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Synthesis of stable ZnO nanocolloids with enhanced optical limiting properties via simple solution method

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ABSTRACT

In present work, we report the synthesis of stable ZnO nanocolloids through a simple solution method which exhibit enhanced optical limiting threshold. The influences of reaction temperature on the crystal structure as well as linear and nonlinear optical properties of prepared ZnO nanoparticles were carried out. The XRD and Raman analysis reveal that the prepared ZnO nanoparticles retain the hexagonal wurtzite crystal structure. HRTEM analysis confirms the effect of reaction temperature, solvent effect on crystallinity as well as nanostructure of ZnO nanoparticles. It has been found that crystallinity and average diameter increase with reaction temperature where ethylene glycol act as both solvent and growth inhibiter. EDS spectra shows formation of pure ZnO nanoparticles. The direct energy band gap of the nanoparticles increases with decrease in particle size due to quantum confinement effect. The third order nonlinear optical properties of ZnO nanoparticles were investigated by z scan technique using a frequency doubled Nd-YAG nanosecond laser at 532 nm wavelength. The z-scan result reveals that the prepared ZnO nanoparticles exhibit self - defocusing nonlinearity. The two photon absorption coefficient and third - order nonlinear optical susceptibility increases with increasing particle size. The third-order susceptibility of the ZnO nanoparticles is found to be in the order of 10^{-10} esu, which is at least three order magnitude greater than the bulk ZnO. The optical limiting threshold of the nanoparticles varies in the range of 54 to 17 MW/cm^2. The results suggest that ZnO nanoparticles considered as a promising candidates for the future photonic devices.

1. Introduction

Nonlinear optical semiconductors are of great importance in current and future technological applications. Since ZnO exhibits interesting nonlinear properties, it is widely used in a variety of applications such as optical switching, optical signal processing and optoelectronic devices [1–3]. Nano-sized ZnO shows large third order optical nonlinearity than that of the bulk counter part due to the increase in surface-volume ratio [1,3,4]. Quantum confinement effect also affects the nonlinear properties of ZnO [5]. In general, quantum confinement effect in semiconductors are classified into two regime, one is strong confinement regime ($R \ll a_B$) , second is weak confinement regime ($R \gg a_B$), where a_B is Bohr radius ($a_B^{ZnO} = 2nm$) [5]. ZnO is a multifunctional n type semiconductor with wide band gap of 3.37eV, high exciton binding energy (60 meV) and high thermal stability [6,7]. The various morphologies of ZnO, including nanowires, nanorods, quantum dot, nanotubes, nanobelts, nanohelixes and nanodisks, play an important role in their linear and nonlinear optical properties [3,8,9]. So the control of size, shape and crystalline structure has been the major challenge in the synthesis of ZnO nanoparticles. Various physical and chemical methods are employed for the production of ZnO nanostructures [10–13]. The solution based methods are attractive because of the mild synthesis condition and simple experimental setup involved [14,15]. In solution method, nucleation process is very fast. Oswald ripening and aggregation are the basic mechanisms in the growth process of nanoparticles [14]. In the present work, ZnO nanoparticles have been synthesized on the basis of solution method using ethylene glycol as a reacting medium. The effects of reaction temperature on its crystalline nature and nonlinear optical properties have been investigated.

2. Experimental

2.1. Synthesis of ZnO nanoparticles

Solution method incorporating ultra sound sonication was employed in the preparation of ZnO nanoparticles using Zinc acetate dihydrate (Zn $(CH_3COO)_2.2H_2O$, Sigma aldrich) and Sodium hydroxide

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(NaOH, Merck) as chemical reagents. Ultra sound sonication in the solution method helps to increase the surface area and size uniformity. 0.1 M Zinc acetate dihydrate and 0.5 M NaOH were dissolved in ethylene glycol under constant magnetic stirring. The NaOH solution was added dropwise to the zinc acetate dihydrate suspension under ultrasound sonication at room temperature. After 10 min, a transparent white solution was formed, which was heated at a constant rate to different temperatures (80°C, 100°C, 120°C and 150°C) for 2 h and kept at room temperature for a day. The resulting white precipitate was centrifuged at 3000 rpm for 20 min and washed several times using distilled water to remove the unreacted ions. Final product was dried at 80°C for 1 h and ZnO particles were obtained without using any additional surfactant/capping molecules.

2.2. Sample characterization

Crystal structure and morphology of prepared samples were analysed by X-ray diffraction crystallography (XRD) and high resolution transmission electron microscopy (HRTEM). Absorption spectra of the prepared ZnO nanoparticles were recorded using JASCO V-570 UV-VIS-NIR spectrophotometer. Elemental composition of sample was analyzed using energy – dispersive X-ray (EDX) spectrometer and Raman spectra of sample was analysed using DPSS laser with 532 nm excitation wavelength.

2.3. Nonlinear optical properties

The nonlinear optical characterisation of ZnO nanoparticles were carried out using Z-scan technique developed by Sheik Bahae et al. using a Q-switched Nd-YAG laser (532 nm,7 ns, 10 Hz) as the light source [16]. Several methods can be used for determining the nonlinear optical properties of the samples, like interferomery, third harmonic generation (THG), degenerated four wave mixing (DFWM) [17]etc. Z-scan method is a simple and high sensitive technique for measuring the sign and magnitude of the nonlinear refractive index and nonlinear absorption coefficient. It is a single beam technique based on spatial beam distortion principle. The samples were mounted on a translational stage and moved in the z direction along the beam focus ($z = 0$). The self focusing/defocusing effect results in the modification of phase of the beam, which in turn modifies the intensity of the laser beam at the detector. Fig. 1 shows schematic experimental setup for Z-scan technique. As an essential prerequisite of the Z-scan technique, the Rayleigh length, $Z_0 = {}^{\pi\omega_0^2}/_{\lambda}$ was estimated and was found to be 7.4 mm, which is greater than the thickness of the sample.

When a material is irradiated with a high intensity laser beam, transmission at the focus increases or decreases with increase in intensity. First category of materials exhibit the saturable absorption (SA) and second category exhibit the reverse saturable absorption (RSA) [1,3,18]. In nanomaterials there occurs several mechanisms such as two photon absorption (TPA), reverse saturable absorption (RSA), transient absorption, free carrier absorption (FCA) and nonlinear scattering that result in nonlinear absorption property [1,18]. In semiconductors TPA and FCA are the basic mechanisms that contribute to the induced absorption. Since the contribution of FCA in nonlinear absorption is negligible, TPA is the most significant mechanism in nonlinear optical studies of semiconductors. In the case of ZnO, free carrier absorption life time is reported to be 2.8 ns [3]. In the present work 7ns laser pulses are used for the irradiation of the sample. So there is a strong possibility for the generation of free carriers by two photon absorption that results in slight deviation from the theoretical curve fitted for two photon absorption [3]. The intensity dependent nonlinear absorption and refraction are expressed by the equations,

$$\alpha(I) = \alpha + \beta$$

$$n(I) = n_0 + n_2 I$$

where α is the linear absorption coefficient, n_0 is the linear refractive index, β the nonlinear absorption coefficient, n_2 is nonlinear refractive index and I the intensity of the laser beam [1].

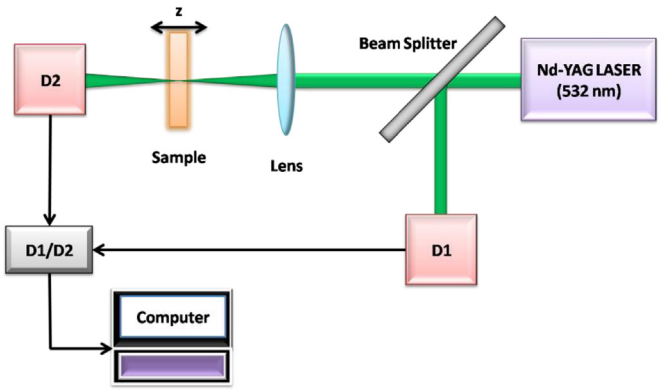

Fig. 1. Z-scan experimental setup.

3. Result and discussion

3.1. Structural properties

As shown in Fig. 2, the XRD pattern of ZnO nanoparticles synthesized at different reaction temperature and constant reaction time, confirms the formation of hexagonal wurtzite phase (JCPDS No: 01-089-1397). It can also be noted that, all diffraction peaks are broadened, which suggests that the crystalline size of ZnO nanoparticles lies in nanometre regime. Debye – Scherrer formula [19,20] was used to calculate the average crystalline sizes of ZnO nanoparticles. The crystalline sizes of ZnO nanoparticles were found to be 9.6 nm (Sample A), 11.2 nm (Sample B), 12.4 nm (Sample C) and 17.7 nm (Sample D). As the reaction temperature increases, the crystalline size increases which in turn results in enhanced crystallinity.

The morphology and size of ZnO nanoparticles were further investigated using TEM analysis as shown in Fig. 3. The diameter distribution of sample A, B, C and D were determined to be 5.6 ± 0.6 nm, 7.5 ± 1.7 nm, 12.5 ± 1.4 nm, and 16.6 ± 2.2 nm, respectively, where all distributions are fitted with a Gaussian distribution.

It is noticed that reaction temperature affects the diameter and crystalline nature of ZnO nanoparticles. With an increase in reaction time, nanoparticles are clearly well separated and less aggregated. The increase in size is in good agreement with XRD results as shown in

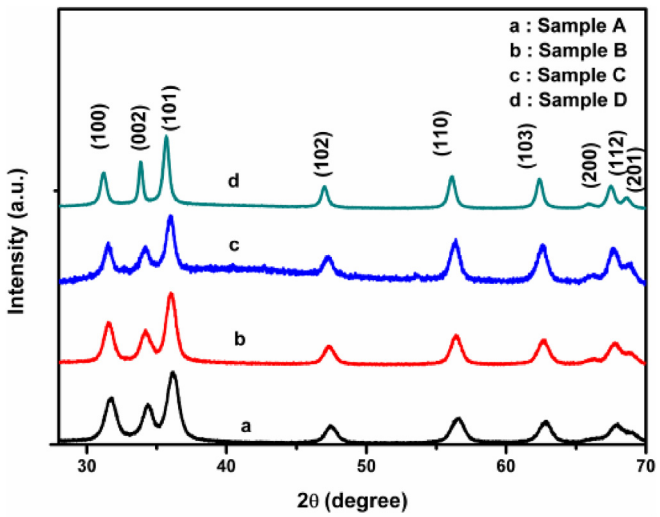

Fig. 2. XRD analysis of ZnO nanoparticles.