Size Dependent Absorption Spectrum of ZnO Nanocrystals

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Abstract To investigate the dependences of the absorption spectrum and electronic structure properties on the ZnO nano-particle size, ZnO nanocrystals were synthesized by a sol-gel method. The absorption onset peak exhibits a systematic blue-shift with decreasing particle size due to the quantum confinement effect, as well as, with decreasing Zn^{2+} concentration. The increase of particle size is mainly controlled by coarsening and aggregation step during the nucleation and growth of ZnO nano-particles. The onset absorption spectrum of ZnO colloids changes from 310 to 355 nm as Zn^{2+} concentration increases from 0.01 to 0.1 mole. The average particle size as a function of aging time can be determined from the absorption spectra. The freshly prepared nanocrystal size was about 2.8 nm.

Key words ZnO, nanocrystals, absorption spectrum, quantum confinement effect.

1. Introduction

In recent years, nano-scale semiconductor particles have attracted much attention due to their distinct properties in comparison with bulk materials.[1-3] When the size of nanocrystals decreases to the exciton Bohr radius, the energy level develops discrete orbits from continuum and the energy gap increases, showing a quantum confinement effect. So, it is promising to tailor the optical, electrical, magnetic, and chemical properties of nanocrystals for specific applications by controlling their sizes and structures. Wide band gap semiconductors are of interest for blue and ultra-violet (UV) optical devices, such as light emitting diodes and laser diodes.[4] Zinc oxide (ZnO) is one of the wide band gap semiconductors with band gap of 3.36 eV at room temperature. ZnO have been investigated intensively for high power devices, surface acoustic wave devices, ferroelectric memories, transparent conductive film used in display, solar cell, and various optoelectronic devices.[5-7] Especially, ZnO with outstanding optical properties, such as high exciton binding energy (60 meV) which is stable even at room temperature, has attracted a great deal of attention for blue emitting optical devices. It is essential to investigate the evolution of the optical and electronic structural properties of ZnO nano-particles from molecular to bulk regime. ZnO films have been grown using several techniques: plasma assisted molecular beam epitaxy, *rf*-magnetron sputtering, metalorganic chemical vapor deposition, and pulse laser deposition, etc. At present, the sol-gel method has been widely used in the synthesis of ZnO nanocrystals because it can control the mole ratio accurately, synthesize monodisperse samples, and increase the solubility.[8]

In this work, the ZnO colloidal suspensions were prepared by a sol-gel method and the growth of ZnO nanocrystals according to the aging times were also characterized. The dependences of optical and electronic structural properties on the ZnO nano-particle size were investigated and discussed by analyzing the absorption spectra.

2. Experimental

The ZnO colloidal solutions were prepared by the sol-gel method that was carried out by Bahnemann and Spanhel with a few modifications.[3,8] For a typical synthesis of ZnO solution, $Zn(Ac)_2 \cdot 2H_2O$ with 1.1 g (0.1 mole) (reagent grade) was dissolved in 50 ml ethanol under vigorous stirring at the temperature of 80°C. This solution was refluxed for 180 min, followed by being cooled to the temperature of 0°C. Next, $LiOH \cdot H_2O$ with 0.29 g (0.14 mole) (reagent grade) was dissolved in 50 n.l ethanol in an ultrasonic bath at room temperature, followed by being

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cooled to 0°C. And then the lithium hydroxide solution was added dropwise to the prepared Zn(Ac)$_2$ solution under vigorous stirring at 0°C. The overall reaction can be written as stated below,

$$Zn(CH_3COO)_2 + 2LiOHZnO \rightarrow 2LiCH_3COO + H_2O \quad (1)$$
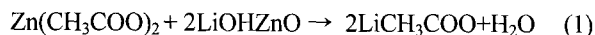
The molar ratio of Zn^{2+} and Li^{+1} was 1:1.4, in favor of the preparation of stable ZnO colloid. Keeping the ratio invariable, we prepared several ZnO colloids with different Zn^{2+} concentrations such as 0.1, 0.05, 0.025, 0.0125, and 0.01 mole. In this work, the fresh ZnO colloids were stored at the temperatures ranging from 2°C to room temperature and were taken at regular intervals for measurements. The growth of ZnO colloids was also characterized with the aging times ranging from 1 to 630 min at room temperature. The absorption spectra were recorded on a spectrophotometer (SHIMADZU RF5301PC).

3. Results and Discussion

3.1. Absorption spectra of ZnO colloid particles

The absorption spectra of ZnO particles aging at room temperature for various times are shown in Fig. 1. The absorption spectra show steep onsets, indicating narrow size distribution.[9,10] The onset absorption spectra of prepared ZnO colloids are found to be 306 nm, substantially moved to be blue-shifted in comparison with the bulk materials with around 388 nm. This result suggests that the ZnO particles are in quantum confinement regime. In addition, the absorption onset is shifted to a lower energy
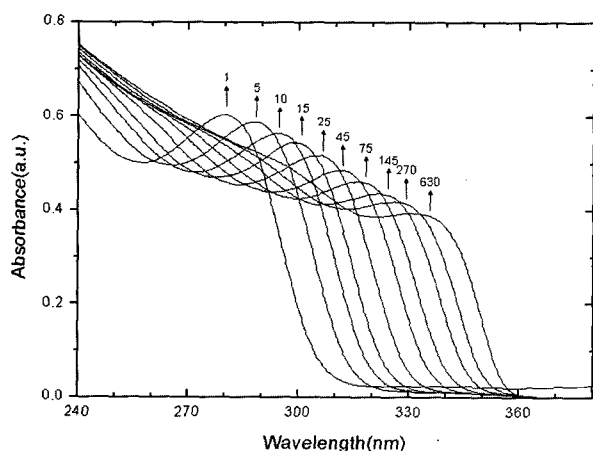

Fig. 1. Absorption spectra of ZnO nanocrystals (0.1 mole) aging at room temperature for 1, 5, 10, 15, 25, 45, 75, 145, 270, and 630 min, respectively.

state, showing the increment of the particle size as the aging time of the ZnO colloids increases.

Pronounced peaks can be seen at the higher energy of the onsets, which can be attributed to the first excited state transition of exciton or from molecular point of view the transition between the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO). At low temperature, a series of peaks in the ZnO absorption edge are resolved, assigned to discrete states of three Wannier excitons.[11] As the particle size decreases, the exciton peak shifts to the higher energy state and the peak intensity increases. These features can explain that the states density of band edge decreases and the exciton oscillator strength increases with decreasing the particle size. The exciton oscillator strength is given by the following formula,[12]

$$f = \frac{2m_e^*}{h^2} \Delta E |M|^2 |U_{(0)}|^2 \quad (2)$$

, where E is the transition energy, M is the transition dipole moment. The oscillator strength per volume, f/v (v being the cluster volume) determines the magnitude of the absorption coefficient. In the strong confinement regime, there is an increased overlap of the electron and hole wave functions, which increases with decreasing the cluster volume. As a result, the exciton oscillator strength, f is weakly dependent on the cluster size. However, the oscillator strength per unit volume (f/v) increases with decreasing the cluster size, and it can be defined roughly by the formula as $(a_B/R)^3$, where a_R and R indicate Bohr radius and cluster size, respectively. The exciton absorption should therefore become stronger as R decreases.[13]

Fig. 2 shows the concentration dependence of the absorption spectra of freshly prepared ZnO colloids. The onset spectrum of ZnO colloids changes from about 310 to 355 nm, indicating that the spectrum shifts to a lower energy state as the Zn^{2+} concentrations of ZnO colloids increases from 0.01 to 0.1 mole. The absorption spectra show exciton peaks below 0.0125 mole, and exhibit a steep absorption edges at the Zn^{2+} concentration of above 0.025 mole.

3.2. Growth of ZnO nanocrystals

The average particle size as a function of aging time is determined from the absorption spectra using the effective mass approximation (EMA) model. Though it has certain limitations in very small size region, where the determined
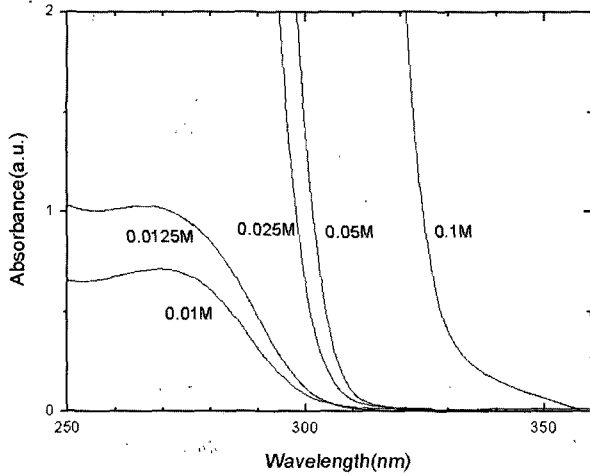
Fig. 2. Concentration dependence of the absorption spectra of freshly prepared ZnO colloids.

Fig. 3. Band gap and corresponding absorption onset as a function of particle radius.

size would be slightly larger than one observed by transmission electron microscopy, this approach has been also confirmed to be valid in the evaluation of the particle size.[11] The size dependence of the band gap (E^*) can be approximated by the following equation,[13]

$$E^* \cong E_g^{bulk} + \frac{h^2\pi^2}{2em^*r^2} - \frac{1.8e}{4\pi\varepsilon\varepsilon_0 r} - \frac{0.124m^*e^3}{h^2(4\pi\varepsilon\varepsilon_0)^2} \quad (3)$$

, where E_g^{bulk} (eV) is the band gap energy of bulk sample, $m^* = 1(1/m_e^* + 1/m_h^*)$ is the effective mass of the exciton, and 0 are the relative and free space permittivity, respectively. In the case of nanocrystals, the size dependence of the band gap is governed by competing terms: the confinement energy which scales as $1/r^2$ the coulomb interaction term which scales as $1/r$; and the exciton Rydberg energy. In addition, the permittivity also affects and relates with these competing terms.

Fig. 3 depicts the band gap and the corresponding absorption onset as a function of particle radius with m_e^*=0.26 , m_h^*=0.59 , ε=8.5, E_g^{bulk}=3.2 eV.[4] As can be seen, the band gap enlargement is pronounced for particle size below 3 nm. For a direct-band semiconductor of ZnO, a is related to the excitation energy hv by $a^2(h\upsilon)$=B(hυ-E$_g$) (for hυ> E$_g$), where B is a coefficient.[9] The absorption onset can be obtained by extrapolating the linear part of the curve to intercept the energy axis (not shown here). The time dependence of the average particle radius obtained from above equation is shown in Fig. 4. The freshly prepared nanocrystal size is about 2.8 nm. Brus and Kayanuma pointed that nanocrystals are in strong confinement regime
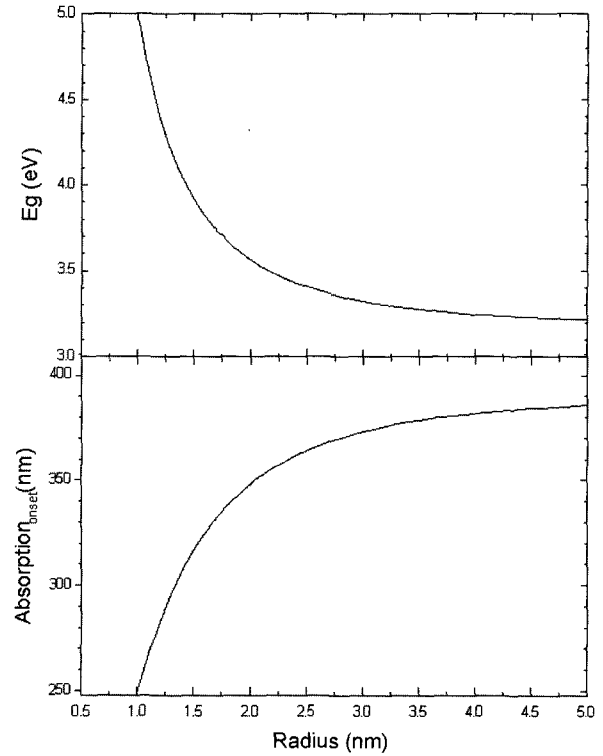
as $r < 2a_B$.[13,14] The Bohr radius, a_B, of the first excitonic state (n=1) is given by a_B=$\varepsilon h^2/.m^*e^2$.[15] The a_B is calculated to be 2.5 nm by using above equation. So the fresh nanocrystals are in strong confinement regime. The ZnO nanocrystals are rapidly grown below 4 nm in the particle size, and then the growth rate is slow down as the particle size increases. Acetate complexes present on the surface of ZnO chelates with Zn^{2+}, which stabilize the particle growth.[3] It is shown that the particle growth is greatly related to the concentration of precursor, surface properties, and temperature.[16]

In solution phase synthesis, process such as coarsening (also known as Ostwald ripening) and aggregation can compete with nucleation and growth in modifying the particle size distribution in the system. The time dependence of the r^3 is shown in the inset of Fig. 4. As can be seen, particle size increases rapidly during the early 150 min, indicating the rapid nucleation and growth of particles. Then the approximate linear region suggests that the increase of particle size is mainly determined by diffusion-limited coarsening. Coarsening process involves the growth of larger particles at the expense of smaller particles and would be governed by capillary effect. The growth law for
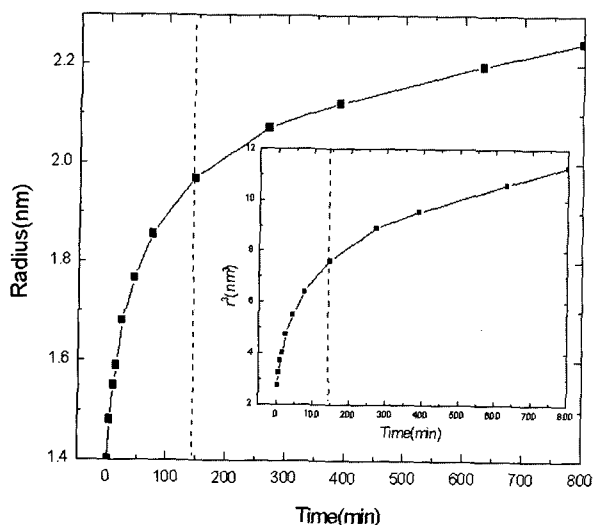
Fig. 4. Particles radius versus time for growth of ZnO nanocrystals aged at RT (inset is the curve of r^3 versus t).

coarsening is given by $r^3 - r_0^3 = kt$, where r and r_0 is the average and initial particle radius, respectively. The t is time and k is the rate constant.[10,16] From the slope of the linear region, we obtain the k value of $4.6 \times 10^{-3} nm^{-3} min^{-1}$. In addition, we found that aggregation influences the increase of particle size because the absorption onset shift decreases when diluting the colloids. However, further work would be needed to ascertain the growth processes of ZnO colloids.

4. Conclusion

We have synthesized stable transparent ZnO colloidal suspensions by a sol-gel route. The sizes of nanocrystals are about 2.8-4.5 nm. The absorption peak shifts to higher energy with decreasing the particle size due to quantum confinement effect, as well as with decreasing the

concentration. The growth of nanocrystals is controlled mainly by processes of coarsening and aggregation during the nucleation and growth. The average particle size as a function of aging time is determined from the absorption spectra. The freshly prepared nanocrystal size is about 2.8 nm. The band gap enlargement is pronounced for particle size below 3 nm.

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