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Electron beam induced synthesis of CdSe nanomaterials: Tuning of shapes from rods to cubes

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ABSTRACT

Cadmium selenide (CdSe) nanomaterials of different shapes have been synthesized in the water pool of the *water-in-oil* microemulsions through 7 MeV electron beam irradiation. The rod shaped CdSe nanomaterials of lengths and breadths up to 1 μm and 200 nm, respectively with aspect ratios from 3 to 5 were grown in the case of microemulsions containing lower water content, water to surfactant concentrations ratio, $w_0 = 10$. In contrast, the cubic shaped CdSe nanomaterials of dimensions about 100 nm were formed in the microemulsions with higher water contents, w_0 values from 20 to 40. Such a transformation of shape from rod to cube was attributed to the change in the hydrophobicity and hydrophilicity of the micro-environment in the microemulsions. The as-grown CdSe nanomaterials were stable at ambient conditions and thus expected to be very useful in the device applications.

1. Introduction

Radiation-induced synthesis of metallic and semiconductor 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. Semiconductor and metallic nanomaterials of different shapes and sizes have been synthesized earlier *via* radiation-chemical routes in aqueous and non-aqueous media using different templates [1–4]. The templates usually determine the shapes and sizes of nanomaterials. Among other semiconductors, CdSe is an important one because of its potential applications in photovoltaics, LEDs and other optoelectronic devices. Several groups including us have reported the radiation-induced synthesis of CdSe nanoparticles in different condensed phases [1–6]. The yield of CdSe nanoparticles depends on the absorbed dose and the concentration of the precursor ions.

Among various templates, *water-in-oil* microemulsions are known as soft templates [7]. Cetyl trimethyl ammonium bromide (CTAB) in solution facilitates the formation of different micro-structures under different conditions [8,9]. In this communication, we have used such soft templates, *water-in-oil* microemulsions consisting of CTAB as the surfactants, cyclohexane as the oil phase, n-butanol as the co-surfactants and the aqueous phase containing the precursor ions for the synthesis of CdSe nanomaterials *via* electron beam irradiations.

2. Experimental

High purity chemicals, CTAB, n-butanol, cyclohexane, cadmium sulfate, selenium powder, sodium sulfite, and tert-butanol were obtained from Sigma-Aldrich and used as received. Nanopure water obtained from a Millipore water purifying system was used for the preparation of aqueous solutions. The concentration of surfactant, CTAB was kept constant, 0.1 M in all the microemulsions. The microemulsions of different water to surfactant concentration ratios, $w_0 = 10$, 20, 30 and 40 were used in the synthesis. The aqueous solution was prepared separately by adding equimolar (5 mM each) ammoniated cadmium sulfate, $[Cd(NH_3)_4]SO_4$, as the cadmium ion precursor and freshly prepared Na_2SeSO_3 as the selenium ion precursor in the presence of 1 M tert-butanol [10,11]. This solution was used as the aqueous phase in the microemulsions. The reaction mixtures are expected to be present only in the water pool of the microemulsions because of the very high solubility of the components in the aqueous phase. The size of the water pool is normally decided by the w_0 value of the microemulsion ($[H_2O]/[CTAB]$) [12,13].

The de-aerated microemulsions were irradiated with 7 MeV electron beam (FWHM 2 μs) obtained from a linear electron accelerator (LINAC). The absorbed dose was measured using a chemical dosimeter, an aqueous solution of 10 mM KSCN [10,11]. The absorbed dose per pulse was kept at 140 Gy and the samples were irradiated with repeated pulses at a rate of 12 pulses per second accounting for a cumulative dose of 25 kGy.

The transmission electron microscopy (TEM) measurements were carried out on model no. 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. The

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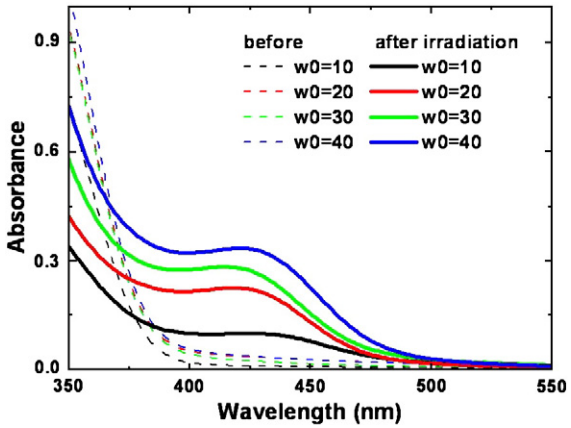

Fig. 1. Absorption spectra of *water-in-oil* CTAB microemulsions containing the precursor ions before (dotted lines) and after (solid lines) electron beam irradiation.

optical absorption spectra were recorded at room temperature using a Jasco V-650 spectrophotometer.

3. Results and discussion

We have previously synthesized CdSe nanoparticles in the aqueous tert-butanol solution containing equimolar (5 mM each) $[Cd(NH_3)_4]SO_4$ and Na_2SeSO_3 upon irradiation with 7 MeV electron beam, which are present in the spherical agglomerated forms of size about 100 nm, due to the absence of any capping agents there [5,6]. In the present work, the same concentrations of these precursors were taken in the water pool of the CTAB microemulsions. Thus, the radiolytic product is expected to be CdSe nanoparticles only. This is evident from the instantaneous change of microemulsion from colorless to greenish-yellow upon irradiation, which was otherwise not observed in normal chemical route. The CdSe nanomaterials were characterized by optical absorption measurements. The optical absorption spectra of the unirradiated and irradiated microemulsions containing CdSe nanomaterials are shown in Fig. 1. The CdSe nanomaterials clearly exhibit excitonic absorption peaks around 420–425 nm. The band gap values and the sizes of the primary CdSe nanoparticles were estimated from the absorption spectra by using Braus equation (Eq. (1)) as shown in Table 1.

$$E_g = E_g(0) + \alpha / d^2 \quad (1)$$

where, $\alpha = 3.7$ eV nm^2, $E_g(0) = 1.7$ eV, d = particle size (nm) and E_g = band gap value in eV. It is found that the size of the primary CdSe nanoparticles in all the microemulsions was about 2 nm.

The CdSe nanomaterials were further characterized by TEM measurements. It was observed that those formed in the microemulsions with lower water content, $w_0 = 10$ were of rod shaped as seen in Fig. 2(a). The lengths and breadths of the rods were up to 1 μm and 200 nm respectively with aspect ratios from 3 to 5. A faint lining outside each rod is clearly visible in the TEM image. From this it is confirmed that the CdSe primary nanoparticles of size 2 nm get associated to form bigger agglomerates which are entangled within the well structured cavities of CTAB microemulsions giving rise to rod shaped materials.

Here it should be mentioned that CTAB microemulsions form rod shaped structures when the volume ratio of oil to water is very less

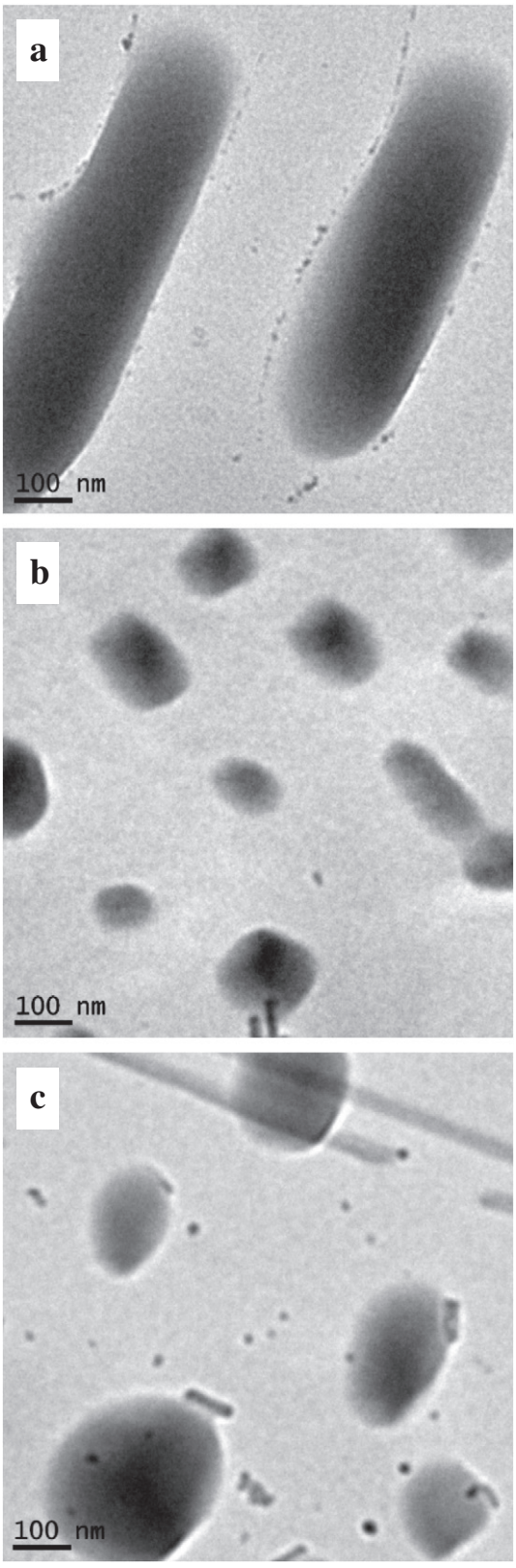

Fig. 2. TEM images of the CdSe nanomaterials grown in *water-in-oil* CTAB microemulsions with (a) $w_0 = 10$, (b) $w_0 = 30$ and (c) $w_0 = 40$.

Table 1
Band gap values and the size of the CdSe primary nanoparticles.

w_0	E_g (eV)	Particle size (nm)
10	2.50	2.14
20	2.59	2.03
30	2.58	2.04
40	2.55	2.08