J Mater Sci (2011) 46:5412–5416
DOI 10.1007/s10853-011-5481-0

Chemical synthesis of CdS nanoparticles and their optical and dielectric studies

Ziaul Raza Khan · M. Zulfequar · Mohd. Shahid Khan

Received: 21 December 2010 / Accepted: 16 March 2011 / Published online: 29 March 2011

Abstract Cadmium sulphide nanoparticles were synthesized by chemical displacement reaction method using cadmium nitrate as cadmium source and ammonium sulphide as sulphur source. The CdS samples are characterized using X-ray diffraction, UV–Vis spectroscopy, FTIR spectroscopy, scanning electron microscopy and impedance spectroscopy. CdS nanoparticles are found to possess cubic structure with the crystallite size ~ 10 nm. The absorption spectra of synthesized CdS nanoparticles revealed the blue shift in excitonic transitions with respect to CdS bulk material, clearly confirming the formation of nanoparticles. The dielectric properties of CdS nanoparticles are studied in the frequency range 10^3–10^7 Hz at room temperature. The dielectric properties of CdS nanoparticles are found to be significantly enhanced specially in the low frequency range due to confinement.

Introduction

Semiconducting optoelectronic materials play functional role in variety of applications due to their extraordinary optical, electrical, magnetic and piezoelectric properties. Modifications of the optical, electrical, magnetic and physical properties of semiconductor materials strictly depend upon the sizes, structures and morphologies [1, 2]. Due to these changes in properties with the crystallites size, researchers interest turn towards the synthesis of semiconductor particle in the few nanometre range with dimensions comparable to the Bohr radius. The semiconductor nanoparticles within the dimension of Bohr radius exhibit strong size dependent properties. Such particles may lead to quantum dot lasers, single electron transistors and also have biological applications [3, 4]. It is important to synthesize nano particle at the desired size within a narrow size distribution and in an easy to handle conditions of precursor, solvent and temperature etc. Cadmium sulphide (CdS) is a brilliant II–VI semiconductor material with a direct band gap of 2.42 eV at room temperature with many outstanding physical and chemical properties, which has promising applications in multiple technical fields including photochemical catalysis, gas sensor, detectors for laser and infrared, solar cells, nonlinear optical materials, various luminescence devices, optoelectronic devices and so on [5–8]. Cadmium sulphide (CdS) has excellent visible light detecting properties among the others semiconductors [9]. In the last decades, many techniques have been reported on synthesis of CdS nanoparticles [10–12]. The possibility of finding new experimental methodologies that can yield very low cost and low size- and shape-dispersion nanoparticles at a low cost. In last few years, researchers have been devoted to the preparation of high-quality CdS nanoparticles and the investigation of their various properties. In this study, synthesis of CdS nanoparticles by simple chemical route using cadmium nitrate and sodium sulphide inorganic precursor, and their characterization by XRD, Optical spectroscopy, FTIR, scanning electron microscopy (SEM), and electrical studies are reported.

Experimental

In this study, we have used Cadmium nitrate $Cd(NO_3)_2$ as a Cd^{+2} ion source and sodium sulphide Na_2S as a chalcogen

Z. R. Khan · M. Zulfequar · M. S. Khan (✉)
Department of Physics, Laser Spectroscopy Laboratory,
Jamia Millia Islamia, New Delhi 110025, India
e-mail: shahidkhan_m@yahoo.com; mskhan@jmi.nic.in

ion S^{-2} source, respectively. For the synthesis of CdS nanoparticles, the 50-mL aqueous solution of (0.1 M) $Cd(NO_3)_2$ and 50-mL aqueous solution of (0.1 M) Na_2S were prepared. The freshly prepared aqueous solution of 0.1 M Na_2S was mixed drop by drop in the 0.1 M $CdNO_3$ solution using strong stirring. As the reaction started, the mixture gradually changed from transparent to pale yellow or cream coloured and after the completion of reaction this turned to dark yellow. The precipitates were washed several times with ethanol and centrifuge and were dried at 70 °C for four hours in vacuum. To remove any type of unreacted impurities, it was then washed three times with methanol and dried by evaporation method. The X-ray diffraction (XRD) pattern was recorded using the Panalytical Diffractometer (Model PW3710) which was operated at 30 kV and 30 mA (Cu K_α irradiation, $\lambda = 1.542$ Å). The optical property of nanoparticles was measured using the double beam spectrophotometer model (Jasco V-570). The IR spectrum was recorded using SHIMADZU FTIR-8400S Japan in the range of 400–4500 cm^{-1}. The CdS nanoparticles were palletized in the form of disk, whose two surfaces were coated with silver coating. The dielectric measurements were carried out using Alfa-A high frequency impedance analyzer (nova control technologies). The entire chemicals used were of analytical grade.

Results and discussion

X-ray diffraction analysis

Figure 1 shows the XRD pattern of the as-synthesized CdS nanoparticles. The XRD pattern of CdS has three strong peaks at the angles (2θ) of 26.56°, 43.79°and 52.85°, which could be indexed to diffracting from the (111), (220) and (311) planes, respectively, of the cubic CdS crystal lattice, which is in very good agreement with the international centre for diffraction data (JCPDS card file no. 75-1546). Average particle size is estimated to be 10 nm according to the Scherer equation ($D = K\lambda/\beta_{2\theta}$ cos θ, where K is a constant taken to be 0.94, λ is the X-ray wavelength ($\lambda = 1.54$ Å), $\beta_{2\theta}$ is the full width at half maximum of the XRD selected diffraction peak on the 2θ scale and the θ is the diffraction angle).

Optical properties

An absorbance spectrum of CdS nanoparticles is shown in Fig. 2. Blue shift is observed in band edge as compared to bulk CdS absorbance spectrum, revealing a characteristics confinement effect on the carriers due to reduction in size within few nano meter dimensions.

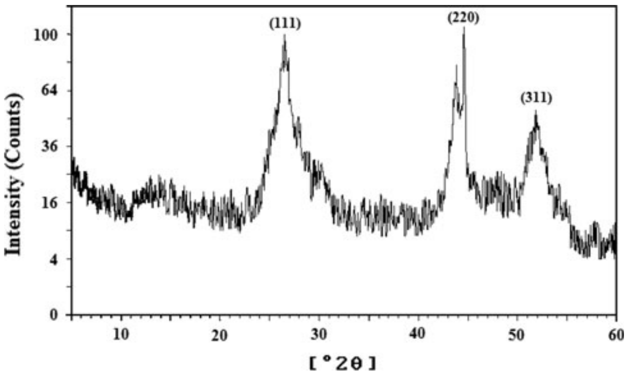

Fig. 1 XRD pattern of Cadmium sulphide nanoparticles

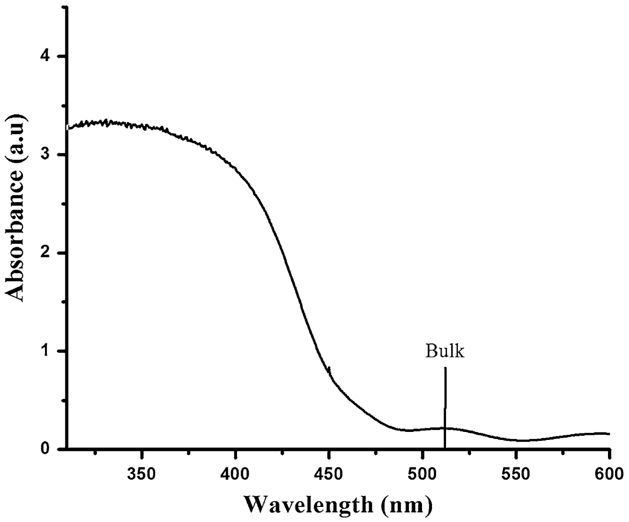

Fig. 2 Absorbance spectrum of Cadmium sulphide nanoparticles

The value of the band gap is found to be 2.54 eV.

The grain size of nanoparticles is estimated adopting the procedure as described elsewhere [13] using the equation given under

$$E^{\mathrm{eff}} = E_g + \hbar^2\pi^2/2\mu R^2 - 1.8\ e^2/4\pi\varepsilon\varepsilon_0 R \qquad (1)$$

with ($1/\mu = 1/m_e^* + 1/m_h^*$), m_e^* is the effective mass of the electron (0.19 m_e), m_h^* is the effective mass of hole (0.8 m_h), R is the radius of the particle, ε is the dielectric constant (5.7) and ε_0 is the permittivity of free space. The particle size of the CdS nanoparticles as estimated using the Brus equation are found to be 12 nm to the size as estimated from the XRD analysis.

FT–IR analysis

FTIR spectrum of CdS nanoparticles is shown in Fig. 3. The strong absorption band observed at 623.01 cm^{-1} is due to the CdS stretch vibrations [14]. The absorption band observed at 1230.64 cm^{-1} is attributed to the nitrate group,

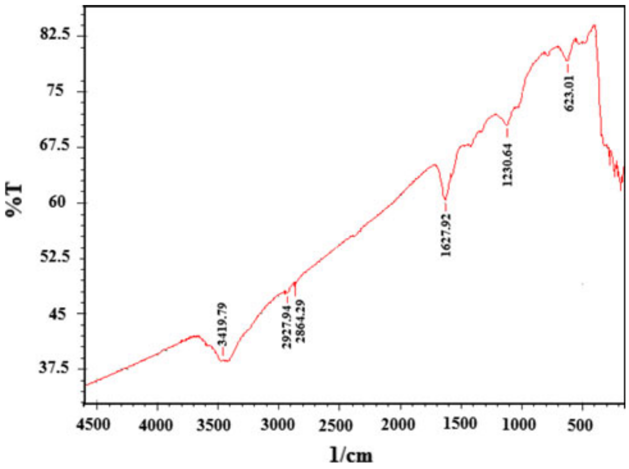

Fig. 3 FTIR spectrum of CdS nanoparticles

which is due to the nitrate group residue from the precursor used for synthesizing the CdS nanoparticles. The bending vibration of water molecules is found at 1627.92 cm^{-1}. The presence of weak symmetric and asymmetric absorption band observed at 2864.29 and 2927.94 cm^{-1} are due to the Cd–O vibrations. The peaks at 3419.79 cm^{-1} correspond to O–H stretch vibrations of water molecules [15].

SEM analysis

Scanning electron microscope is a suitable technique to study the particle size of materials. SEM micrographs recorded at different resolution of as-synthesized CdS nanoparticles are shown in Fig. 4. From these SEM images it is noticed that the surface morphologies are in the form of assemblies of nanoparticles having round shape. The CdS nanoparticles are uniformly distributed over the entire surface as can be observed in Fig. 4. The particle size of nanoparticles as seen in the SEM micrographs is of the order of tens of nanometres. It is also important to mention here that the grain size of CdS nanoparticles estimated from XRD and that obtained using SEM is nearly equal.

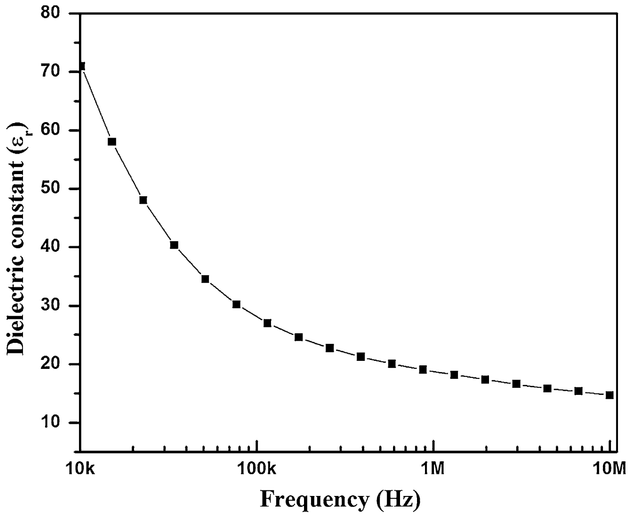

Fig. 5 Variation of dielectric constant of CdS nanoparticles with frequency

Dielectric properties

Relative dielectric constant (ε_r) of as-synthesized CdS nanoparticles measured in the frequency range of 10^3–10^7 Hz is shown in Fig. 5. The relative dielectric constant of CdS nanoparticles is found to show usual behaviour, i.e. ε_r is found to decrease rapidly from 10^3 to 10^4 Hz whereas it decreases slowly in the range of 10^5–10^7 Hz. The value ε_r of CdS nanoparticles is found to be very high as compared to bulk cadmium sulphide, which is in good agreement with earlier reports [16]. Interpretation of high value of ε_r is very remarkable, we cautiously explain these data. According to Zhang and co workers [17], specific surface of nanosized materials is of the order of 10^{19}, much larger than that of the corresponding bulk

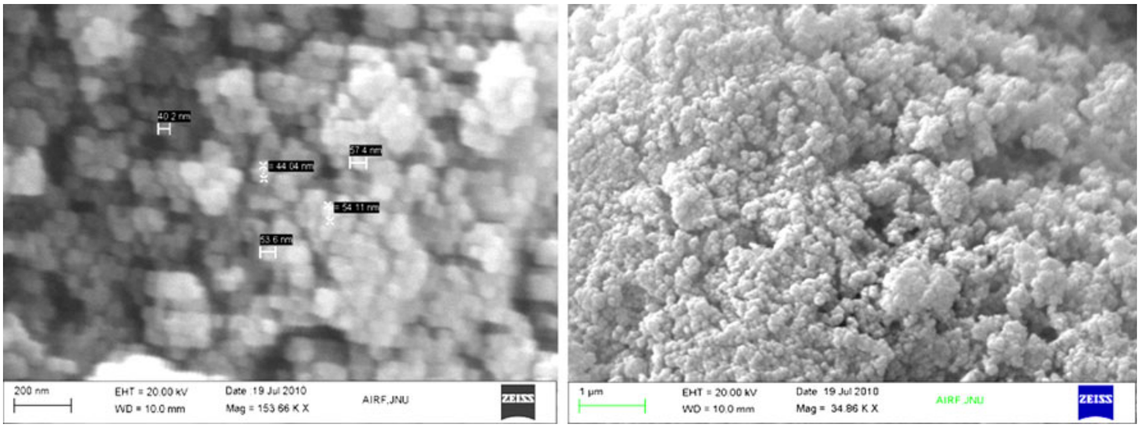

Fig. 4 SEM micrographs of CdS nanoparticles

solids. In this experiment, palletised nanoparticles using very high pressure (5 Ton) have been used, so interfaces with this kind of large volume fraction in the nanosized samples must contain a great deal of defects including micro porosities, vacancies, vacancy clusters and dangling bonds. These defects can cause a change of positive and negative space-charge distributions in the interfaces. The pallets exposed to an external electric field, positive and negative charges on interfaces moves towards the negative and positive poles of electric field, respectively. Meanwhile, a great number of dipole moments are unavoidably formed after they have been trapped by defects. Consequently, space-charge polarization occurs in the interfaces of CdS nanoparticles, which results in the much larger ε_r for CdS nanoparticles. For conventional CdS powders, it is impossible to observe space-charge polarization due to the smaller specific surface.

The dielectric loss (tan δ) of as-synthesized CdS nanoparticles is shown in Fig. 6. In the low frequency region high energy loss is observed, this may be due to the dielectric polarization, space-charge and rotation-direction polarization occurring in the low frequency range. The value of tan δ is found to be 1.2 in the frequency range $f < 10^5$ Hz and for $f > 10^5$, the value of tan δ is observed to be 0.2. The value of dielectric loss is found to be higher than that its value for the bulk CdS in the low frequency region.

The a.c. conductivity of CdS nanoparticles is shown in Fig. 7. The conductivity can be explained by the power law reported by Almond and West [18]. The a.c. conductivity σ in CdS is found to increase with the frequency. The relaxation is observed in entire frequency range as a gradual increase in conductivity with increasing frequency. The nature of dielectric permittivity related to free dipoles oscillating in an alternating field may be described in the following way. At very low frequencies ($\omega \ll 1/\tau$, τ is the relaxation time), dipoles follow the field and as the frequency increases ($\omega > 1/\tau$), dipoles lag behind the field and conductivity increases slightly. When frequency reaches the characteristic frequency ($\omega = 1/\tau$), the conductivity increases. At very high frequencies ($\omega \gg 1/\tau$), dipoles can no longer follow the field and conductivity increases rapidly.

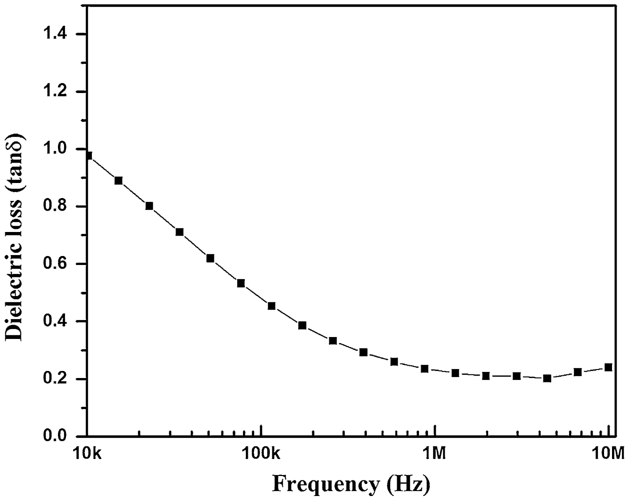

Fig. 6 Dielectric loss of CdS nano particles, as a function of frequency

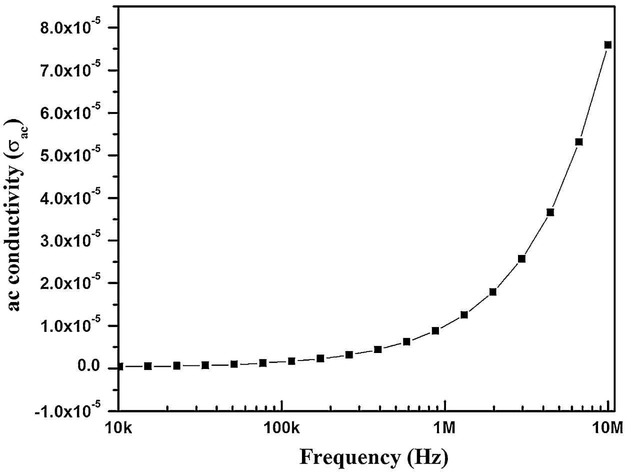

Fig. 7 A.c. conductivity of CdS nanoparticles as a function of frequency

Conclusion

CdS nanoparticles with cubic phase were successfully synthesized by chemical precipitate method using $Cd(NO_3)_2$ and sodium sulphide (Na_2S) inorganic precursor. We have observed a blue shift in band edge of absorption spectrum. The value of band gap is found to be 2.54 eV. The relative dielectric constant, dielectric loss and a.c conductivity of synthesized CdS nanoparticles are measured in the frequency range 10^3–10^7 Hz at room temperature. The relative dielectric constant of CdS nanoparticles is found to be much larger than that of the bulk CdS powder. This enhancement in dielectric properties is due to the confinement of grain size in Bhor’s radius.

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