 Sol-gel method

Sol-gel method also known as chemical solution deposition is based on the hydrolysis of liquid precursors and formation of colloidal sols (Kundu *et al*., 2011). They stipulated that sol-gel method is a low cost chemical process if compared to physical synthesis methods. The formation of nanosized semiconductor or metal elements permits system with peculiar

optical and electrical properties. In the experiment performed by Kundu and co-workers (2011), sol-gel process can be applied in the production of uniformly dispersed ZnO nanoparticles. They also investigated the effect of different synthesis conditions and sintering on particle size, crystallinity and morphology. In their work, PVA **(Figure 9)** was used as capping agent. PVA molecules contribute active OH groups which have the ability to form metal ion-polymer complex by ligand reaction. The function of PVA is important in acquiring high and stable UV sensitivity. Hence, the surface-modified ZnO nanoparticles signified the construction of stable structural organization that promoted optical emission. Schematic diagram of the sol-gel process is represented in **Scheme 3**.

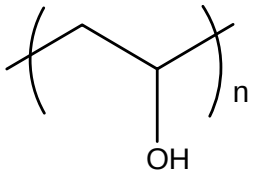
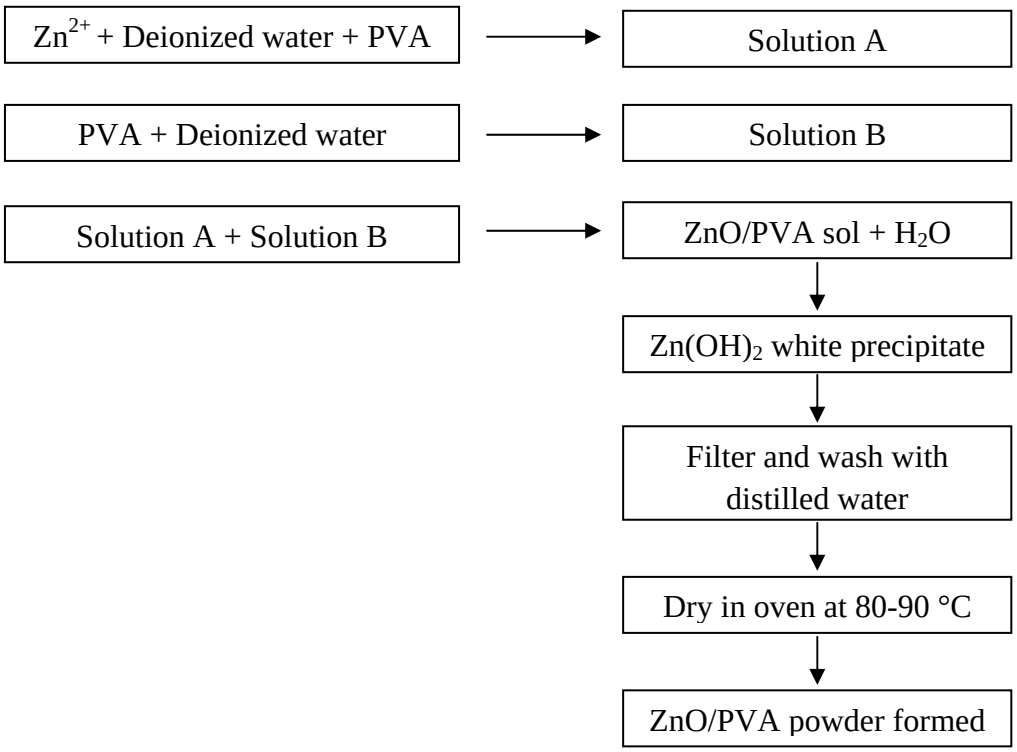


Figure 9: Structure of polyvinyl alcohol (PVA)



Scheme 3: Flow chart of the synthesis of ZnO nanoparticles by sol-gel process