Research Article

Quantum Size Effect in ZnO Nanoparticles via Mechanical Milling

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ZnO nanocrystals were successfully produced by mechanical milling. It is shown that mechanical milling is very effective and simple to produce ZnO nanoparticles with the possibility of obtaining large quantities of materials. Size effects in ZnO nanoparticles were probed by XRD and UV-vis and photoluminescence (PL) spectroscopy. Absorption due to free electron was clearly observed, whereas strong PL lines were recorded in the UV and blue region. The absorbance and photoluminescence were found to increase with reduction in particle size. Blueshift of excitonic and emission peaks was observed as a consequence of the size quantization effect. Formation of pure ZnO phase was confirmed from XRD pattern and the optical spectroscopy.

1. Introduction

Compared to bulk materials, nanoscale materials exhibit large specific surface area and size-dependent quantum confinement effects. Nanoscale materials often have distinct electronic, optical, magnetic, catalytic, and thermal properties. They provide a unique opportunity to observe the evolving electronic structure of materials growing from molecules to bulk. The investigations on size-dependent electronic structure have revealed interesting properties including discretization of electron energy levels, concentration of oscillator strength, highly polarizable excited states, and increased electron-electron correlation [1–4]. ZnO nanoparticles are one of the important multifunctional materials due to their unique optical and electronic properties [5–9]. It has a wide band gap semiconductor, having high exciton binding energy of 60 meV and has stable wurtzite structure with lattice spacing $a = 0.325$ nm and $c = 0.521$ nm. Several authors have reported high photoluminescence (PL) efficiencies in ZnO nanostructures [10, 11]. Optical techniques are the most common techniques to study the quantum size effects. Here, we report studies on the optical properties of zinc oxide (ZnO) nanoparticles, synthesized by a mechanical route. We have emphasized UV-vis and PL spectroscopic studies, to examine the size-induced effects.

Various techniques have been used to synthesis ZnO nanoparticles including mechanical milling [12], hydrothermal synthesis [13], sol-gel method [14], and spray pyrolysis [10].

2. Experimental

Commercially obtained ZnO powder with size ~ 200 nm and purity 99% was milled in a zirconia jar with zirconia balls with a ball-to-powder weight ratio of 14. The mechanical milling was performed in a horizontal ball mill operating at 200 rpm for different milling times (5, 10, 15, and 20 h). No solvent was used in this process.

The optical properties were investigated by using Cary, 50-probe UV-vis spectrophotometer, and Perkin Elmer (LS-55) Luminescence Spectrophotometer (PL). X-ray diffraction patterns were performed using SIEMEN D500 X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.5418$ Å) irradiated with a scanning rate of 0.02°s^{-1} . The particle size was calculated from the effective mass equation using data from UV-vis spectroscopy.

3. Results and Discussion

Figure 1 shows the XRD pattern of the ZnO powders before and after milling. All the peaks corresponding to the

FIGURE 1: XRD pattern for ZnO particles before and after milling.

reflections of hexagonal phase ZnO match well with standard diffraction data (JCPDS card no. 80-0075), as well as with that for high-purity powder. With increasing milling time, the corresponding peaks become less intense and broader. No major change is observed on the lattice parameters. The considerably broad reflections are mainly a consequence of a small grain size with a small contribution from internal strain induced by the severe mechanical deformation.

Figure 2 shows the UV absorption spectra of ZnO powders milled at different milling times. Absorption peaks corresponding to 5, 10, 15, and 20 h are obtained at 284.97, 281.98, 279.94, and 276.95 nm, respectively. As seen from Figure 2, the absorption spectra for all the samples show sharp excitonic peaks and blue shifted due to quantum confinement effect. The absorbance increases as the milling time increases. Therefore, the optical properties get enhanced with the increasing ratio of surface to volume in ZnO powder.

The particle size was determined from the effective mass equation below [13]:

$$E = E_{\text{bulk}} + h^2 \pi^2 \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{(1.8e^2)}{4\pi\epsilon'\epsilon'_0 R}, \quad (1)$$

where E and E_{bulk} are the band gap of synthesized and bulk (3.3 eV) ZnO particles, respectively, R is radius of the particle, m_e is the effective mass of electron ($0.28 m_0$), m_h is the effective mass of hole ($0.49 m_0$), ϵ' is the dielectric constant of material (2.1), ϵ'_0 is the permittivity of free space, and h is the Planck's constant.

Table 1 shows the size of ZnO particles are decreases as the milling time increases.

Figure 3 shows the room temperature photoluminescence (PL) spectra of ZnO nanoparticles milled for 5, 10,

FIGURE 2: UV-vis spectra of ZnO nanoparticles at various milling times with respect to their (a) wavelength and (b) energy.

TABLE 1: Characteristics of ZnO powders at various milling times.

Milling time (h)	FWHM (eV)	UV emission peak (nm)	BE emission peak (nm)	Particle size from (1) (nm)
5	0.46	309.0	414.0	2.32
10	0.51	308.5	430.0	2.24
15	0.52	306.5	418.0	2.18
20	0.54	307.0	417.5	2.10

15, and 20 h. ZnO nanoparticles exhibited two prominent emission PL bands at around 309 and 418 nm. The PL peak at 309 nm which is intense and sharp is assigned to near-band-edge emission (UV emission) attributed to free electron recombination [15]. This peak intensity is decreased

FIGURE 3: Photoluminescence spectra of ZnO powders at various milling time.

and blue shifted as the particle size decreases. Blue shift in the UV emission peak is due to the quantum confinement effect. The peak around 430 nm is blue emission (BE) which is attributed to intrinsic defects such as oxygen and zinc interstitials [16]. It can be observed that only small changes in the parameters are observed for the sample milled 20 h, which is wider and less-quantum efficiency. The mechanical milling produces different kinds of defects in the powders giving place to an increase in the possible recombination mechanisms. Table 1 summarized the UV and PL characteristics of the samples.

4. Conclusion

ZnO nanoparticles were successfully synthesized at room temperature via mechanical milling. Absorption spectra

demonstrate sharp excitonic peaks and blue shifted corresponding to quantum confinement effect. The absorbance was increased as the milling time increases. Strong PL lines were recorded in the UV and blue region. The crystal structure of ZnO nanoparticles is the same as that of bulk ZnO, though some amount of internal strain induced by the severe mechanical deformation.

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