Synthesis, optical and morphological studies of Sol-Gel derived ZnO/PVP one dimensional Nano-composite

S. Ravichandran*, G.Ramalingam
Department of Physics, Sathyabama University, Chennai-600 119.Tamilnadu, India

*email: rs_ravichandran@yahoo.com

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Abstract. The ZnO nanorods were characterized by means of transmission electron microscopy (TEM) X-ray diffraction (XRD). From the XRD pattern, the particle size is found to be 30-37 nm. A sharp absorption edge of 400 nm is observed from UV-Vis studies. The photoluminescence is performed at room temperature with an excitation wavelength of 350 nm. The unusual properties are observed in the optical studies. The influence of experimental conditions, such as reaction time, quantity of PVP and concentration of Zn\textsuperscript{2+}, etc. on the quality of the growth mechanism for the formation nanorods were discussed.

Introduction

Chemical synthesis is one of the important techniques which can be performed using a range of precursors and synthesis conditions like temperature, time, concentration, pH of reactant, etc. Optimization of these parameters leads to nanoparticles of different size, shape and showing different optical properties [1]. It is indicated that the addition of capping molecule could greatly influence the size confinement of zinc oxide nanostructures, which in turn affects the physical properties. A significant variation in the size of the ZnO nanoparticles is noted with the addition of capping molecules [2]. The novelty of this procedure can be supported by the successfully well ordered growth of perfect crystallized zinc oxide nanoparticles under easily controlled and mild conditions. Therefore, it is necessary to study the relationship between reaction conditions and zinc oxide morphologies for exploring an effective and simple route to control the morphology of ZnO for practical applications [3].

Among the different capping agents employed to prepare ZnO nano particles, CTAB (C\textsubscript{19}H\textsubscript{42}BrN) and PEG has been identified as excellent capping agents for 1D ZnO nanostructure. The chain length of non-polar moiety in the CTAB surfactant is sufficient to form proper capping, resulting in the formation of nano sized ZnO [8]. The hydrothermal synthesis of ZnO nanoparticles carried out by Maiti et al confirmed that with optimised CTAB concentration, it will be possible to develop high optical quality one dimensional ZnO nano structure for UV nano laser application and for field emitter in emission display industry [9]. Jiaqiang et al (2006) prepared ZnO nanorods by a hydrothermal process with CTAB and zinc powder. The gas sensing characteristics of ZnO nanorods were investigated and the results indicate that the ZnO nanorods show much better sensitivity and stability than the conventional materials [6].

In recent years, one dimensional (1D) nanostructures in the form of nanorods, nanowires or nano tubes, appear as an exciting research area for their great potential of addressing space-confined transport phenomena as well as applications in nano devices [4]. Though many methods have been proposed to synthesize 1D ZnO structures; the high processing temperatures are unfavorable to make ZnO nanorods because of the problems with scale-up and high energy consumption and also the employment of catalysts or template introducing impurities into the desired products, thus, the preparation of ZnO nanorods with high purity and at low cost calls for a convenient, low temperature and tractable methods [4]. In this regard, few research groups have successfully demonstrated the low cost synthesis of ZnO materials with 1D structure, using hydrothermal method [5-7]. However, the controlled organization of rod-like building blocks and the growth of nanorods in ordered aggregative structures are still challenging research topics [4]. Hence, inquiry into reaction conditions that affect the growth of 1D material will throw light on the growth mechanism of the 1D material [4].
Li et al (2003) developed PEG assisted route to prepare 1D ZnO nanostructures, and nanowires and nanorods can be selectively synthesized by using a short chain polymer (PEG 400). Another interesting capping agent to prepare ZnO nanoparticles is water soluble polymer like PVP. It is a large polymer molecule (MW = 40,000) although; it could form a sort of capping on the surface of ZnO nanoparticles. For the role of PVP, the surface-regulating polymer is believed [2] to play a key role in preventing the flocculation of particles, controlling the particles size and its morphology. The achievement of desired particle sizes over the largest particle range, narrow size distribution, good crystallinity, high luminescence and desired surface properties are the parameters that are considered to be the characteristics of the high quality of the chemically prepared semiconductor nanocrystals [10].

Experimental

Zinc acetate is the chemical compound with the formula Zn (O₂CCH₃)₂, which commonly occurs as a dihydrate Zn(O₂CCH₃)₂.2(H₂O). Its molecular weight is 219.49 g/mol. Zinc acetate is used as a precursor in preparing transparent semiconductor zinc oxide in wet chemical methods. Potassium hydroxide is the inorganic compound with the formula KOH. Its molecular weight is 59.11 g/mol. Its dissolution in water is strongly exothermic, meaning the process gives off significant heat. In the present work, high purity zinc acetate (Zn (CH₃COO)₂.4H₂O) Merck) and potassium hydroxide (KOH, Merck) were used as the starting materials. Both the precursors were of high purity and no further purification was done.

Synthesis of PVP capped Zincoxide nanoparticles

Zinc nitrate and sodium hydroxide salts salt dissolved in double distilled water to get the required solution. Sodium hydroxide (0.2 M) is added with zinc nitrate solution by drop wise method at room temperature while constantly stirring for 2h. The white precipitate formed was washed thoroughly with double distilled water to remove all the ions; then it was centrifuged at 3000 rpm for a short time. The procedure was repeated several times until the precipitate was free from Na⁺ and NO₃⁻ ions. Then, H₂O₂ was added to the precipitate to make a translucent sol, maintaining the temperature. The obtained sol was dried in hot air oven and further calcinated at a particular high temperature for 6hrs to form ZnO nano crystals. To prepare the composite film less weight of zinc oxide nanoparticles were added with Polyvinylpyrrolidone solution and mixed uniformly by magnetic stirring. The prepared solution was caste on a glass substrate uniformly and kept in vacuum desiccators. Due to solvent evaporation, a film of PVP-ZnO NPs was obtained.

The powder XRD pattern for the as prepared ZnO nanopowder was recorded by a RICH SEIFER, X-ray diffractometer using monochromatic nickel filtered CuKα (λ=1.5416 Å) radiation. Scanning electron microscope (SEM) was employed for morphological study using a JEOL JSM 6310 operated at 10 kV with Energy Dispersive X-ray analyser (EDAX). The optical absorption spectrum of the sample was taken in the range between 200-800 nm using double beam CARY 5E UV-Vis-NIR spectrophotometer. The photoluminescence study was done using a JOBIN YVON FLUROLOG-3-11 spectrofluorimeter with an excitation wavelength (λex) of 300 nm. TEM images were recorded on a JEOL JEM 3010 with an accelerating voltage of 200 kV.

Results and discussion

X-ray powder diffraction

Figure 1 shows the X-ray diffraction pattern of the synthesized products of PVP co-polymer caped ZnO in aqueous solutions. The XRD patterns indicate that most of the prominent peaks are present in all the samples without any exemption. The peaks assigned to diffractions from various planes correspond to hexagonal structure of ZnO. The diffraction peaks for different ZnO nanopowders were conveniently indexed to the hexagonal ZnO phase (Wurtzite structure) by comparison of the obtained data with the standard JCPDS (PDF NO 80-0075) data. The Bragg’s peaks indexed at (100), (002), (101), (102), (110) and (103), are analogous to bulk hexagonal structure. The most striking feature is that for all the samples with different capping agents as well as for the pure sample the (1 0 1) peak is the strongest one. Further, the strong and narrow diffraction peaks reveal the high purity, good crystallinity and size of the as prepared products.
Hexagonal wurtzite ZnO can be described schematically by hexagonal close packing of oxygen and zinc atoms in point group 3m and space group P6₃mc with zinc atoms in tetrahedral sites. O²⁻ and Zn²⁺ ions are alternatively along the c-axis. From the XRD pattern, the particle size of the ZnO nano particle is found to be 30-37 nm by using the schriffer formula.

**UV-visible absorption spectrum**

The optical studies were performed to evaluate the potentially useful optical qualities of the nanoparticles. The UV-Vis absorption spectra of the as prepared PVP capped hexagonal ZnO nanocrystals are shown in Figure 2a-d. A sharp absorption edge of 400 nm is observed for pure ZnO. Thus, there is a significant red shift in the excitonic absorption for the ZnO nanoparticles capped with surfactants when compared to the bulk exciton absorption of 373 nm (3.324 eV). The red shift in the exciton absorption clearly indicates the quantum confinement property of nanoparticles. In the quantum confinement range, the band gap of the particles increases resulting in the shift of the absorption edge to higher wavelength, as the particle size increases. As we capped different amount PVP (.0.25gm, 0.50gm, 0.75 and 1 gm) but there no significant change in both UV and PL spectrum.

Usually, for small size ZnO nanoparticles, the blue shift will be very large. However in this present case, it was observed only the red shift. The reason is that, the Bohr exciton radius (2.23 nm) for ZnO is too small, which is not comparable to the size of the nanoparticles prepared in the present study. The size distribution may be another reason. For 1D nanostructure, the quantum confinement effect has to depend on the change of the width or diameter. It is different from the ZnO nanoparticles [11], further supports the typical characteristic of one dimensional semiconductor materials [12].

**Photoluminescence (PL) study**

To investigate the optical properties of the ZnO nanostructures, the photoluminescence is performed at room temperature with an excitation wavelength of 350 nm. The photoluminescence spectra of the ZnO nanoparticles were recorded in the spectral range of 300-700 nm and the PL spectra are shown in Figure 3. Study of photoluminescence spectra is an effective way for investigating the defect structures of ZnO nanoparticles. The PL spectra of PVP capped ZnO samples show a strong emission peak which lies in the UV region and another relatively weak emission peak in the visible region centered around at 450 nm. A weak band in UV emission region and a strong band emission in the visible region were observed. It is interesting to note that when the ZnO nanoparticles are capped with the surfactants, the peak positions are shifted towards the higher wavelength side. A close examination of PL spectra of a sample indicates that ZnO nanoparticles with 1D nanostructure have their UV emission peak stronger.

**Transmission electron microscopy (TEM)**

The morphology of the pure ZnO particle was examined from TEM images, and it is shown in Figure 4 a, b. The results confirmed with the TEM observation that the nanorods synthesized were straight. Though the nanorods are predominant, there are also few particles with polyhedral shapes. The average diameter and length of the nanorods are estimated to be 30-40 nm and 40-50 nm respectively.
In this polyol synthesis of ZnO, water plays an important role in determining the particle morphology since water can induce hydrolysis and condensation reactions of the Zn precursor. In the case of particles obtained by heating the precursor solution, water is present in the reaction medium together with Zn ions, such that nucleation and growth would start before the solution temperature reaches 180°C. It was observed that the solution became milky-white at 150°C. Under these conditions, it is expected that nucleation events are sluggish, and the number of nuclei is small due to the lower reaction temperature. Upon reaching 180°C, the additional heat supply causes further nucleation and its growth. Because heterogeneous nucleation is preferred over homogeneous nucleation, it is thought that Zn ions in the solvent tend to condense on the surfaces of pre-existing nuclei, rather than forming new nuclei [13].

The presence of many nuclei prevents preferential growth along the c-axis due to a limited amount of Zn ions available for monomeric addition onto the pre-existing, growing particles. Under these conditions, the ZnO grows into relatively equiaxial particles. Unstable particles may undergo aggregation due to an increased possibility of inter-particle collisions. We obtained ZnO particles free of aggregation when a higher amount of PVP was added (results not shown here). PVP is a water-soluble polymer, consisting of N-vinyl pyrrolidone monomer that can form a coordinate bond with the Zn ions on the growing particles. This leads to PVP being strongly adsorbed on the surface of particles, preventing the nanoparticles from aggregating. Fig. 3 illustrates the different particle growth mechanisms that occur depending on the method of capping molecules.

In the wurtzite structure of ZnO, the growth rates of each crystallographic plane differ somewhat according to the crystal orientation. When the growth process is relatively slow, there is a greater chance for the particles to grow into rods, because the material deposits on the most stable spots on the surface by which the overall surface energy can be minimized. The c-axis is known to be the direction for fast growth in wurtzite ZnO since the (001) plane has the lowest surface energy [14-16]. Our XRD analysis also supports that rod-shaped ZnO particles have a tendency to grow in the c-axis direction.

Conclusion

We have demonstrated the synthesis of ZnO nanorods with controlled morphology and size by a simple sol-gel method. The method of addition of water, the hydration ratio, and the concentration of PVP play important roles in determining the characteristics of the synthesized particles. From the XRD pattern, the particle size of the ZnO nanoparticles is found to be 30-37 nm by using the schriffer formula. A weak band in UV emission region and a strong band emission in the visible region was observed. It is interesting to note that when the ZnO nanoparticles are capped with the surfactants, the peak positions are shifted towards the higher wavelength side. When the growth process is relatively slow, there is a greater chance for the particles to grow into rods, because the material deposits on the most stable spots on the surface by which the overall surface energy can be minimized. The as prepared nanorods will be used in making of nanobuildings and optoelectronics devices etc.
References