

Comparative study on the freezing temperature synthesised CdSe nanoparticles before and after annealing

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Thioglycolic acid-capped CdSe nanoparticles have been synthesised at 273–279 K. A comparative study on the structural and optical characteristics of the as-synthesised and annealed samples is done using state-of-the-art instruments and software. Based on these studies here the authors report a colossal change in crystallinity, particle size and red shift in the absorption spectra upon annealing. Lattice strain is also found to increase by 18.77% upon annealing. Excitation wavelength-dependent photoluminescence with giant Stokes shift and narrow full-width at half-maxima of both the samples is also reported, which may be useful for device application.

1. Introduction: Owing to its widely existing and potential use in various fields such as solar cells [1, 2], light-emitting diodes [3, 4], lasers [5, 6] and biomedical tags [7, 8] semiconducting cadmium selenide (CdSe), nanoparticles have been vibrant research topics for many years. Extensive work is going on inventing new synthesis procedures or modifying existing ones along with various post-synthesis treatments [9, 10]. In the chemical route to synthesise CdSe nanoparticles, reactants molar ratio, synthesis temperature and pH value always play a pivotal role [11–16]. It has been found that reaction temperature controls the diameter of the CdSe nanoparticles, which in turn have significant influence on the luminescent properties [11]. Reduction in size polydispersibility and good photoluminescence (PL) quantum yield can be obtained by optimising the ratio of the precursors and capping agent [12, 14, 15]. The capping agent used also plays a vital role [17–19] in preventing agglomeration and to have better solubility. So the quest to obtain a breakthrough with the ‘hot injection’ reaction method [13] using tri-*n*-octylphosphine (TOP)—tri-*n*-octylphosphine oxide (TOPO), is now focusing on smarter, cheaper and greener approaches [20–25]. Again as at nanoscale the influence of the surface atoms, defect states [26] and lattice strain [27, 28] on its properties can be significant; it is worth mentioning that proper optical [11–16] and structural characterisations [29–31] of the synthesised nanoparticles must be done for better understanding and fruitful application. However, the previous studies discussed in detail the synthesis of CdSe nanoparticles with varying precursor concentrations and at different temperatures ranging from room temperature to high temperature. Reports of freezing temperature synthesis of CdSe nanoparticles are still rare in the literature. Recently reported work on the freezing temperature of synthesised CdSe focused mainly on optimising the PL property [32]. However, we have emphasised here not only on the synthesis at freezing temperature, but also on comparative study of their properties after annealing. So here we briefly report the scale-up synthesis of thioglycolic acid (TGA)-capped CdSe nanocrystals at freezing temperature via a soft chemical route in an aqueous medium without using toxic chemicals such as TOP—TOPO and we have also done their structural and optical characterisations before and after air annealing. We have chosen to synthesise at 273–279 K (freezing temperature) to slow down the nucleation growth of CdSe nanocrystal [21] and to have an account of low-temperature effect on the formed nanoparticles, which may be useful while synthesising some low-temperature in-situ CdSe polymer nanocomposites.

2. Experimental

2.1. Synthesis of TGA-capped CdSe nanoparticles: There are several reports existing in the literature about the use of thiol/

TGA as the size limiting as well as stabilising agent in the synthesis of high quality of CdSe nanoparticles or quantum dots at high, room and recently at freezing temperature [12, 20, 23, 33]. Here our approach was with a modified scaled-up synthesis procedure in which at first 0.05 mol of cadmium acetate was dissolved in 100 ml of water. 7 ml of TGA was then added to this aqueous solution under continuous magnetic stirring, resulting in a turbid solution. 1 M of NaOH was added until the solution became transparent (pH ~ 12). This is marked as precursor A — the Cd²⁺ source. Then Na₂SeSO₃ solution was prepared by dissolving 0.05 mol of Se powder in aqueous solution of 0.10 mol Na₂SO₃. After refluxing for 4 h at 373 K, the nearly transparent solution was filtered to remove any unreacted selenium, which if not filtered might give an unwanted X-ray diffraction (XRD) peak. This was marked as precursor B — the Se²⁻ source. Now the freshly prepared precursor B was added drop wise with the precursor A under continuous magnetic stirring at 273–279 K with some specially designed experimental setup. After complete addition, the solution turned greenish yellow, and was left for 1 h under continuous magnetic stirring. Then the colloidal solution was centrifuged at 273–279 K with 10 200 rpm and washed with distilled water several times to completely remove the excess TGA. The washed precipitate was then collected and dried at 333–343 K under vacuum. In the total synthesis procedure, the molar ratios between different chemicals were maintained as follows — Se powder: Na₂SO₃ = 1:2; Se powder: cadmium acetate = 1:1; cadmium acetate: TGA = 1:2. The pH variation during the synthesis was as — pH of cadmium acetate aqueous solution ~ 5; after mixing the TGA to the above aqueous solution pH ~ 3; after addition of 1 M NaOH pH ~ 12. After drying the samples were ground to powder form and divided into two parts. One part was annealed at 473 K for 2 h. The other part was kept as synthesised.

2.2. Characterisation: The XRD pattern of the powdered sample was recorded in an X’pert Pro MPD diffractometer (PANalytical) using X’Celerator operating at 40 kV and 30 mA using Cu K_α radiation from 10 to 90°. Fourier transform infrared (FTIR) spectra were measured in the range 400–4000 cm⁻¹ in potassium bromide pellets using a Thermo Scientific Nicolet iS10 FTIR spectrometer. The morphology and estimation of sizes of the investigated samples were done with JEOL, 2011 high-resolution transmission electron microscopy (HRTEM). A Hitachi UV—vis spectrophotometer and a Hitachi F 2500 fluorescence spectrophotometer were used to study the UV—vis and PL spectroscopy, respectively.

3. Results and discussion

3.1. XRD studies: The comparative XRD profile of the samples and the Reitveld analysis [34, 35] of the profiles, using 'X'pert high score plus software' (PANalytical) [36], are shown in Figs. 1 and 2 for the as-synthesised and annealed samples, respectively. From Figs. 2a and b, we observe that the fitted curves matched well with the raw data, which confirms that all peaks are of CdSe and the investigated samples are CdSe in cubic phase with space group F-43 m (ICSD code 41528). It was clearly observed that the annealed sample's diffraction peaks were sharper and narrower, which infer that the sample attains better crystallinity with calcination at the cost of increased crystallite size. The calculated values of the microstructural parameters by Reitveld refinement are shown in Table 1. It is to be noted that the lattice

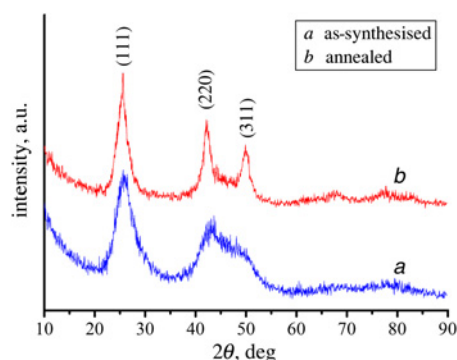


Figure 1 XRD profile of the as-synthesised and annealed CdSe nanoparticles

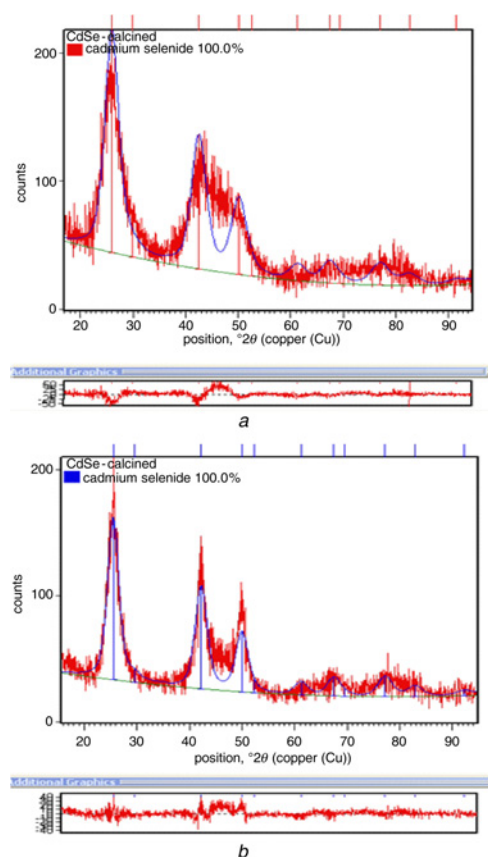


Figure 2 XRD pattern along with difference plot as obtained by Rietveld analysis of the as-synthesised and annealed CdSe nanoparticles
a As-synthesised
b Annealed CdSe nanoparticles

Table 1 Comparison of calculated microstructural parameters of the as-synthesised and annealed CdSe nanoparticles extracted from Reitveld analysis

CdSe sample	Cell parameters, nm	Cell volume, nm ³	Crystallite size, nm	Lattice strain, %
as-synthesised	0.6110	0.2280	2.80	0.064
annealed	0.6052	0.2217	3.53	0.341

strain is increased by 18.77% in the annealed sample with respect to the as-synthesised sample, which is also reflected in the cell dimensions.

3.2. HRTEM and selected area electron diffraction (SAED) studies: Again from the HRTEM images, it was observed that the particle size of the as-synthesised sample is 4.4 nm (Fig. 3a) whereas it increases to 7 nm (Fig. 3b) after annealing. The interplanar distances with assigned planes are shown within the corresponding Figures. From the HRTEM image it is also noted that upon annealing, it appeared to be a nearly perfect crystal. From Fig. 3c, we note some diffused ring pattern for the as-synthesised sample, whereas spotty selected area electron diffraction (SAED) pattern was observed for the annealed sample (Fig. 3d), which in turn supports our previous conclusion that the sample attains better crystallinity after annealing. The particle sizes and interplanar distances were calculated using 'Image J' software.

3.3. FTIR studies: To study the efficient capping of CdSe by TGA we performed FTIR spectroscopy (shown in Fig. 4). As the flash point of TGA is 405 K, so annealing at 473 K is supposed to eliminate unreacted TGA, if any. In the FTIR spectrum, the broad peaks about 1631 and 3410 cm⁻¹ are because of OH stretching vibration of the absorbed H₂O [37]. Absence of a peak at 2560 cm⁻¹ is a clear indicator of S—Cd bonds between TGA and CdSe. Although the two samples exhibit nearly the same 'fingerprint', there are some differences regarding the increased or reduced intensity of peaks such as, in the annealed sample the peaks at 1639, 1331, 771, 620 and 520 cm⁻¹ are pronounced, whereas the peaks at 2922, 2850, 1559 and 1065 cm⁻¹ are diminished. Among these the peaks about 771 cm⁻¹ correspond

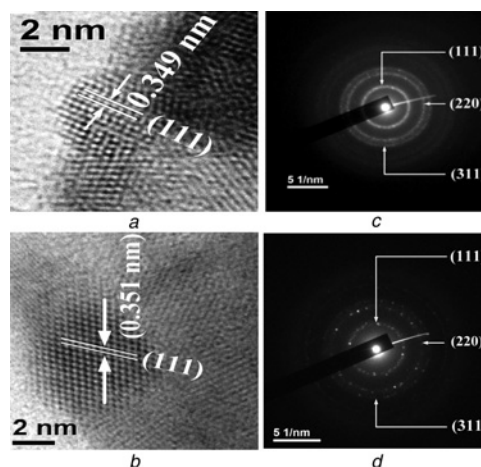


Figure 3 HRTEM and SAED images of the CdSe nanoparticles
a HRTEM image of the as-synthesised CdSe nanoparticles
b HRTEM image of the annealed CdSe nanoparticles
c SAED image of the as-synthesised CdSe nanoparticles
d SAED image of the annealed CdSe nanoparticles

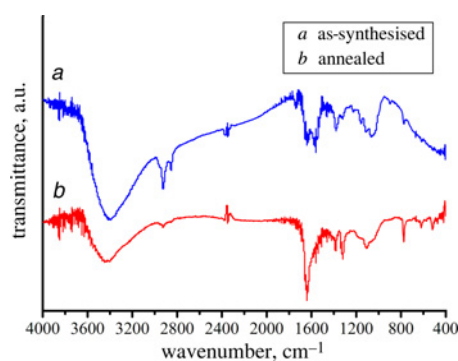


Figure 4 Comparative FTIR spectra of the as-synthesised and annealed CdSe nanoparticles

to the Cd–Se bonds [29, 38] and all others to the TGA or its bonding with the sample [39]. As annealing removes excess TGA and crystallite size increases, the corresponding fingerprint is trimmer. So the FTIR study confirms the formation of capped CdSe.

3.4. UV–vis spectroscopy studies: UV–vis absorption spectra of the samples were studied by dispersing both the samples in a polar solvent (methanol). It was observed that the as-synthesised sample absorbs about 560 nm corresponding to a bandgap of 2.22 eV, whereas the annealed sample absorbs about 660 nm corresponding to a bandgap of 1.88 eV, respectively, (Fig. 5). The particle sizes were calculated using the Brus equation [40]

$$\Delta E = E_g^{\text{nano}} - E_g^{\text{bulk}} = \left(\frac{h^2}{8\pi m^* m_0 R^2} \right) \left(\frac{1.8e^2}{4\pi\epsilon\epsilon_0 R} \right)$$

where E_g^{bulk} and E_g^{nano} are the bandgap of the bulk and nanoCdSe, respectively. R is the particle radius. m_0 is the electron rest mass and ϵ_0 is the permittivity of free space. $m^* = (m_e m_h / m_e + m_h)$ is the electron–hole pair reduced mass and for CdSe the taken values are $m_e = 0.119$, $m_h = 0.820$ and $\epsilon = 10.2$ [41]. Using these values particle size ($2R$) came out to be 4.6 and 7.6 nm for the as-synthesised and annealed sample, respectively, which is close enough to the value obtained from HRTEM images. Apart from these excitonic peaks, we observe small humps at about 280 and 310 nm (for the as-synthesised and annealed samples, respectively) which are because of the formation of smaller nanoclusters.

3.5. PL studies: The PL spectra of the samples are shown in Fig. 6. It was observed that when excited with 220 nm both the samples give emission in the UV range and the annealed sample's PL has

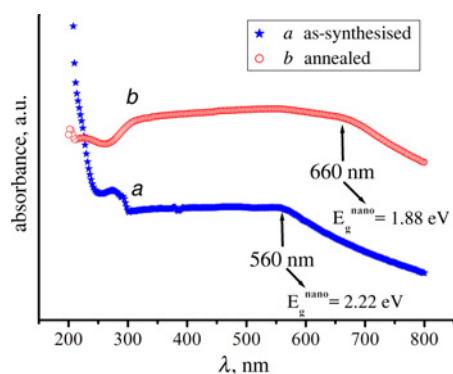


Figure 5 Comparative UV–vis absorption spectra of as-synthesised and annealed CdSe nanoparticles

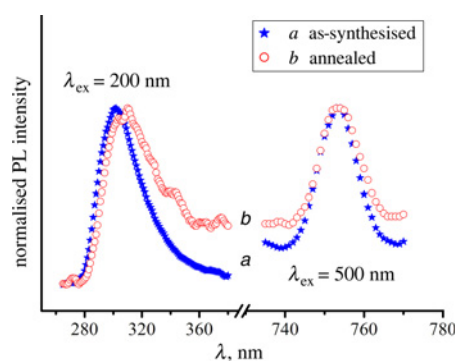


Figure 6 Comparative PL emission curves of the as-synthesised and annealed CdSe nanoparticles with excitation wavelength (λ_{ex}) = 220 and 500 nm

The excitation wavelengths (λ_{ex}) are indicated within the figure

multiple peaks because of the removal of surface capping agent. However, when excited with visible light (e.g. 500 nm) both of these samples show a giant Stokes shift and emit at 753 nm with full-width at half-maxima (FWHM) of 11 and 12 nm for the as-synthesised and annealed samples, respectively. Although the input precursor ratio of cadmium and selenium was 1:1, the energy-dispersive X-ray study (not shown here) yields that in the synthesised nanoparticles Cd:Se = 63.3: 36.6 (atomic %), the synthesised nanoparticles are cadmium rich. We consider that this unstoichiometry in composition coupled with improper surface passivation at low temperature may lead to defect states, which in turn gives rise to the observed Stokes shift in PL [42]. However, as the samples emit both in the UV and visible regions with narrow FWHM, depending upon the excitation, it can be a promising candidate for light-emitting device fabrication.

4. Conclusion: To conclude, we observe that CdSe nanoparticles synthesised at low temperature are poor in crystallinity and must be annealed to improve it. Again this happens at the cost of increased particle size. A corresponding colossal change of lattice strain, shifting of absorption peak was also observed. However, this low-temperature cadmium-rich synthesis of CdSe may also give rise to some defect states, which can again serve as non-radiative recombination centres leading to a giant Stokes shift. However, as it displays excitation wavelength-dependent PL in UV and visible regions, we may exploit this feature in device applications.

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