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Polyvinyl pyrrolidone assisted low temperature synthesis of ZnO nanocones and its linear and nonlinear optical studies

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ABSTRACT

ZnO is synthesized by low temperature solution precipitation technique using polyvinyl pyrrolidone (PVP) as capping agent and at varying pH of the precipitating solution. The as-synthesized ZnO has a cone shape with rough surface, due to the chemisorption of PVP. The results show that PVP has a significant role in the nucleation and growth of ZnO at low temperature and a pH of 11 is required for the formation of the ZnO phase. When it is calcined at 550 °C, the morphology is modified to smooth nanocones. As the ZnO is calcined, optical bandgap is decreased and altered the nonlinear absorption properties of nano ZnO. The optical limiting property of ZnO colloids is investigated using Z-scan technique. Enhanced optical limiting is observed for ZnO calcined at 550 °C.

1. Introduction

Recently numerous researchers have been focusing on new synthetic methods to control shape, size and crystallinity of semiconductor nanomaterials, which are important in tailoring their physical and chemical properties. Among these nanomaterials ZnO, n-type semiconductor material with a wide and direct band gap of 3.37 eV and a large exciton binding energy of 60 meV [1] at room temperature, has been identified as a good optoelectronic material used in optical limiting devices [2], solar cells [3], light emitting diodes [4], photocatalyst [5] and gas sensors [6]. The tremendous interest in ZnO is provoked by its multifunctional character, which can be varied by controlling the morphology and crystallinity. Recent advances in chemical synthesis have enabled the achievement of ZnO nanocrystals (NCs) with an increased degree of structural complexity and shape. For example, there are reports on the synthesis of ZnO NCs with different morphologies like rods [7], wires [8], belts [9], sheets [10], cubes [11], etc. Several interesting ZnO nanostructures can be synthesized by chemical vapour deposition [12] and thermal evaporation [13]. However, complex process control and sophisticated equipment are needed for the vapour methods. For large scale use, simple and cost-effective synthesis approaches are required. The facile solution method is simple and effective way to prepare large scale and highly crystalline ZnO nanostructures at low growth temperature.

The optical properties of wide bandgap materials are currently the subject of tremendous interest because of the industrial demand for optoelectronic devices that could be operated at short wavelength. Also there is an increased demand for high nonlinear optical (NLO) materials, which can be incorporated in optoelectronic device with relatively high damage threshold. ZnO have attractive nonlinear optical properties, which make them good candidate for NLO based devices. Because of the high damage threshold, ZnO find its application as an optical limiter. Optical limiters exhibit a decrease in transmittance with increase in incident intensity and this nonlinear absorption (NLA) is referred as reverse saturable absorption (RSA).

Herein, we present a simple low temperature wet chemical approach to synthesize ZnO nanostructures in presence of Polyvinyl pyrrolidone (PVP) at ambient pressure. The influence of reaction conditions on the size and shape of ZnO is discussed. The as-obtained ZnO nanopowder has cone shape with rough surface and when it is calcined at 550 °C and the morphology is modified to smooth nanocones. The optical behaviour of ZnO is substantially changed because the optical bandgap is changed upon calcination. We compared the optical limiting behaviour of all the ZnO nanostructures by evaluating the nonlinear absorption coefficient (β) and saturation intensity (I_{sat}) by Z-scan measurement. The optical limiting efficiency of ZnO nanocolloid increases with increase in calcination temperature.

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2. Experimental

2.1. Materials and synthesis

The starting material in this work are Zinc acetate dihydrate ($Zn(Ac)_2 \cdot 2H_2O$, Merck), Polyvinyl pyrrolidone (PVP, Mol. Wt. 40,000, Sigma–Aldrich), Acetic acid (98%, Merck), De-ionised water and Sodium hydroxide (NaOH, Merck). Zinc acetate dihydrate is stirred with 0.05% PVP solution (in 1% acetic acid) for 24 h to form Zinc acetate-PVP complex. ZnO is precipitated from this complex using NaOH solution. The molar ratio of Zinc acetate and NaOH solution is 1:6. The stirring is continued for 12 h to complete the precipitation. The precipitate is filtered and dried at 100 °C. This method of synthesis is already reported from our group [14]. To study the effect of pH on the growth of ZnO at low temperature, the synthesis was repeated by varying the pH of the precipitating solution. A part of ZnO nanopowder dried at 100 °C is calcined at 550 °C, for studying the effect of calcination temperature on the morphology and optical properties of ZnO. The ZnO nanopowder obtained by heating at 100 °C and 550 °C are indicated as ZnO@100 and ZnO@550 respectively.

2.2. Characterization

X-ray Diffraction (XRD) analysis of the obtained powder was performed with a Bruker AXS D8 Advance X-ray diffractometer using Cu Kα (λ = 1.54 Å). The powder XRD can be used for phase identification and to calculate the crystallite size. The crystallite size can be evaluated using Scherrer formula (Eq. (1)).

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

where D is the crystallite size, λ is the wavelength of X-ray radiation, and B is the line width at the half maximum height.

The morphology and crystallinity of the products were characterized by FEI Quanta High Resolution Transmission Electron Microscope (HRTEM). The UV–vis absorption spectra of ZnO dispersed in methanol was obtained on a Varian Cary Bio 100 UV Spectrophotometer at room temperature in the wavelength ranging from 210 nm to 600 nm. A diffused Reflectance Fourier Transform Infrared (FTIR) spectrum was recorded on Perkin-Elmer Spectrum 100 Spectrometer. Thermogravimetric Analysis (TGA) was performed with TA Q-50 apparatus at the heating rate of 10 °C/min in nitrogen atmosphere.

3. Results and discussion

3.1. Low temperature growth of nano ZnO using PVP

The Zn^{2+} precursor is dissolved in 1% acetic acid solution and subsequently 0.05% aqueous solution of PVP is added. The transparent solution is stirred for 24 h to form Zn^{2+}/PVP complex. The pH of Zn^{2+}/PVP solution is found to be 4. When NaOH solution is added dropwise, pH of the solution slowly increases and turbidity starts to appear at a pH value of 6.4. The addition of NaOH is continued till the pH of the final solution is raised to 11. The reaction mixture is stirred for 12 h at 30–35 °C. The TEM image shown in Fig. 1a is dominated by cone nanostructure with rough surface average size of 90 nm (base) × 170 nm (height). Fig. 1b shows the High Resolution Transmission Electron Microscope image of as-formed ZnO. The fringe spacing of 0.28 nm agrees well with the spacing of (1 0 0) lattice planes of ZnO. The XRD patterns (Fig. 2) confirm that ZnO nanostructures formed are hexagonal wurtzite structure. The sharp peaks indicate that the product formed is well crystallized and oriented, further confirming the room temperature crystallization of ZnO by this method. The crystallite size evaluated by Scherer formula is found to be 24 nm. This reveals that cone shaped nanostructures are formed by the crystallization of nanocrystallites with size of 24 nm.

3.2. Effect of calcination on the morphology of as-synthesized ZnO

When ZnO@100 is heated to 550 °C, the PVP chemisorbed on the surface of ZnO get decomposed and the surface of the nanostructures get smoothened and resulted in a cone shape (Fig. 3a). These cone shaped nanostructures are polydispersed and have an average size of 70 nm (base) × 120 nm (height). The XRD pattern of ZnO@550 is shown Fig. 3b. The crystallite size is calculated from XRD pattern and it shows that there is no significant variation in crystallite size, when it is calcined from 100 °C to 550 °C. Thus the ZnO nanocones are polycrystalline with an average crystallite size of 24 nm.

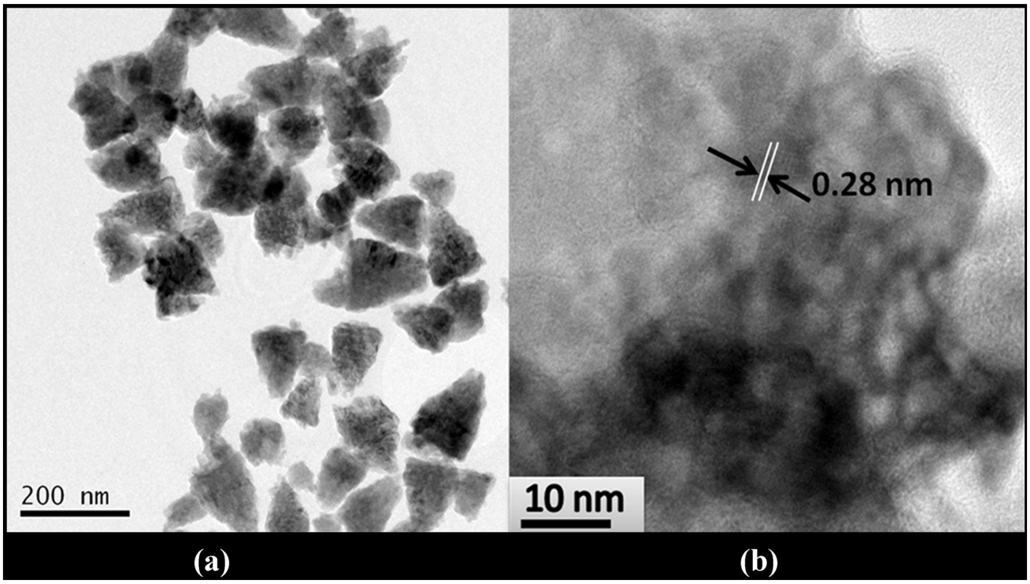

Fig. 1. (a) TEM micrograph and (b) HRTEM micrograph of ZnO@100.