

Shape evolution of CdSe nanomaterials in microheterogenous media

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ABSTRACT

Cadmium selenide, CdSe nanomaterials were synthesized in microheterogenous media consisting of *water-in-oil* type microemulsions using the surfactant, cetyl trimethyl ammonium bromide (CTAB) and cyclohexane as the oil, under two different experimental conditions. In one set of experiments, the synthesis was carried out by normal chemical route at room temperature, named as green chemistry route. In another set, the synthesis was carried out through radiation-chemical route using 7 MeV electron beam using a linear electron accelerator (LINAC). In the previous case, the shape of CdSe nanomaterials was found to evolve from isotropic spherical to anisotropic rod like structures in lower w_0 microemulsions with time. Similar observations were obtained in the case of CdSe nanomaterials synthesized *via* electron beam irradiation. The photoluminescence was found to be different in the CdSe nanomaterials formed by these two different routes. In the former case, the band gap photoluminescence was observed from the immediately produced nanomaterials, however with aging after a day there were two distinct band gap photoluminescence as well as trap state photoluminescence observed at room temperature. On the contrary, in the case of electron beam induced CdSe nanomaterials the trap state photoluminescence was always dominating irrespective of the aging. Copyright © 2013 VBRI press.

Keywords: Shape; CdSe nanomaterials; CTAB microemulsion; electron beam irradiation; green chemistry.



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Introduction

II–VI quantum dots and their related nanostructures have numerous potential applications in optoelectronics, quantum dot lasers, and bio-labeling [1,2]. Cadmium selenide (CdSe), which is a band gap material with an energy band gap of 1.75 eV at 300 K, is one of the most important II–VI semiconductors. This material has been widely used for optoelectronic devices [3,4]. In the past decade, lot of research has been done on controlling the size, shape and crystal structure as these affect their optical properties [5,6]. The optical properties of the semiconductor nanomaterials can be tuned by the band gap engineering, which could be achieved by varying their shapes and size. The tuning of photoluminescence in CdSe nanoparticles has been reported earlier by controlling the surface states [7,8].

Several methods including normal chemical route, electrochemical, photochemical, radiation-chemical, etc have been employed for their synthesis in condensed phase. Radiation-induced synthesis of nanomaterials has been an extensively used method for its simplicity and effectiveness. In this process, the synthesis in the aqueous media mainly proceeds through the reaction of the solvated electrons, e_{aq}^- , with the precursor ions [9–11]. Nanomaterials of different shapes and sizes have been synthesized earlier *via* radiation-chemical routes in aqueous and non-aqueous media using different templates. Several stabilizing agents have been reported in the literature, including various surfactants, organic or inorganic polymers, thiols, amines and polyphosphates [12–14]. The use of *water-in-oil* (w/o) microemulsions has proved to be a powerful way to synthesize and stabilize size-controlled nanoparticles [15,16]. Water droplets inside the microemulsions can be considered as nano-reactors for the controlled growth and nucleation of nanoparticles [17]. Therefore, controlling the structure and dynamics of microemulsions, one can effectively manipulate the size and shape of nanoparticles. Using *water-in-oil* type of microemulsions, we have earlier reported the synthesis of CdSe nanomaterials by chemical as well as radiation chemical routes [18,19].

Experimental

Reagents

High purity chemicals, cyclohexane, n-butanol (spectroscopic grade), cadmium sulfate, sodium sulfite and selenium powder were obtained from Sigma-Aldrich and were used without any further purification. Cetyl trimethyl ammonium bromide (CTAB), was from Sigma-Aldrich, was recrystallized twice from ethanol. Ammoniated cadmium sulfate, $(Cd[NH_3]_4SO_4)$ solution was used as cadmium precursor. Sodium selenosulfate, Na_2SeSO_3 solution was used as the selenium precursor, which was prepared by the reported procedure. To prepare the microemulsion, 0.1 mol dm^{-3} CTAB was added to cyclohexane and 1-butanol was added to this solution to achieve a 1-butanol/surfactant ratio of 5:1. Water was added to this system to obtain w_0 values of 20, 30 and 40. The samples were sonicated or vigorously shaken as and

when required to obtain a homogeneous and transparent solution adequate for optical absorption measurements.

Chemical synthesis of CdSe nanomaterials

The concentrations of the stock precursors used in the synthesis were 100 and 150 mM. Equimolar precursors were added in nanopure water obtained from a Millipore water purifying system. This solution was used to make the water pool inside the reverse micelle for the water-in-oil microemulsion. The microemulsions containing the precursor solutions inside the water pool were kept at constant stirring for about 2 hrs [18]. The colorless microemulsion transformed into greenish yellow or light orange color after 2 hrs depending on the experimental parameters variations and this sol was used for the further studies.

Electron beam induced synthesis of CdSe nanomaterials

The concentrations of the stock precursors used in the synthesis were 10 mM. Equimolar precursors were added in nanopure water obtained from a Millipore water purifying system. This solution was used to make the water pool inside the reverse micelle for the water-in-oil microemulsion. The microemulsions containing the precursor solutions inside the water pool were irradiated with $2 \mu\text{s}$ electron pulses obtained from a 7 MeV linear electron accelerator (LINAC) with rep rate of 12.5 pps with a total absorbed dose of about 25 kGy [19]. The colorless microemulsion transformed into greenish yellow or light orange color after irradiation and this sol was used for the further studies.

Characterization of CdSe nanomaterials

The optical absorption spectra were recorded at room temperature using a Jasco V-650 absorption spectrophotometer. Photoluminescence (PL) studies were performed using a Hitachi model 6526 Fluorescence spectrometer at room temperature. The high-resolution transmission electron microscopy (HRTEM) measurements were carried out on model number FEI, TECNAI-F30. Samples for TEM measurements were prepared by depositing a drop of the above sol on thin carbon coated copper grid and allowing the solvent to evaporate.

Results and discussion

CdSe nanomaterials through chemical synthesis

The synthesis of CdSe nanomaterials was carried out in microheterogeneous media such as *water-in-oil* type of microemulsions with lower water content, ($w_0 \leq 20$). The microemulsions containing the precursor solutions turned greenish yellow color after stirring for about 2 hrs at room temperature. Further, it was noticed that the sols were stable at normal laboratory conditions. We have previously reported the chemical synthesis of CdSe nanoparticles from the mixtures of these precursors [18]. Therefore, the CdSe nanomaterials are formed inside the water pool of microemulsions only; as the precursors are in the aqueous phase [20] and the size of these nanoparticles should be limited by the size of the water pool. The TEM image of immediate synthesized CdSe nanomaterials (Fig.1a)

showed the formation of isotropic homogeneous spherical shaped nanomaterials. They have strong absorption peak at 525 nm as seen in the absorption spectra shown in **Fig. 2**. The room temperature PL peak was seen at 500 nm with hump at 560 nm (**Fig. 3**) indicating that the band gap PL (BG-PL) dominates over trap state PL (TS-PL). The as-grown CdSe nanoparticles were allowed to age for 1 day and then all these measurements were performed, which was quite different from those obtained from the immediately prepared sols.

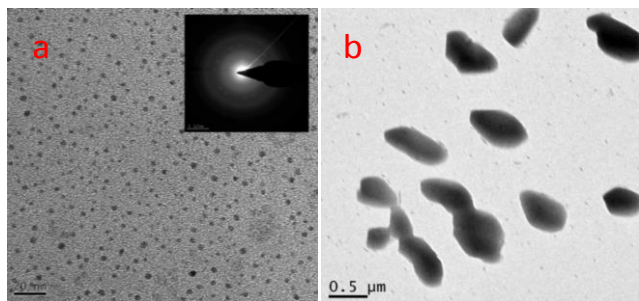


Fig. 1. TEM images of CdSe nanoparticles synthesized at room temperature in microemulsion of $w_0 = 20$ and stock precursor concentration = 100 mM taken (a) immediately (b) after 1 day.

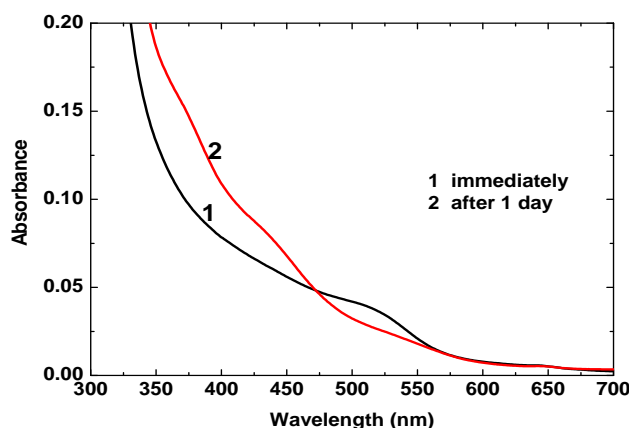
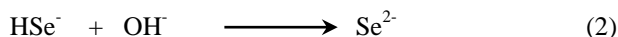
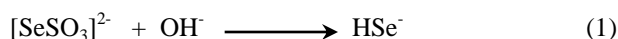


Fig. 2. Optical absorption spectra of CdSe nanoparticles synthesized at room temperature in microemulsions of $w_0 = 20$, stock precursor concentration = 100 mM, recorded at different time intervals.

The formation mechanism of CdSe nanoparticles, $(\text{CdSe})_{\text{np}}$, through the chemical route in alkaline aqueous environment is given below [21]:



The formation of anisotropic rod shaped CdSe nanomaterials were confirmed from the TEM images (**Fig. 1b**). Absorption peak was slightly red shifted (**Fig. 2**) and room temperature PL peak was observed at 560 nm with hump at 500 nm (**Fig. 3**) indicating TS-PL dominates over BG-PL. This could be attributed to change in shape of nanomaterials with time which are known to change their optical properties. This study was limited to the *water-in-*

oil type microemulsions with lower w_0 values compare to other report where shape changes were observed with increase in w_0 values [18, 19].

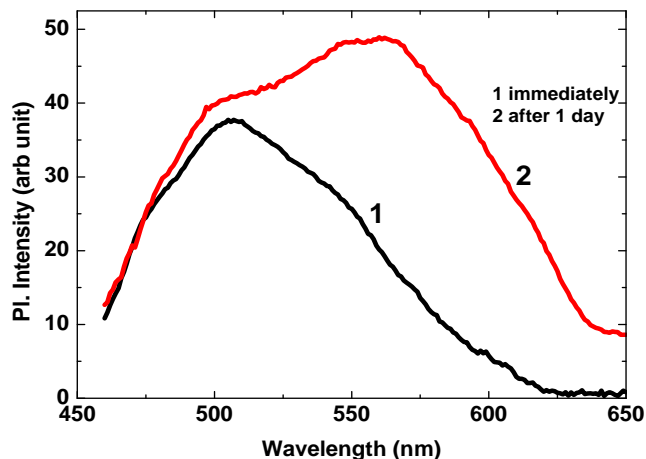
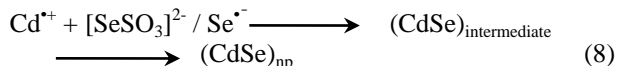
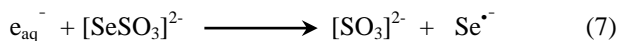
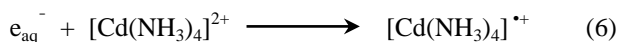
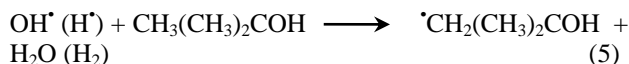
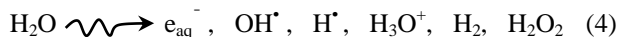


Fig. 3. Photoluminescence spectra of CdSe nanoparticles synthesized at room temperature in microemulsions of $w_0 = 20$, stock precursor concentration = 100 mM, recorded at different time intervals.

CdSe nanomaterials through electron beam irradiation

Similarly, the synthesis of CdSe nanomaterials was carried out in microheterogeneous media such as *water-in-oil* type of microemulsions with lower water content, ($w_0 < 20$) and irradiated using a 7 MeV electron accelerator. Water radiolysis yields three major primary radical species, e_{aq}^- , OH^\cdot and H^\cdot , out of which e_{aq}^- and H^\cdot are reducing and OH^\cdot is oxidizing in nature [22]. Tert-butanol ($\text{CH}_3(\text{CH}_3)_2\text{COH}$) is added to the aqueous solution to scavenge the $\text{OH}^\cdot/\text{H}^\cdot$ radicals and leaving behind the hydrated electrons, e_{aq}^- in the solution. This can be called as a perfectly reducing condition where the reduction is occurred mainly *via* the e_{aq}^- radicals. These hydrated electrons then react with the precursor ions to form CdSe nanomaterials [23,24]. Following are the various important reactions pertinent to the above conditions.

Radiolysis of water:



The radiolytic products are CdSe nanomaterials, evidenced by the instantaneous change of colorless microemulsion to the greenish-yellow color upon irradiation, which confirms our previous report [19]. However, these CdSe nanomaterials were less stable in

ambient condition as compared to nanomaterials synthesized by green chemistry route discussed in the previous section. The TEM image (Fig. 4a) of the immediately prepared CdSe sols showed isotropic spherical shaped nanoparticles (of size less than 5 nm) agglomerated to relatively bigger sizes. The optical absorption spectra of the same had strong absorption peak at 450 nm as shown in Fig. 5.

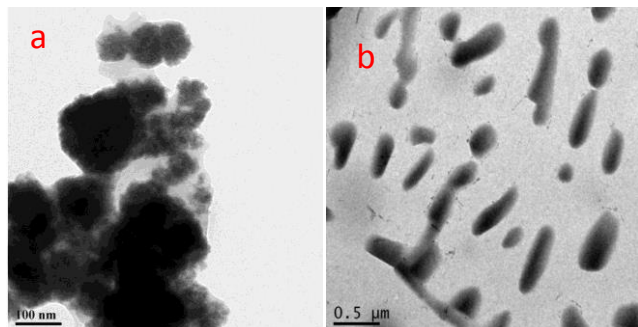


Fig. 4. TEM images of CdSe nanoparticles synthesized via electron beam irradiation in microemulsion of $w_0 = 10$ and stock precursor concentration = 10 mM taken (a) immediately, (b) after 1 day.

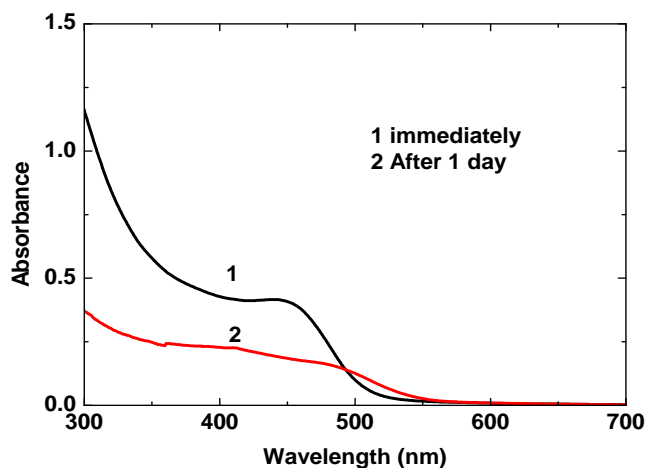


Fig. 5. Optical absorption spectra of CdSe nanoparticles synthesized via electron beam irradiation in microemulsions of $w_0 = 10$, stock precursor concentration = 10 mM, recorded at different time intervals.

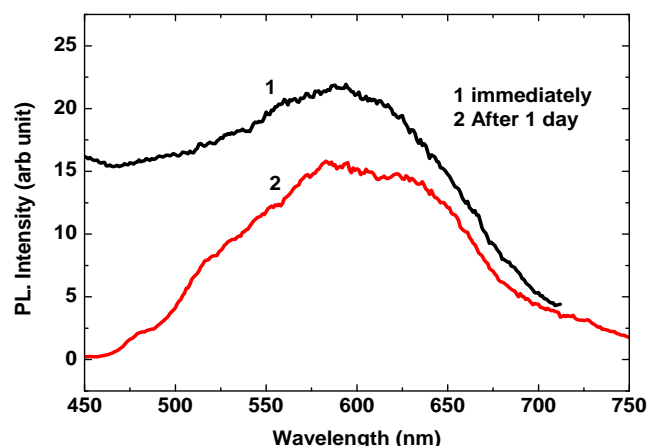


Fig. 6. Photoluminescence spectra of CdSe nanoparticles synthesized via electron beam irradiation in microemulsions of $w_0 = 10$, stock precursor concentration = 10 mM, recorded at different time intervals.

The room temperature PL peak was at 600 nm with hump at 525 nm (Fig. 6) showing TS-PL dominates over BG-PL. The sols were allowed to age for about 24 hours. After a day, the TEM image (Fig. 4 b) confirmed the formation of rod shaped CdSe nanomaterials. Absorption peak was also slightly red shifted as seen in Fig. 5. The room temperature PL peak was at 600 nm with hump at 525 nm (Fig. 6) showing that the TS-PL dominates over BG-PL which was further dominated with aging. This observation was quite different from that obtained from the green chemistry route. This could be due to related to their internal structure and the defect density. It is well known that the nanomaterials formed by the radiation-chemical route utilizing high-energy electron beam in a LINAC, have a disordered structure with low crystalline and high amorphous nature and high defect density [9,10,24]. On the contrary, those formed by normal chemical route (green chemistry) are of more crystalline and have less defect density. Therefore, the observed photoluminescence behavior in the present case might be arising due to these above-mentioned properties of the CdSe nanomaterials.

Conclusion

We have successfully synthesized CdSe nanomaterials, which exhibited a slow evolution in shape leading to rod-shaped structures with time, in microheterogeneous medium such as *water-in-oil* type microemulsions with lower water content ($w_0 \leq 10$) by two different routes, green chemistry and electron beam irradiation. In both the cases the immediately formed CdSe nanomaterials transformed to rod shaped structures with aging for a day. Those formed by green chemistry route exhibited higher band gap photoluminescence as compared to trap state photoluminescence at an early time. However, this observation was reversed when the measurements were taken after a day. In the case of CdSe nanomaterials formed by electron beam irradiation, trap state photoluminescence was observed at an early time, which almost remained unchanged when the measurements were taken after a day. This was attributed to the structure of immediately formed and aged CdSe nanomaterials. The rod shaped structures obtained after aging for a day by both the routes are found to be highly luminescent in different wavelength range in the visible region. Therefore, it is expected that the shape evolution of CdSe nanomaterials in microheterogeneous media could be of potential use in nanoscience and technology.

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