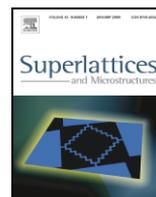




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Large scale synthesis of cadmium selenide nanowires using template synthesis technique and their characterization

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ABSTRACT

We report the fabrication, and structural and optical characterization of CdSe nanowires. Large scale uniform nanowires with length 40 micron and diameter 100 nm were grown using the simple chemical reaction technique. Morphological study of CdSe nanowires was done using scanning electron microscopy (SEM). X-ray diffraction (XRD), and Raman studies show the crystalline structure of CdSe nanowires. Energy dispersive X-ray fluorescence (EDXRF) technique was used to study the composition of CdSe nanowires. UV-Vis absorption studies show a blue shift of 0.26 eV in the optical band gap of CdSe nanowires.

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1. Introduction

Chemically synthesized semiconductor nanowires are drawing increasing attention as building blocks for the bottom-up approach to the invention of nanoscale devices and sensors [1,2]. CdSe is an important II–VI semiconductor material, and has exclusive physical properties such as direct band gap of 1.74 eV and electron mobility of 450–900 cm²/V s [3–7]. Because of high photosensitivity, CdSe has been extensively used in photoconductive devices [8–11].

Different techniques like cation-exchange route [12], γ -irradiation [13], solvothermal synthesis [14], electrodeposition [15,16], hydrothermal-assisted thermal evaporation [17], DNA template

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driven [18], solution based approach [19], multiple injection method [20] etc. have been used for the synthesis of CdSe nanowires. CdSe nanowires grown using vapor transport deposition process exhibits superparamagnetic behavior [21]. CdSe nanowires doped with sulphur could be used in color-tuned photodetectors, nanolasers, biological labels, and nanoelectronics [22].

In this paper, we report the generation of CdSe nanowires using simple chemical reaction method through the pores in Anodic Alumina Membrane (AAM). Chemical reaction takes place inside the pores and the reaction yield is deposited in the pores. The morphological, structural and optical characterization of CdSe nanowires is also reported.

2. Experimental details

AAM (Whatman) is used for the fabrication of CdSe nanowires. The pore size is 100 nm. All the reagents used for the chemical solution are of pure analytical grade. Triply distilled water is used for the preparation of solutions.

Two compartment cell is used for the generation of CdSe nanowires. Alumina template is fixed between the two compartments so that it acts as semi permeable membrane. In the first compartment, an aqueous cadmium acetate solution (0.2 M with some drops of NH_4OH) was added and allowed to diffuse through the membrane for 30 s prior to the introduction of the second reagent Na_2SeSO_3 (0.2 M) in the second compartment. Both solutions diffuse toward each other through the pores of the membrane and react to yield the CdSe. The synthesis process was continued for 60 min at room temperature.

For the SEM characterization, the prepared sample of CdSe nanowires embedded in the alumina membranes was put in the solution of NaOH to dissolve the alumina membrane. The concentration of NaOH solution was taken to be very small (0.5 M) so that it should not damage the CdSe nanowires. It takes long time to completely remove the host membrane. After that nanowires were washed with distilled water and ethyl alcohol several times. Then a small drop of alcohol containing the nanowires was taken for the SEM characterization.

The dried sample of CdSe nanowires were coated with gold–palladium alloy using Jeol JFC sputter coater and then examined under Jeol, JSM 6100 scanning electron microscope. The crystallographic studies of CdSe nanowires embedded in AAM were carried out using Panalytical X'pert X-ray Diffractometer in 2θ range from 20° to 80° using $\text{Cu } k\alpha$ radiation. The optical absorption measurements were recorded using a Shimadzu double beam double monochromator (UV-2500) equipped with an integrating sphere assembly ISR-240A in the wavelength range of 190–900 nm with a resolution of 0.5 nm.

The Raman studies of CdSe nanowires were carried out using the WiTec CRM 2000 Raman spectrometer coupled with a high resolution confocal optical microscope. With this combination it is not only feasible to obtain a Raman spectrum of a sample but also to combine its chemical information with a lateral resolution in the sub-micrometer regime. In Raman studies excitation was done using the 514.5 nm line of an Ar^+ laser. The microscope objective used was Nikon 100X, with a working distance 0.26 unit. Thus, the laser beam diameter at the focus is approximately in submicron regime. All the measurements were carried out at room temperature, in order to avoid heating effects in the spectra.

3. Results and discussion

Fig. 1 shows SEM image of CdSe nanowires. It can be seen that diameter of nanowires is about 100 nm that closely corresponds to the diameter of pores of AAM used and also all the CdSe nanowires have analogous orientation and the length, diameter and direction of growth of CdSe are reasonably uniform which is due to the confined growth of nanowires in the ordered pores of AAM template.

X-Ray diffractogram of CdSe nanowires embedded in AAM template is shown in Fig. 2. The spectrum depicts three peaks at 25.2° , 42.1° and 50.1° that correspond to (111), (220) and (311) planes, respectively. A investigation of broadening of XRD peaks imply that CdSe nanowires so synthesized are possibly not single crystalline but are assembled from nanocrystallites [23]. Zinc

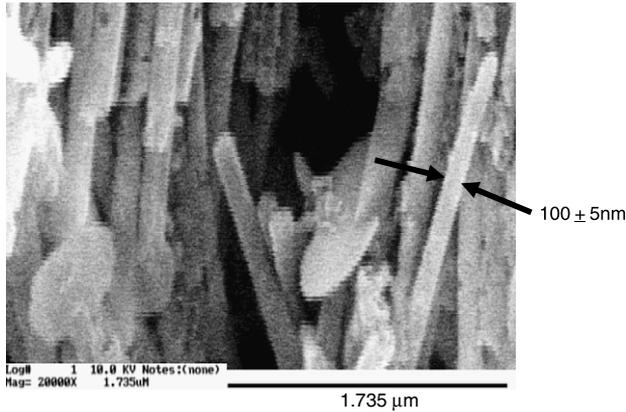


Fig. 1. SEM image of template synthesized CdSe nanowires.

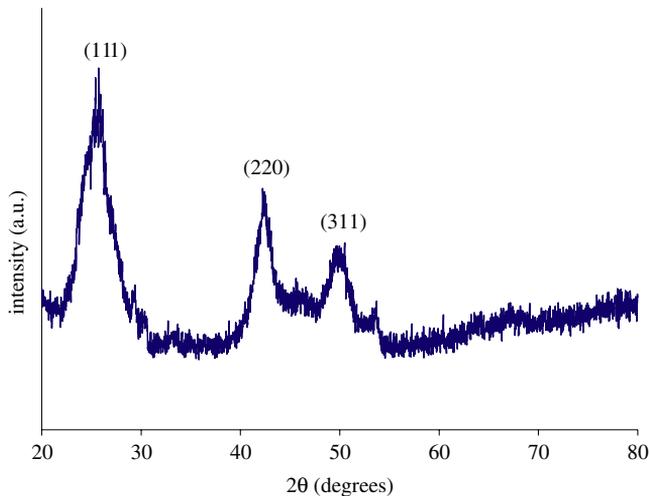


Fig. 2. X-ray diffractogram of CdSe nanowire arrays.

blende type nature of nanocrystallites is observed after comparison of observed d values with standard d values [24].

Crystallite size can be estimated by using Debye–Scherrer formula [25]:

$$D = 0.93\lambda / \beta \cos \theta$$

where D is the diameter of the particles; $\lambda = 1.518 \text{ \AA}$ (CuK α radiation wavelength); β = full width at half maxima; θ , is the Bragg's angle. By substituting these values, the size of the nanoparticles was found to be about 3.6 nm.

To verify the chemical composition of CdSe nanowires energy dispersive X-ray fluorescence (EDXRF) technique was used. The EDXRF spectrum is shown in Fig. 3 which clearly reveals that nanowires are composed of Cd and Se. There is also a peak corresponds to chlorine, may be due to some chlorine residue as remains in the sample holder during previous measurements. But the exact reason for the small amount of Ni and Zn is not found.

The Fig. 4 presents the absorption spectrum of CdSe nanowires. The optical band gap found from absorption spectrum is 1.96 eV, which is higher than normal band gap (1.7 eV) for bulk CdSe [26], showing a blue shift of 0.26 eV in band gap. Quantum confinement effect is responsible for the blue

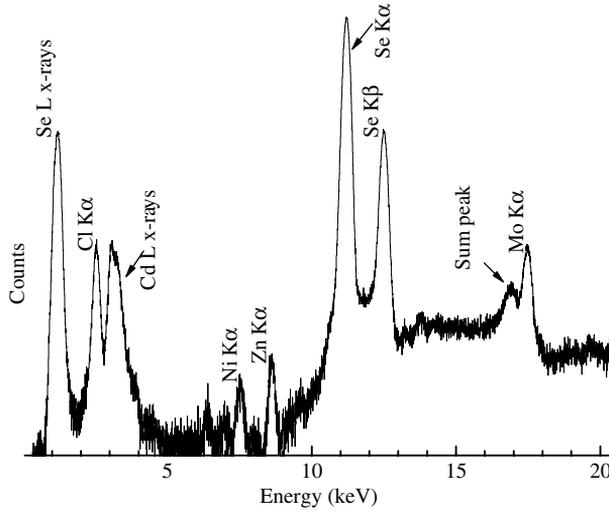


Fig. 3. EDXRF spectrum of CdSe nanowires.

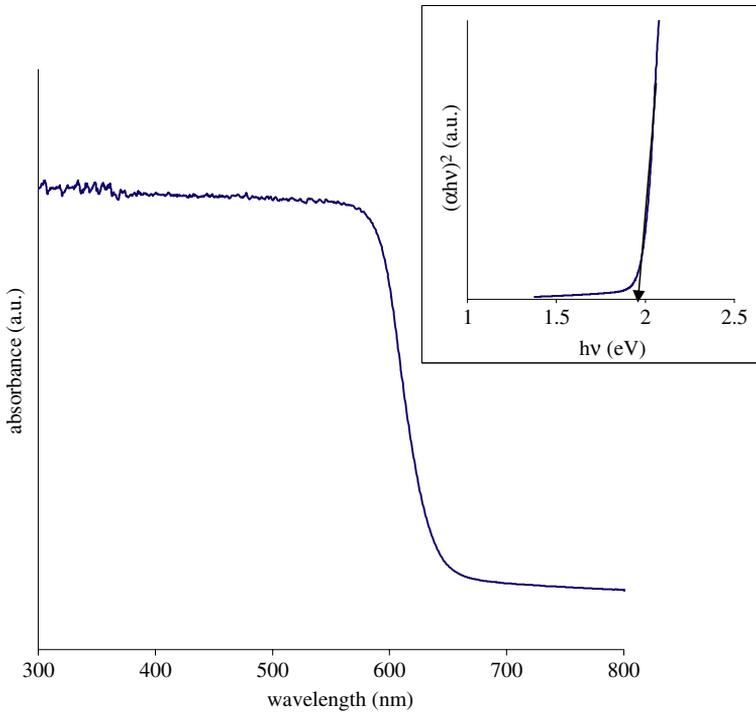


Fig. 4. Plot of absorption (α) versus wavelength (λ). Inset shows the plot of $(\alpha hv)^2$ versus $h\nu$ for CdSe nanowires.

shift in band gap [27,28]. Because of the localization of electrons and holes in the semiconductor nanocrystallites, quantum confinement effect occurs. This effect causes a change in electronic band structure and consequently a higher value of optical band gap is observed as compared to that of the bulk.

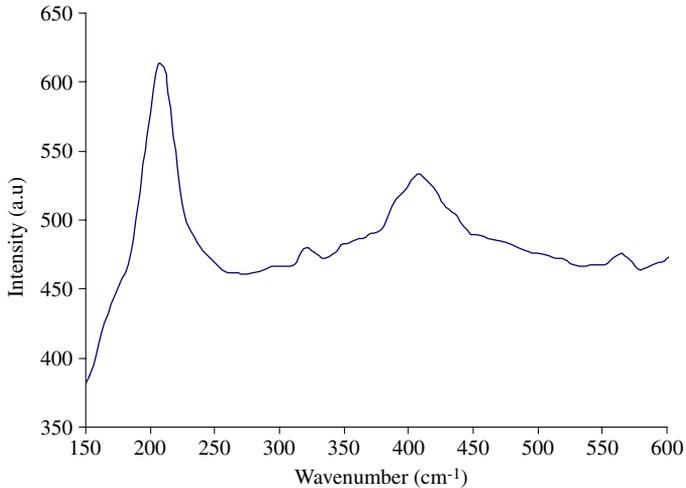


Fig. 5. Micro-Raman spectrum of CdSe nanowires.

A room temperature Raman spectrum of the CdSe nanorods (Fig. 5) presents the phonon frequencies of the longitudinal optical (LO) and its overtone (2LO) modes of CdSe nanowires to be 210.4 and 409 cm^{-1} , respectively. This blue-shift of 2LO peak can be compared to the wave numbers for bulk CdSe of 418 cm^{-1} [29,30]. In our case CdSe nanowires have diameters that exceed 40 nm, so quantum confinement of the phonon motion due to the size effect is insignificant, and therefore size is not likely to contribute appreciably to this spectra shift. Venugopal et al. [31] and Zhang et al. [32] reported that lattice contraction may be the real basis for peak shift when they investigated free-standing CdSe quantum dots and CdSe sheets. In our case there is a blue shift in 2LO peak of the order of 9 cm^{-1} . This shift may be due to the lattice contraction during growth. This lattice contraction can be attributed due to the surface tension experienced during surface reconstruction when the nanocrystallites grow and this contraction happens mostly on the surface [32].

4. Conclusion

Simple chemical reaction (non-galvanic) technique is a constructive technique for the large scale growth of CdSe nanowires. XRD shows the zinc blende (cubic) nature of CdSe nanowires. Blue shift of the order of 0.26 eV is observed in the optical band gap of 100 nm CdSe nanowires. Micro-Raman spectrum indicates the CdSe nanowires have good crystalline nature.

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