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CdSe nanoparticles grown via radiolytic methods in aqueous solutions

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ABSTRACT

Cadmium selenide, CdSe, nanoparticles have been synthesized in aqueous solution containing equimolar ammoniated $CdSO_4$ and Na_2SeSO_3 as the starting materials without any capping agents, using gamma and electron beam irradiation under a reducing condition. The radiolytic processes occurring in water result in the formation of CdSe nanoparticles through the reactions mediated by hydrated electrons, e^-_{aq}. TEM measurements revealed that the CdSe nanoparticles were found to exist in agglomerates of dimension of about 100 nm, consisting of primary nanoparticles of dimensions within 5 nm. The as-grown nanoparticles were of cubic crystalline phase as supported by the XRD measurements. These bare CdSe nanoparticles exhibit room temperature ferromagnetic (RTFM) behavior. However, the RTFM behavior was found to be 30% higher in the case of CdSe nanoparticles prepared on electron beam irradiation as compared to those obtained by gamma irradiation, which was attributed to their relatively smaller size (2–3 nm) and disordered structures as compared to those obtained in the later case (3–5 nm).

1. Introduction

The radiation-induced synthesis of metal and semiconductor nanoparticles in aqueous solutions is a very powerful technique, which was reported earlier by Henglein (1989), Hayes et al. (1989), Swayambunathan et al. (1990) and Marignier et al. (1985). The work on the radiolytic synthesis of compound semiconductor like CdS has inspired the researchers to synthesize other related semiconductor nanoparticles, such as CdSe, by this method. CdSe nanoparticles have attracted the researchers for their potential applications in various optoelectronic devices (Ashkenasy et al., 2002; Oertel et al., 2005; Kamat, 2008). The synthesis of CdSe nanomaterials of various shapes and sizes by employing different chemical routes has been reported by several researchers in the past (Murray et al., 1993; Peng and Peng, 2001; Qu et al., 2001). The preference is for an easy, economical synthesis of stable CdSe nanoparticles. In these chemical methods different capping agents such as TOP, TOPO and other polymeric materials are often used for controlling their sizes. This requires certain stringent laboratory conditions, such as high temperature, glove box, moisture-free atmosphere, etc. To circumvent these complications, the synthesis of CdSe nanoparticles is also carried out in the polymeric host matrices under ambient laboratory conditions. Several groups have employed these methods for getting stable CdSe nanoparticles (Khanna et al., 2006; Dayal et al., 2009). The radiolytic syntheses of these nanomaterials using various starting reagents, different capping agents as well as different solvent matrices under gamma irradiation have recently been reported in the literature (Xie et al., 1999; Hu et al., 2003; Ge et al., 2001; Qiao et al., 2000). Synthesis of CdSe quantum dots in PVA matrix using ammoniated cadmium sulfate ($CdSO_4$) and sodium selenosulfate (Na_2SeSO_3) as the starting precursor materials by radiolytic methods has been recently reported by our group (Biswal et al., 2010). The polymer film, PVA, containing CdSe quantum dots were very stable and exhibit room temperature excitonic absorption patterns. We have reported the reversibility effect on the formation of CdSe nanoparticles in aqueous solutions by high-energy electron beam irradiation (Singh et al., 2010) using the above precursors. The as-grown CdSe nanoparticles in the aqueous solutions were found to decompose on exposure to air/oxygen and the decomposed solution again produced CdSe nanoparticles on irradiation with electron beams. On the contrary, these nanoparticles were quite stable when dispersed in organic solvents. The radiation-induced synthesis of the CdSe nanoparticles in aqueous solutions and their material characteristics still need to be thoroughly investigated.

In this paper, we have reported in detail on the radiation-induced synthesis of the CdSe nanoparticles in aqueous solutions and their materials properties like magnetic behavior. Based on our previous studies (Rath et al., 2007; Singh et al., 2010), we have

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used equimolar ammoniated cadmium sulfate ($CdSO_4$) and sodium selenosulfate (Na_2SeSO_3) in aqueous solutions to prepare CdSe nanoparticles by radiation-induced routes. The bare nanoparticles so produced were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and optical spectroscopy. Interestingly such bare CdSe nanoparticles exhibited room temperature ferromagnetism (RTFM). By using gamma radiation and electron beam irradiation under different experimental conditions, we have been able to get an insight of the formation mechanism of these nanoparticles.

2. Experimental

2.1. Chemicals

The starting reagents, $CdSO_4$ and Na_2SeSO_3 solutions, were freshly prepared from the high purity chemicals obtained from Aldrich. Na_2SeSO_3 solution was prepared by refluxing the solution containing 1 g Se powder and 10 g Na_2SO_3 in 50 ml nanopure water at 70 °C for 7 h (Pramanick and Bhattacharya, 1982). Nanopure water from Milipore water purifier was used for preparing the solutions. The reaction mixture for synthesis of CdSe nanoparticles was prepared in the line of chemical bath deposition (Rath et al., 2007), where a required quantity of 25% ammonia was added to a 25 ml $CdSO_4$ (10 mM) solution until a clear ammoniated $CdSO_4$ solution appeared. Fresh 25 ml Na_2SeSO_3 solution (10 mM) was added to this solution. Tert-butanol ($CH_3(CH_3)_2COH$) was added to scavenge the $OH^\bullet$ radicals, allowing only the e^-_{aq} reactions to occur. The final concentration of the precursor ions in the reaction mixture was 5 mM each. In another set of experiments, aqueous solutions saturated with N_2O gas for allowing the OH reactions during the radiolysis processes. The samples were de-aerated by purging with high purity argon gas in the case of e^-_{aq} reactions.

2.2. Irradiation

A ^{60}Co gamma source was used for the radiolysis experiments for the synthesis of CdSe nanoparticles by gamma irradiation. The absorbed dose rate in this gamma source was 1.5 kGy/h. The samples were irradiated with a dose of about 40 or 100 kGy. Such a very high dose was delivered because of the complete transformation of the reagents to the products and for getting a homogeneous stable product. CdSe nanoparticles were also synthesized by irradiating the reaction mixtures with 7 MeV electron beam (FWHM 2 μs) from a linear accelerator (LINAC) (Guha et al., 1987) at repetition rate of 12 pulses per second with a total absorbed dose of 40 kGy. In this case the dose rate was very high as compared to the gamma irradiation. The pulse radiolysis experiments were carried out for measuring the reaction rate constant involving e^-_{aq} and precursor ions using a kinetic spectrometer coupled with the LINAC. The transient intermediate species formed during the pulsed electron beam (FWHM 500 ns, absorbed dose 40 Gy/pulse) irradiation were monitored by the kinetic spectrometer using a 450 W xenon lamp kept at 90° angles to the electron beam. The absorbed dose was determined by using a chemical dosimeter, aqueous solution containing 10 mM KSCN.

2.3. Characterization

Optical absorption measurements were carried out by using a Chemito Spectrascan 2600 absorption spectrophotometer. Steady-state fluorescence measurements were carried out at room temperature by using a Hitachi F 4500 spectrofluorimeter. X-ray diffraction (XRD) measurements were recorded on a Phillips X-ray diffractometer, model PW 1710 system, using a monochromatic Cu Kα source ($\lambda = 0.154$ nm). The electron diffraction and high-resolution transmission electron microscopic (HRTEM) images were acquired on a TEM, model no. FEI, TECNAI-F30. The preparation of samples for HRTEM analysis involved sonication of methanol for 2–5 min and deposition on a carbon-coated copper grid. The accelerating voltage of the electron beam was 300 kV. DC magnetization measurements, as a function of field, were carried out using an E.G. & G P.A.R vibrating sample magnetometer (model 4500).

3. Results and discussion

Water radiolysis yields three major primary transient species, e^-_{aq}, $OH^\bullet$ and $H^\bullet$, out of which e^-_{aq} and $H^\bullet$ are reducing and $OH^\bullet$ is oxidizing in nature (Spinks and Woods, 1976). In the radiation-induced synthesis of metallic nanoparticles normally a reducing condition is employed. Tert-butanol ($CH_3(CH_3)_2COH$) is added to the aqueous solution to scavenge the $OH^\bullet/H^\bullet$ radicals and leaving behind the hydrated electrons, e^-_{aq}, in the solution. This can be called as a perfectly reducing condition where the reduction occurred mainly via the e^-_{aq} radicals. These hydrated electrons then react with the precursor ions to produce the desired products. However, in the presence of an electron scavenger like N_2O, these hydrated electrons will have a competitive kinetics between the precursor ions and the N_2O molecules. Such a condition can be called as a partially reducing condition. Hence the yield of formation of the desired product will depend on the reactivity between these two reactions. Following are the various important reactions pertinent to the above conditions.

Radiolysis of water:

$$H_2O \rightsquigarrow e^-_{aq}, OH^\bullet, H^\bullet, H_3O^+, H_2, H_2O_2 \quad (1)$$

$$OH^\bullet\ (H^\bullet) + CH_3(CH_3)_2COH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O\ (H_2) \quad (2)$$

$$e^-_{aq} + N_2O \xrightarrow{H_2O} N_2 + OH^- + OH^\bullet\ (k = 9.1 \times 10^9\ M^{-1}\ s^{-1}) \quad (3)$$

(Janata et al., 2002)

3.1. Radiolytic synthesis using gamma irradiation

3.1.1. Radiolytic synthesis in the presence of tert-butanol

Gamma irradiation was performed in the de-aerated aqueous solution containing 10 mM ammoniated $CdSO_4$ and 10 mM Na_2SeSO_3 in the presence of 1 M $CH_3(CH_3)_2COH$. After radiolyzing the reaction mixture continuously inside a gamma chamber for an absorbed dose of about 100 kGy, an orange colored product was formed. The radiolyzed product was collected by centrifugation and was repeatedly washed with water and methanol and finally air-dried for further studies. Blank run was carried out by keeping the above reaction mixture for the same time period without any irradiation. The optical absorption spectra of the reaction mixture before irradiation, blank run, the supernatant of the radiolyzed solution and the product obtained on irradiation dispersed in methanol were measured (Fig. 1). It is clear from this figure that no reaction takes place in the blank run. We emphasize the advantage of the radiation-induced synthesis of CdSe nanoparticles in the present situation, because the synthesis of these nanoparticles takes place only on irradiation, which otherwise does not proceed by normal chemical reaction. The supernatant of the radiolyzed solution also did not show any absorption in the visible region, indicating that the reaction between the two precursors is completed within the employed time. Similar observation was exhibited with different absorbed doses (40 kGy). Therefore, it is established that the reaction between the two individual precursors is mediated through the hydrated