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Synthesis of CdSe nanoparticles by solvothermal route: Structural, optical and spectroscopic properties

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ABSTRACT

We have developed successfully the synthesis of highly yielded CdSe nanoparticles (NPs) at 60 ^{0}C by solvothermal route in which the cadmium and selenium precursors have been dissolved in deionized water, ethylene glycol and hydrazine hydrate. This route is very facile, inexpensive and less hazardous and ensures almost complete yield of the precursors. The powder product was well characterized by powder X- ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), UV-Vis spectroscopy, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) .It is investigated that as synthesized powder has a hexagonal (Wurtzite) structure of CdSe with diameters of the particles are in the range of 10-15 nm. The formation mechanism is also discussed. Copyright © 2012 VBRI Press.

Keywords: Nanoparticles; chemical synthesis; electron microscopy; X-ray diffraction; optical properties.

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Introduction

Nanostructured materials have attracted a great transaction of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. Owing to the quantum size effects and surface effects, nanoparticles can display novel optical, electronic, magnetic, chemical and structural properties that might find many important technological applications. An extremely active and prolific field in nanomaterials is finding ways to control size and morphology of the nanoparticles since the properties and applications of the nanoparticles are largely dependent on their size and morphology. The most evident manifestation of properties is the optical light emission in the blue–red spectral region characterized by a blue shift at smaller crystallite dimensions [**1**]. Such properties construct semiconducting nanostructures suitable for several kinds of applications, from anti reflecting coatings [**2**] to biomolecular detection [**3**] and light emitting devices [**4**]. In the past decade, II–VI semiconductor nanoparticles attracted much attention because of their size-dependent (and thus tunable) photo- and electro-luminescence properties and promising applications in optoelectronics. Among the family of II–VI semiconductors, ZnS [**5, 6**], CdS [**7**], ZnO [**8**], CdSe [**9**], are the foremost candidates since of their favorable electronic and optical properties for optoelectronic applications. In particular CdSe quantum dot (QD) is an important II–VI semiconductor having a wide optical band gap, making it a very attractive material for optical applications, especially in nanocrystalline form. CdSe can have two different crystal structures cubic zinc blende and hexagonal wurtzite and a direct band structure. CdSe quantum dots of appropriate size can have an absorption edge and emission peak anywhere in the visible spectrum. This led to CdSe nanoparticles to be used for opto-electronic devices, laser diodes, nanosensing and biomedical imaging [**10**].

In 1D nanostructure synthesis, solvothermal processes have emerged a powerful tool for the fabrication with some significant advantages, such as controllable particle size and low temperature, cost-effective and less-complicated techniques. Semiconductor nanocrystals are of great interest because of their quantum confinement effect. Among them, CdSe nanocrystals with uniform shape and size have been deeply and methodically researched not only because their synthesis was a milestone in the history of colloid nanocrystals [**11**] but also their unique properties in superlattices [**12**], core/shell structures [**13**], light-emitting diodes [**14**], solar cells, photoluminescence [**15**] and biological labels [**16**]. Compared with the conventional dyes, CdSe-based colloidal nanoparticles render higher photostability, their emission is narrow ensuring no crosscoupling of signals and numerous colors can be excited by a single source allowing for multiplex detection. Therefore, it is a great challenge for the chemists to prepare CdSe nanocrystals and solve the problem of toxicity, biocompatibility and water solubility [**17**].

There are several methods involving many variables for the synthesis of CdSe QDs and are based on highly toxic Cd and Se ingredients. There are reports on room temperature synthesis of CdSe nanoparticles involving costly and hazardous techniques with or without surfactant/stabilizing reagents [**18-20**]. Recently, we have developed a general low temperature, facile aqueous solution-phase strategy to grow nanostructured metal chalcogenides which is low cost and less hazardous [**21-24**].

We report one-pot, template free, single step, straight-forward, simple and environmental friendly solvothermal technique for synthesis of CdSe nanoparticles. It has to guarantee a production of nanoparticles with high quality (a narrow size distribution and a high quantum yield) and desired sizes. Less hazardous aqueous solution process for the preparation of hexagonal (wurtzite) CdSe nanoparticles in ethylene glycol and hydrazine hydrate using cadmium chloride as a precursor is described. The present study tries to satisfy all of these requirements to the large-scale production of CdSe nanoparticles.

Experimental

Synthesis of CdSe nanoparticles

In the typical synthesis of CdSe, highly pure $CdCl_2$ powder (99.9%) and elemental Selenium (99.999%) purchased from Alfa was used without further purification. Ethylene glycol and Hydrazine hydrate purchased from Loba pvt. Ltd., Germany. In this synthesis process, $CdCl_2$ (4.0 g) and elemental selenium (2.0 g) was taken with deionized water, ethylene glycol and hydrazine hydrate in the volume ratio of 7:3:1 respectively in a 200 ml capacity conical flask. Then, the solution was refluxed under vigorous stirring at 60°C for 6 hrs. The black precipitates was collected and washed with anhydrous ethanol and hot distilled water several times, then dried in vacuum at 50°C for 5 h.

Characterizations of CdSe nanoparticles

The X-ray diffraction pattern of as synthesized, freshly dried CdSe powder was recorded by Rigaku Rotoflux rotating anode diffractometer (operating at 40 kV, 100 mA) with Cu-K_α radiation (wavelength 1.54Å).Scanning electron microscopy (SEM) was applied to investigate the size and morphology, which was carried out with a scanning electron micro-analyzer using a JEOL-JSM6700 microscope, operating at 10 A and 15 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) investigations were carried out using a Tecnai $20G^2$-TEM, employing 200 kV typical e-beam voltage using JEOL-JSM-5600.UV–Visible spectra was recorded by UV-Vis160 Spectrophotometer (Shimadzu, Japan) in the spectral range between 200 and 800 nm using a spectral bandwidth of 1nm absorption, experiments were performed at room temperature. The Raman spectra were measured using a 514.5 nm Ar-ion laser excitation by Renishaw, micro-Raman (RM 2000) model. Fourier transform infrared spectroscopy (FTIR) analysis has done using Jasco-5300 (Japan) Fourier transform infrared spectrometer at room temperature with the sample milled in KBr.

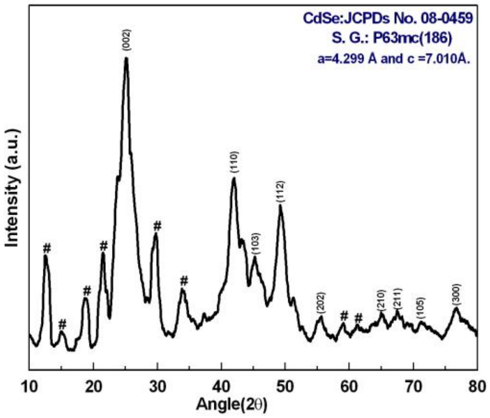

Fig. 1. Powder X-ray diffraction pattern of as synthesized CdSe NPs at 60 °C. The peaks marked by # correspond to impure phase of CdSe.

Results and discussion

X-ray diffraction pattern of the as prepared CdSe sample is shown in **Fig. 1**. The XRD measurements of CdSe nanoparticles shows that the position of several diffracted peaks match well with the standard powder diffraction data (a = 4.299 Å and c = 7.010 Å). The several peaks of CdSe have been obtained due to diffraction form (002), (110), (103), (112), (202), (210), (211), (105) and (300) planes of Hexagonal (Wurtzite) CdSe which are in very good agreement with hexagonal (P63mc) structure (Joint

Committee on Powder Diffraction Standards) JCPDS CAS No. 08-0459 (a = 4.299 Å and c =7.010 Å). Some additional peaks are also observed in the XRD pattern due the presence of other phase in our sample. Pure and single phase CdSe has not been successfully obtained under the present conditions. The size of the nanocrystallites was estimated using the Debye-Scherrer formula:

$$A = \frac{0.94\lambda}{\beta Cos\theta} \quad (1)$$

where, *A* is coherence length, β is the full-widths-at-half maximum (FWHM) of the diffraction peak, *λ* (1.5418 Å) is the wavelength of X-ray radiation, and *θ* is the angle of diffraction. From different *θ* values, the calculated average particle size is about 15 nm. Inherent stress inside a nanocrystal could contribute to broadening of the XRD peaks.

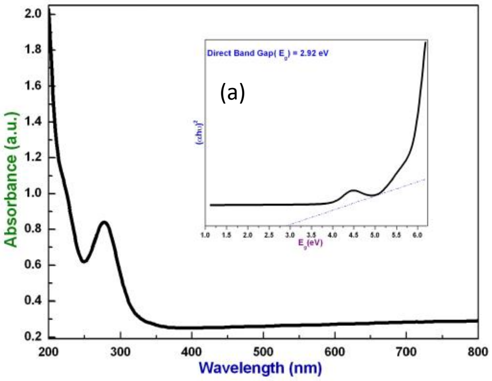

Fig. 2. Absorption spectra of CdSe NPs at room temperature and (a) The variation of $(\alpha h\upsilon)^2$ versus hυ for direct band gap calculation of CdSe sample.

UV-Vis. absorption spectrum of CdSe NPs is shown in **Fig. 2**.The absorption spectra of the CdSe NPs were considered without taking into account the reflection and transmission losses. It is a useful absorption characterization to analyze nanomaterials. The absorption spectroscopy is very useful to calculate the optical band gap (E_g). From the classical relationship of near edge optical absorption of semiconductors:

$$\alpha = \frac{k(h\nu - E_g)^{\frac{n}{2}}}{h\nu} \quad (2)$$

where k is constant , E_g is the optical band gap and n is a constant equal to 1 for direct band-gap semiconductors. The plot of $(\alpha h\nu)^2$ vs. hν is shown in **Fig. 2(a)**. Extrapolating the straight line of this plot for zero absorption coefficient it gives the direct band gap of NPs which is shown in **Fig. 2(a)**. The direct band gap energy (E_g) of CdSe NPs was found to be 2.92 eV that represent the 'blue shift' of 1.82 eV from standard bulk band gap (E_g = 1.10 eV). The blue shift might be caused by nanosize effect and structural defects of nanocrystals.

TEM images are shown in **Fig. 3 (a)**; indicate the high-yield growth feature of as synthesized CdSe NPs by solvothermal route. On the basis of the TEM images of the NPs, it can be revealed that the morphology of the CdSe NPs is not uniform and contains many small irregular NPs with the average size ranging from 10-15 nm, **Fig. 2** shows selected area electron diffraction (SAED) pattern of as synthesized CdSe NPs which shows the polycrystalline nature. HRTEM image of nanoparticles in **Fig. 3(c)** confirm that the NPs are crystalline in nature. The average size of the particles is about 15nm, which is in very good agreement with value obtained from XRD.SEM images of as synthesized CdSe NPs are shown in **Fig. 3(d)** which shows that the particles are well agglomerated.

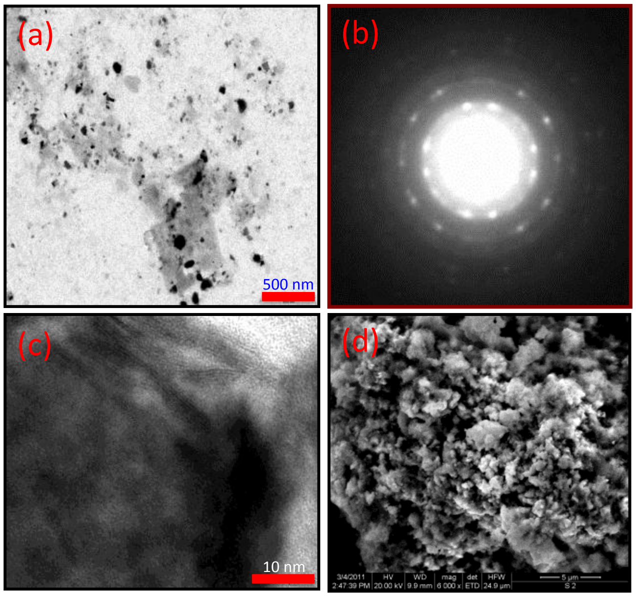

Fig. 3. (a) TEM micrograph (b) SAED pattern shows polycrystalline nature (c) HRTEM micrograph and (d) SEM micrograph of as synthesized CdSe NPs.

Raman scattering spectroscopy is a powerful characterization for the study of the different modes of as synthesized CdSe nanoparticles. For Raman measurements, the spectrum was taken at room temperature in backscattering configuration excited by Ar^+ laser at wavelength IR (λ_{exc}) = 514.5 nm (2.41 eV) for which our synthesized sample CdSe is transparent. The out coming beam is focused through a microscope objective on CdSe samples in 1 µm circular spot with power density 50 kW/cm^2. Raman spectrum is recorded at a fixed power level. Sample damage is avoided under such measurement conditions.

Fig. 4 shows a typical Raman spectrum of CdSe NPs in the range from wavenumber (ν) 150 to 550 cm^{-1}. An overview Raman spectrum of the CdSe NPs under study whose peaks are related to scattering by the longitudinal optical (LO) phonon and its first overtone (2LO) are observed near ν_{LO} = 200 cm^{-1} and ν_{2LO} = 400 cm^{-1}, respectively. The observation easy to make from fig. 4 is that the LO peak for λ_{exc} =514.5 nm is several wavenumber lower than that of bulk CdSe (ν_{LO} = 210 cm^{-1}, indicated by a dashed line in the **Fig. 4**). This shift is an indication of the phonon confinement (PC) effect in the present NPs, in accordance with a number of earlier experiments [**25-28**].

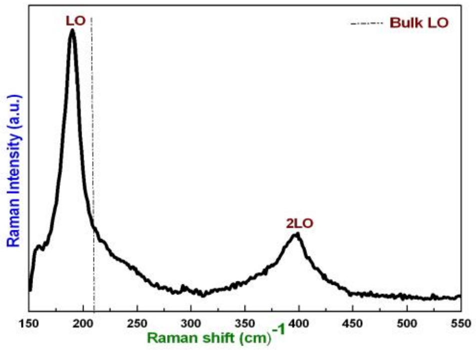

Fig. 4. Raman spectra of the CdSe NPs in the region of the LO and 2LO phonons at λ_{exc}= 514.5 nm. The dashed line shows the position of the LO peak for bulk CdSe.

A simple way to take into account the PC effect on phonon spectra of NPs was proposed by Richter [**29**] within a simple spatial correlation model, being in use until now with some modifications [**30-32**]. Later, a rigorous continuum theory [**26, 33, 34**] and microscopic lattice dynamics calculations [**35**] were applied considering discrete confined optical vibrational modes (vibrons), with the dominant contribution to the resonant Raman spectrum of the modes [**34**]. Any PC model employs the phonon dispersion of the bulk material to predict the ν_{LO} in NPs.

Fig. 5 shows the FT-IR spectrum of as-prepared CdSe NPs. Initially, the sample was washed with absolute ethanol and hot distilled water several times and then dried in a vacuum. We determined the IR absorption of the obtained CdSe powder with KBr. From the **Fig. 5**, it can be seen that the broad peak at 3448 cm^{-1} is assigned to –OH stretching intra molecular hydrogen bonds due to the small quantity of H_2O on the sample. N-H stretching vibration peak is observed at 3282 cm^{-1} due to the presence of hydrazine hydrate in our sample. The peak observed at 1602 cm^{-1} is assigned to OH of water absorbed from the molecular precursors. C-N stretching vibration peak is positioned at 1142 cm^{-1} is due to the interaction of ethylene glycol with the hydrazine hydrate and regular periodic structure of molecular precursors.

The exact mechanism for the formation of CdSe nanoparticles is still unclear, but it is reasonably concluded that the appropriate ratio of solvents volume may play the significant role for the formation of CdSe NPs. On the basis of the above observations, a growth mechanism of the CdSe NPs is proposed. In the present work, Se source can be easily converted into Se^{2-} by N_2H_4, which results in a high monomer concentration. In the initial step, hydrazine hydrate ($N_2H_4.H_2O$) complexes with Cd^{2+} and forms the transparent soluble complexes solution, which effectively decreases the concentration of Cd^{2+} and avoids the precipitation of $CdSeO_3$, and thus provides a more homogeneous solution environment for the reaction. The chemical reaction involved in the entire synthesis of CdSe NPs could be formulated as the following:

$$2Se + N_2H_4 + 4OH^- \longrightarrow 2Se^{2-}\downarrow + N_2 + 4H_2O$$

$$2Cd^{2+} + 4OH^- \longrightarrow 2CdO + 2H_2O$$

$$CdO + Se^{2-} + H_2O \longrightarrow CdSe\downarrow + 2OH^-$$

$$2Cd^{2+} + 6OH^- \longrightarrow 2Cd(OH)_3^-$$

$$Cd(OH)_3^- + Se^{2-} \longrightarrow CdSe\downarrow + 3OH^-$$

So, the application of N_2H_4 as the coordination agent is determinable for this phase of the products. Thus, it can be drawn that the complexing ability of groups containing atom N (such as NH_2 or NH_3) can effectively determine the final phase of the products. Compared with the CdO deposit, it is easier for $Cd(OH)_3^-$ to release Cd^{2+}, which can facilitate growth of nanoparticles under nonequilibrium kinetic growth conditions with a high monomer concentration. A similar phenomenon was found during preparation of PbSe and Cu_2Te nanostructures using $N_2H_4.H_2O$ as complexing agent and the exact mechanism was fully understood [**21, 36**].

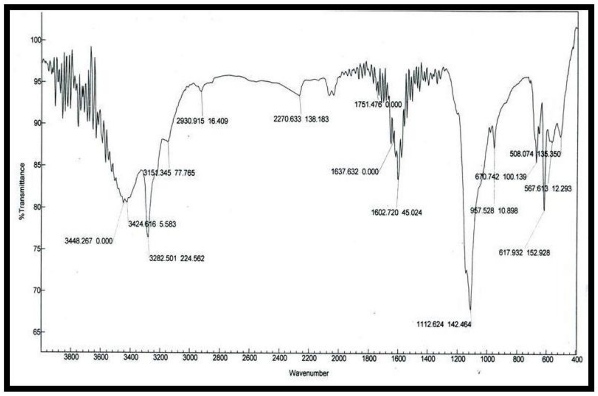

Fig. 5. FT-IR analysis of as prepared CdSe sample milled in KBr at room temperature

Conclusion

In conclusion, a facile and general solvothermal route has been successfully established to synthesize hexagonal (wurtzite) CdSe nanoparticles in the presence of hydrazine hydrate and ethylene glycol at 60^0 C. This route is simple, convenient, less hazardous and inexpensive than hydrothermal route, microwave-assisted method, electrodepositing method etc. We have synthesized CdSe nanocrystals with an average particle size 15 nm at low temperature. The longitudinal optical (LO) phonon and its first overtone (2LO) are also observed near ν_{LO} = 200 cm^{-1} and ν_{2LO} = 400 cm^{-1}, respectively. The experimental results revealed that hydrazine hydrate played multiple roles in the formation of CdSe NPs, it served not only as reduction agent which helps to dissolve Se in the mix solvent but also as a complexing agent, reaction controller and as the stabilizing agent. The UV-Vis spectra shows that the direct band gap of the CdSe NPs were 2.92 eV.

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