

Synthesis and analysis of ZnO and CdSe nanoparticles

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Abstract. Zinc oxide and cadmium selenide particles in the nanometer size regime have been synthesized using chemical routes. The particles were capped using thioglycerol in case of ZnO and 2-mercaptoethanol in case of CdSe to achieve the stability and avoid the coalescence. Zinc oxide nanoparticles were doped with europium to study their optical properties. A variety of techniques like UV-Vis absorption spectroscopy, X-ray diffraction (XRD), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM) were used to carry out structural and spectroscopic characterizations of the nanoparticles.

Keywords. Nanoparticles; chemical capping; photoluminescence; doping.

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1. Introduction

Semiconductor nanoparticles is a very important topic in the ongoing research activity across the world. As the semiconductor particles exhibit size-dependant properties like scaling of the energy gap and corresponding change in the optical properties, they are considered as the front runners in the technologically important materials.

Zinc oxide is attracting tremendous attention due to its interesting properties like wide direct band gap of 3.3 eV at room temperature and high exciton binding energy of 60 meV. Zinc oxide is widely used in a number of applications like photocatalysis [1], gas sensors [2], varistors [3], low-voltage phosphor material [4] and so on. Recent prediction by Dietl *et al* [5] have increased the importance of transition metal-doped ZnO as a potential candidate in spintronics.

Cadmium selenide is another material which is technologically important. It shows a strong fluorescence which can be tuned according to the particle size. CdSe has been considered useful in many applications like optoelectronic devices [6], light sensors [7], biological labels [8], chemical libraries [9] etc.

A variety of techniques like spray pyrolysis, thermal decomposition, molecular beam epitaxy, chemical vapor deposition, laser ablation etc. have been widely used in the synthesis of nanomaterials and nanostructures. Chemical synthesis is one of the important techniques. It can be performed using a range of precursors and synthesis conditions like temperature, time, concentration of reactants etc. Variation of these parameters leads to different size selection and geometries of resulting particles.

We show here chemical routes to synthesize nanoparticles of ZnO and CdSe. Simple and inexpensive routes compared to those reported earlier have been devised. Thioglycerol was used as a capping agent in case of ZnO and 2-mercaptoethanol in case of CdSe nanoparticles. Synthesis route for ZnO was extended further to produce europium-doped ZnO nanoparticles. As europium has intense emission lines in the visible region (red), it is considered as an important red phosphor material.

2. Experimental

2.1 ZnO nanoparticles

Chemical synthesis of ZnO nanoparticles has mostly been tried in alcoholic media like ethanol, methanol or propanol. In alcoholic media growth of oxide particles is slow and controllable [10].

Different solutions were prepared by dissolving 0.2725 g of ZnCl₂ (10⁻¹ M, 20 ml), 0.4 g NaOH (10⁻¹ M, 100 ml) and X M (discussed later) thioglycerol in methanol. Thioglycerol (TG) solution was slowly added to NaOH solution while it was continuously stirred. The resulting solution was stirred for one hour before adding ZnCl₂ solution to it. After three hours of constant stirring a milky white solution was obtained. Size selective precipitation was carried out using acetone as a non-solvent. The precipitate was washed in methanol and methanol was allowed to evaporate at room temperature to obtain ZnO nanoparticles in white powder form. By changing the thioglycerol concentration we could vary the particle size from 2.6 nm to 3.3 nm. Water was added to increase the size further up to 4.0 nm.

To dope ZnO nanoparticles with europium, europium acetate was dissolved in 2 ml methanol and was added dropwise to the stirring solution of zinc chloride before addition of thioglycerol. Same procedure was followed further. By changing the concentration of europium acetate in the reacting solution we can change the doping percentage.

2.2 CdSe nanoparticles

Solution of cadmium acetate ((CH₃COO)₂Cd·2H₂O) was prepared by dissolving 0.5875 g of cadmium acetate dihydrate in 50 ml dimethyl formamide (DMF)

(equivalent to 2.2 mM) and stirred in ambient atmosphere. Mercaptoethanol solution of 0.25 ml (10^{-2} M) was mixed with constant stirring and then 0.0579 g of $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ (sodium selenite pentahydrate) dissolved in 8 ml water (0.2 mM) was added to the above solution. The resulting solution was stirred for 30 min and further refluxed for 3 h at $\sim 80^\circ\text{C}$ without stirring.

Size selective precipitation was carried out using acetone as a non-solvent. The resulting precipitate thus obtained was washed five times in methanol and then dried in vacuum to obtain CdSe nanoparticles (sample A) in powder form. CdSe (sample B) was synthesized using the above procedure except that concentration of 2-mercaptoethanol used was 10^{-1} M. Thus, size of the particles could be varied by changing the concentration of the capping agent.

3. Results and discussion

3.1 ZnO nanoparticles

In the present work we have synthesized ZnO nanoparticles in the quantum confinement regime. Direct band gap of 3.3 eV in case of bulk ZnO should give rise to an absorption edge at ~ 375 nm. However, as seen from figure 1 the absorption spectra for all the samples viz. ZnO-TG1 (10^{-2} M TG), ZnO-TG2 (10^{-4} M TG) and ZnO-TG3 (5×10^{-5} M TG) are not only blue-shifted with respect to 375 nm absorption wavelength expected for bulk ZnO but also exhibit sharp excitonic peaks. ZnO particle size was controlled using appropriate amounts of organic capping agent viz. thioglycerol. The blue-shift of all these spectra clearly indicates that particles smaller than 5.0 nm have been achieved. A deliberate addition of water was made to increase the particle size. Spanhel *et al* [11] have used this approach earlier. In figure 1 optical absorption spectra for ZnO-WT1 (10% water) and ZnO-WT2 (50% water) also are shown. Shift in excitonic peak due to addition of water is quite clear. Sharp absorption edges and well-developed excitonic peaks further indicate that synthesized particles are rather monodispersed.

The scaling of energy gap with particle size has been explained in the effective mass approximation [12] as well as tight-binding approximation [13]. The particle sizes calculated for the samples ZnO-TG1, ZnO-TG2 and ZnO-TG3 using effective mass approximation (EMA) are 2.6, 3.0 and 3.3 nm respectively and that for ZnO-WT1 with excitonic peak at 332 nm and for ZnO-WT2 with peak at 340 nm are 3.6 and 4.0 nm respectively. Synthesized particles are found to be stable over a long time.

X-ray diffraction analysis (not shown here) of the samples showed that the particles have a wurtzite structure. Figure 2 shows the TEM photograph for ZnO-TG3 sample along with electron diffraction pattern. Particles with ~ 3.8 nm size can be seen. This size is close to that estimated using EMA. Diffraction pattern shown at the right-hand top corner depicts hexagonal symmetry in agreement with XRD results. Two of the particles seen in figure 2 are (101) oriented. Lattice spacing of 0.252 nm, measured from TEM, is slightly larger than 0.248 nm for (101) plane in ZnO. Third particle clearly shows hexagonal plane.

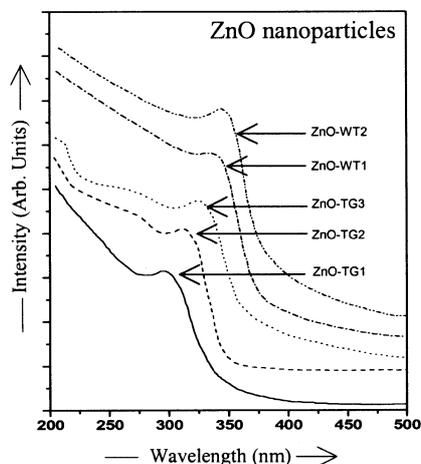


Figure 1. UV-Vis absorption spectra for ZnO nanoparticles.

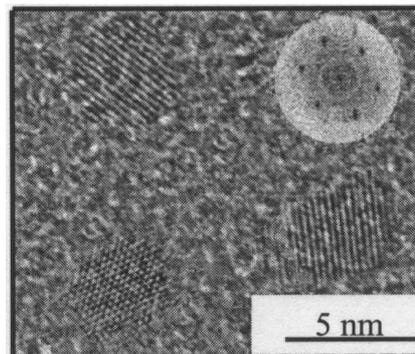


Figure 2. High resolution transmission electron micrograph of ZnO nanoparticles.

Presence of TG could be detected by performing FTIR spectroscopy (not shown here). Comparison of spectrum due to thioglycerol with those of TG-capped ZnO clearly indicates the presence of thioglycerol on the nanoparticle surfaces. It appears that Zn-S or Zn-O bonds are also present, given by the peak at $\sim 390\text{ cm}^{-1}$.

The synthesis method could be extended to dope europium at room temperature during the synthesis of ZnO nanoparticles. Photoluminescence from ZnO nanoparticles doped with Eu was studied. A broad peak at 517 nm was observed which is caused by defect level, occurring mainly due to oxygen vacancies in the bulk of nanoparticles (deep-trapped hole) and excess oxygen on the surface, which might be in the form of OH^- ions [14]. After annealing at 150°C , the intensity of the broad emission band at 517 nm decreases and two weak bands around 590 and 615 appear. These bands are characteristic emissions due to Eu^{3+} corresponding to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions respectively [15,16]. Thus it is possible to dope ZnO nanoparticles with Eu by the chemical route described here. It will be interesting to study further whether europium ion is incorporated at a substitutional site or present on the surface of the particle using a technique like extended X-ray absorption fine structure (EXAFS). The synthesis method described here can also be extended to produce high quality ZnO nanoparticles doped with other transition and rare earth ions.

3.2 CdSe nanoparticles

Figure 3 shows UV-Vis absorption spectra of the thiol-capped samples. The samples show excitonic peaks at 360 nm (sample A) and 385 nm (sample B) respectively. For bulk CdSe, direct band gap is 1.74 eV. An absorption peak for CdSe is therefore expected at $\sim 716\text{ nm}$ [17]. Thus there is a strong blue-shift in the absorption spectra for both the samples A and B, indicating that particles must be smaller than the Bohr radius of exciton which is 5.4 nm for CdSe [18].

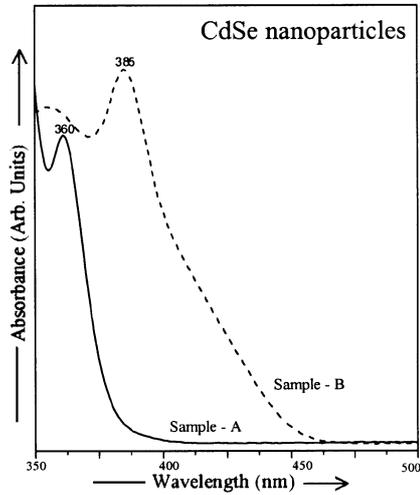


Figure 3. UV-Vis absorption spectra for CdSe nanoparticles.

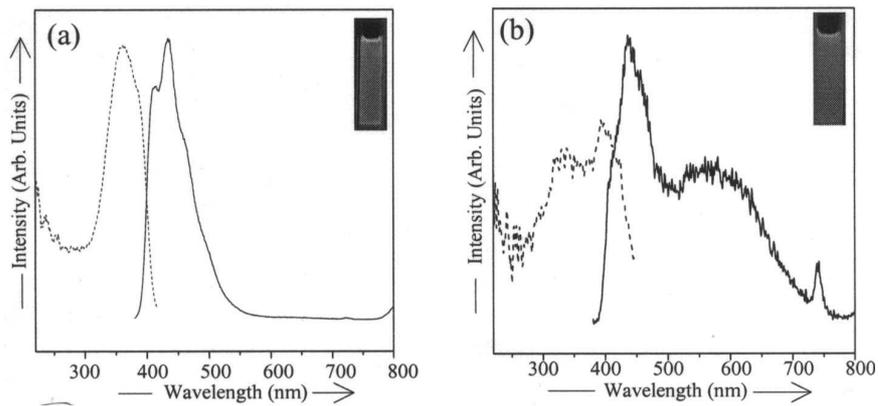


Figure 4. Photoluminescence spectra for CdSe nanoparticles: (a) Sample A (inset shows blue luminescence as seen under UV light). (b) Sample B (inset shows red luminescence as seen under UV light).

Using the effective mass approximation (EMA) [12], the particle size calculated turns out to be ~ 2.8 nm (sample A), and ~ 3.7 nm (sample B) respectively. (The constants used are $m_e = 0.13$, $m_h = 0.6$ and $\epsilon = 6.1$ [18].)

From X-ray diffraction pattern (not shown here), average sizes of the thiol-capped nanoparticles as calculated using the Scherrer formula were ~ 2.4 nm (sample A) and 3.1 nm (sample B). The structure determined by comparing with JCPDS data (8-459) is hexagonal (wurtzite).

Figure 4a depicts the photoluminescence spectra, for sample A, while figure 4b shows the PL spectra for sample B. The excitation wavelength was $\lambda_{ex} = 362$ nm, for CdSe sample A showing blue luminescence (see the inset). Emission spectrum

exhibits a sharp peak at 435 nm and a weak peak at ~ 414 nm. In case of sample B showing red luminescence (see the inset) the excitation wavelength was $\lambda_{\text{ex}} = 371$ nm. Emission spectrum exhibits broad peak at 581 nm which may be due to the formation of defect levels, along with peak at 437 nm.

4. Conclusion

Nanoparticles of zinc oxide and cadmium selenide were synthesized using simple chemical routes. Stability of the particles was achieved by thiol capping. Synthesis method for ZnO particles was further extended to dope these particles with europium. CdSe particles were found to be highly luminescent.

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