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Quantum confinement effect in ZnO nanoparticles synthesized by co-precipitate method

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ABSTRACT

Quantum mechanical effects such as an increased bandgap of semiconductors with reduction of size are viewed as having strong potential for future applications. In the present work, zinc oxide (ZnO) nanoparticles (NPs) were synthesized via the co-precipitate method. Very narrow particle size distribution of the ZnO nanoparticles was achieved through careful control of the synthesis conditions. The structural, morphological, and optical characterization was carried out using X-ray diffraction, atomic force microscopy, and UV–vis reflectance techniques, respectively. The results indicated that increasing the temperature from 60 to 65 °C caused a subsequent increase in particle size from ~4 to 12 nm. An associated increase in bandgap with decrease in particle size was also noticed which is a strong indication of the quantum confinement effect.

1. Introduction

Zinc oxide (ZnO) has been recognized as one of the promising materials because of its wide bandgap (3.37 eV) and relatively large exciton binding energy (60 meV) at room temperature [1–5]. It is one of the most important oxide semiconductors because of its unique properties and potential applications, such as transparent electronics, ultraviolet (UV) light emitter, surface acoustic wave (SAW) devices and spin electronics [6,7]. Various methods have been employed to prepare ZnO with small diameters including precipitation of colloids in solution [8], sol–gel methods [9], thermal transport methods [10,11], pulsed laser deposition (PLD) [12] and metal-organic chemical vapor deposition (MOCVD) [13]. It is well known that preparation of ZnO via solution-based chemical processing routes provides a promising option with control of particle size, shape, and crystallinity representing some of the key issues in this area [14–16].

Quantum confinement effect in ZnO is a research area that is aggressively being pursued for numerous interesting electronic and optical applications [15]. An increase in the efficiency of radiative recombination by several orders of magnitude has been reported in quantum dots of indirect gap semiconductors [17]. Confinement of optical and acoustic phonons also leads to interesting changes in the phonon spectra [18].

In the present study, size control of ZnO nanoparticles (NPs) with narrow particle size distribution is demonstrated by carefully controlling the synthesis temperatures. UV–vis spectroscopy results suggested that tuning of optical properties of ZnO NPs is possible by controlling the size. AFM studies give direct evidence of the morphology and size distribution of ZnO NPs.

2. Experimental procedure

Zinc acetate dihydrate (Sigma-Aldrich, 0.9789 g, 4.46 mmol) and 1 ml of distilled water were added to a flask containing 42 ml of methanol. The mixture was divided into three equal parts and heated at 60, 63, and 65 °C with sample IDs S_1, S_2, and S_3, respectively. In another beaker, potassium hydroxide (Sigma-Aldrich, 0.4051 g, 7.22 mmol) was dissolved into 23 ml of methanol. This stock solution was then added drop by drop to the flasks containing S_1, S_2 and S_3, and the solution was then stirred for 2.5 h. Gradual addition of KOH turned the transparent solution opaque, which in turn, transformed into a clear solution again after 10 min.

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The solution so obtained was centrifuged to separate ZnO powder from other solvents. NPs were repeatedly washed in distilled water and ethanol, and subsequently dried in the oven at 60 °C.

The size and shape of the NPs was determined using atomic force microscope (SPM5200, JEOL) in non-contact (NC) and tapping (AC) modes. The micro-fabricated cantilever (NSC35; μmasch) probe employed for this purpose was 130 μm long with spring constant, resonance frequency, and nominal tip radius of 4.5 N/m, 150 kHz, and <10 nm, respectively. For AFM studies, ZnO nanoparticles were dispersed onto atomically smooth highly oriented pyrolytic graphite (HOPG) surface by placing a droplet on it from the suspension and drying off the liquid medium. The compositional analysis as well as particle size measurement was done using X-ray diffractometer (JDX-11, Japan). Optical characterization was carried out by measuring the diffuse reflectance spectroscopy (DRS) at room temperature using Lemda-950 Perkin-Elmer.

3. Results and discussion

Since AFM-measured nanoparticle's height is considered to be an excellent indicator of the particle diameter, particle height histograms for ZnO were used as a means for determination of particle size and the relative standard deviations. The area scans for ZnO NPs with sample IDs of S_1, S_2, and S_3 along with their respective histograms of particle heights are presented in the Fig. 1. It was noticed that AFM sample preparation through formation of a colloidal suspension resulted in uniformly dispersed nanoparticles. For the selected scan area, the number of nanoparticles was high enough to give insight into the particle shape and size that is representative of the bulk powder sample. Several measurements of the particle height were made to determine the values of mean particle size and standard deviation. Fig. 1 clearly suggests an increase in the average particle size for higher synthesis temperatures. The particle sizes were estimated to be 4.11 ± 0.82, 8.03 ± 2.11, and 11.5 ± 2.52 nm, for synthesis temperatures of 60, 63, and 65 °C, respectively (Table 1). Nanoparticles were found to be nearly spherical in shape with narrow particle size distribution. A series of experiments (results not shown here) indicated the important role of stirring toward control of size distribution. It was noticed that intermediate stirring offered precise control over particle size, producing nanoparticles with very narrow size distribution.

Fig. 2 shows XRD patterns of ZnO NPs grown at 60, 63, and 65 °C. All major peaks correspond to hexagonal Wurtzite crystal structure with (1 0 1) as the highest intensity peak (JCPDS card # 65-3411). FWHM is also narrowing with the increase in synthesis temperature, suggesting increase in particle size (inset, Fig. 2). Average size of these nanoparticles was calculated by using Scherer's formula, giving 5.32, 7.10, and 8.23 nm at 60, 63, and 65 °C, respectively (Table 1).

Optical characterization is an important tool to measure bandgap and quantum confinement effects. The UV–vis DRS of S_1, S_2, and S_3 are shown in Fig. 3 (inset). The diffuse reflectance, R, of the samples is related to the Kubelka–Munk function $F(R)$ by the relation $F(R) = (1-R)^2/2R$, where R is the percentage reflectance [19]. The spectra used for the bandgap calculations are plotted in terms of $F^2(R)$. The bandgap energy of the ZnO NPs were calculated from their diffuse reflectance spectra by plotting the square of the Kubelka–Munk function $F(R)^2$ vs. energy in electron volts. The linear part of the curve was extrapolated to $F(R)^2 = 0$ to get the direct bandgap energy. Fig. 3 illustrates the graph between $F(R)^2$ and the band-energy of ZnO NPs grown at different temperatures. It was observed that the energy

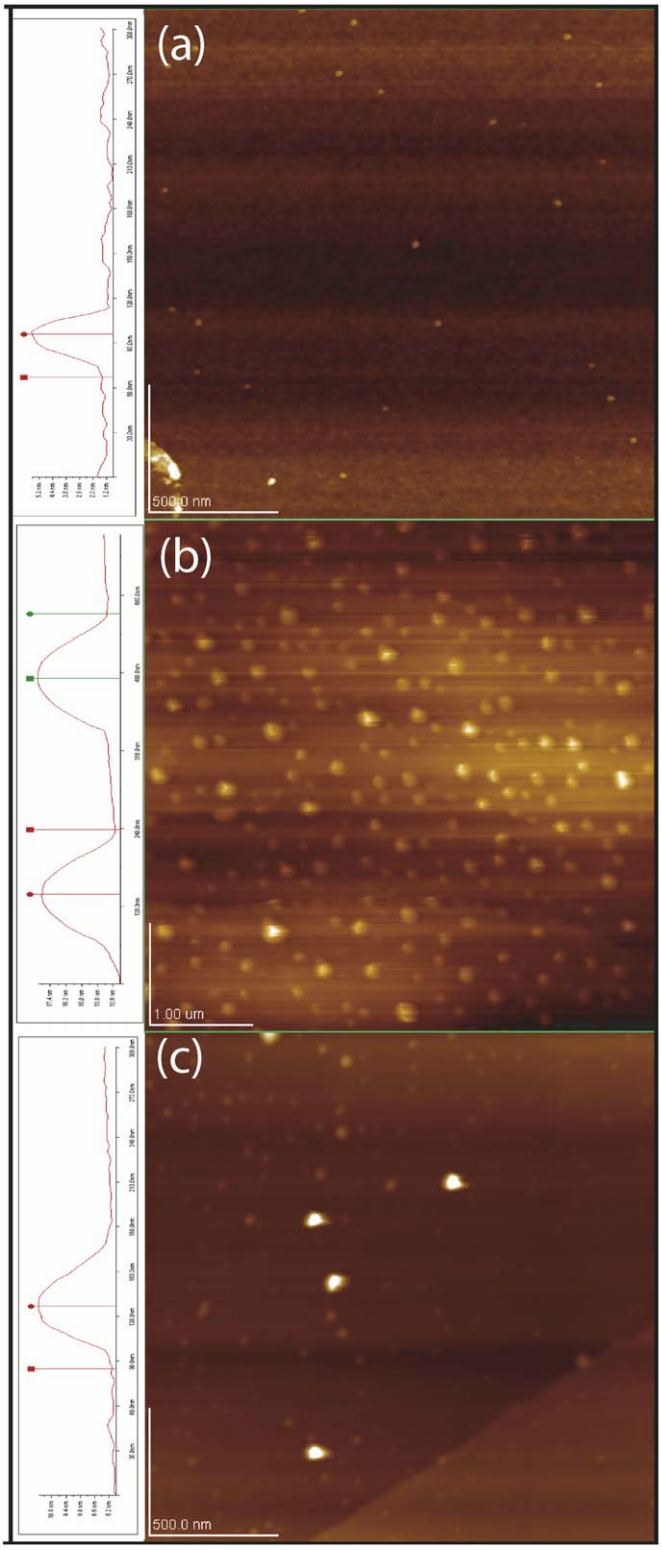

Fig. 1. AFM images of ZnO NPs synthesized at (a) 60 °C (S_1), (b) 63 °C (S_2), and (c) 65 °C (S_3). The graphs beside each image correspond to the respective particle height histograms.

systematically increases as the particle size decreases (Table 1). The energies are 3.29, 3.26, and 3.15 eV for S_1, S_2, and S_3, respectively. ZnO NPs synthesized at higher temperatures are bigger in size with much wider particle size distribution and also lower bandgaps (results not shown). As the size of the particle

Table 1
Summary of results with synthesis temperature, average particle sizes, and bandgaps of ZnO NPs.

Sample ID	Particle size		Bandgap (eV)
	AFM (nm)	XRD (nm)	
S_1	4.11 ± 0.82	5.32	3.29
S_2	8.03 ± 2.11	7.10	3.26
S_3	11.5 ± 2.52	8.33	3.15

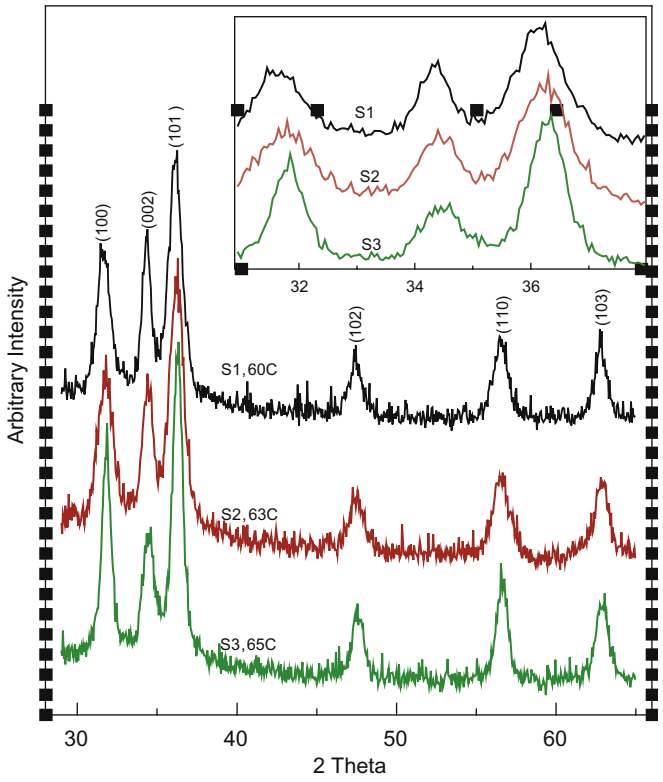

Fig. 2. XRD results of ZnO NPs synthesized at different temperatures suggesting that all the peaks corresponds to ZnO. The inset shows that FWHM decreases with increase in synthesis temperature.

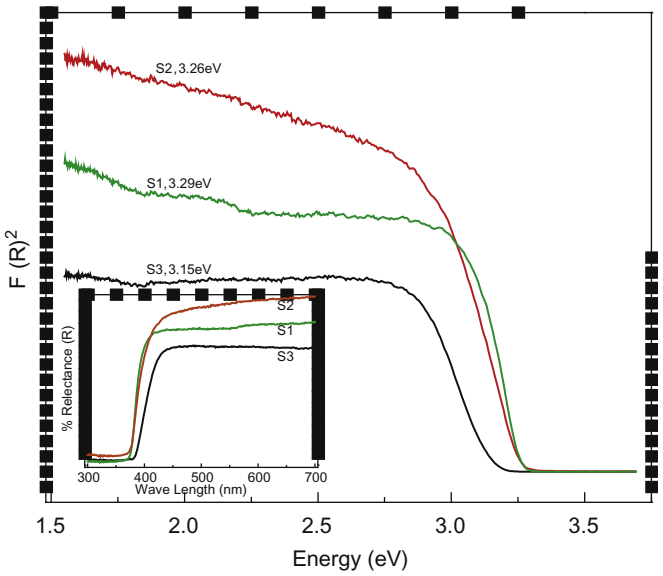

Fig. 3. UV–vis reflectance spectroscopy data was plotted between $F(R)^2 = (1-R)^2/2R$ (where R = optical reflectance) and the band-energy of ZnO NPs, suggesting systematic blue shift with change in particle size. The inset is the raw UV–vis data plotted between %reflectance (R) and wavelength.

became comparable with exciton radius, optical properties of semiconductors change significantly [20]. Stronger exciton effect is an important character of quantum confinement effect in nanosemiconductors, the reason mainly comes from the carriers being confined in a very small space, this makes the electrons and holes move only in a potential well. At the same time, it can enhance the coupling interaction with each other and the exciton bounded stronger and the probability of binding increased. Therefore, more apparent exciton absorption peak can be observed with decrease in particle size. The exciton Bohr radius of bulk ZnO is 2.34 nm [21] and sizes of ZnO NPs synthesized in this study are slightly larger than the above value, suggesting confinement in moderate to strong regime. Synthesis of ZnO nanoparticles/quantum dots and size-dependent quantum confinement effect has been reported by many independent research groups. In many cases ZnO was either confined inside a matrix [22,23] or size controlled by post-synthesis annealing at higher temperatures [24]. In this study, NPs were synthesized at different temperatures by co-precipitate method with smaller sizes than some earlier reports, i.e. 20–40 nm [25].

4. Conclusion

ZnO nanoparticles were synthesized by co-precipitate method and the size was controlled by carefully controlling synthesis temperatures. AFM analysis clearly suggested narrow particle size distribution and the presence of discrete particles. XRD results show good crystallinity and peak broadening with decrease in particle size. Size-dependent blue shift of reflectance spectra is attributed to the quantum size effect.

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