Low-Temperature Synthesis of ZnO Nanorods Stabilized with PVP

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Abstract: Small-diameter ZnO nanorods with lengths of 35-50 nm were synthesized by solvothermal treatment route at low temperature (70 °C) for 48, 96 and 144 hours using polyvinylpyrrolidone (PVP) as stabilizing agent. The optical band gap energy of nanorods was calculated by Tauc’s approximation, obtaining values of 3.30-3.21 eV. By X-ray diffraction (XRD) it was determined that ZnO samples crystallize in Wurtzite hexagonal structure and present changes in lattice parameters. Also XRD patterns reveal a preferential growth of ZnO nanostructures along the plane with Miller indices (002). Stabilization process of ZnO nanoparticles and nanorods was studied by Fourier-transform infrared (FT-IR) spectroscopy, determining that the presence of amide group in polymer structure confers the ability to interact electrostatically with ZnO nanostructures surface. FT-IR results revealed that O and N atoms of amide group interact strongly with the surface of ZnO nanostructures. The length/diameter ratio of ZnO nanorods at 48 and 96 hours of reflux was 2.3 and 2.7, respectively.

Key words: ZnO, nanorods, PVP, stabilization, low-temperature synthesis.

1. Introduction

Nanocomposites based in metal oxide and polymer have quite a few applications due to electron transport, their optical and mechanical properties and engineering technology and medical applications [1]. The ZnO is very interesting material due to their high electronic mobility, their forbidden band gap (3.37 eV at room temperature) and their high exciton energy of 60 meV. Its potential applications in optoelectronics in the blue and ultraviolet region include light emitting diodes [2], laser diodes [3], photo detectors [4], short wavelength light emitting diodes [5], transparent conductors [6], dye-sensitized solar cells [7], piezoelectric materials [8], gas sensors [9], photovoltaic cells [10], varistors (also called variable resistors) [11], as well as high resistance semiconductor devices [12] and thin films of fully transparent transistors [13]. One-dimensional nanostructures of ZnO have received special attention recently due to their unique properties [14], such as piezoelectricity, transparency, biocompatibility and large-area fabrication. In 2003, Liu and Zeng [15] reported the synthesis of nanorods of ZnO, with diameters around 50 nm, whereas in 2006 Zhu and coworkers [16] also obtained nanorods of ZnO with diameters about 70 nm. In 2009, Baruah and Dutta [17] reported the synthesis of ZnO nanostructures by hydrothermal method, in the same year, Eskarandi et al. [18] reported the synthesis of nanorods using polyvinylpyrrolidone (PVP) as stabilizing agent. In 2014 Gutul and coworkers [19] synthesized colloidal nanoparticles also in the presence of PVP, in that same year Parra and Haque [20] studied the structural and optical properties of nanorods synthesized in presence of PVP. The chemical methods for the preparation of ZnO nanorods commonly use temperatures above 100 °C [21] using an autoclave,
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which is so more expensive and the lengths of those nanorods become microns. In the present work, we present the synthesis of ZnO nanorods at low temperatures (at 70 °C) by solvothermal treatment of ZnO nanoparticles used PVP as stabilizing agent. The obtained ZnO nanostructures are characterized by ultraviolet-visible (UV-Vis) absorption spectroscopy, transmission electron microscopy (TEM) and Fourier-transform infrared (FT-IR) spectroscopy. Our results show that the ZnO nanostructures are stabilized by the electrostatic interaction of the O and N atoms of PVP with the surface of ZnO.

2. Experimental

2.1 Materials

Polyvinylpyrrolidone (PVP, (C₆H₉NO)ₙ, Mₘ ~40,000 gmol⁻¹), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, > 98%) and sodium hydroxide (NaOH, 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals used were of analytical grade and were used as received without any further purification.

2.2 Preparation of ZnO Nanoparticles

ZnO nanoparticles were synthesized through a modified Ge method [22] by the general chemical reaction of Eq. (1). Briefly, a typical experiment is as follows: first, 0.88 g (0.004 mol) of Zn(CH₃COO)₂·2H₂O was dissolved in 80 mL of ethanol, under magnetic stirring and at room temperature. At the same time, 0.42 g (0.010 mol) of NaOH was dissolved in 80 mL of ethanol, also under magnetic stirring. On the other hand, a solution of the PVP polymer was prepared at a concentration of 1,000 ppm. The PVP solution was added to the solution of Zn(CH₃COO)₂·2H₂O under vigorous magnetic stirring. Then, the NaOH solution was added to the mixture within one minute and left under vigorous stirring for 20 minutes. The mixture was then subjected to ultrasonic vibration for 10 minutes. The final product was recovered by ultracentrifugation by performing two cycles of 1,600 rpm and a time of 10 minutes. Finally, the product was washed several times with ethanol, acetone and deionized water. The obtained powder sample was dried under vacuum in an oven at 90 °C for two hours. The experimental yield for ZnO synthesis was 78%.

\[
\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \\
\text{PVP (1,000 ppm)} \xrightarrow{25 \degree \text{C}} \text{ZnO} + 3\text{H}_2\text{O} \\
+ 2 \text{Na(CH}_3\text{COO)}
\]

2.3 Preparation of ZnO Nanorods

Synthesis of ZnO nanorods was carried out by the following procedure: 200 mg of purified ZnO nanoparticles stabilized with PVP were dispersed in 200 mL of ethanol, into a two-necked flask of 250 mL equipped with a magnetic stirrer, a thermometer and a condenser. The reaction mixture was refluxed at constant temperature of 70 °C under vigorous magnetic stirring for 48 hours. Subsequently, the solid was purified in the same manner as the ZnO nanoparticles. A yield of 72% was obtained. The same procedure was repeated at 96 and 144 hours of reflux.

2.4 Characterization of ZnO Nanostructures

UV spectra were taken on a Perkin Elmer UV-Vis spectrophotometer, model Lambda 2S. Measurements were carried out in the range of 800 nm to 300 nm at room temperature, using 1 cm × 1 cm × 3 cm quartz cells and water as a dispersing medium. X-ray diffraction (XRD) patterns were performed on an INEL X-ray diffractometer, model Equinox 2000. Measurements were made on the powder samples using monochromatic Co-Kα radiation. The infrared spectra were obtained on a Perkin Elmer FT-IR spectrophotometer, model Frontier MIR, in the range of 4,000-400 cm⁻¹. The powder samples were analyzed using the attenuated totally reflection method. TEM images were taken with a JEOL transmission
electron microscope, model JEM-2100, operating at 200 KV. The samples for TEM were made by depositing the colloidal solution on carbon-coated copper grids and dried in vacuum.

3. Results and Discussion

3.1 Morphology and Structure

Fig. 1 shows a TEM image of ZnO particles prepared in absence of PVP, we can observe the presence of big particles, which are formed by the aggregation of smaller particles. This result confirms that without some stabilizing agent and due to the high surface energy, the small particles interact and therefore form agglomerates with sizes of several tens of nanometers. It is important to mention that the lack of stabilization of ZnO nanoparticles in the solution causes their aggregation and this agglomerates precipitate from the solution.

On the other hand, when ZnO nanorods were attempted to be obtained by preferential growth of ZnO nanoparticles without PVP, it was found that particle growth does indeed occur, but this growth is uncontrolled and therefore large particles are formed with sizes of several hundred nanometers, some particles have hexagonal shape and other with elongated form. Fig. 2 shows the TEM images of ZnO nanostructures obtained by the solvothermal treatment of ZnO particles not stabilized.

However, in the synthesis of ZnO in presence of polyvinylpyrrolidone a significant change in morphology and size of ZnO particles was found. The TEM images of ZnO nanoparticles obtained in presence of PVP are shown in Fig. 3. In this image it can be observed that the nanoparticles have a homogeneous size and although they are very close, they are not agglomerated. The ZnO nanoparticles stabilized with PVP have an average size of 14 nm and a quasi-spherical shape. This shows that PVP polymer is able to control the size of the particles, besides serving as a stabilizer that prevents that the particles are agglomerating and precipitating.

When ZnO nanoparticles stabilized with PVP were subjected to solvothermal treatment, elongated particles, like a rod, were formed through preferential growth of the nanoparticles. Fig. 4 shows TEM images of ZnO nanorods prepared at different reaction time. When analyzing the images, it was determined a length-diameter ratio of 2.3 and 2.7 for ZnO nanorods at 48 and 96 hours of solvothermal treatment, respectively. At 144 hours of reflux, the growth of the nanorods is greater. The average diameter of nanostructures obtained at 48 hours of solvothermal treatment is 15 nm and for nanostructures at 96 hours of reflux, the average diameter is 14 nm.
Fig. 3  TEM images of ZnO nanoparticles prepared in presence of PVP and their particle size distribution histogram. Average particle size and standard deviation were calculated from Gaussian fitting of the histogram.

Fig. 4  TEM images of ZnO nanorods stabilized with PVP and synthesized by solvothermal treatment at: (a) 48 h, (b) and (c) 96 h and (d) 144 h.

Fig. 5 shows the XRD patterns of the samples prepared without PVP. Diffraction pattern of the nanoparticles without PVP revealed eleven well-defined diffraction lines in the range of 20 from 35 to 95 degrees. By comparison with the X-ray pattern of the JCPDS Card No. 96-900-4181 of ZnO in Wurtzite hexagonal phase, the pattern of ZnO nanoparticles was identified and indexed. Thus, the observed peaks correspond to the reflections of the crystallographic planes with Miller indices: (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202), all belonging to the Wurtzite hexagonal structure of ZnO [23]. It is important to mention that the diffraction pattern does not show peaks of some other phase. In the XRD pattern of ZnO nanostructures obtained at 144 hours of reflux and in absence of polymer all of peaks belong to the Wurtzite hexagonal phase of ZnO. In this case, the peaks are
very well defined and are very sharp which is characteristic of a bulk material. An important feature in the pattern is the high intensity of the peak corresponding to the plane (002), which reveals a clear preferential growth of the ZnO nanostructures.

On the other hand, the XRD patterns of nanoparticles and nanorods of ZnO obtained in the presence of PVP are shown in Fig. 6. In all diffraction patterns it is possible to appreciate a widening of the peaks in comparison to those obtained in ZnO without polymer, it is known that the widening of the peaks is characteristic of nanometric systems [24]. However, it is noted that as the reflux time increases, the peaks are better defined, the widening of the peaks is reduced and a higher preferential growth is observed along the plane with Miller indices (002).

![XRD patterns of ZnO nanostructures prepared in absence of PVP: (a) ZnO nanoparticles and (b) ZnO nanostructures at 144 hours of reflux.](image)

![XRD patterns of ZnO nanoparticles and ZnO nanorods at three times of reflux, prepared in presence of PVP.](image)
From the XRD patterns presented above, it can be seen that there are certain shifts in the position of the diffraction peaks. Using the following equations [25], the values of the parameters \(a\) and \(c\) were calculated:

\[
a = \frac{\lambda}{\sqrt{3} \sin \theta}
\]
\[
c = \frac{\lambda}{\sin \theta}
\]

In Eqs. (2) and (3), \(\lambda\) is the wavelength of the radiation, for our case \(\lambda = 1.7890\) Å (Co-K\(\alpha_1\)). The parameter \(a\) was calculated using the angle \(\theta\) corresponding to the plane with Miller indices (100) and the parameter \(c\) using the angle \(\theta\) of the plane (002) [26], both taken from the experimental diffraction patterns. For the sample of ZnO nanoparticles in presence of PVP, the values for \(a\) and \(c\) were 3.2774 Å and 5.2509 Å, respectively. For samples of ZnO nanorods in presence of PVP, the following values for \(a\) and \(c\) respectively were found: 3.2543 Å and 5.2157 Å for the sample at 48 hours of solvothermal treatment, 3.2450 Å and 5.2020 Å for the nanorods at 96 hours and 3.2408 Å and 5.2032 Å for the nanorods at 144 hours. According to the results and considering that the lattice parameters for ZnO in bulk are 3.2494 Å and 5.2038 Å for \(a\) and \(c\) respectively [27], it can be determined that there are tensions and compressions in the lattice of the nanocrystals. It could be assumed that the polymer, when interacting with the surface of ZnO nanostructures, is exerting forces that cause this tension or compression. First, the ZnO nanoparticles have a tension in the lattice and as the solvothermal treatment time increases, the lattice of ZnO nanostructures tends to contract. This type of stresses or compressions, could be affecting the optical properties of ZnO nanostructures.

On the other hand, from XRD patterns, it is possible to calculate the crystal size of the nanostructures. To make this calculation, the Scherrer formula was used:

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

Table 1. Crystal size values of ZnO nanoparticles and ZnO nanorods prepared in presence of PVP.

| Sample                        | Crystal size (nm) |
|-------------------------------|-------------------|
| ZnO nanoparticles            | 9.45              |
| ZnO nanorods at 48 h          | 14.60             |
| ZnO nanorods at 96 h          | 13.38             |
| ZnO nanorods at 144 h         | 13.36             |

where \(k\) is the Scherrer’s proportionality constant, \(\lambda\) is the wavelength of X-ray radiation, \(\beta\) is the width of the diffraction peak, and \(\theta\) is the Bragg diffraction angle [28]. For the calculations, a value of 0.94 was used for \(k\) and \(\lambda = 1.7890\) Å. For ZnO nanoparticles in presence of PVP, a crystal size of 9.45 nm was obtained. The values obtained from the crystal sizes of all samples are presented in Table 1.

3.2 Optical Properties

Fig. 7 shows the UV-visible absorption spectra of ZnO nanostructures obtained in absence of polymer. It is observed that the absorption spectrum for nanoparticles has a maximum absorbance at 366 nm and for ZnO nanostructures at 144 hours of reflux, said absorption maximum occurs at 377 nm, very close of value (380 nm) reported for ZnO in bulk [29]. The absorption band is due to the electronic transition that is carried out by the excitation of the electrons that are in valence band and are promoted to the conduction band of the semiconductor. The hypsochromic effect (displacement towards smaller wavelengths) observed in ZnO nanoparticles spectrum in absence of polymer with respect to the value of ZnO in bulk, is due to effects of particle size, since despite that this sample is composed of agglomerates, said agglomerates are made up of smaller particles of nanometric size. The hypsochromic effect is very small in the case of ZnO nanostructures prepared with 144 hours of reflux, since in this case the nanostructures grew sufficiently and therefore practically the behavior of ZnO in bulk is obtained.

On the other hand, Fig. 8 shows the absorption spectra of ZnO nanostructures in presence of PVP. A maximum absorption was obtained at the following
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Fig. 7  UV-visible absorption spectra of (a) ZnO nanoparticles and (b) ZnO nanostructures after 144 h of solvothermal treatment, in the absence of polymer. Dot line indicates the value of the absorption band reported for ZnO in bulk.

Fig. 8  UV-visible absorption spectra of ZnO nanoparticles and ZnO nanorods in presence of PVP.

wavelengths: 339.78, 346.72, 349.19 and 352.29 nm, corresponding to ZnO nanoparticles and ZnO nanorods at 48, 96 and 144 hours of solvothermal treatment respectively. In this case, the hypsochromic effect in the UV-Visible absorption spectra of the nanostructures is more evident, being higher in the ZnO nanoparticles. Such phenomenon is due to effects of quantum confinement, as a consequence of reduced the crystal size [30]. For ZnO nanorods samples, it is observed that when the solvothermal treatment time increases, the size of the nanostructures increases, and the value of the wavelength of maximum absorption also increases, because the size of the rods is larger.

Optical transitions in ZnO nanostructures can be easily understood by determining the energy of the optical band gap using the Tauc’s plot by the following expression:

\[
E_g = \frac{\hbar c}{\lambda} - \frac{A}{\lambda^2}
\]
\[ \alpha h v = B (h v - E_g)^n \]  

where \( \alpha \) is the absorption coefficient, \( B \) is a parameter that depends on the inner transition probability of bands, \( h v \) is the energy of the incident photon, \( E_g \) is the optical band gap energy and \( n \) is an index that characterizes the nature of the electronic transitions which cause optical absorption. \( n \) can take values of 1/2, 3/2, 2 and 3 for direct, direct forbidden, indirect and forbidden indirect transitions, respectively [31].

For this study we used the value of 1/2 for \( n \), since direct transitions in ZnO occur between the energy bands [32-34].

Making use of the data obtained by UV-visible spectroscopy, a numerical treatment is performed to obtain the Tauc’s plot. Fig. 9 shows the relationship between \((\alpha h v)^2\) as a function of incident photon energy \((h v)\) for ZnO nanoparticles and ZnO nanorods in the presence of PVP at different reflux times. By making an extension of the curve toward the value \((\alpha h v)^2 = 0\), we can find the energy value of the optical band gap of the nanostructures.

The values obtained by the Tauc’s method are smaller than the band gap value of the bulk material (3.37 eV). Several authors report values also below 3.37 eV for the optical band gap energy of ZnO nanostructures [35-38].

Also, the calculation of the band gap energy can be realized by UV-visible spectroscopy, using diffuse reflectance (RD) technique [39]. The values of reflectance spectra were applied the function of remission or Kubelka-Munk function denoted by \( F(R_\infty) \), defined as follows:

\[ F(R_\infty) \equiv \frac{(1 - R_\infty)^2}{2R_\infty} \]

where \( R_\infty = \frac{R_{\text{sample}}}{R_{\text{standard}}} \). A numerical treatment similar to the Tauc plot is performed to obtain the value of the bandwidth energy, using the expression

\[ [F(R_\infty h v)]^2 = C_1 (h v - E_g) \]

where \( C_1 \) is a constant of proportionality, \( h v \) is the energy of the incident photon and \( E_g \) is the band gap energy. Fig. 10 shows the reflectance spectra under the Kubelka-Munk transformation of ZnO nanostructures in the presence of PVP.

Fig. 9  Tauc’s plot for determination of optical band gap of ZnO nanostructures prepared in presence of PVP: (a) ZnO nanoparticles and (b) ZnO nanorods at solvothermal treatment time of 48 h, (c) 96 h and (d) 144 h.
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Fig. 10  Kubelka-Munk transformed reflectance spectra of (a) ZnO nanoparticles and (b) ZnO nanorods at solvothermal treatment time of 48 h, (c) 96 h and (d) 144 h, all in presence of PVP.

Table 2  Optical band gap energy values obtained by Tauc’s method and Kubelka-Munk transformed reflectance spectra.

| Sample                      | $E_g$ (eV) (Tauc) | $E_g$ (eV) (RD) |
|-----------------------------|-------------------|-----------------|
| ZnO nanoparticles          | 3.18              | 3.33            |
| ZnO nanorods at 48 h        | 3.30              | 3.26            |
| ZnO nanorods at 96 h        | 3.29              | 3.22            |
| ZnO nanorods at 144 h       | 3.21              | 3.26            |

Table 2 shows the optical band gap energy values of ZnO nanostructures, found by both methods.

3.3 IR Spectra and Stabilization Mechanism of Nanostructures of ZnO

Fig. 11 shows the IR spectra of the PVP, the ZnO and the composite formed by ZnO nanoparticles and the PVP. In the PVP spectrum several absorption bands are observed which are due to the vibration modes of the different functional groups present in the polymer. The broadband located around 3,447 cm$^{-1}$ corresponds to the stretching vibration mode of the hydroxyl (OH) group [40]. The bands around 2,950 and 2,882 cm$^{-1}$ are due to the asymmetric and symmetric stretching vibration modes of the methylene (CH$_2$) group, respectively [41]. The band observed at 1,655 cm$^{-1}$ corresponds to the elongation of the carbonyl group (C=O) [42]. While the band observed at 1,460 is caused by the vibration mode of elongation of the C-N and the bands in 1,421 and 1,284 cm$^{-1}$ are due to the bending modes of the CH$_2$ groups of the pyrrole ring of PVP. On the other hand, the spectrum of ZnO nanoparticles without polymer shows a very intense absorption band located below 500 cm$^{-1}$ corresponding to the $E_2$ mode characteristic of ZnO in the hexagonal phase, such mode is reported as active in spectroscopy Raman [43]. With respect to the spectra of the ZnO nanostructures (particles and rods) stabilized by PVP, it is observed that it presents few absorption bands, the most intense is located between 400 and 500 cm$^{-1}$ and corresponds to the $E_2$ mode of ZnO. In addition, the spectrum reveals two medium-intensity bands located at 1,572 and 1,409 cm$^{-1}$ which are assigned to the C=O and C-N elongation modes of the PVP amide group, a band with low-intensity at 3,432 cm$^{-1}$ that is due to the stretching vibration mode of the OH group and several low intensity bands located in the range between 1,100 and 600 cm$^{-1}$ that could be
assigned to the stretching vibration of C=O attributed to zinc acetate and the bending mode of carbonate [44]. Comparing the spectrum of the composite with those of PVP and ZnO, it can be seen that the bands due to the C=O and C-N of the PVP amide group are considerably displaced with respect to the values of 1,655 and 1,460 cm\(^{-1}\) of the spectrum of PVP. In this respect, Gutul et al. [19] reported a displacement of the C=O band from 1,645 (in PVP) to 1,560 in ZnO-PVP and associated it to the oxygen interaction of the carbonyl group with the zinc ion of ZnO.

Fig. 11  IR spectra of PVP, ZnO nanostructures without and with PVP.

Fig. 12  Scheme of the stabilization process of ZnO nanoparticles by PVP.
Thus, from our study of the interaction ZnO-PVP by IR, it is determined that a strong interaction of the PVP with ZnO occurs, through the atoms of O and N of the amide group of the polymer and the Zn ion of the surface of the ZnO nanoparticles. Such interaction is responsible for the stabilizing capacity of PVP, which achieves to stabilize the ZnO particles by an electrostatic and also steric effect, where the steric effect is due to the high molecular weight of PVP. In Fig. 12 we present the mechanism of stabilization of ZnO nanoparticles in presence of PVP. First, the ZnO molecules formed in the solution are bound together to form stable ZnO crystallites. Then, the polymer present in the solution interacts with the surface of the crystallites; on one hand, the long chain of the polymer surrounds the crystallites controlling their growth, so that the particles formed are stabilized by a steric effect. On the other hand, oxygen and nitrogen atoms of the amide group present in the PVP repeating units interact strongly with the zinc ions in the surface of the nanostructure, providing an electrostatic stabilization of the nanostructures. In this way is how the nanostructures of ZnO can be very close to each other without agglomerating.

In the case of the ZnO nanorods stabilized with PVP, the same type of interaction between the PVP and ZnO was observed, that is to say, the atoms of the polymer involved in the interaction with the surface of ZnO nanorods are the atoms of O, C and N of the amide group, which is confirmed by the IR spectra.

4. Conclusions

ZnO nanoparticles and nanorods were synthesized by the colloidal method and solvothermal method using PVP to stabilize and control the size and shape of nanostructures. TEM images determined that the average size of ZnO nanoparticles is 14 nm, in addition it was found that the ZnO nanorods in presence of PVP have a length/diameter ratio of 2.3 and 2.7 after 48 and 96 hours of growth, respectively. The optical band gap energy and the wide bad gap of ZnO nanostructures were calculated, with values ranging from 3.18 to 3.30 eV for the optical band gap and from 3.33 to 3.38 eV for the band gap. X-ray diffraction results revealed that the crystal size of ZnO nanostructures varies between 9 and 15 nm and the presence of the polymer causes tensions and compressions in the lattice of ZnO nanocrystals. It was confirmed that the preferential growth of the ZnO nanorods is carried out along the planes with Miller indices (002). From the study of the interaction ZnO-polymer, it was found that the O and N atoms of amide group present in the polymer structure interact with the surface of the nanostructures, carrying out an electrostatic stabilization through this functional group.

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