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Influence of lanthanide ion on the morphology and luminescence properties of cadmium sulphide nanocrystals

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ABSTRACT

An interesting shape evolution of cadmium sulphide nanocrystals is observed in the presence of a multidendate ligand, ethylenediamine tetra acetic acid (EDTA). In our study, EDTA is used as a capping agent and a ligand forming complex with the trivalent gadolinium ion for the synthesis of cadmium sulphide (CdS) nanoparticles. EDTA-capped CdS nanocrystals and gadolinium (Gd) doped CdS nanoneedles have been synthesized using wet chemical route. Addition of Gd as a dopant to the nanocrystals resulted in formation of luminescent CdS nanoneedles. Fourier transform infrared spectroscopy, energy dispersive X-ray analysis, X-ray diffraction, optical absorption, photoluminescence measurements, scanning and transmission electron microscopic measurement techniques were employed to characterize the samples. Photoluminescence investigation revealed the highly luminescent behavior of the CdS nanoneedles. Further, cathodoluminescence mapping confirmed the excellent luminescent properties, which can be exploited for the fabrication of optoelectronic devices.

1. Introduction

Much research has been devoted to the investigation of the optical properties of II–VI semiconductor nanocrystals doped with luminescent centers such as transition metal ions [1], lanthanide ions [2] and donor–acceptor impurities [3]. Many authors have synthesized zinc sulphide (ZnS) and cadmium sulphide (CdS) nanoparticles in the presences of Eu^{3+}, Tb^{3+} and Er^{3+} using various techniques [4]. The trivalent lanthanide ions are very attractive luminescent centers for their high color purity and relatively longer lifetimes of the excited states as a result of transitions within the partially 4f shells of the ions. The unusual photoluminescence properties of rare earth ions have been exploited for the applications in optoelectronic devices, fiber amplifiers and solid state lasers [5,6]. Synthesis of uniform nanostructures by accurate control of morphology at nanoscale is a scientific challenge. In recent years, much effort has been directed to the fabrication of nanostructures, which are potentially useful in electronics, optics, catalysis and biomedicine. Nanostructures such as nanorods, nanowires, nanoribbions and nanotubes have attracted much attention due to their unique properties and applications in nanoscale devices [7,8]. It is reported that the modification of the surface chemistry of the nanocrystals through the attachment of organic ligands may lead to the organized assembly of nanocrystals [9].

CdS, a direct band gap ($E_g = 2.42$ eV) material, is being widely used for photovoltaic conversion solar cells, light-emitting diodes for flat panel displays and other optical devices based on its non linear properties [10,11]. CdS nanoparticles show a significant improvement in sensor sensitivity [12] and are used as oligonucleotide labeling tags for the detection of DNA hybridization [13]. CdS semiconducting nanowires have been intensively studied because of its vital optoelectronic applications for laser light-emitting diodes and optical devices based on nonlinear properties [14–16]. Since the band gap of CdS corresponds well with the spectrum of sunlight and conduction band edge is more negative than H^+/H_2 redox potential, these properties enable it to be used efficiently in the process of photocatalytic hydrogen evolution [17]. A number of new methods have been reported for the synthesis of CdS based nanostructures. Most of the methods adopt reaction temperatures above 100 °C. He and Goa synthesized flower-shaped multipods of CdS by hydrothermal route at 180 °C [18]. Li et al. synthesized rod-like and granular shaped CdS nanocrystals by hydrothermal method at temperature at 120 °C [19]. One-dimensional (1D) CdS nanowires have been prepared by many groups at temperature above 100 °C [20–22]. Although these approaches are promising, it is still a challenge for material scientist to develop controllable methods for the synthesis of nanostructures, with 1D anisotropy with simple experimental set up and at temperatures less than 100 °C. Although CdS nanowires with a wide

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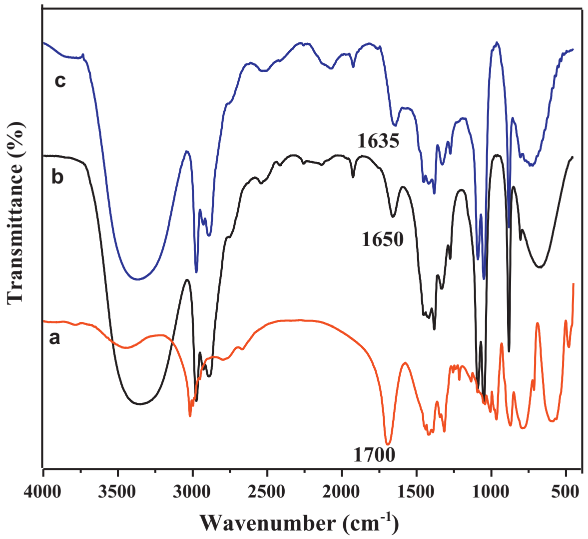

Fig. 1. FTIR spectrum of (a) EDTA, (b) EDTA-capped CdS nanoparticles, and (c) Gd-doped CdS nanoneedles.

distribution of sizes have been achieved by individually tailored routes, there are no reports on concerning the growth of luminescent CdS nanoneedles, which can also be versatile nanoscale building blocks for electronic and photonic nanodevices similar to nanowires.

Incorporation of rare earth ions into the lattice of nanoparticle is a difficult technological task. Generally rare earth ions get physically absorbed onto the surface and hence easily dissociate from surface of the nanoparticles. This will greatly affect their luminescence property and hence seriously limit their applications. To overcome this difficulty, EDTA, a versatile ion-chelating compound was used. It has six binding sites, four carboxylic groups and two pairs of electron on nitrogen. It can simultaneously chelate with cadmium ions on the CdS surface and with free rare earth ion [23]. In this paper, we report a two step process in synthesis of Gd-doped CdS nanoneedles by a simple wet chemical route at temperature below 100 °C. In the first step, EDTA-capped CdS nanocrystals of different shapes are obtained from the same solution at 50 °C for 1 h reaction time. In the second step, Gd is added as a dopant to the EDTA-capped CdS at a slightly higher temperature (70 °C) for longer reaction time (5 h) to obtain luminescent CdS nanoneedles. Formation of CdS nanoneedles is explained on the basis of oriented attachment process, which potentially controls the development of size and morphology [24].

2. Experimental details

In this work, a simple wet chemical route is adopted to prepare EDTA-capped CdS nanoparticles and Gd-doped CdS nanoneedles. All the chemicals were of analytical purity and were used without further purification. 0.201 g of cadmium chloride was dissolved in 50 ml of ethanol (sol A). 0.19 g of thiourea and 0.292 g of EDTA were separately dissolved in another 50 ml of ethanol (sol B). Under vigorous stirring, the solution B was injected into sol A. The mixture was heated at about 50 °C for 1 h. Gradual color change to yellow indicated the formation of CdS nanoparticles. Further, the synthesized yellow color precipitate was washed and centrifuged with water for several times. Finally, the product was dried in vacuum for 5 h and was stored for characterizations. To prepare Gd-doped CdS sample, 0.5 g of EDTA-capped CdS and Gd ions (Gd^{3+}) were extracted from Gd compounds and were added to 50 ml of ethanol and heated to about 70 °C for 5 h. The final precipitate was washed with water thrice to remove the free Gd^{3+} ions and dried in vacuum for 5 h. The products were characterized with Fourier transform infrared measurements (FTIR, Perkin Elmer), X-ray diffraction (XRD, X'per PRO PANalytical), ultraviolet (UV, Varian Cary 5E UV–vis–NIR spectrophotometer), photoluminescence measurements (PL, Fluorolog-3-11 Jobin Yvon spectrophotometer, excitation wavelength 300 nm) and scanning electron microscopy (SEM, Hitachi S-3400) attached with an energy dispersive X-ray spectrometer (EDAX) and transmission electron microscopy (TEM, JEM 3010 JEOL).

3. Results and discussions

FTIR spectra in Fig. 1(a)–(c) show the formation of EDTA-capped CdS nanoparticles and the coordination of trivalent Gd ions (Gd^{3+}) through EDTA to the nanoparticles surface. For unionized EDTA, the strong absorption bands due to the carboxylic group (–COOH) can be identified in the region 1750–1550 cm^{-1}, 1350–1340 cm^{-1} and 950–800 cm^{-1} [25–27], whereas the absorption occurs in the region 1650–1350 cm^{-1} for coordinated EDTA [28]. In comparison with the spectrum of EDTA, the spectra of the EDTA-capped CdS and Gd-doped CdS show quite similar absorption band structure except the strong band at 1700 cm^{-1} (due to free –COOH) shifts to lower wave number 1650 cm^{-1} and 1635 cm^{-1}, respectively. This shift is due to the chelation of carboxylic groups with the metal ions [29]. In addition, some subtle bands vanish in the fingerprint region less than 1550 cm^{-1}. All these data indicate the formation of EDTA-capped CdS and the coordination of Gd to CdS via EDTA. Further, the presence of the dopant, Gd along with CdS is confirmed by EDAX curve as shown in Fig. 2.

Fig. 3(a) and (b) indicates the XRD spectra of the EDTA-capped CdS and Gd-doped CdS which are assigned to hexagonal structure of CdS (JCPDS Card, File No. 75-1545). On doping with Gd, the three peaks around 26.9° are well distinguished. The two diffracted peaks from planes (1 0 2) and (1 0 3) are characteristics of hcp phase. These results are in agreement with the XRD results [30], which are based on the influence of Cd source on the crystal structure. Moreover, there is no peak related to gadolinia in XRD pattern, which indicates that these ions are not incorporated in the lattice but are absorbed

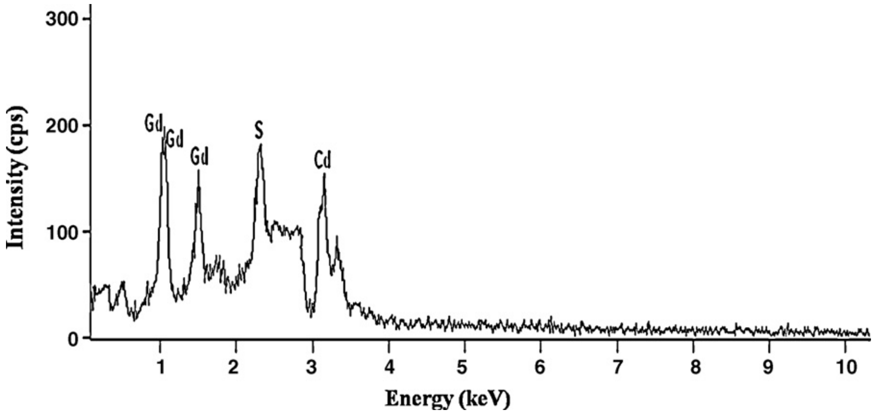

Fig. 2. EDAX analysis of Gd-doped CdS nanoneedles.

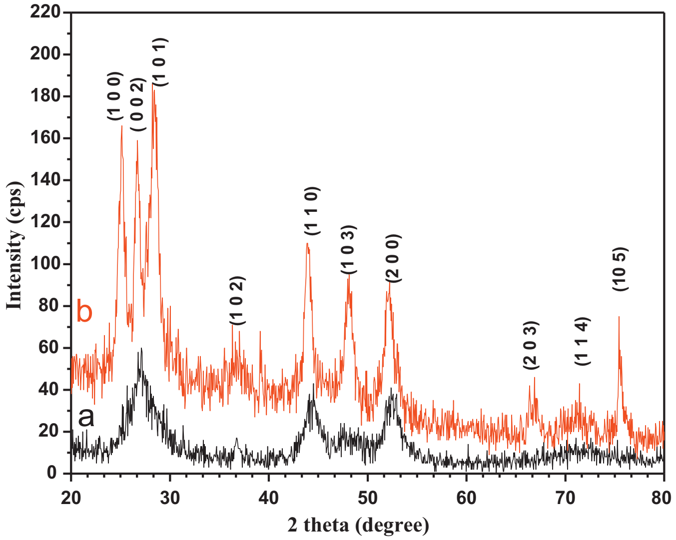

Fig. 3. XRD patterns of (a) EDTA-capped CdS nanoparticles and (b) Gd-doped CdS nanoneedles.

on the surface. This might probably be due to low synthesize temperature adopted for synthesis [4].

It is well known that the optical and electronic properties of the semiconductor would be obviously changed when the particle size is comparable or less than excitonic Bohr radius. The well defined 'excitonic shoulder' in Fig. 4 (curves a and b) of the synthesized sample is the indication of quantum confinement effect. The UV spectrum of the EDTA-capped CdS (curve a) sample shows two excitonic peaks with a step-like absorption [31]; this is possibly relative to the different shapes of nanoparticles present in the sample as shown in TEM (Fig. 6).

Fig. 4 (curves c and d) compares the PL spectra of the EDTA-capped CdS nanocrystals and Gd-doped CdS nanoneedles. Emission peak of the EDTA-capped CdS nanocrystals at 347 nm is assigned to the band edge luminescence. No peaks related traps were observed. The doped sample shows a high luminescent intensity when compared to the EDTA-capped CdS. The lanthanide ion has the inherent ability to form complexes with various Lewis bases in interaction of these functional groups with f-orbital of the lanthanide ions [32]. The enhancement of the fluorescence emission of Gd-doped CdS nanoneedles is due to the chelation of the EDTA with the Gd^{3+} ion. This effectively increases the rigidity of the ligand and reduces the loss of energy by radiation with less decay of the intraligand emission excited state [33]. Hence, the origin of the strong luminescence emission is attributed to ligand–metal charge transfer (LMCT). Further, the luminescence property was verified by cathodoluminescence (CL) mapping image in Fig. 5. Cathodoluminescence technique is used to investigate the optical properties of nanostructures, because of its spatial resolution and surface sensitivity [34].

The size and morphology of the EDTA-capped CdS and Gd-doped samples were investigated using TEM and SEM, respectively. The morphology of the nanoparticles could be facilely controlled through adjusting the experimental parameters like the concentration of the capping agent, reaction time, and temperature [35]. A striking observation of the representative TEM patterns of the EDTA-capped CdS is that the nanoparticles feature various shapes and sizes. The nanoparticles exhibited mixed morphologies of spherical, hexagonal, triangular and rod-like as shown in Fig. 6(a)–(d). Fig. 6(a) shows nanoparticles of uniform size and spherical morphology. The size distribution histogram shows that the particle size ranges from 1 nm to 6 nm, with maximum number of particles around 2 nm. The Fig. 6(b) shows a large number of spherical nanoparticles around 2 nm and a few larger ones of hexagonal shape. Fig. 6(c) and (d) exhibited nanoparticles in different shapes and with the size 30 nm. In all these cases, the nanoparticles are absolutely free from agglomeration.

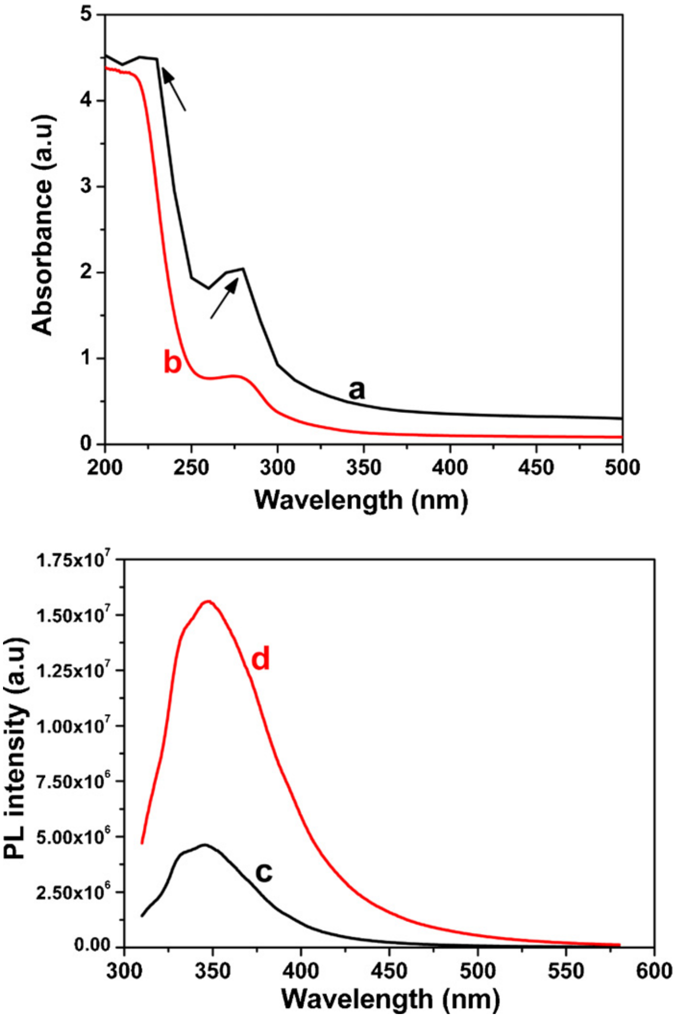

Fig. 4. Room temperature optical absorption (a and b) and photoluminescence spectra (c and d) of EDTA-capped CdS nanoparticles (continuous line) and Gd-doped CdS nanoneedles.

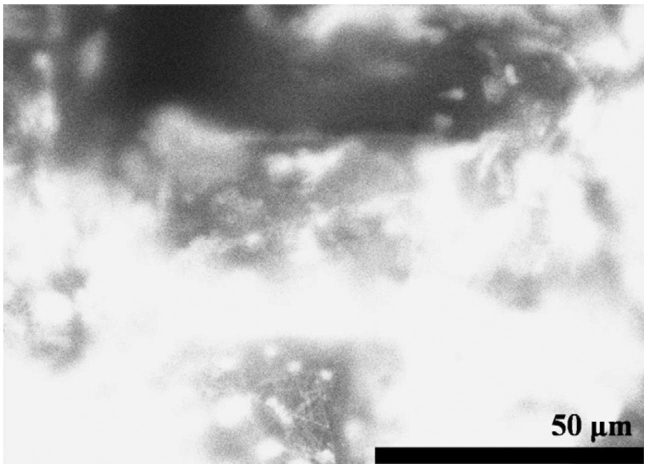

Fig. 5. Cathodoluminescence image of Gd-doped CdS nanoneedles.

The HRTEM image in Fig. 7 shows clear crystal fringes which indicate the formation of high quality CdS nanocrystals. Selected

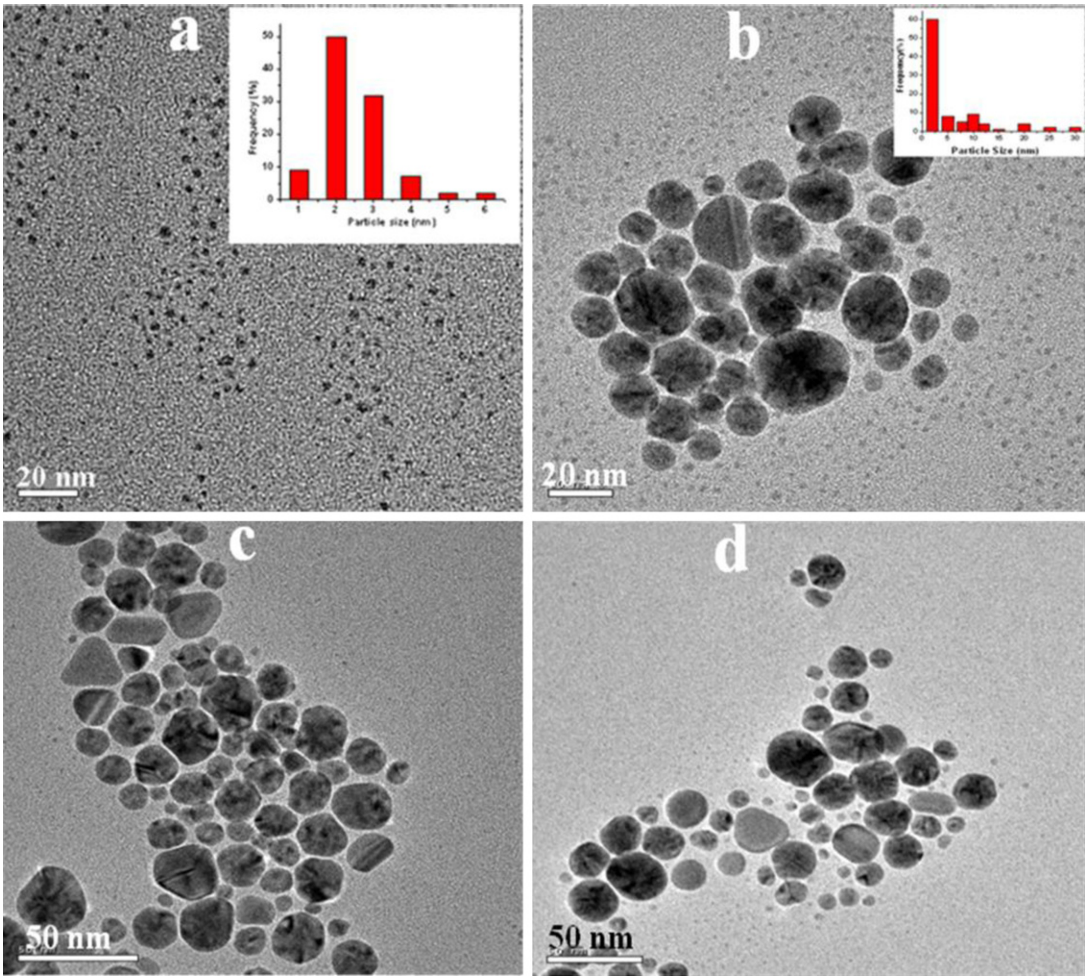

Fig. 6. (a–d) TEM images of EDTA-capped CdS nanoparticles. [Inset: particle size distribution of EDTA-capped CdS nanoparticles.]

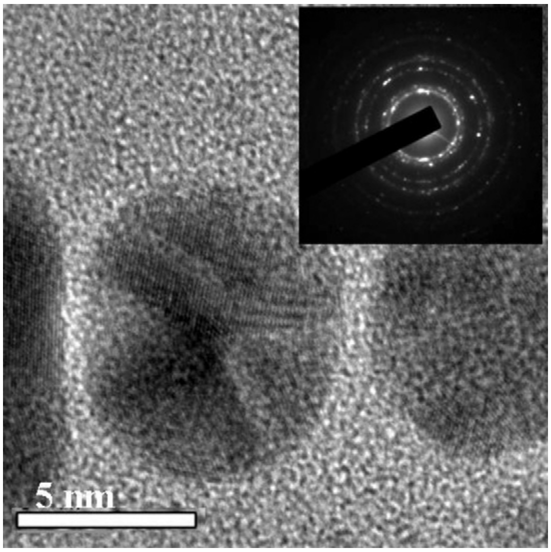

Fig. 7. HRTEM image of individual EDTA-capped CdS nanoparticles. [Inset: SAED pattern of EDTA-capped CdS nanoparticles.]

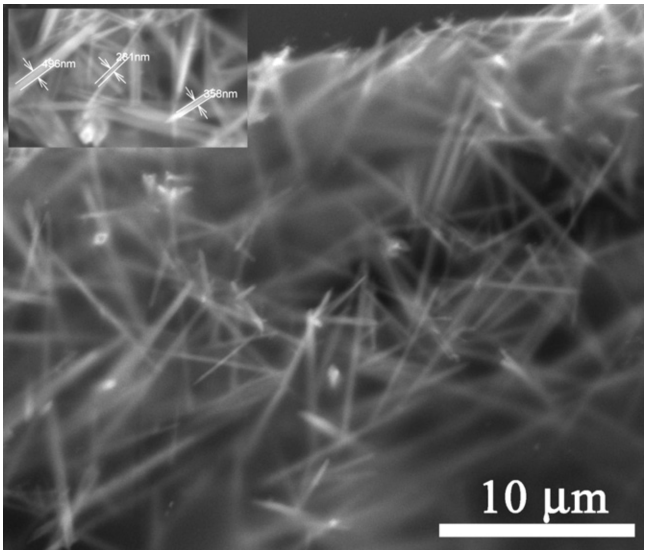

Fig. 8. SEM image of Gd-doped CdS nanoneedles.

area diffraction pattern (SAED) inset shows multiple rings corresponding to wurtzite structure of CdS nanocrystals. Though we have succeeded in getting a regular shaped CdS nanocrystals using EDTA as a capping agent, the reaction parameters must be tailored to get a uniform well-defined shapes. Many researchers have reported high quality nanocrystals of well-defined shape using a bisurfactant system, such as hexylphosphonic acid and trioctylphosphine oxide [36], oleylamine and dodecanthiol [37]. Unlike the EDTA-capped CdS nanocrystals, the SEM image of the

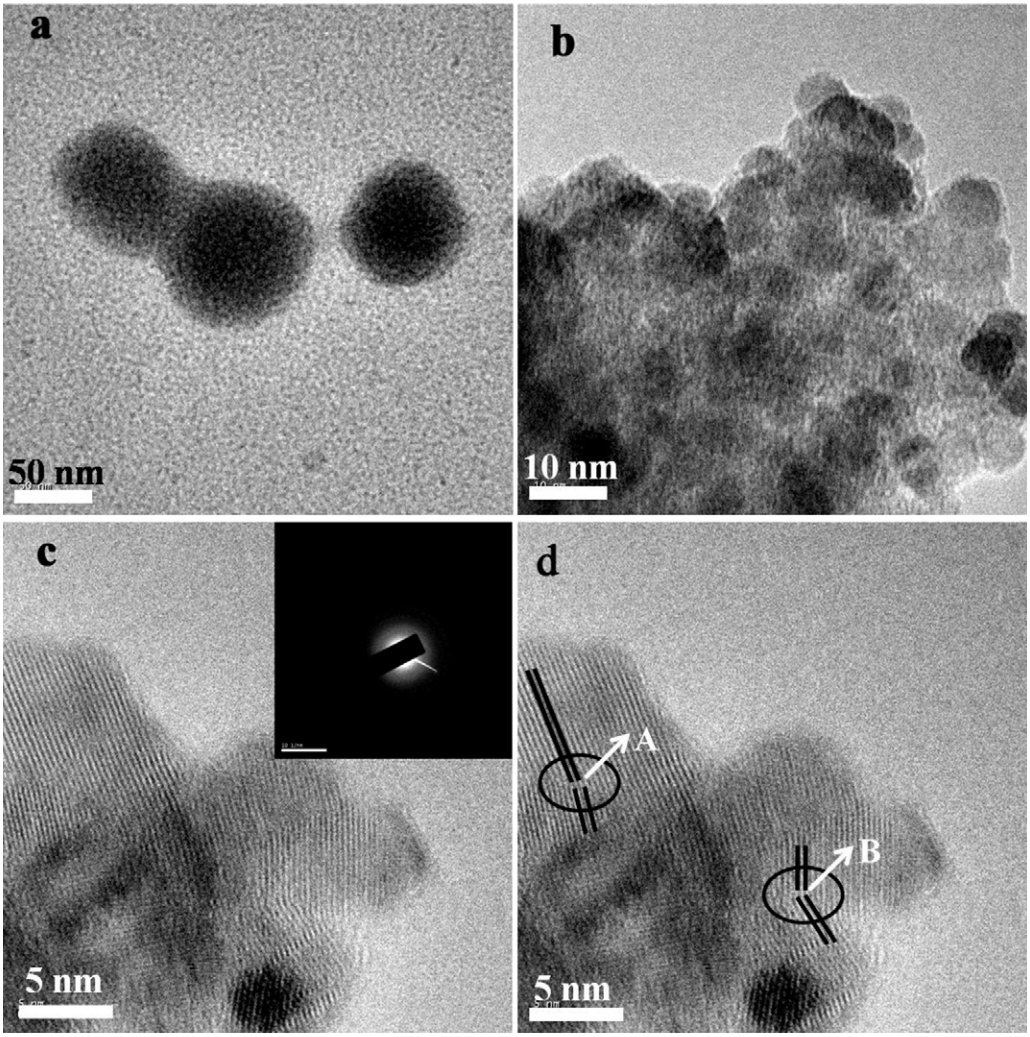

Fig. 9. (a) Oriented attachment of spherical nanoparticles to form CdS nanoneedles. (b) TEM micrographs showing aggregation of CdS nanoparticles resulting in the formation of CdS nanoneedle. (c) HRTEM image shows nanoparticles attached to each other in the common crystallographic orientation. [Inset: SAED pattern of Gd-doped CdS nanoneedles.] (d) The marked regions (A) and (B) shows the interface between assembly units.

Gd-doped samples in Fig. 8 clearly reveals the formation of luminescent CdS nanoneedles. The diameter of the nanoneedles ranges from 255 nm to 650 nm with their length in micrometer range. TEM images of these luminescent CdS nanoneedles in Fig. 9(a) reveal the spontaneous self-organization of adjacent CdS nanoparticles resulting in the formation of nanoneedles. HRTEM images (Fig. 9(b) and (c)) confirm the oriented attachment mechanism, which shows plenty of randomly aggregated nanoparticles trying to share a common crystallographic orientation. The circled regions (A) and (B) in Fig. 9(d) shows the interface between the assembly units. SAED pattern (inset of Fig. 9(c)) of these structures shows diffuse rings indicating the polycrystalline nature. In recent years, several reports on the formation of 1D nanostructures from corresponding nanoparticles by solution-based synthesis have been published [38,39]. Deng et al. [40] reported the formation of sharp tipped nanorods, ultra thin nanowires and three-dimensional sheaf-like and broccoli-like nanostructures of lanthanide compounds by varying the concentration of EDTA. Pacholski et al. reported the formation of ZnO nanorods from self-assembly of ZnO nanoparticles based on “oriented attachment” [39]. Zhang et al. [41] reported the formation of CdS nanorod bundles from the self-assembly of CdS nanoparticles. Nie et al. [42] explained the anisotropic of the CdS nanocrystals taking into account the structure of the intermediate formed during the reaction. Norsten et al. [43] explained the formation of large aggregates of capped gold nanoparticles in the presence of metal ions as a metal directed assembly process. He reported that overall strength of the assemblies can be controlled through choice of bridging metal atom. In our case, the EDTA molecule attached on the surface of CdS facilitates the attachment of the nanoparticles at higher temperature for longer reaction times [17]. These reaction parameters enhance the particle-to-particle attachment which resulting in the formation of CdS needles. The Gd ions attach to the free binding sites of EDTA molecule and impart excellent luminescence to these CdS needles.

4. Conclusions

In this paper, we present a facile route for the size and shape-controlled synthesis of CdS nanostructures. Ethylenediamine tetra acetic acid serves as a good surface-active agent. It plays a significant role as a contributor to growth mechanism and an efficient sequestering agent. Higher temperature and longer reaction times assist EDTA to produce uniform morphology of CdS nanoneedles. Formation of CdS nanoneedles is explained on the basis of oriented attachment of the nanoparticles. High luminescent behavior of these nanoneedles is attributed to ligand–metal charge transfer. The CL measurement shows that these materials serve as a promising candidate for phosphor in display devices.

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