

Dynamics of radiolytic formation of CdSe quantum dots in aqueous solution containing different alcohols: A pulse radiolysis study

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ABSTRACT

The dynamics of radiolytic formation of CdSe quantum dots in aqueous solution containing equimolar ammoniated cadmium sulphate, $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ and sodium selenosulphate, Na_2SeSO_3 as precursors for Cd and Se respectively, have been investigated in the presence of different aliphatic alcohols, namely methanol, ethanol, 1-propanol, 2-propanol or 1-butanol by electron pulse radiolysis studies. The mechanism of CdSe quantum dots formation was studied in N_2O saturated aqueous solutions to investigate the formation through reactions with different aliphatic alcohols. The formation of the CdSe quantum dots was found to proceed via the formation of short lived transient intermediate species having and absorption at around 500 nm, which are formed through the reaction of different aliphatic alcohol radicals with the cadmium and selenium precursors. The rate constants for the formation and decay of these intermediate species have been determined. Optical properties of these quantum dots were found to be different in the presence of different alcohols.

1. Introduction

The synthesis of semiconductor quantum dots has been the area of great interest for the researchers in the recent years due to their unique optical, electronic and other properties (Smith and Nie, 2010; Alivisatos, 1996; Woggon and Alivisatos, 1998). Owing to these properties, semiconductor nanomaterials are used in the areas of photovoltaics (Nozik et al., 2010; Semonin et al., 2012), light emitting diodes (LED) (Qingjiang et al., 2007; Rogach et al., 2008;), sensors, biological imaging (Medintz et al., 2005; Jin and Hildebrandt, 2012), photodynamic therapy (Samia et al., 2003; Joshi, 2016) etc. CdSe is one of the most important II-IV semiconductors with a medium energy band gap (E_g) of 1.75 eV at 300 K (Yu and Brock, 2008; Huynh et al., 2002; Klimov et al., 2000). CdSe quantum dots have been synthesized using different methods like high temperature organometallic route, sonochemical, microwave assisted, hydrothermal, photochemical, radiation chemical and green chemistry route etc. (Murray et al., 1993; Murcia et al., 2016; Xuan et al., 2013; Jamble et al., 2017; Singh et al., 2018, 2017; Liu et al., 2008). Out of all these existing methods radiation chemical route is a very efficient and powerful one, due to several advantages over other routes like, (a) no need of any additional reducing agents, (b) synthesis can take place with a very low concentration of precursors, (c) free radicals generated in-situ act as reducing agents, (d) the process is very fast, (e) large scale production can be possible

with ease and (f) tuning of shape and size is achieved by controlling the dose and dose rate (Guleria et al., 2015; Dispenza et al., 2015).

In the radiation chemical route, the solvent media play very important role in controlling the shape, size and morphology and hence properties of quantum dots. The high radiation energy when interacts with water, generates free radicals (OH^\cdot , H^\cdot and e_{aq}^-), which are the primary reactive species. In aqueous solution, hydrated electrons, e_{aq}^- are mainly used in the synthesis of metallic and semiconductor nanoparticles (Rath et al., 2016; Gonzalez-Martinez et al., 2016). In such case, OH^\cdot and H^\cdot radicals are quenched by the addition of tert-butanol. However, in aqueous solutions containing alcohols like 2-propanol, OH^\cdot and H^\cdot radicals react with alcohol molecules to produce the secondary radicals, 2-hydroxy-2-propyl radicals, $(\text{CH}_3)_2\text{C}^\cdot\text{OH}$, which are again highly reducing in nature ($E^\circ = -1.5 \text{ V vs NHE}$) (Wardman et al., 1989) and can be used for the synthesis of these nanoparticles. Several researchers have studied the reactions pathways involved in the formation of metallic/semiconductor nanomaterials in aqueous and non-aqueous polar organic solvents (Henglein, 1989; Belloni et al., 1998; Belloni, 2006). The reaction pathways depend upon the precursor ions/molecules and the solvent system.

We have earlier studied the dynamics of radiolytic formation of CdSe nanoparticles in aqueous solution containing equimolar cadmium and selenium precursors in the tert-butanol which acts as the OH^\cdot radical scavenger (Singh et al., 2011). The formation of CdSe

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nanoparticles was found to occur through the formation a short-lived transient intermediate species having an absorption maximum at 520 nm which was formed via the reactions of hydrated electrons with these precursors. The CdSe nanoparticles were relatively less stable at ambient conditions and do not exhibit any photoluminescence at room temperature. In this study, we have synthesized CdSe quantum dots through different aliphatic alcohol radicals instead of hydrated electrons and investigated the reaction dynamics of their formation by the pulse radiolysis studies. These quantum dots were found to exhibit room temperature photoluminescence contrary to those obtained through the reactions with hydrated electrons. A probable mechanism of their formation has been proposed here.

2. Experimental

2.1. Chemicals

High purity chemicals Cadmium sulphate, Sodium sulphite, Se powder methanol, ethanol, 2-propanol, 1-propanol and 1-butanol were purchased from Sigma Aldrich and used without further purification. Ammoniated cadmium sulphate, $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ and sodium selenosulphate, Na_2SeSO_3 were used as precursors for cadmium and selenium respectively. $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ solution was prepared by adding desired quantity of 25% NH_3 solution to freshly prepared CdSO_4 solution until cleared transparent solution was obtained. 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 obtained from Millipore water purifying system was used for preparing the solutions. 4% (v/v) of different alcohols were taken in reaction mixture of 0.5–1 mM concentration of the both the precursors.

The reaction mixture was saturated with N_2O (2.5×10^{-2} M) before the electron beam irradiation to quench the hydrated electrons, e_{aq}^- to allow reduction/reaction of precursors with alcohol radicals and not hydrated electrons. Different aliphatic alcohols will react with $\text{H}^\bullet/\text{OH}^\bullet$ radicals formed after electron beam irradiation to generate corresponding alcohol radicals (Buxton et al., 1982; Janata, 2002a). These secondary radicals (alcohol radicals) react with the precursors to form different transient intermediate species. The concentrations of both the precursors were changed accordingly to allow the secondary radicals to react with the specific precursor.

2.2. Pulse radiolysis

Pulse radiolysis experiments were carried out with a 7 MeV linear electron accelerator (LINAC) coupled with a kinetic spectrometer. The solutions were irradiated with electron pulses of FWHM about 500 ns inside a 10 mm x 10 mm flow quartz cell with all the sides transparent to the visible light. The white light from a 450 W xenon lamp at a 90° angle to the electron beam irradiation was used for the detection of the transient species produced upon radiolysis. The details of the set up are given elsewhere (Guha et al., 1987). The absorbed dose was determined by using a chemical dosimeter solution of 10 mM potassium thiocyanate (KSCN), kept in a quartz cell of similar dimensions. The absorbed dose in the pulse radiolysis experiments were 40 Gy. The time-resolved spectra and the kinetic profiles at different probe wavelengths for the formation and decay of the transient intermediate species produced during radiolysis were obtained during the pulse radiolysis experiments.

2.3. Characterization

UV-vis absorption spectra of the reaction mixtures were recorded using a spectrophotometer with a model no. JASCO V650 and a quartz cell with a 10 mm path length. Room temperature steady state photoluminescence spectra were recorded using spectrofluorometer with a

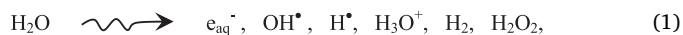
model no. Hitachi F-450. X-ray diffraction (XRD) measurements of CdSe QDs were carried out by using a Panalytic model X-Pert pro instrument using Cu K- α source. The transmission electron microscopy (TEM) images were recorded using a Libra 200FE instrument operated at 200 kV accelerating voltage.

3. Results and discussion

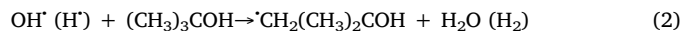
3.1. Synthesis of CdSe quantum dots

Radiation-induced synthesis of any materials mainly directed by the process of radiolysis of water because the water molecules are present in ample amount in aqueous solution so the radiation primarily interacts with water molecules leads to radiolysis of water. Radiolysis of water produces three major species, e_{aq}^- , H^\bullet and OH^\bullet radicals. Out of these the e_{aq}^- and H^\bullet are reducing while OH^\bullet is oxidizing in nature (Spinks and Woods, 1976). By suitably modifying the solvent medium, it is possible to investigate the reaction of any one of these three primary radicals with the reagents of our interest. A reducing environment containing only hydrated electrons, e_{aq}^- , can be achieved by adding tert-butanol ($(\text{CH}_3)_3\text{COH}$), which quenches OH^\bullet radicals. On the contrary, an oxidizing environment can be made by saturating the solution with N_2O (Singh et al., 2011) which generate OH^\bullet radical by reacting with e_{aq}^- . Similarly, a reducing environment can also be created by adding different aliphatic alcohols along with saturating the solution with N_2O , where the OH^\bullet radicals can react with the alcohols to produce secondary radicals, which are reducing in nature. The rate constant of reaction between OH^\bullet and aliphatic alcohols (ROH) is interestingly very high (Table 1) (Buxton et al., 1988)

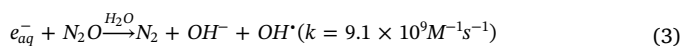
Radiolysis of water:



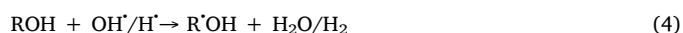
In the presence of tert-butanol:



In the presence of N_2O :



In the presence of aliphatic alcohols, other than tert-butanol as mentioned above ROH, where R stands the aliphatic chains with carbon atoms varied from one (in the case of methanol) to four (in the case of 1-butanol).



The tert-butanol radicals ($\cdot\text{CH}_2(\text{CH}_3)_2\text{COH}$) are inactive and therefore do not interfere in the subsequent reactions. However, the aliphatic alcohol radicals ($\text{R}^\bullet\text{OH}$) formed in the reaction (4), are highly reactive (particularly in reducing nature) and therefore are used for the subsequent reactions as discussed in the present study (see Table 2).

The radiolytic synthesis and the pulse radiolysis study of CdSe quantum dots using electron beam irradiation in aqueous solution containing equimolar $\text{Cd}(\text{NH}_3)_4\text{SO}_4$ and Na_2SeSO_3 and tert-butanol

Table 1

Rate constants of reactions of H^\bullet , OH^\bullet radicals with alcohols (Buxton et al., 1988).

Alcohols	k ($\text{M}^{-1} \text{s}^{-1}$)	
	H^\bullet	OH^\bullet
methanol	2.6×10^6	9.7×10^8
ethanol	1.7×10^7	1.9×10^9
1-propanol	2.4×10^7	2.8×10^9
2-propanol	7.4×10^7	1.9×10^9
1-butanol	5.5×10^7	4.2×10^9

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