Low Temperature Synthesis of ZnO nanoparticles and Nanorods via Wet Chemistry Route

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Abstract:In this study, we report the synthesis and characterization of colloidal ZnO nanoparticles (NPs) and nanorods. The colloids were prepared by precipitation method at room temperature. The X-ray diffraction (XRD) patterns of nanoparticles and nanorods, revealed hexagonal wurtzite structure and the diffraction peaks matched well with the JCPDS (card no 80-0075) standard data. The Scanning electron microscopy (SEM) revealed the spherical nanoparticles and clustered nanorods. The optical absorption of the nanoparticles at ~340 nm was more intense than that of the nanorods. The green emission from defects was more intense than the excitonic UV emission in the case of the nanoparticles, while the excitonic UV emission was more intense in the case of the nanorods. The ZnO nanoparticles and nanorods were investigated for possible applications in transparent electrodes in solar cells and gas sensors.

1. **Introduction**

ZnO optical and structural properties have drawn so much attention in the past decades. ZnO nanostructures such as quantum dots (QDs), nanoparticles (NPs), nanobelts, nanowires and nanorods have been widely investigated [1]. Moreover, it has been reported that nano-sized ZnO exhibit a unique luminescence properties different from that of bulk ZnO because nanoparticles posses an enormous surface-to-volume ratio [2]. At room temperature ZnO typically exhibit a UV emission due to recombination of free excitons and emission in the visible spectral range attributed to defects [3]. Different physical and chemical processes such as chemical bath deposition, solid state and hydrothermal technique have been used to prepare ZnO particles with different morphologies, However wet chemical synthesis technique offers many advantages in comparison with other techniques because of their realiability, reproducibility at lower temperatures, higher yields and well defined nanostructures [1,4]. With its well-known wide bandgap (~3.37 eV at room temperature), large exciton binding energy (60 meV) and excellent chemical stability, ZnO has attracted extensive attention due to its potential applications in laser diodes, solar cells, field emission display and gas sensors [5]. In this study a simple precipitation method was used to synthesize ZnO NPs and nanorods and we report the structure, morphology and photoluminescence of the ZnO nanostructures.

2. Experimental

2.1. ZnO nanoparticles synthesis

Zinc acetate and tetramethylammonium hydroxide (TMAH) were used as precursors. TMAH dissolved in 30ml ethanol was added dropwise to 2g of zinc acetate dissolved in dimethylsulfoxide (DMSO) solution followed by an hour stirring at room temperature. The resulting precipitation was washed at least three times in a mixture of heptane:ethanol (1:3) and ZnO NPs were dispersed in ethanol. Colloids of ZnO nanoparticles with different concentrations of zinc acetate ranging from 0.1 – 0.8 M were prepared and the UV-vis absorption and fluorescence spectra of the colloids were

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recorded. The precipitate was later separated by centrifugation and was dried in oven at 100°C for 1hour for X-ray diffraction (XRD) characterization.

2.2. ZnO nanorods synthesis

3g of zinc nitrate tetrahydrate was dissolved in 100 ml of distilled water and stirred for 30 minutes. Simultaneously, a 10 ml of sodium hydroxide (NaOH) was added dropwise into aqueous zinc nitrate solution and stirred for an hour. The resulting precipitate was washed at least three times in a mixture of heptane:ethanol same ratio as in 2.1. The colloids of ZnO nanorods with different concentrations of NaOH ranging from 0.1 – 1.0 M were prepared and the UV-vis absorption and fluorescence spectra of the colloids were recorded. The precipitate was later separated by centrifugation and was dried in oven at 100°C for 1hour for XRD characterization.

The crystalline structure was analyzed by XRD using Bruker AXS D8 Advance diffractometer. The optical absorption was recorded by Perkin Elmer Lambda 950 Spectrophotometer. Scanning electron microscopy (SEM) images were obtained by JEOL-JSM 7500F, Field Emission. SEM and PL measurements were carried out at room temperature using a Varian Cary Eclipse fluorescence spectrophotometer.

3. Results and discussion

Diffraction peaks corresponding to the hexagonal wurtzite structure of ZnO were observed from both dried ZnO nanoparticles and nanorods. The spectra in figure 1, show the XRD pattern with the nanorods having a narrow peaks indicating better crystallinity as compared to that of nanoparticles. Average particle size estimated by Scherer equation was ~10-20 nm for nanoparticles and 30-50 nm for nanorods in diameter. The peaks matched well with the JPCDS standard data (card no 80-0075).

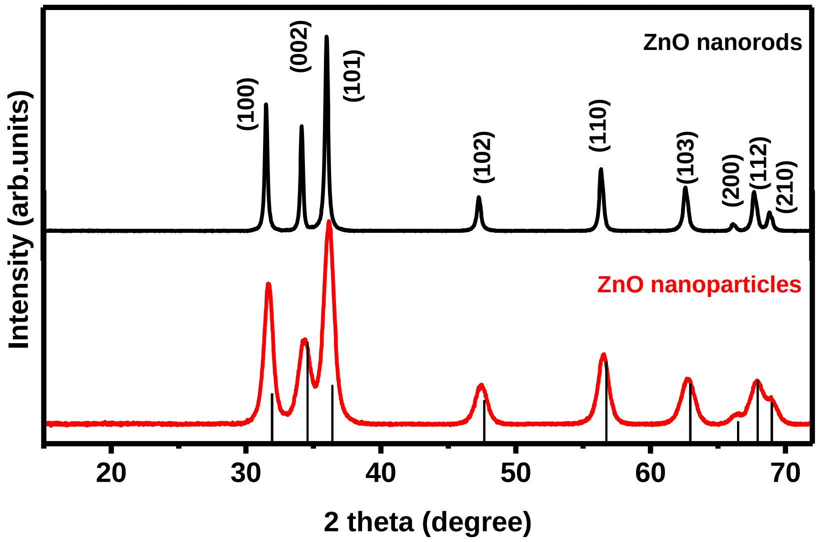

Figure 1: XRD patterns of ZnO nanorods, nanoparticles and standard JPCDS match (card no 80-007)

SEM images in figure 2(a) and (b) showed spherical nanoparticles and clustered nanorods. The clustering may be due to the sample preparation or the process of rods formation might be incomplete resulting to particles and chunks of clustered nanorods. The absorption spectra in figure 3, shows a well defined excitonic absorption for nanoparticles and the weak absorption for nanorods colloids both at ~ 340 nm (3.65 eV). This absorption peak is blue-shifted from the bulk absorption at 3.37 eV. This blue-shift can be ascribed to the confinement of charge carriers in restricted volume of smaller particles [6,7]. The PL spectra measured at room temperature using Xe lamp as an excitation source with an excitation wavelengths of 260 nm and 200 nm is shown in figures 4 (a) and (b) respectively. The colloidal nanoparticles exhibited dual emission in the UV and visible regions. The UV emission consists of two bands at ~364 nm (3.41 eV) and ~380 nm (3.26 eV) which can be ascribed to donor-acceptor transition and recombination of free excitons respectively [8,9,10]. The intense green emission ~527 nm (2.35 eV) is ascribed to oxygen or zinc vacancies. The inset in figure 4(a), shows how the maximum PL intensity varies with zinc acetate concentration. In Figure 4 (b), the colloidal nanorods on the other hand, showed an intense near band-edge emission and a weak red-shifted defects emission at ~723 nm. Similarly, the near band-edge emission consists of two bands at at ~364 nm (3.41 eV) and ~380 nm (3.26 eV). The red shifted emission at ~723 nm is attributed to excess oxygen [3] and OH groups attached the nanostructures [9,11]. Note that the origin of different defect emissions in ZnO is not fully established yet and it is still a subject of intensive research.

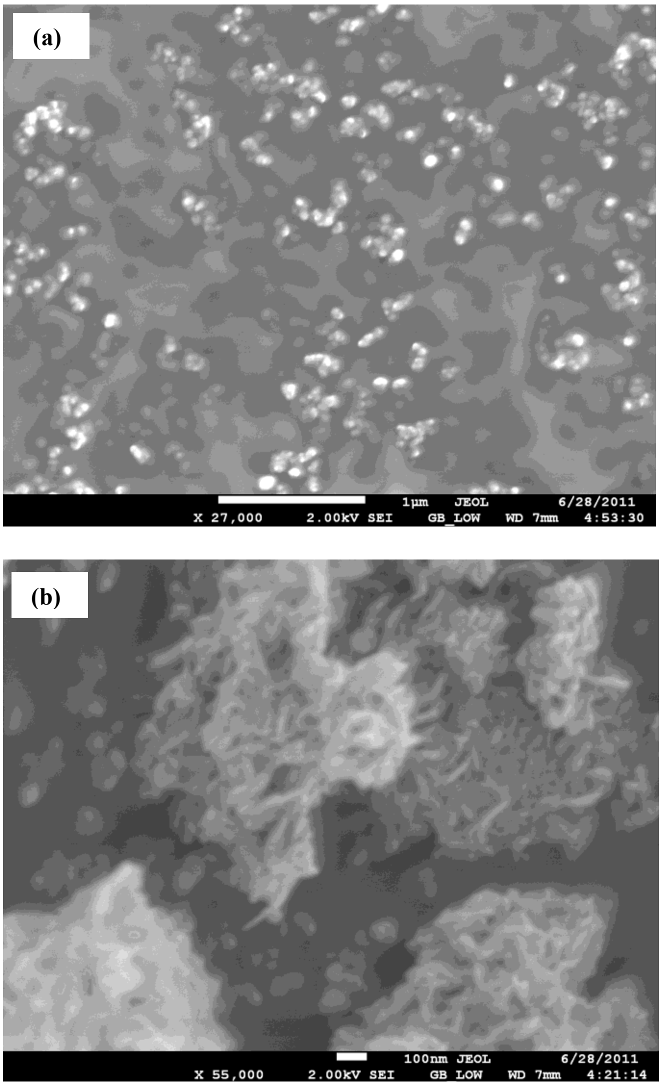

Figure 2: SEM images of ZnO (a) Nanoparticles and (b) clustered Nanorods

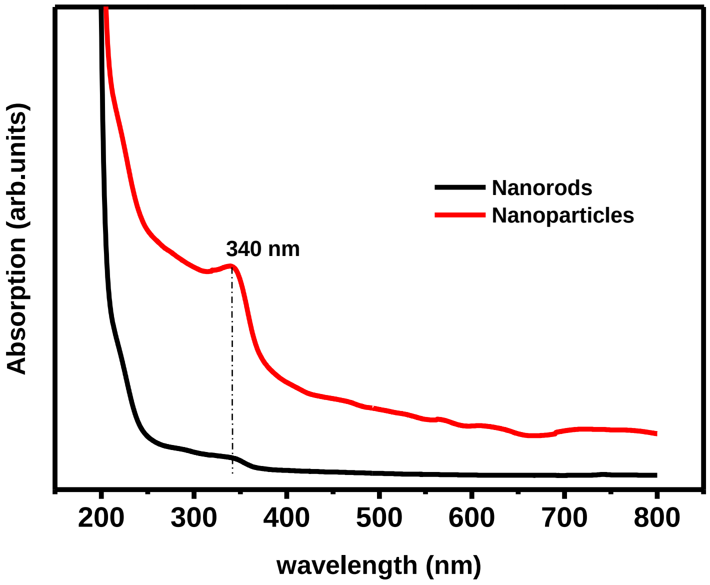

Figure 2: Absorption spectra of both colloidal ZnO nanorods and nanoparticles

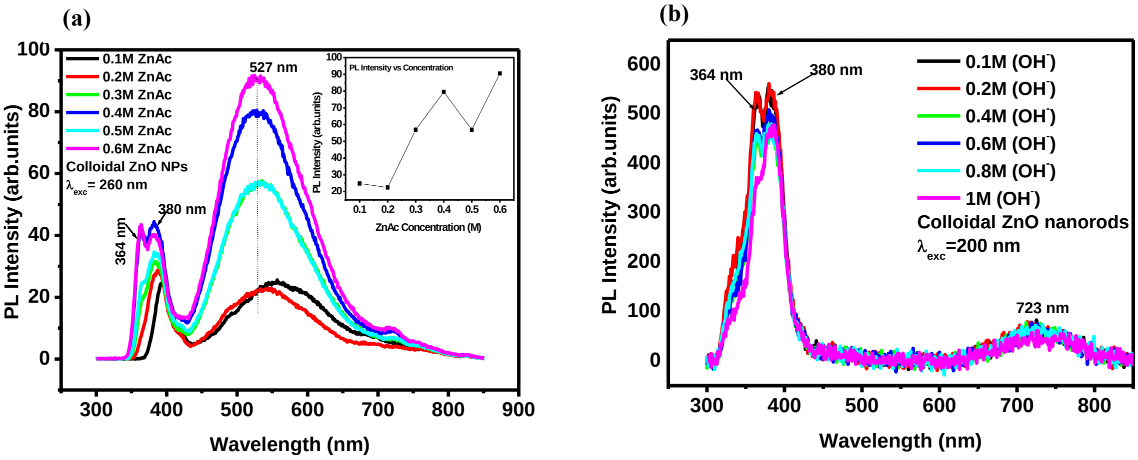

Figure 4: The PL spectra of colloidal (a) ZnO nanoparticles, the inset shows the PL intensity vs concentration of zinc acetate, (b) ZnO nanorods.

4. Conclusion

Colloidal ZnO nanoparticles and nanorods were synthesized by a simple wet chemistry route at low temperatures. Both nanoparticles and nanrods showed dual emission in the UV and visible region of the electromagnetic spectrum associated with excitonic recombinations and defects. In the case of ZnO nanoparticles, the green defects emission was more intense than the UV emission while the UV emission from the nanorods was more intense than the red-shifted defects emission. The red-shifting of the defects emission was attributed to excess oxygen and surface OH group.

5. Acknowledgement

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