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Impedance Study of Nanostructure Cadmium Sulfide and Zinc Sulfide

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Abstract

A simple chemical route for the synthesis of inorganic semiconductor nanoparticles has been reported. CdS and ZnS nanoparticles have been synthesized using respective metal precursors and DMF as a stabilizing agent. The samples have been analysed by XRD, UV-VIS, fluorescence spectroscopy and TEM. Crystalline nature and particle size calculated from broad peaks in the diffraction pattern along with blue shift in absorption spectra confirms the formation of nanoparticles with the particle size less than 10 nm. Illumination of these semiconductor colloids generates holes and electrons and the recombination of charge carriers is accompanied by emission of light which is observed in fluorescence spectra. TEM micrograph also reveals the nanosized particles of CdS and ZnS. Impedance analysis of the samples was carried out to reveal the variation of impedance with frequency at room temperature. These results shows the capacitive admittance associated with the nanoparticles and hence nanostructure CdS and ZnS can have potential applications in the electronics as nano-tuned devices in which resonant frequency can be adjusted by controlling the size and shape of the nanoparticles.

Keywords*:* Nanostructure; impedance; fluorescence; nano-tuned device; CdS; ZnS

INTRODUCTION

In recent years, study of nanomaterials is becoming the fast growing area of research due to their numerous applications in almost all areas of utilities. This is because it gives an opportunity to understand the physical properties in low dimensions which explore totally different properties than that of bulk materials like blue shift in optical absorption spectrum, increased effective surface area, reactivity, phase-phase transformation, strength etc. Semiconductor nanomaterials have attracted much research interest because of their novel properties originating from quantum confinement effect. Interest in semiconductor nanomaterials is driven by their unique properties. One example of the unique properties of these materials is illustrated by the discovery of solvothermally synthesized quantum dots (QDs) of CdS had a blue shift in the visible absorption and emission spectra compared with bulk CdS.[1,2] Among various nanomaterials, II-VI class

inorganic semiconductor nanomaterials like CdS, ZnS, CdSe, ZnSe etc are proved to be versatile materials because of their applications in optoelectronic devices due to large variation of band gap as a function of particle size. Cadmium Sulfide (CdS) and Zinc Sulfide (ZnS) nanomaterials have attracted considerable interest in recent years. CdS is a wide band gap semiconducting material having band gap energy 2.4 eV and widely used because of its size dependent photophysical, photochemical and non-linear optical properties etc.[3-5] ZnS (band gap energy 3.6 eV) is also most widely used nanomaterials in solar cells, electro luminescent devices for the cathode ray tube, field emission display and scintillator as one of the most frequently used phosphors.[6-8]

A lot of work has been done on the synthesis of these nanomaterials but a wet chemical method is most suitable and accepted as a promising technique because of the ability of the production of various size and large quantities of nanoparticles. Hence, in this investigation, chemical precipitation method has been used for the synthesis of CdS and ZnS nanomaterials using DMF (N,N-Dimethyl Formamide). Most of the study related to CdS and/or ZnS nanomaterials is focused on the optical properties.[9] In this investigation, emphasis has been given on the impedance study of the CdS and ZnS nanomaterials which shows the use of these nanomaterials in the field of electronics as quantum dot tuned electronic devices. Now a days, devices based on the nanomaterials are replacing the traditional ones and are forefront of research in almost all areas of modern technologies. In this study, nanomaterials have been characterized by XRD, UV-VIS, fluorescence spectroscopy and TEM. The impedance study of these nanomaterials provide the futuristic scope in electronics circuits.

MATERIALS AND METHODS

Experimental

CdS and ZnS nanoparticles have been synthesized using respective metal precursors, i.e. cadmium nitrate and zinc acetate and for a source of sulfur, sodium sulfide (Na_2S) was used. All the chemicals used were of AR grade. Initially specific molar concentration of metal precursor was stirred with 100 ml DMF for 10 minutes and then equimolar sodium sulfide in aqueous solution was added dropwise. The stirring was continued for 2 hours for the completion of precipitation reaction. Then precipitate was filtered, washed with acetone and dried in vacuum oven at 60^{o}C. Bright yellow powder of CdS and light gray powder of ZnS nanocrystallites have been obtained.

The samples have been characterized by XRD to confirm the crystalline phase of the samples, (Philips–PW-700 automatic X-ray diffractometer using CuKα radiation (λ= 1.5404Å), UV-VIS absorption spectroscopy (UV-1800 Shimadzu double beam spectrophotometer), Fluorescent spectroscopy (RF-5301 Spectrofluorophotometer) and TEM (PHILIPS model- CM200 with resolution 2.4Å) to know the formation of nanosized CdS and ZnS. Impedance measurement was done using Agilent Precision Impedance Analyzer-4294A to study the variation of impedance with frequency at room temperature. For this, powdered samples were molded in to pellets of equal thickness by applying the pressure of 4 tons in hydraulic press.

RESULTS AND DISCUSSION

The broadness of the diffraction peaks as obtained in XRD spectra (fig. 1) gives the direct consequence of the reduced particle size and crystalline phase of CdS and ZnS indicating the nanocrystallites with (111), (220) and (311) planes corresponding to broad peaks around 2θ values of 26.56^o, 44.06^o and 52.8^o for CdS and 28.66^o, 47.56^o and 56^o for ZnS. The broadness of

peaks indicates the formation of nanoparticles and sharp peaks indicates the crystalline nature of the materials. The increased in the peak width is the evidence of decrease of particle size as also noticed in the optical results. The average particle size was found to be 9.3 nm for CdS and 8.7 nm for ZnS, calculated using following Debye Scherrer formula.[10]

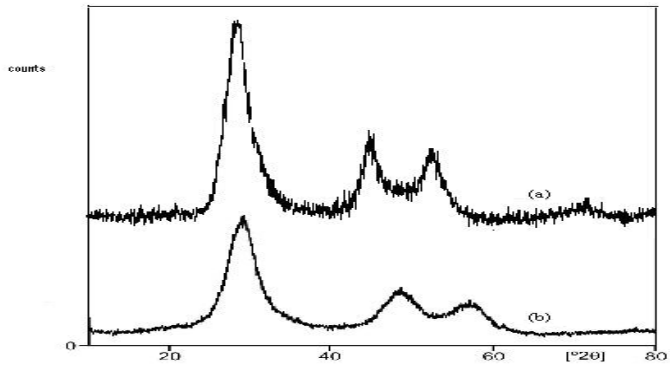


Fig.1: XRD spectra of (a) CdS, (b) ZnS nanomaterials

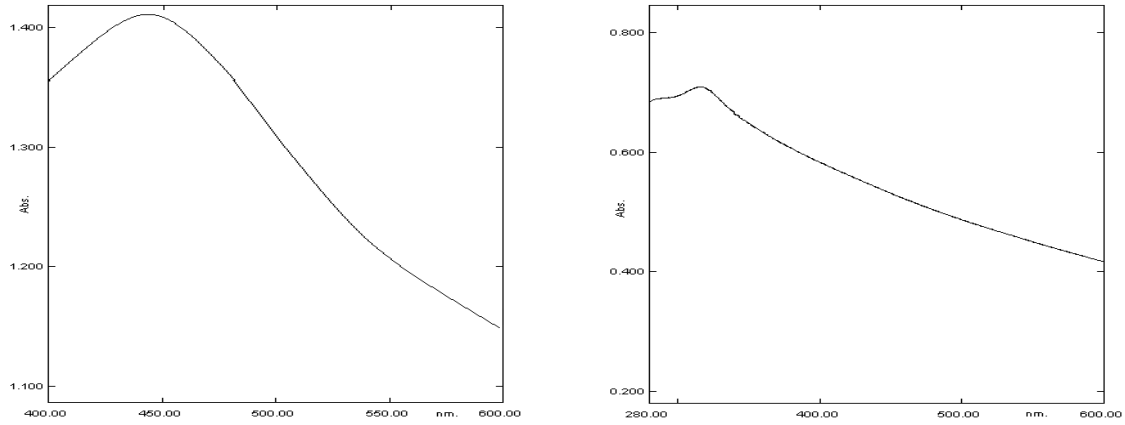
UV-VIS absorption spectra (fig. 2) of the samples show a strong blue shift. From the blue shifted absorption edge, the particle size has been assessed by using following Brus formula.[11]

$$E_{gn} = \left[E_{gb}^2 + \left\{ \frac{2h^2 E_{gb} \left(\frac{\pi}{R} \right)^2}{m^*} \right\} \right]^{1/2}$$

where, R is radius of the particle size, E_{gb} is band gap of bulk material, E_{gn} is band gap of nanomaterial (calculated from strong absorption edge in absorption spectra), h is planck's constant and m^* is the effective mass of specimen (1.82×10^{-31}Kg and 3.64×10^{-31}Kg for CdS and ZnS respectively). Observed absorption maxima for CdS is at 440 nm and for ZnS it is 310 nm, while for bulk materials these values are reported to be 517 nm and 337 nm respectively.[12] The blue shift clearly indicates the formation of nanoparticles. The band gap energy of the synthesized CdS and ZnS, determined from the absorption spectra are found to 2.82 eV for CdS and 4.01 eV for ZnS. The average particle size estimated was 8.2 nm for CdS and 7.6 nm for ZnS which are in consistent with the result obtained from XRD and TEM micrographs. Table 1 shows the average particle size determined using XRD and UV-VIS spectra.

Table 1: Average particle size determined using XRD and UV-VIS spectra

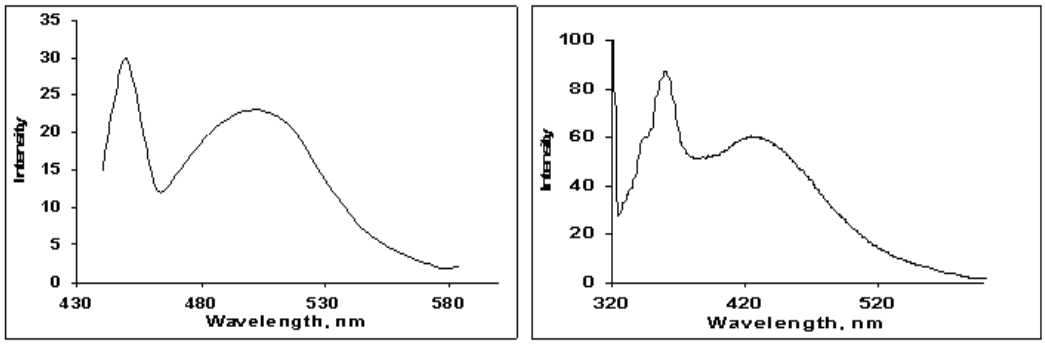
Sample	Average particle size (nm) particle size (nm) from XRD from UV-VIS	Average
CdS	9.3	8.2
ZnS	8.7	7.6



(a) (b)

Fig.2: UV-VIS spectra of (a) CdS (b) ZnS nanomaterials

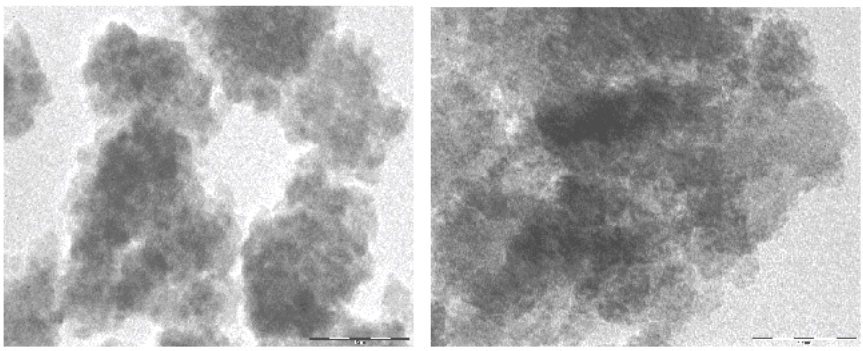
Illumination of these semiconductor colloids generates holes and electrons and the recombination of charge carriers is accompanied by emission of light which is observed in fluorescence spectra. Fluorescence spectra of CdS and ZnS have been presented in fig. 3. Fluorescence spectra of CdS shows a sharp band gap emission at about 450 nm and surface state emission approximately at 506 nm when excited at 440 nm which is the maximum absorption peak observed in UV-VIS spectra, indicating the blue shift due to nano size particles of CdS. Similarly, fluorescence spectra of ZnS shows a peak at 360 nm and 425 nm corresponding to band gap emission and surface state emission when excited at 310 nm which is the maximum absorption peak observed in UV-VIS spectra of ZnS also indicating the blue shift due to nano size particles of ZnS.



(a) (b)

Fig. 3: Emission spectra of (a) CdS (b) ZnS nanomaterials.

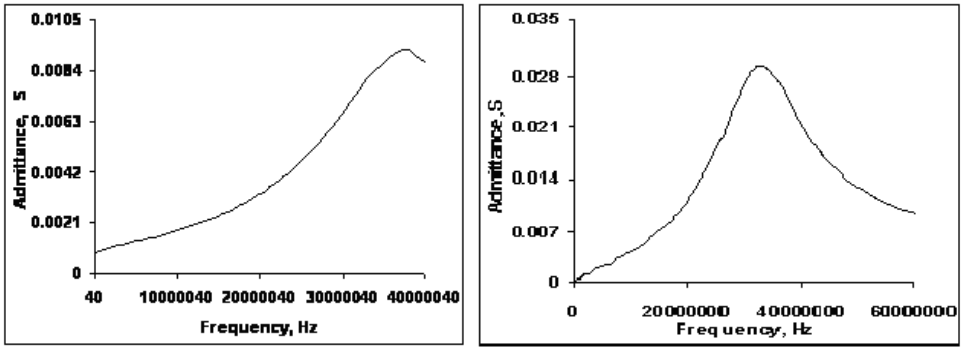
TEM micrographs of synthesized CdS and ZnS are shown in fig. 4, which clearly indicate the formation of nanosize particles with the average particle size around 10 nm.



(a) (b)

Fig. 4: TEM of (a) CdS (b) ZnS nanomaterials. (Scale bar indicates 50 nm)

Impedance study of CdS & ZnS nanomaterials was carried out to analyze the variation of impedance (Z) in terms of admittance (Y) with frequency, shown in fig. 5. It is observed that initially admittance increases slowly for lower frequencies and then rapidly up to certain frequency called resonant frequency and then decreases at higher frequency. The values of critical frequency and corresponding minimum impedance and maximum admittance are listed in table 2. Such variation of impedance with applied frequency shows the capacitive impedance associated with the nanomaterials. Quantum dots are associated with capacitance and quantum dot impedance (or admittance) is basically due to capacitance in the specimen.[13, 14]



(a) (b)

Fig. 5: Variation of admittance of (a) CdS and (b) ZnS nanomaterials with frequency.

Table 2: Maximum Admittance, minimum Impedance corresponding to resonant frequency

Sample	Resonant frequency (MHz)	Max. Admittance (S)	Min. Impedance (Ω)
CdS	37.95	0.0093	107.88
ZnS	33.60	0.0290	34.06

Due to variation in size as well as shape, capacitive impedance and critical frequencies for the samples are different. Impedance analysis indicates that materials under investigation, displays steep rise and fall of admittance at a particular frequency. This is the property of electronic tuned circuit and the frequency at which maximum admittance is attained may be compared to the resonant frequency of a conventional tuned circuit and this frequency may be called ‘equivalent

resonant frequency'. In a conventional tuned circuit, resonance frequency is adjusted by tuning passive components (R & C), whereas in a quantum dot tuned devices the 'equivalent resonant frequency' can be adjusted by controlling the size and shape of the quantum dots. Bulk materials of CdS and ZnS do not show any variation in admittance.[12] Therefore CdS and ZnS nanomaterials can be used in nanotuned devices.

CONCLUSIONS

Nanomaterials of CdS and ZnS were synthesized successfully by precipitation method. Broad peaks in X-RD pattern and blue shift in absorption maxima clearly indicates the formation of nanoparticles with the particle size less than 10 nm, which is also confirmed by TEM micrographs. Impedance analysis shows that synthesized materials have minimum impedance at a particular frequency which is 37.95 MHz for CdS and 33.6 MHz for ZnS nanoparticles. The variation of impedance with frequency indicates the capacitive impedance associated with these nanomaterials. Such materials can be used in electronic nano-tuned devices.

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