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A simple route to shape controlled CdS nanoparticles

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ABSTRACT

We report the synthesis of CdS nanoparticles in the form of spheres, triangles and wire-like structures. The method involves the reaction of reduced sulfur with a cadmium salt followed by thermolysis in hexadecylamine (HDA). The different shapes were obtained by variation of reaction conditions such as reaction time, temperature and cadmium source. The optical studies show the particles to be quantum confined and luminescent at room temperature.

1. Introduction

Semiconductor nanoparticles have attracted much attention in recent years due to their potential applications in optoelectronics, photocatalysis, solar energy conversion, biological labeling and water pollutant photodegradation amongst others [1–8]. Cadmium sulfide is a metal chalcogenide material which shows variation in one-dimensional (1D) morphology when the reaction conditions such as monomer concentration, reaction temperature and reaction time is varied. The so called 'hot-injection' route involving the thermolysis of dual or single source precursors in high boiling point coordinating solvents has proved to be an efficient route to achieve the shape control of nanoparticles. In the case of CdS nanoparticles, $CdCl_2$ [9,10], Cd-oleate [11] or CdO [12,13] have been used as cadmium precursors and dodecanthiol [11] or a solution of elemental sulfur in oleylamine [10] or in octadecene [13] were identified as sulfur precursors. The related single-molecular precursor route has also been very successful in producing CdS nanoparticles with varying morphologies. Dithiocarbamate complexes of cadmium have been extensively used as precursors for CdS nanoparticles [14–18]. CdS particles in the form of one dimensional (1D) nanowires (NWs) have recently attracted considerable attention due to their unique band and/or ballistic charge transport capabilities [19], dielectric contrast effects [20] and intrinsic polarization sensitivities [21].

In the present work we have used a simple route to CdS nanoparticles with varying morphologies. Sulfur is reduced by sodium borohydride in solution to produce sulfide ions, followed by the reaction with a cadmium salt to give CdS which is then dispersed in tri-n-octylphosphine (TOP) followed by thermolysis in hexadecylamine (HDA). Our previous work using this method has shown that by varying the metal salt the particle morphology can be engineered [22,23]. The synthetic procedure employed in the work is simple, environmentally benign and cost-effective methodology without the need to sacrifice on sample quality, crystallinity, monodispersity and purity, while allowing control over size, shape and morphology.

2. Experimental

2.1. Materials

Cadmium chloride, cadmium nitrate, sodium borohydride ($NaBH_4$), methanol, toluene, acetone, hexadecylamine (HDA) and tri-n-octylphosphine (TOP) were purchased from Aldrich. Sulfur powder was purchased from Merck. All the chemicals were used as purchased.

2.2. Synthesis of CdS nanoparticles

The procedure employed for preparing CdS nanoparticles is as follows. In a typical reaction, sulfur powder (0.64 mmol) was mixed with deionised water (20 mL) in a three neck flask. A solution of $NaBH_4$ (1.58 mmol) was carefully added to this reaction mixture and the flask was immediately purged with nitrogen to facilitate an inert atmosphere. After 12 h, cadmium salt (0.64 mmol) was added to the reaction mixture. The suspension was stirred for 30 min. followed by the addition of excess methanol. The resultant suspension was then centrifuged. The precipitate was dispersed in tri-n-octylphosphine (6.0 mL) and injected into hot hexadecylamine (6.0 g) at 230 °C, and the reaction was allowed to continue for 1–2 h. After heating excess anhydrous methanol was added to the solution resulting in HDA capped CdS nanoparticles. Several experiments were repeated with the above reaction procedure. The injection temperature was

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changed to 190 °C and 270 °C. The cadmium source was also varied by using cadmium nitrate in place of cadmium chloride.

2.3. Characterization

The crystalline phase was identified by X-ray diffraction (XRD), employing a scanning rate of 0.05 $^{\circ}$min^{-1} in a 2θ range from 20° to 80°, using a Bruker AXS D8 diffractometer equipped with nickel filtered Cu Kα radiation ($\lambda = 1.5418$ Å) at 40 kV, 40 mA and at room temperature. The morphology and particle sizes of the samples were characterized by a JEOL 1010 TEM with an accelerating voltage of 100 kV, Megaview III camera, and Soft Imaging Systems iTEM software. The detail morphological and structural features were investigated by using a JEOL 2010 high resolution transmission electron microscope operated at an accelerating voltage of 200 kV. A Varian, Cary 50 Conc UV–Visible spectrophotometer was used to carry out the optical measurements and the samples were placed in silica cuvettes (1 cm path length), using toluene as reference solvent. A Perkin Elmer, LS 55 Luminescence spectrometer was used to measure the photoluminescence of the particles. The samples were placed in a quartz cuvette (1 cm path length).

3. Results and discussion

HDA capped CdS nanoparticles were synthesized by the thermolysis of pre-formed CdS in hexadecylamine (HDA) at 230 °C. The initially formed CdS was synthesized by reacting cadmium chloride or cadmium nitrate with reduced sulfur in water. Fig. 1 shows the TEM images of the well-defined HDA capped CdS nanoparticles. The particles obtained after 1 and 2 h reaction time when cadmium chloride was used as cadmium source consist of a mixture of both spherical and triangular shaped particles. The average particle sizes of the spherically shaped nanocrystals were estimated to be 6.70 ± 0.82 nm and 7.71 ± 0.83 nm in diameter for the 1 h and 2 h reaction time respectively. The formation of the triangular shaped CdS nanoparticles was limited when compared to the number of the spherical nanoparticles formed in the ensemble as shown in Fig. 1(a and b). The formation of triangular shaped CdS nanoparticles has been previously reported [24,25]. Triangular shaped CdS with sizes up to 50 nm were grown at 240 °C by injecting a solution of sulfur dissolved oleylamine into a hot solution of $CdCl_2$ in oleylamine [24]. The corresponding HRTEM image shows that the CdS nanocrystals were highly crystalline, confirmed by the clearly observable lattice fringes in Fig. 1c. All the triangular and spherical nanoparticles observed were single crystals with no discontinuities in their lattices. There seemed to be no change in the particle shape when the reaction temperature was increased to 270 ºC. Close to spherical and triangular particles are observed in the TEM images of the 1 and 2 h samples (Fig. 2). The diameter of the spherical shaped nanocrystals estimated from the TEM image are 5.37 ± 0.92 nm and 6.29 ± 0.74 nm for the reaction at 1 h and 2 h respectively. The crystallinity of the as-prepared CdS nanocrystals from $CdCl_2$ source was investigated by X-ray diffraction (XRD), as shown in Fig. 3. The major diffraction peaks could be indexed as (100), (002), (101), (102), (110), (103) and (112) of hexagonal CdS structure. Compared with the standard diffraction pattern, no peaks of impurities were detected, indicating the high purity of the products.

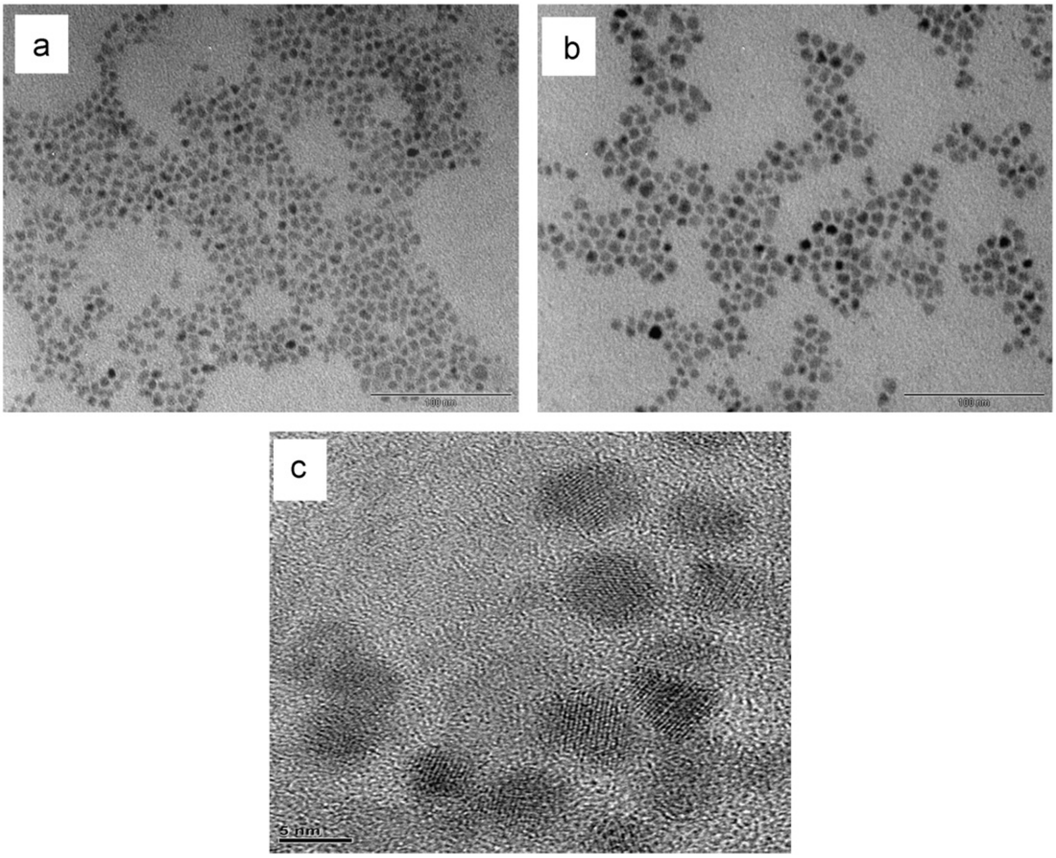

Fig. 1. TEM images of CdS nanocrystals from $CdCl_2$ source at 230 °C (a) after 1 h reaction time, (b) after 2 h reaction time and (c) HRTEM image CdS nanocrystals after 2 h reaction time.

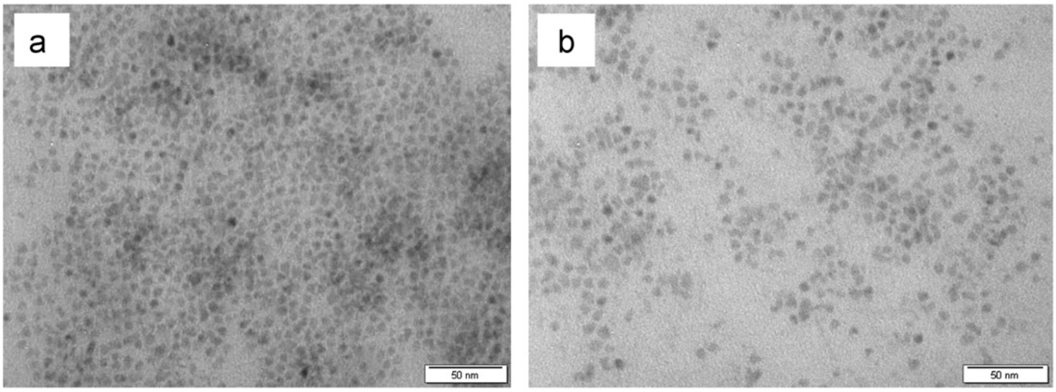

Fig. 2. TEM images of CdS nanocrystals from $CdCl_2$ source at 270 °C (a) after 1 h reaction time and (b) after 2 h reaction time.

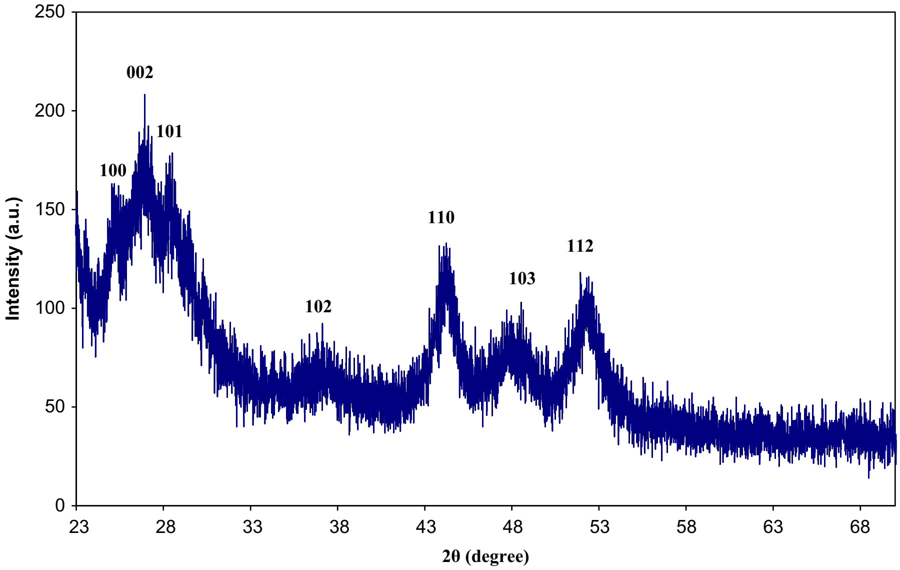

Fig. 3. XRD patterns of the CdS nanocrystals from $CdCl_2$ source at 230 °C after 2 h reaction time.

To investigate the effect of the cadmium source on the growth morphology of the nanocrystals formed, cadmium nitrate was used as cadmium source when forming the pre-formed bulk and thermolysis was carried out at 190 °C and 270 °C. During the growing process, the reaction time was found to play an important role. At 190 °C, the initial growth stage (reaction for 1 h) shows the formation of both rod-like and spherical nanoparticles (see Fig. 4a). The rod-like shaped CdS nanocrystals has an average length of 24.30 ± 11.27 nm and width of 3.9 ± 0.99 nm. The average diameter of the spherical particles is estimated to be about 5.33 ± 1.30 nm. When the reaction proceeded for 2 h, a drastic transformation of almost all the nanoparticles into one-dimensional nanorods with an average length of 72.65 ± 29.60 nm and breadth of 5.88 ± 0.91 nm were formed as shown in Fig. 4b.

When the growth temperature was increased to 270 °C narrow CdS structures in the form of elongated rods closely resembling nanowires were observed. The average length of these rods/wires was 107.41 ± 29.16 nm and breadth of 5.69 ± 3.83 nm (Fig. 5). The elongated growth of the CdS nanoparticles when cadmium nitrate is used can be explained when considering the growth mechanism of particles. Anisotropic shape control is mainly through the preferential growth of a particular crystallographic surface of nanocrystals during a kinetically controlled growth process [18,26,27]. After the formation of a preferred crystalline phase seed, the surface energy of the crystallographic faces has a dominant effect on the anisotropic growth pattern. The HDA seems to increase the growth rate in the (001) direction under high temperature conditions [18]. It is also possible that undissolved cadmium nitrate also adsorbs onto the crystalline faces thereby accentuating the difference in surface energy and modulating growth along the (001) plane. This explains the presence of wire-like structures at the growth temperature of 270 °C.

The size/shape-dependent optical properties of semiconductor nanocrystals can be used as convenient probes to study the growth and shape evolution of nanocrystals. The growth of the CdS nanocrystals was monitored as a function of time by recording the optical absorption spectrum of aliquots taken after 15 min, 30 min, 1 h and 2 h of reaction time. Fig. 6 shows the evolution of absorption spectrum over time for the rod-like shaped CdS nanocrystals synthesized at a growth temperature of 270 °C when $Cd(NO_3)_2$ was used as the cadmium source. A distinct excitonic shoulder is observed in all spectra. The absorption band edges as estimated using the direct band gap method are 2.73 eV (454 nm, $t=15$ min), 2.82 eV (440 nm, $t=30$ min), 2.68 eV (464 nm, $t=1$ h) and 2.62 eV (473 nm, $t=2$ h). The absorption edges for all samples are blue-shifted from that of CdS bulk crystal (2.52 eV, 490 nm) [15] a clear indication of quantum size effects. These results are in agreement with the value of the reported literatures [15–17,28].

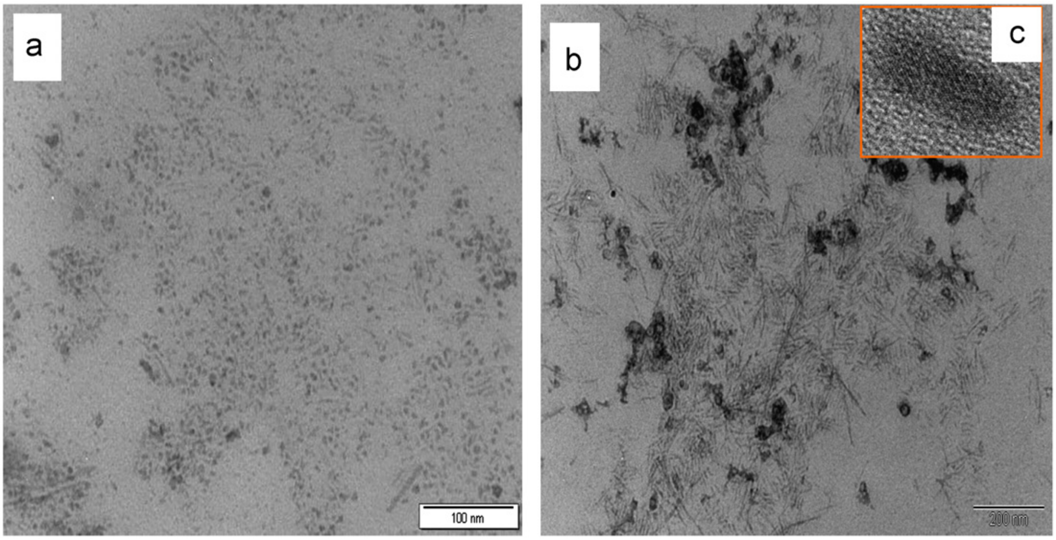

Fig. 4. TEM images of CdS nanocrystals from $Cd(NO_3)_2$ source at 190 °C (a) after 1 h reaction time, (b) after 2 h reaction time and (c) HRTEM image CdS nanocrystals after 2 h reaction time.

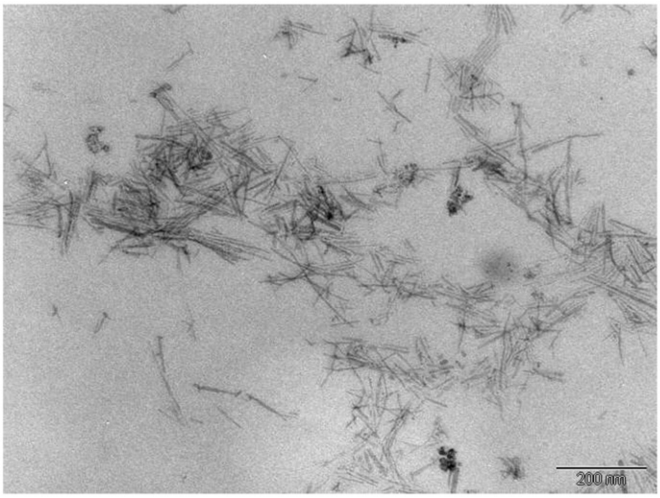

Fig. 5. TEM image of CdS nanocrystals from $Cd(NO_3)_2$ source at 270 °C after 2 h reaction time.

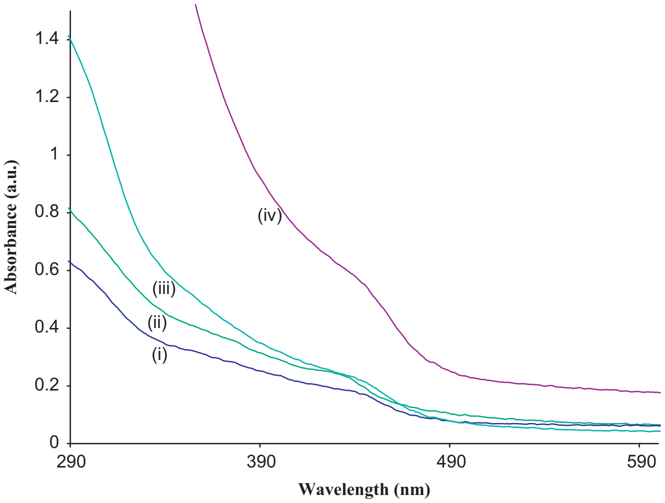

Fig. 6. UV–Visible spectra of CdS nanocrystals synthesized from $Cd(NO_3)_2$ source at 270 °C after (i) 15 min (ii) 30 min (iii) 1 h and (iv) 2 h reaction time.

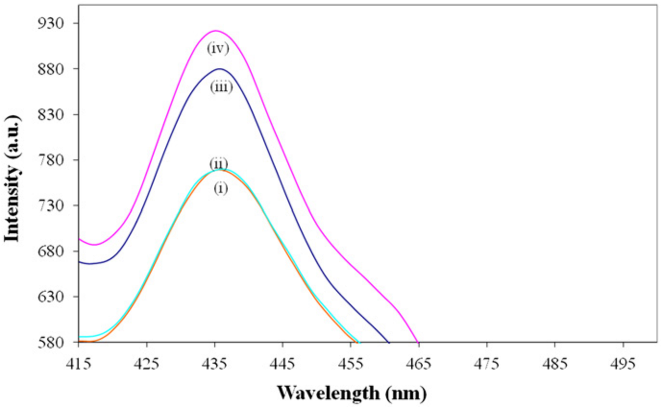

Fig. 7. Photoluminescence spectra of CdS nanocrystals synthesized from $Cd(NO_3)_2$ source at 270 °C after (i) 15 min (ii) 30 min (iii) 1 h and (iv) 2 h reaction time.

Fig. 7 shows typical room temperature luminescence spectra of CdS nanocrystals prepared from $Cd(NO_3)_2$ at 270 °C. The as-prepared CdS nanocrystals only show a band edge emission and the emission maximum appear at about 436 nm for reaction time of 15 min, 30 min, 1 h and 2 h as shown in Fig. 7. The emission peaks of samples are identical because the fluorescence involves the same initial and final state despite differences in the reaction time. This also implies that there is only one emitting species in the samples. The emission peaks of the samples have identical narrow shape, which is an indication of monodispersed particles that are well passivated. The presence of smooth single peaks is also indicative of the existence of predominantly simple morphology.

4. Conclusions

In summary, we have successively synthesized HDA capped CdS nanocrystals with spherical, triangular and rod-like shape. The as-prepared CdS nanocrystals have good crystallinity and a good surface chemical environment with a narrow size distribution. The experimental results show that the morphologies of CdS nanocrystals were significantly influenced by the reaction temperature and different cadmium sources. The shape evolution from spheres to rods is evident with increase in reaction temperature. The optical absorption of the as-prepared nanocrystals is obvious blue shifted in relation to the bulk band-gap of CdS which is due to the quantum-confinement effect of CdS nanocrystals.

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