

Structural, Morphological and Optical properties of Samarium-doped CdS nanocrystals

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ABSTRACT

In this section, we have demonstrated the effective preparation of CdS nanocrystals by the inclusion of samarium rare earth ions using a straightforward the coprecipitation approach. The cubic structure's diffraction peaks are apparent in the X-ray diffraction (XRD) study of CdS: Sm³⁺ nanocrystals. Energy dispersive X-ray analysis (EDX) powder composition shows that samarium is present in the CdS. The FESEM image makes it abundantly evident that the extremely tiny particles in these powders aggregated to form clusters. The actual grain forms and size distribution are displayed in the HRTEM picture. Results from EDX analysis show that samarium is integrated into host CdS. Micro Raman spectroscopy shown peaks at 293 and 589 cm⁻¹ matches with the first and second order scatterings of the longitudinal optical phonon modes. In addition to the structure-induced instability caused by the insertion of Sm rare earth ions as well as optical phonon confinement, the 1LO and 2LO modes, which were originally at 299 cm⁻¹ and 599 cm⁻¹, respectively, migrated towards a lower frequency. In this work, structural, morphological and optical features of produced CDS: Sm nanocrystal have been explored.

Keywords: Sm doped CdS. Co-precipitation. XRD, EDX, Raman spectroscopy.

I. Introduction

Investigators have recently become quite interested in cadmium sulfide (CdS) nanocrystals due to their size-dependent optical characteristics, variable band gap, and distinct energy levels. For several decades, Group II–VI semiconductor materials have been at the intersection of extensive theoretical and experimental investigation. A common broad direct bandgap II–VI semiconductor, CdS has a room temperature band gap of 2.42 eV and is widely utilized in solar cells, light emitting diodes, biological imaging, and labeling devices [1]. It is anticipated that the surface and structural flaws would also significantly impact the quantum dots' (QDs) optical and other physical characteristics. It was previously reported lately [2] to synthesize CdS nanoparticles doped with various rare earth elements and to examine the impact of doping on the optical and structural characteristics of CdS nanocrystals. The electrical structure of ions made up of rare earths varies from their counterpart elements due of incompletely filled 4fⁿ shells. The exceptionally sensitive phonon effect of inorganic nanocrystals triggered by rare earth or transition metal ions makes them particularly attractive due to their confined electronic states. Since the ionic radius of Ln³⁺ (> 0.85 Å) is generally larger than that of Cd²⁺ (0.78 Å) in fourfold coordination for blende-type structures [3], the Ln³⁺ dopant ion is not easy to be incorporated into the lattice of host nanocrystals. Limited literature was available on the structural characteristics and Sm³⁺ doping of CdS nanocrystals.

The synthesis of Sm doped CdS nanocrystals using the chemical co-precipitation technique is reported in this paper, along with the impact of doping on the structural characteristics of CdS nanocrystals. The incorporation and influence of dopant ions on the structural, morphological, composition analysis, and Raman spectroscopy were investigated and reported.

II. Experimental Details

Synthesis

Using the coprecipitation approach, Sm³⁺ doped CdS nanocrystals were created. Doped CdS nanocrystals were created using samarium nitrate hexahydrate as the doping reagent at a dosage of 5 mol% samarium. Aqueous solution of cadmium acetate dihydrate (Cd(CH₃COO)₂·2H₂O) and required amount of samarium nitrate hexahydrate (Sm(NO₃)₃·6H₂O) were stirred for 2 hr at room temperature. All chemicals are prepared with 0.1 molarity solution. Aqueous solution of potassium sulfide (K₂S) was added drop wise to the solution (cadmium acetate + samarium nitrate) with constant stirring. pH was maintained at ~ 10 with aqueous ammonia. The mixture was refluxed at ~ 67°C for 1:30 hr to get a saturated solution of CdS: Sm³⁺. To prevent the formation of the most aggregated particles, the resulting precipitate was ultrasonically treated for two hours. The leftover residues in the nanocrystals were then removed by washing with ethanol and deionized water. The sample was vacuum-sealed after being dried in a hot air oven. The above-discussed method was used to synthesize both of the CdS nanocrystals doped with 5 mol% Sm³⁺ ions.

Characterization

The X-ray diffraction (XRD) patterns were recorded using PANalytical X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Morphology and elemental composition were analyzed with Hitachi S-3400 FE-SEM-EDX. A high-resolution transmission electron microscope (HRTEM) was implemented at 200 keV using JEOL JEM-3010 with LaB6 filament, to further investigate the particle size and morphology. Micro-Raman spectra were recorded in the spectral range of 200–1000 cm^{-1} , using a Horiba Jobin-Yvon T64000 photon design, micro-Raman spectrometer that employed an Ar ion laser at a power source of $\sim 50\text{mW}$ with an excitation wavelength of 515 nm.

III. Results and discussion

X-ray diffraction Analysis

Fig. 1 shows the XRD patterns of the represented products having all the peaks corresponding to the cubic phase of the CdS zinc blende structure of the JCPDS card no. 75-0581 [4]. The obtained XRD peaks were specified as the (111), (220), and (311) planes. We observed no peak shift for 5 % Sm: CdS which indicates some dopant ions entered the interstitial sites and some stay on the surface of CdS nanocrystals. The primary peak (111) was slightly moved towards the lower diffraction angle by an increase in dopant ions, which allowed the crystal lattice deformation (lattice expansion) to begin. This implies that without changing the crystal structure, the Sm^{3+} ions replace the Cd^{2+} position inside the CdS crystal lattice. Because Sm^{3+} ions deposit on the edges of grains, the addition of Sm^{3+} ions inhibit grain development. The X-ray powder diffraction measurement's line widening indicates that the produced products are nanoscale. Using Scherrer's equation [5], the crystallite size was derived from the high intensity (111) plane. The estimated grain size was determined to be $\sim 3.6 \text{ nm}$, and we observed that the particle sizes of our samples did not change with the amount of samarium present.

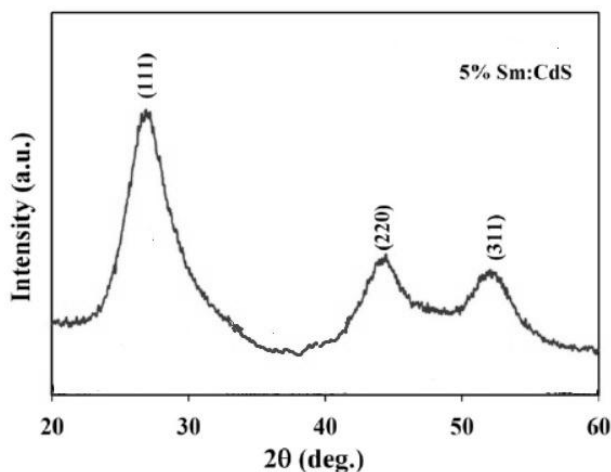


Fig. 1. XRD Patterns of Sm doped nanocrystalline CdS.

The average nanocrystallite size [D] was calculated in according to Debye–Scherrer formula [9]:

$$D = k\lambda / \beta \cos\theta$$

where k is a constant, λ is the X-ray wavelength (1.5405 \AA), β is the full width at half maximum (FWHM) of the main diffraction line, and θ is the diffraction angle. The calculated result indicates that the mean crystalline size of CdS: Eu (QDs) sample is approximately $\sim 3.6 \text{ nm}$.

FESEM Analysis

Fig. 2 shows the FESEM image of the as-synthesized Sm doped nanocrystalline CdS. It clearly reveals that these powders comprised of aggregation of very small particles to form clusters.

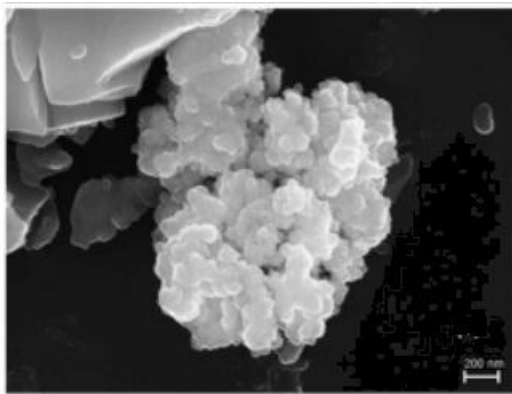


Fig. 2. FESEM image of Sm doped nanocrystalline CdS.

HRTEM Analysis

High resolution transmission electron microscopy (HRTEM) has been employed to evaluate Sm doped CdS in powder form and examine the microstructure of the produced nanocrystals. The HRTEM image shown in Figure 3 demonstrates that the tiny nanocrystal grains that make up agglomerated nanoparticles are numerous. Additionally, it is evident that the injection of rare-earth metal ions caused very little aggregation in the formation of spherical nanocrystals. Lattice fringes are clearly visible in the photograph, showing that the nanocrystals have strong connectivity and crystallinity. In accordance with XRD observations, the high-resolution TEM picture indicates a grain size of around 3.4 nm. It is crucial to remember that the HRTEM picture displays the actual grain forms and their size distribution, whereas the SEM image displays the aggregate particles' characteristic morphology.

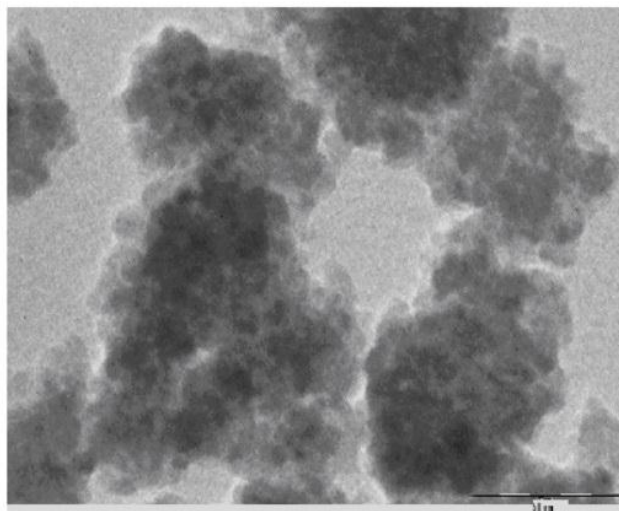


Fig. 2. HRTEM image of Sm doped nanocrystalline CdS.

EDX Analysis

The various components for cadmium, sulfur, and samarium peaks are present in the elemental composition of the Sm doped CdS nanocrystals, as measured by EDX, and is displayed in Fig. 3. As a consequence, and in line with the XRD data, the EDX results show that samarium is integrated into CdS.

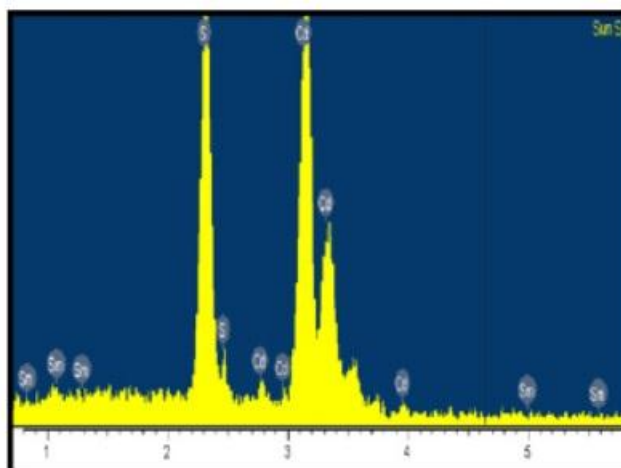


Fig. 4. EDX of Sm doped nanocrystalline CdS.

Raman Spectrum Analysis

A significant contribution of the surface modes is the Raman spectra, which have also been characterized using an equivalent macroscopic method [6]. The CdS nanocrystals were characterized at room temperature using Raman spectroscopy stimulated by an Ar ion laser with a wavelength of 515 nm. Figure 5 displays the micro-Raman spectra of pure CdS and CdS nanocrystals doped with 5% samarium. The produced samples are in the nanoscale range, as confirmed by the Raman spectra's broadness. The spectra clearly identify the first-order (1LO) and second-order (2LO) longitudinal optical phonon modes of RE doped CdS, which are situated approximately at ~ 293 and ~ 589 cm^{-1} , respectively. These modes exhibit typical Raman shifts that are similar to those of pure crystalline CdS [7]. For Sm doped CdS, the fundamental optical phonon mode (1LO), dominates the spectra and shifts from 299 to ~ 293 cm^{-1} and the weak first overtone mode (2LO) shifts from 599 to ~ 590 cm^{-1} for both samples. The most apparent peak for pure CdS nanoparticles is found at around 292 cm^{-1} . It has been discovered both experimentally and conceptually that a substantial asymmetry and frequency shift towards the lower frequency results from the reduction in particle size [8, 9]. The lattice extension and consequent bond weakening, which lowers the resonance frequency, also contributed to this drop (red shift) in the phonon frequency. The quantum confinement manifests as an asymmetric widening of the phonon line beyond the red shift. In some instances, the proportion of intensity of a resonance to the basic phonon vibrations can be used to determine the strength of exciton-phonon coupling in semiconductors. When in comparison to pure CdS, the I_{2LO}/I_{1LO} values for Sm³⁺ doped CdS NCs in this instance suggest that the exciton-phonon coupling became stronger during doping.

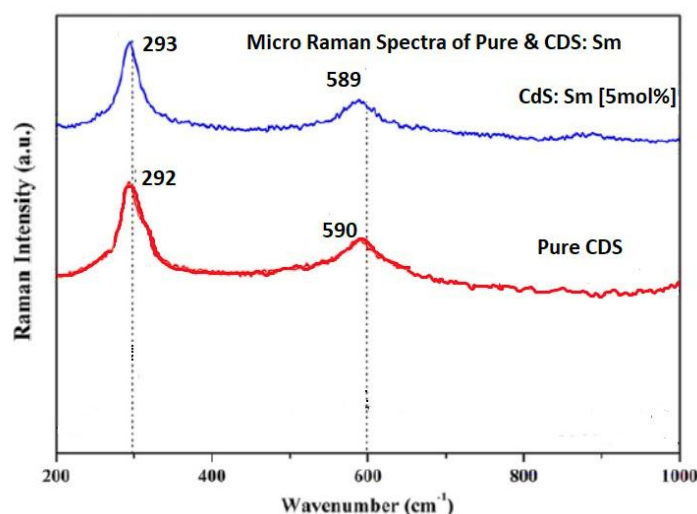


Fig. 5. Micro-Raman spectra of pure and samarium doped CdS nanocrystals.

IV. Conclusion

We present the structural, compositional, and vibrational characteristics of CdS nanocrystals produced by the coprecipitation technique and doped with rare-earth samarium ions. The cubic crystal structure was validated by the XRD and HRTEM investigations, and the Sm: CdS nanocrystals had a size of around 3.4 nm. The HRTEM picture also demonstrated the aggregated nanoparticles made up of several tiny nanocrystal grains. EDX was used to confirm the existence of the Sm ion. The existence of dopant (Sm³⁺) incorporation, which results in optical phonon confinement and CdS lattice expansion, is supported by the shift in the LO peaks and the alteration in the brightness ratio in Raman spectra. The results suggest that the rare earth ions (Eu³⁺, Tb³⁺, Sm³⁺, Nd³⁺, Er³⁺, etc.) can easily be doped into the CdS nanocrystals, which can be used in many fields as chemical sensors, fluorescent probes and as a down-conversion material for harvesting higher energy UV photons for solar cell.

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