EFFECT OF AGING PERIOD ON THE STRUCTURAL CHARACTERIZATION OF FRESH AND THERMALLY-ANNEALED CdS NANOPARTICLES

M.F. Kotkata^a, A.E. Masoud^b, M.B. Mohamed^c, E.A. Mahmoud^{b*}

^a Physics Department, Faculty of Science, Ain Shams University, Cairo-11566, Egypt

^b Physics Department, Faculty of Science, Al-Azhar University for Girls, Cairo-11884, Egypt.

^c National Institute of Laser Enhanced Sciences (NILES), Cairo University, Cairo, Egypt.

Different samples of CdS nanoparticles capped by cetyltrimethyl ammonium bromide (CTAB) have been prepared under two different aging conditions before filtration via coprecipitation method. A blue shift in the band gap has been observed in the UV-Visible absorption spectra indicating the formation of nanoparticles of size about 8 nm for the samples prepared. Transmission electron micrographs prove the previous result. The nature, thermal-induced phases (RT : 350°C) and their structure as well as surface stability have been investigated using FT-IR, Raman scattering, DSC, XRD and heat stage X-ray diffraction (HSXRD). Analysis of the obtained data reveals that 5 days aging period greatly enhances the stability of the structure of the CdS nanoparticles as well as its surface stability.

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1. Introduction

Nanomaterials have drawn interests owing to their special characteristics which differ from that of bulk solids and molecules. Since novel properties of nanomaterials depend on their size, structure and shape, a new direction for synthetic methods and an understanding of the mechanisms by which the size, structure and shape of the nanocrystals can be easily varied are key issues in nanoscience [1].

II-VI semiconductor (SC) nanoparticles have received extensive attention for their practical applications in optoelectronics and photonics [2]. Branched II-VI SC nanocrystals, such as; arrows, bipods, tripods and tetrapods, are presently of great interest for their shape dependant applications. They have been produced at high yield using chemical synthesis, achieving a narrow distribution of sizes by many research groups and with various methods [3-8]. What underlies this work is the polytypism of the bonded structures, such as those of the II–VI SCs; their lattice has a common crystal plane, which can be used to achieve branching. The (111) plane of the cubic zinc blende lattice structure is atomically identical to the \pm (001) plane of the hexagonal wurtzite structure. Their synthesis was achieved by performing the initial nucleation in the zinc blende phase, followed by the growth of arms in the wurtzite phase [9].

The ability to separate between the zinc blende (metastable phase) & wurtzite (stable phase) structures, is then the main key. This key needs an intensive study on the phase changes in these systems, and enhancing the stability of their zinc blende phase.

Cadmium sulphide CdS is an important semiconductor. It has many opto-electronic applications including solar cells, photodiodes, light emitting diodes, nonlinear optics and heterogeneous photo catalysis [2]. Within this vision, CdS was selected, as an interesting II-VI compound, to be the scope of the present paper.

^{*} Corresponding author e-mail: prof ea@yahoo.com

2. Experimental

Zero aging CdS (sample 1), was prepared via coprecipitation method. Typically, 12.4 g of Cd(NO₃)₂.4H₂O {Riedel-de Haën, 99%} and 2.5 g of cetyltrimethyl ammonium bromide (CTAB) {PARK-Scientific Limited, 99%} were dissolved in 100 mL of re-distilled water under stirring at room temperature (RT~25 °C). In another flask, 3.1 g of Na₂S was dissolved in 100 mL of re-distilled water, and then added to the former solution under stirring. Once the reaction takes place, the solution is filtered, washed several times (5-10 times) by re-distilled water, and left in a dark and dry place till complete dryness.

5 Days aging CdS (sample 2), was prepared with the previously mentioned method, under the same conditions; the only difference is that the sample was left in its reaction vessel for 5 days before being filtered.

UV-Visible spectrum of the prepared two samples, dispersed in distilled water, is recorded using Bio-Cary50 Model spectrophotometer in the wavelength range 300-900 nm. Transmission electron micrographs of the sample, dispersed in absolute ethanol ultrasonically, were collected by (TEM) type 1230 JOEL, West Germany, operating at power=100 kV. The structure, the phase changes, and the surface stability of the two samples were examined by BRUKER D₈ ADVANCE heat stage X-ray diffraction (HSXRD) using CuK α (λ =0.15406 nm), at a power of 1600 Watts (40kV & 40mA), and heating rate of 60 deg/min. differential scanning calorimetry (DSC) curves for the two samples were recorded using SETARAM analyzer (LabsysTM TG DSC1) with a heating rate of 8 deg/min in the temperature range (RT-400°C). The final produced phases after annealing the samples during the DSC runs were examined by XRD.

3. Results and discussion

Structural nature of as-prepared samples

The ICCD card no. 89-0440 for zinc blende CdS, the recorded patterns for both asprepared (fresh) samples, together with the XRD pattern of Ref. [2] are shown in figure 1. Here, there is an indication for three broad peaks for both investigated CdS samples. The first one extends from 22° to 32° in 20 angular units, having the highest intensity in both recorded patterns. The second peak extends from 40° to 48° and the third one extends from about 48° to 56° in both samples.



Fig. 1. A comparison between XRD patterns of the investigated CdS samples 1 and 2 with the ICCD card and that of Ref. [2].

Fig. 2, shows the FT-IR curves for the as prepared CdS samples 1 and 2. The peaks at 719 and 668 cm⁻¹ have been assigned to Cd–S stretching [10]. The bands appear at the same positions in both samples but there is some extent of sharpness and relative increase in intensity in the peaks of sample 2 rather than sample 1. More details and analysis of the FT-IR data will be published elsewhere [11].



Fig. 2. FT-IR for both samples measured by FT-IR Raman JASCO (6300 Type A).

The DSC curves with different heating rates are obtained for the two samples for thermal analysis and kinetic studies [12]. As an example, the DSC curves for both CdS samples with heating rate=10 deg/min are shown in figure 3. As it is obvious from the DSC curves, there is an endothermic peak at T~100°C, in both samples, attributed for adsorbed water. In sample 1, there are three exothermic peaks due to crystallization at T~278, 358 and 435°C. While in sample 2, there are only two exothermic peaks appear at T~278 and 515 °C.



Fig. 3. DSC curves for the zero aging (a), and 5 days aging (b) CdS samples. Heating rate=10 deg/min.

A study 6f the structural change during heating the sample, in the DSC apparatus at a constant rate, is performed. Here, sample 1 was heated up to a temperature corresponds to the end

of the first exothermic crystallization peak , $\sim 300^{\circ}$ C, where the DSC apparatus was switched off and the sample was to cool to RT at a rate of ~ 50 deg/min. Hence, an XRD scan was recorded and the result is given in figure 4(a). The CdS sample is heated again with the same heating rate up to nearly the end of the second exothermic crystallization peak, $\sim 400^{\circ}$ C, where the corresponding XRD pattern is shown in figure 4(b). The same process is repeated once more where the sample is heated up to $\sim 550^{\circ}$ C, i.e. the end of the third exothermic peak. The recorded XRD pattern at this stage is shown together with the previous patterns in figure 4(c). Identification of the three recorded XRD patterns indicates the growth of a rather complete zinc blende structure at 300°C. A beginning of the growth of the wurtzite structure together with a complete growth of CdO zinc blende phase is observed at $\sim 400^{\circ}$ C, further details on the existing oxides will be discussed later. However, the growth of a complete wurtzite structure at 550°C is observed.



Fig 4. XRD pattern after each exothermic peak appears in the DSC curve for sample 1 (a) at T~300, (b) at T~400, and (c) at T~550°C.

Heating of sample 2 up to 400°C with a rate of 10 deg/min leads to a direct formation of a zinc blende material and a beginning of the wurtzite structure formation (Fig. 5a). While heating the sample up to 800 °C indicates the formation of a complete wurtzite structure (Fig. 5b).



Fig. 5. XRD pattern after each exothermic peak appears in the DSC curve for sample 2 (a) at T~400, (b) at T~800°C.

Combining the results of the previous figures (1:5), one can conclude that both fresh (asprepared) CdS samples are exploiting two different states of structure lie between amorphous and zinc blende. However, sample 2 (5 days aging), has a more stable zinc blende structure than sample 1 (zero aging). This is observed from the noticeable increase of the lines intensities in the XRD pattern of sample 2 rather than those of sample 1. A further confirmation is established form the big difference between the peak temperatures attributed to the wurtzite structure in DSC curves of both samples 1 and 2. Finally, this stability is clear from the higher sharpness and relative increase in intensity of the IR peaks of sample 2 rather than those of sample 1. These conclusions can be regarded to that the particles of sample 2 had the sufficient time needed

for partially arranging themselves in a more ordered structure, the zinc blende structure, when they had been left in the reaction vessel for 5 days.

Evaluation of particles size

Figs. 6 (a, b) show the respective TEM pictures of CdS nanoparticles sample 1 and 2. The images clearly show that the nanoparticles of both samples are dot-like with a high uniformity in size and shape. Furthermore, the dots appear quite spherical and no shape asymmetry is observed. The average particle size that can be estimated from these figures is ~ 9 nm and ~ 7 nm for the respective samples 1 and 2. It is also observed that there are a lot of agglomerations of nanoparticles in sample 2 rather than in sample 1. This is regarded to that the sonication time was not sufficient to break the intermolecular interactions between the nanoparticles of sample 2 as it did for sample 1. This is attributed to a certain amount of arrangement or compactness exists in sample 2 nanoparticles.



Fig. 6: TEM for sample 1, (a), and sample 2, (b).

As it is well known, UV-Visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum-sized particles. The absorption spectrum of the CdS prepared samples, sample 1 (zero aging) and sample 2 (5 days aging), are shown in figure 7.

The figure shows that the two recorded spectra exhibit well-defined absorption edges at \sim 485 and 475 nm corresponding to respective energy gaps \sim 2.56 and 2.62 eV for samples 1 and 2. These edges are assigned to the optical transition of the first excitonic state. Generally, the wavelength of the maximum exciton absorption decreases as the particle size decreases as a result

of quantum confinement of the photo generated electron-hole pairs. The values of the energy gaps, estimated from figure 7, reflect a considerable blue-shift relative to the absorption band edge of bulk CdS (515 nm and 2.41 eV), [13]. In fact, such observed blue shift reveals quantum size effect in prepared CdS samples, [14, 15]. Similar conclusions were observed in different II-VI nanoparticles [c.f. [16] and references therein].



Fig. 7: UV-Visible spectrum of zero aging (a), and 5 days aging (b) CdS nanoparticles.

In literature, many models have been reported concerning size confinement effect (SCE). A simple model was firstly adapted by Efros et al. [17] in 1982 to spherical clusters with infinite potential walls as boundary conditions. These authors assumed an energy dispersion close to the valence band maximum (VBM) and the conduction band minimum (CBM) with effective masses of CBM electron and VBM hole. This model is called the "effective mass approximation" (EMA). A further development of the EMA model has been made by Brus et al., [18]. The latter's introduced the Coulomb interaction, leading to the following equation:

$$E_{g}^{nano} - E_{g}^{bulk} = \frac{h^{2}}{8r^{2}} \left(\frac{1}{m_{e}^{*}} + \frac{1}{m_{h}^{*}}\right) - \frac{1.8e^{2}}{4\pi\varepsilon\varepsilon_{o}r} - 0.248E_{Ry}^{*}$$

where E_g^{nano} and E_g^{bulk} are the respective nanoparticles and bulk energy band gaps, r is the radius of the particle, $m_e^* \& m_h^*$ are the reduced masses of the conduction band electron & valence band hole in units of the electron mass, ε_o is the vacuum permittivity, ε is the high-frequency dielectric constant, and $E_{R_V}^*$ is the effective Rydberg energy given by:

$$E_{Ry}^{*} = \frac{e^{4}}{2\varepsilon^{2}h^{2}} \left(\frac{1}{m_{e}^{*}} + \frac{1}{m_{h}^{*}}\right)$$

Applying the previously mentioned Brus' equation, 8 and 7 ± 0.1 nm has been estimated for the particles size of the respective precipitated CdS samples 1 and 2.

Effect of heat treatment on structure characteristics

Figure 8 shows the effect of annealing on the structure of the two as-prepared CdS samples at different heating stages; 35, 150, 200, 250, 300, 350°C. At 150°C, sample 1 (zero aging sample) has a zinc blende structure (z), this can be easily identified by comparing the peak positions with that included in ICCD card no. 89-0440. There is an indication for the (111), (220), and (311) planes appear at respective $2\theta=26.46^{\circ}$, 43.891°, and 51.971°. At 200°C, two phases of CdS, zinc blende and wurtzite, are present in sample 1. The wurtzite structure (w) can be easily indexed from the characteristic peaks of (100), (101), and (103) planes appear at respective $2\theta=24.81^{\circ}$, 28.186°, and 47.837° [compared by ICCD card no. 41-1049]. Unlike sample 1, the zinc blende structure still persists in sample 2 (5days aging sample) at this degree of temperature. Above 250°C, the CdS wurtzite structure is enhanced by further increase of temperature is sample 1, and the structure is completely wurtzite at 350°C. However, in sample 2 the wurtzite structure begins slightly to appear at ~250°C. The phase is enhanced by further increase of temperature, but it does not completely formed till 350°C.



Fig. 8. XRD for samples 1 and 2, recorded at different heating stages.

Thus, the zero aging sample begins the transformation to the wurtzite structure earlier than the 5 days aging sample which begins that transformation at temperatures higher than 250°C. Hence, the zinc blende structure of sample 2 is much more stable than that of sample 1. This is because the zinc blende phase is formed in sample 2 (5 days aging) without forcing its production by any external energy such as annealing, i.e. the produced phase, zinc blende, is settled down with the lowest amount of internal energy.

Surface stability of nanocrystals

Because of the high surface-to-volume ratio of nanoparticles, the surface properties have significant effects on their structural and optical properties [19]. Modifying the surfaces of nanoparticles with various organic or inorganic species is expected to remove their surface defects and influence their optical properties. Organic capping of nanoparticles with surfactants would give rise to a barrier to aggregation and electronic passivation of the particles. In this respect, the appearance of peaks at 2θ =33°, 38.283°, 55.305°, and 65.94°, figure 8, in sample 1 (zero aging) at T~200°C indicate the presence of CdO cubic phase at this stage. These peaks can be attributed to the respective (111), (200), (220), and (311) planes [compared by ICCD card no. 75-0592]. CdO may be formed from the oxidation of CdS by some nitrate of the starting material still present in the as-prepared sample. Above 250°C, it can be observed that another phase begins to appear which is the CdO₂ cubic phase, this is concluded from the peak at 2θ = 57.483° for the (311) plane [compared by ICCD card no. 78-1125]. A decrease of the CdO lines intensity and

increase of CdO_2 lines intensity can be observed by further increase of the temperature indicating that CdO is decomposed into CdO_2 . However, this is not the case in sample 2 (5 days aging); there is no appearance of any peak related to CdO or CdO₂ structures.

The appearance of CdO and CdO₂ in sample 1 (zero aging) and their absence in sample 2 (5 days aging) though they have been heated at the same environment and conditions, is attributed to that the CTAB, the capping agent, has the time to be perfectly distributed on the surface of sample 2 than on that of sample 1. This last conclusion has been achieved during the analysis of the recorded Raman spectra. Figure 9 gives the Raman spectra for both investigated samples together with that of CTAB. Comparing these spectra reflect the existence of surface enhancement Raman scattering (SERS) of CTAB in both samples; whereas the SERS for sample 2 is relatively higher than that of sample 1. A detailed investigation of SERS will be given elsewhere, [11].



Fig. 9. Raman spectra for CdS samples and CTAB measured by FT-IR Raman JASCO (6300 Type A).

4. Conclusion

The preparation and characterization of the two samples of CdS nanoparticles (zero and 5days aging), with particle size of about 7-8 nm, leads to the following conclusions:

- In fresh samples, a more stable zinc blende structure was observed in sample 2 (5 days aging) more than that observed in sample 1 (zero aging) as a result of the factor of the aging period before filtration.
- The stability of zinc blende structure of sample 2 was proved by the observed delay in the structure transformation to wurtzite structure, due to annealing.
- The surface stability is remarkably enhanced in sample 2 rather than sample 1 as a consequence of well capping achieved by the aging period.

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