

Research Article

A Quick Process for Synthesis of ZnO Nanoparticles with the Aid of Microwave Irradiation

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Reaction between sodium hydroxide and zinc acetate leads to the formation of zinc hydroxide, $\text{Zn}(\text{OH})_2$. The as-prepared $\text{Zn}(\text{OH})_2$ was then decomposed by using conventional heating process or with the aid of microwave irradiation. The nanoproducts of both methods were ZnO nanostructures of different size and shape, but the microwave irradiation method shows many advantages in yield and reaction time. Some surfactants such as SDS, CTAB, or PVP were then used to cap the product for studying the influence on the morphology and properties of the nanostructures.

1. Introduction

Zinc oxide has been famous for a wide range of applications in the functional devices, photo-catalysts, optical materials, cosmetics, nanostructure varistors, UV absorbers, gas sensors, and industrial additives [1–5]. Until now, many different methods have been developed for the production of ZnO nanopowders [1–3, 6–10]. Mechanochemical processing, sol-gel, or hydrothermal processing methods constitute pertinent examples. However, many of these methods, or at least some of their varieties, are overly costly and constitute demonstrations of laboratory interest only.

Nowadays, microwave energy has become a very efficient means of heating reactions. Chemical reactions that took long time to complete can now be accomplished in minutes with the aid of microwave [8–12]. Microwave assisted synthesis not only helped in implementing GREEN chemistry but also led to the revolution in organic synthesis. Microwave irradiation is well known to promote the synthesis of a variety of compounds, where chemical reactions are accelerated because of selective absorption of microwave by polar molecules.

In this paper, we report an effective method for the preparation of ZnO nanoparticles by using microwave irradiation. The microwave irradiation method considered herein is fast, mild, energy-efficient, and environment-friendly and, hence, it is not a weak substitute of the conventional method.

2. Experimental

Synthesis of ZnO nanopowders was achieved by dissolving 0.1 mol zinc acetate (Merk, 99% purity) in propanol 2 to make 50 mL solution of 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2$ (Merk, 99% purity). While stirring, 50 mL of 0.3 M NaOH in propanol 2 (Merk, 99% purity) was added dropwise. The resulting solution was then heated to obtain ZnO nanopowder. To clarify the advantages of microwave irradiation, the above solution was heated in two different ways: heating with microwave oven system (Figure 1) or normal heating with an electric cooker.

For microwave heating, the mixture of precursor solution was placed in a microwave system. The microwave power was set to 150 W. The reaction time was 5 minutes. During the microwave irradiation the temperature of the solution reached 82.5°C (boiling point of propanol 2). After 5 minutes, a white product precipitated.

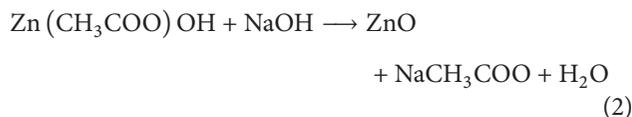
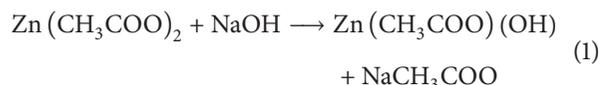
In the normal heating process, the solution of precursors was heated to boiling point of propanol 2 by an electric cooker of power of 500 W. The designed temperature was attained after 20 minutes of heating. A white precipitate was also obtained at the end of the heating process.

ZnO nanopowders were prepared according to the following equations (1), (2) and the residual sodium salt



FIGURE 1: Image of microwave irradiation system.

CH_3COONa was removed by washing the sample with absolute ethanol and distilled water for several times:



The washing process was repeated until the pH of the solution was 7. Finally the product was dried to obtain ZnO nanopowder.

Some different surfactants were also used to study their influence on the morphology and properties of the nanoproductions. In case of using surfactants, the weight ratios Zn^{2+} /surfactant was denoted as R . The as-prepared samples were summarized in Table 1.

The particle morphologies and structures of the products were investigated by a transmission electron microscope (TEM JEM 1010-JEOL) and X-ray diffractometer (Bruker-AXS D5005). Photoluminescence (PL) measurement at room temperature was carried out on a 325 nm He-Cd laser. A UV-vis spectrophotometer PU 8700 was used to record the UV-visible absorption spectra.

3. Results and Discussion

Figure 2 is the powder X-ray diffraction patterns of the ZnO nanoproductions prepared by two different heating processes. The diffraction patterns and interplane spacings can be well matched to the standard diffraction pattern of wurtzite ZnO, demonstrating the formation of wurtzite ZnO nanocrystals. The particle diameter d was calculated using the Debye Scherer formula [7]. The (100) peak at 31.8° in Figure 2 gives the ZnO particle diameters of 32, 18 nm for ZnO nanoparticles prepared by conventional (sample 1) and

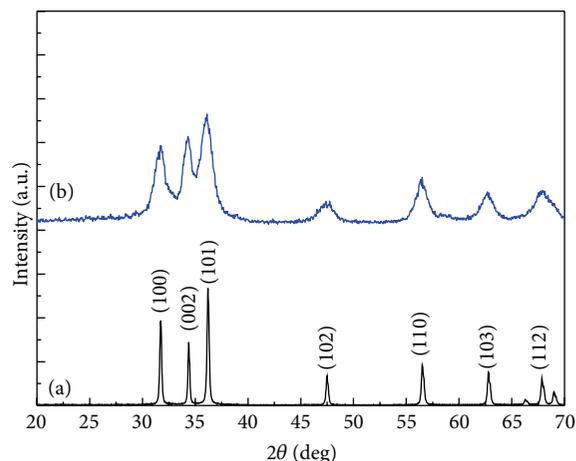


FIGURE 2: X-ray diffraction patterns sample 1 (a) and sample 2 (b).

microwave assisted heating (sample 2) process, respectively. It appears that the ZnO nanoparticles prepared with different heating process have different sizes due to the influence of temperature gradient and reaction time.

Figure 3 shows the TEM images of ZnO nanoparticles prepared by normal and microwave irradiation assisted heating process. It is clearly seen that ordinary heating by electric cooker leads to the formation of aggregated clusters of particles of which size distribution is quite large while the nanoparticles obtained from reactions in microwave irradiation field have small size of only several tens nanometer. Furthermore, these particles are much more uniform in size and shape compared with the products of conventional method. The effectiveness of microwave irradiation in the preparation of nanoparticles can be explained by the pre-eminent advantages of microwave as a means of heating. The mechanism of traditional heating process is conductive heat or heating by convection currents and hence this is a slow and energy inefficient process due to the energy lost at the wall of the vessel. Normally the wall of the vessel absorbs heat first then heat is transferred to the liquid inside so the temperature on the outside surface needs to be in excess of the boiling point of liquid for the temperature inside the liquid volume to reach boiling point. These disadvantages can be overcome easily by applying microwave technique because when heating with microwave, vessel wall is transparent to MW and solvent/reagent absorbs MW energy directly. The direct in-core heating and instant on-off pulse of heat leads to the formation of a homogenous temperature gradient and reduces the reaction time. These advances in turn produce smaller particles of uniform size and shape.

ZnO nanoparticles have been successfully fabricated by microwave irradiation method. However, after the nucleation and growth process are completed, the average size of the particles continues to increase due to diffusion limited coarsening. This process reduces the quality of ZnO nanoparticles so restraining the particles from coarsening is a very important quest. We have investigated the influence of some surfactants such as SDS, CTAB, and PVP on the growth of

TABLE 1: Some preparation parameters of the as-prepared sample.

| Sample | Sample preparation method | Used surfactant | Morphology and size (estimated from TEM image) |
|--------|---------------------------|--|--|
| S1 | Normal heating | No | >100 nm |
| S2 | Microwave irradiation | No | Quasi-spherical Diameter: 20–40 nm |
| S3 | Microwave irradiation | Sodium dodecyl sulphate (SDS) $R = 0.9$ | >100 nm |
| S4 | Microwave irradiation | Hexadecyltrimethylammonium bromide (CTAB) $R = 0.9$ | >100 nm |
| S5 | Microwave irradiation | Polyvinylpyrrolidone (PVP) $R = 0.6$ | Quasi-spherical Diameter: 10–15 nm |
| S6 | Microwave irradiation | Polyvinylpyrrolidone $R = 0.9$ | Rod Diameter 10–15 nm Length 30–50 nm |
| S7 | Microwave irradiation | Polyvinylpyrrolidone $R = 1.2$ | Rod Diameter 20–30 nm Length 40–50 nm |

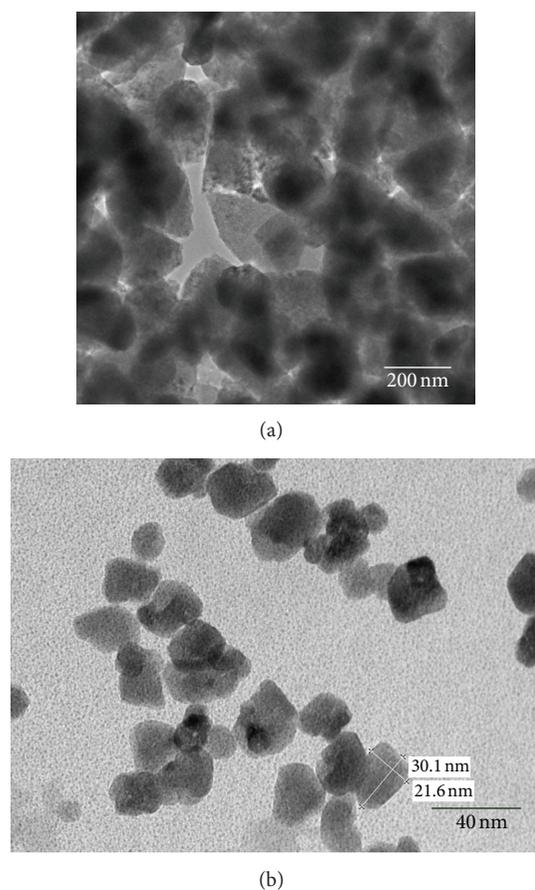


FIGURE 3: TEM images of sample 1 (a) and sample 2 (b).

ZnO nanoparticles. These surfactants were dissolved into the solution of sodium hydroxide before the reaction with zinc salt. PVP reveals to be the most suitable surfactant to prepare ZnO nanoparticles with small size and homogenous shape.

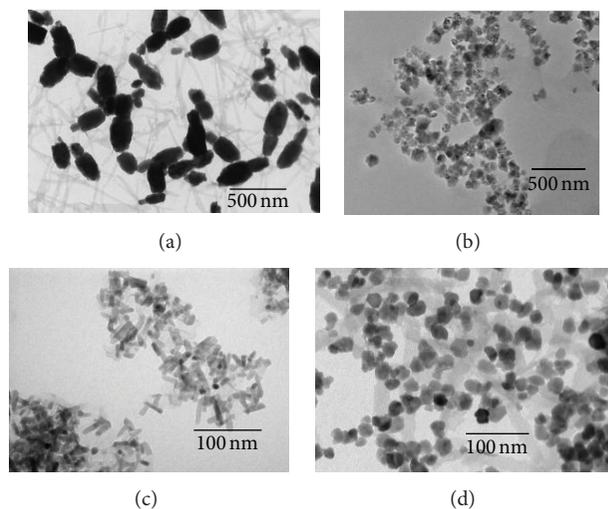


FIGURE 4: TEM images of ZnO nanoparticles precipitated in the presence of different surfactants: (a), CTAB (S4), (b) SDS (S3), (c) PVP (S6), (d) nanoparticles precipitated in the absence of surfactant (S2).

The surfactant on the surface of ZnO plays two roles: firstly, it helps to reduce the defects in nanocrystals during nucleation and secondly, it attaches to the surface of nanoparticles so as to affect on the size of the particles. TEM images of ZnO nanoparticles with different surfactants are shown in Figure 4. It is clear that SDS and CTAB are not suitable to produce ZnO nanoparticles because the products are aggregated to make large particles of several hundreds nanometer. In case of using PVP with $R = 0.9$ (sample S6), we can see that these particles are well separated particles with diameter of about 10 nm and length of 20–40 nm while nanoparticles precipitated without using surfactants have spherical shape with diameter of 25–35 nm. TEM images

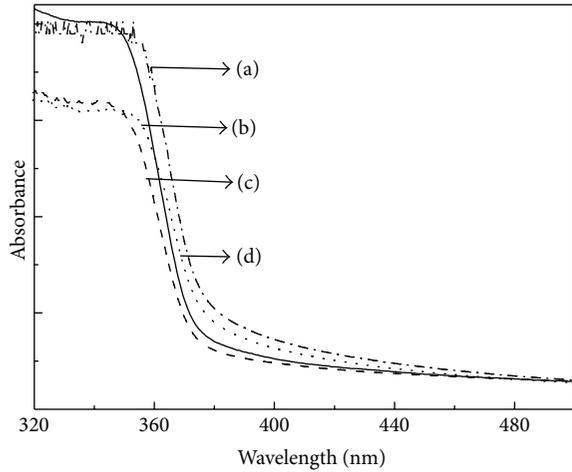


FIGURE 5: Absorption spectrum of nanoparticle prepared with different surfactants: (a) CTAB (S4), (b) SDS (S3), (c) ZnO nanoparticles prepared without surfactant (S2), and (d) PVP (S6).

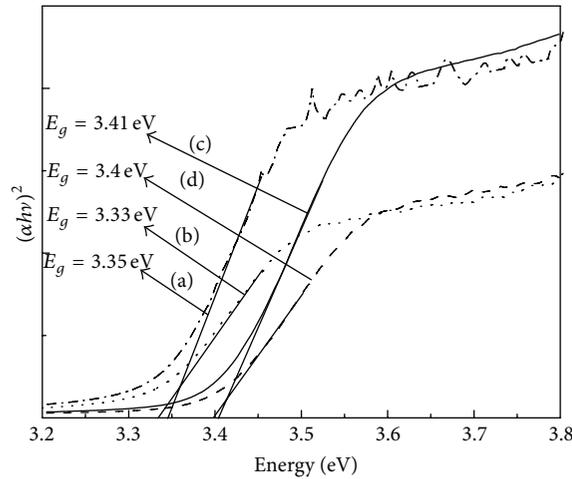


FIGURE 6: Plot of $(\alpha hv)^2$ versus hv of nanoparticle prepared with different surfactants: (a) CTAB (S4), (b) SDS (S3), (c) PVP (S6), and (d) without surfactant ZnO (S2).

obviously show that PVP is quite a good surfactant to reduce the size of ZnO nanoparticles.

The absorption properties of ZnO nanoparticles precipitated in the absence of surfactant, or in the presence of SDS, CTAB, and PVP have been also analyzed. All absorption curves exhibit an intensive absorption in the range 200–370 nm, with the absorption edge between 300 and 370 nm. It can be seen that there is a significant blue shift in the excitonic absorption of the nanoparticles prepared in the presence of PVP compared to that of the bulk ZnO (373 nm). The blue shift in the excitation 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 absorption edge to lower wavelength, as the particle size decreases. All our four samples (curves (a) to (d); Figure 5) exhibit excellent UV

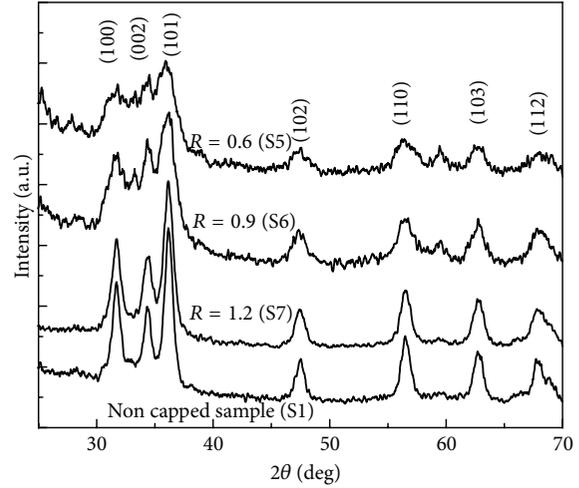


FIGURE 7: X-ray diffraction patterns of ZnO nanosamples prepared with different PVP concentrations.

absorption capacity (Figure 9) and high transparency in the visible range.

From the plot of $(\alpha hv)^2$ versus hv in Figure 6, the band gaps of our samples are estimated as 3.33, 3.35, 3.40, and 3.41 eV for S3, S4, S2, and S6 samples, respectively. Then the average particle size in colloid can be obtained from the absorption onset using the effective mass model [6] where the band gap E_g (in eV) can be approximated by

$$E_g = E_g^{\text{bulk}} + \frac{\pi^2 \hbar^2}{2er^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e}{4\pi\epsilon\epsilon_0 r} - \frac{0.124e^3}{\hbar^2 (4\pi\epsilon\epsilon_0)^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)^{-1}. \quad (3)$$

Due to small effective masses of ZnO ($m_e^* = 0.26m_0$, $m_h^* = 0.59m_0$, $\epsilon = 8.5$ [6]), band gap enlargement gives us the expected particle size of about 9 nm for nanoparticles prepared without surfactant or in the presence of PVP while in the presence of SDS, CTAB the products do not show any band gap enlargement. These results imply that the particles precipitated in the presence of SDS and CTAB are so large that it is not expected to observe any band gap enlargement in these samples.

In order to further decrease the size of the nanoproducts, various amounts of PVP were used to investigate the effect of this surfactant on the ZnO particle size and shape under the same conditions of preparation. Samples with different $\text{Zn}^{2+}/\text{PVP}$ weight ratios (denoted as R) were prepared and checked with X-ray diffraction, absorbance, and photoluminescence spectroscopy. The X-ray diffraction patterns of the samples with $R = 0.6, 0.9$ and 1.2 were shown in Figure 7. All the patterns confirmed that the products were ZnO of wurtzite structure. As increasing the concentration of PVP, the width at half maximum of the diffraction lines in the X-ray patterns grows quickly, which means that the particle size is decreased under the increase of the surfactant PVP.

The smallest value of the particle size is 9 nm, attained when $R = 0.6$.

The effect of PVP on ZnO nanoparticle was confirmed directly from the TEM image of the samples. In Figure 8(a), R was equal 0.6 and it can be seen clearly that the diameter and length of particles are 8–10 nm and 35–45 nm, respectively. Figure 8 shows that when increasing the Zn^{2+}/PVP ratio ($R = 1.2$), the sizes of ZnO nanorods were increased. Their diameters are up to 30–40 nm and the lengths are up to 60–70 nm. The results demonstrate that PVP plays an important role in controlling the ZnO nanoparticle size and shape. As the quantity of PVP increases, the size of ZnO nanoparticle reduces by two or three times. The preeminent advantages of PVP in reducing the particles size are understandable because PVP, a bulky and highly charged adsorbents, serves as an ionic liquid, which results in the so-called electrosteric stabilization. The fact that PVP meets the conceptions of steric and electrostatic stabilization simultaneously makes it a much better stabilizers than those which only have stabilization mechanism of steric or electrostatic [13].

Figure 10 shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ for colloidal ZnO precipitated with different concentration of PVP. The linear portion of the curves when extrapolating to $\alpha = 0$ was an optical band gap value of the product. In this study, we obtained the optical band gap of about 3.45, 3.41, and 3.38 eV at $R = 0.6$, $R = 0.9$, and $R = 1.2$, respectively. The obtained values of the band gap are larger than that of bulk ZnO (3.30 eV) in [6]. It is clear that the optical band gap shifted to higher energy (blue shift) with increasing PVP concentrations or decreasing the particle size.

The photoluminescence spectra of the above samples were taken to study the influence of PVP on the optical properties of the nanoparticle. The green band emission is attributed to the radiative recombination of photo-generated hole with an electron belonging to a singly ionized vacancy in the surface and subsurface. The observation of strong green band emission relative to bulk ZnO indicates the existence of oxygen vacancies concentrated on nanoparticles surface. For nanomaterials, the ratio surface/volume is large and hence it is normal to observe a high green band compared with the peak in the ultraviolet region.

It is noted that in our samples, compared with the sample prepared without surfactant, the ultraviolet peaks in the samples using PVP as the surfactant become much more evident. On increasing the concentration of PVP, the ZnO nanoparticles precipitated in the presence of PVP with $R = 0.6$ showed the highest ultraviolet emission and also the peaks are blue shifted. The increasing in the intensity of the ultraviolet compared with the visible band shows the role of PVP in passivating the trap states at the surface and reduces defects such as oxygen vacancies or Zn interstitials. The blue shifts of these peaks (see the inset of Figure 11) are explained by the reducing particle size as PVP concentration reach higher value. The fluorescence properties of the ZnO nanosamples prepared with PVP indicate that these samples are of better quality than the samples prepared without using surfactants.

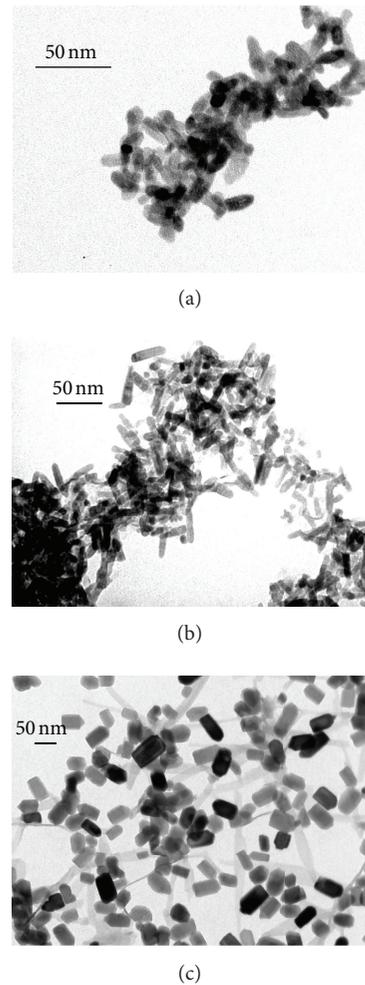


FIGURE 8: TEM images of ZnO nanoparticle with different values of R : (a) $R = 0.6$ (S5); (b) $R = 0.9$ (S6); (c) $R = 1.2$ (S7).

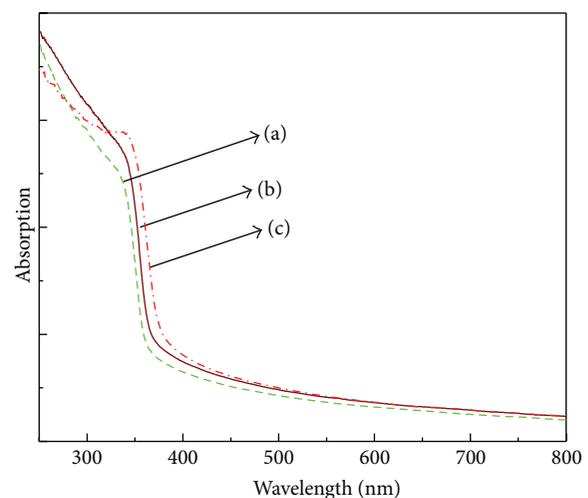


FIGURE 9: UV-vis spectra of the prepared ZnO with different values of R : (a) $R = 0.6$ (S5); (b) $R = 0.9$ (S6); (c) $R = 1.2$ (S7).

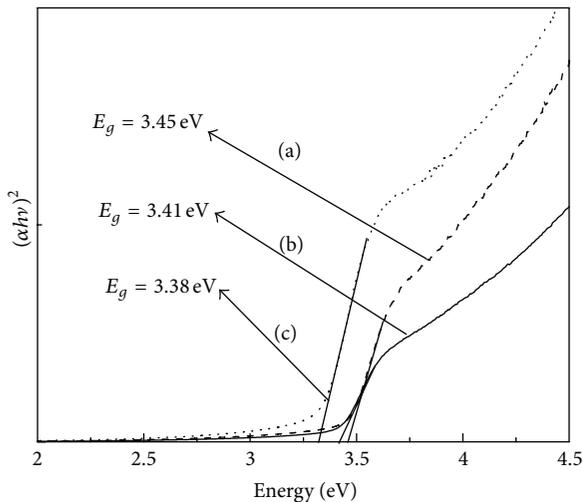


FIGURE 10: Plots of $(\alpha hv)^2$ versus hv for ZnO nanopowder modified with PVP at different R values: (a) $R = 0.6$ (S5); (b) $R = 0.9$ (S6); (c) $R = 1.2$ (S7).

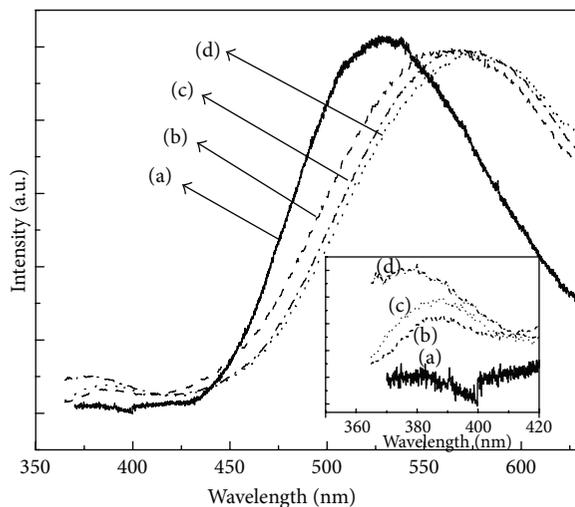


FIGURE 11: Photoluminescence spectrum of ZnO nanoparticles (a) precipitated in the absence of surfactant (S2), and in the presence of PVP with different values of R : (b) $R = 1.2$ (S7), (c) $R = 0.9$ (S6), (d) $R = 0.6$ (S5).

4. Conclusion

ZnO nanoparticles of different size and shape were successfully fabricated by conventional and microwave method. The sample synthesis with the aid of microwave shows some preminent advantages compared with conventional method and results in the formation of small ZnO nanoparticles of uniform size and shape.

Particle size of the ZnO nanoproducs prepared with microwave method can be further reduced by using surfactants. Among the used surfactants, PVP is the most suitable one. The average diameter of the smallest ZnO particles prepared with PVP is less than 10 nm with narrow size distribution. The quantum confinement of the as produced

products was confirmed by the blue shift of the absorption edge in the absorbance spectrum. The increasing in the ratio of the intensity of ultraviolet/green peak in the photoluminescence spectra of these ZnO samples precipitated in the presence of PVP shows that PVP not only reduces the particle size but also the number of trap states at the surface of the nanoparticles.

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