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Study of influence of refluxing on uncapped CdTe nanoparticles synthesized by a facile route

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Abstract:

Semiconductor CdTe is of great interest for use in optoelectronic devices. CdTe nanoparticles ~10 – 25 nm differ remarkably in properties from their bulk making them potential candidates for photovoltaic applications. CdTe nanoparticles are synthesized by low cost, simple and application oriented co-precipitation technique. De-ionized water was used as solvent whereas cadmium chloride ($CdCl_2$) was used as cadmium source. CdTe sol was prepared by refluxing the product at 90° *C for 0 – 120 minutes.*

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Solution was then centrifuged at 5000 rpm for 10 minutes. Resultant precipitates were annealed at 50 - 100°C for different time intervals. CdTe nanocrystals with hexagonal phase were confirmed by X-Ray Diffractograms. Grain size was tuned to ~11 nm, as observed by SEM, by changing the synthesis conditions and refluxing time. Previous studies showed preparation of CdTe nanoparticles in the presence of organic solvents and some surfactants, whereas in this research work simplest route of CdTe nanoparticles' synthesis only by using de-ionized water is explained. Optical properties revealed that the band-gap of these CdTe nano-particles is slightly different from the bulk values. High absorption of the solar spectrum warrants their use in solar cells with the added advantage of increased surface area.

Key words: CdTe nano-particles, Refluxing, surfactant free, solution chemistry

1. Introduction

Optical and electronic properties of semiconducting nanoparticles are strongly size dependent because of the quantum confinement effect. Highly luminescent II-VI semiconductor nanoparticles have been extensively studied since they are promising materials for next generation optical and electronic devices (Gaponik 2011, Gallardo 2007). Most of the research involves cadmium telluride nanocrystals since the high photoluminescence (PL) quantum efficiencies of CdTe make it an interesting material for use in applications such as light emitting devices (Chen 2002, Gaponik 1999, Gaponik 2000, Rogach 2007) photovoltaic devices (Khan 2011, Kumar 2004) and biological labels (Wang 2006, Green 2007).

Solution chemistry and organometallic methods have remained regular synthetic routes for the preparation of CdTe (Mntungwa 2011, Sathyamoorthy 2010, Rogach 2000, Talapin 2001). However, there have also been several reports for growth of nanoparticles via physical methods such as ball milling (Tan 2003) and laser ablation (Ruth 2006).

Organometallic routes are generally toxic and expensive providing less stability in air and less reproducibility. Whereas, reactions comprising of aqueous chemistry are not only environmentally benign but they also have merits like stability, simplicity and reproducibility. When the nanoparticles prepared via aqueous solution chemistry are extracted as free-standing powders, they can be exploited in thin film preparation for device formation application. Most of the aqueous syntheses are carried out using capping agents like TOPO or thiol stabilizers such as Mercaptopropionic acid (MPA), Mercaptoacetic Acid (MMA) or 2-Mercaptoethanol (ME) (Abd El-sadek 2011). The use of these capping agents is to control the shape and size of growing particles through charge transfer and to prevent agglomeration of particles thus making them stable and passivating them against oxidation. Capping agents, however, are not always sought-after since for many applications efficiency of nanoparticles is affected by the surfactant molecules that are covalently bonded with the surface atoms of nanoparticles. For example, for organic photovoltaic hybrid solar applications, where charge transfer between nanoparticles and conjugated polymer are required, surfactant may cause hindrance in the charge transfer. Therefore, often the exchange or removal of surfactant from the surface of nanoparticles is an additional step.

CdTe is considered ideal for photovoltaic (PV) application due to its high absorption coefficient in the visible spectrum and high carrier mobility (Mathew 2004). There are reports of CdTe nanoparticles mixed with a suitable polymer to prepare a hybrid absorber layer where the capping agents are found to be causing hindrance in the desired charge transfer between nanocrystals and conjugated polymers thus causing low cell efficiencies (Verma 2009).

Keeping in view the potential of nanocrystals to be used in solar cell applications, efforts are made to produce surfactant free nanocrystals and the size of particles is controlled with the help of refluxing. 0.5M CdCl2. 2.5 H20 is used as cadmium source and potassium tellurite is used as tellurium source to prepare nanocrystals of different sizes at different pH values. Size is controlled via refluxing and reaction conditions. As prepared CdTe nanocrystals are isolated by the addition of methanol followed by centrifugation and drying in vacuum at room temperature.

2. Experimental

2.1. Chemicals

Cadmium chloride, potassium tellurite, potassium hydroxide, deionised (DI) water, nitrogen gas, methanol were all used as-purchased without any further purification.

2.2. Synthesis of CdTe nanoparticles

0.5M CdCl2 . 2.5 H20 solution was prepared in 20mL DI water at room temperature. pH of the solution was maintained at ~10 by drop wise addition of 1M KOH solution. The solution was then placed in a three-necked flask and was bubbled with N2. 0.4 M potassium tellurite solution was prepared in 20 mL DI water and was stirred for 2 hours. Dark grey color of the solution indicated the nucleation of CdTe after refluxing and condensation. Resulting powder was separated by centrifugation at 5000 rpm for 10 minutes and dried in vacuum at room temperature. 5 samples naming S1, S2, S3, S4, and S5 with different refluxing time were obtained.

2.3. Characterization

X-ray diffraction patterns of dried nanoparticles and films were studied by using Rigaku D/Max II-A X-ray diffractometer (XRD). CuKα radiations (1.5405Å) were used for diffraction.

Voltage of 35kV and 25 mA current was used to produce X-rays. Size and morphology of nanoparticles was observed by Hitachi S-3400N Scanning electron microscope (SEM). Optical characterization was done by using JA Woolam's variable angle spectroscopic ellipsometer (VASE).

3. Results And Discussion

3.1. Structural properties

XRD pattern of as-synthesized CdTe nanoparticles, at different reflux times, is shown in Fig.1. XRD patterns shows two distinct peaks at angles (2^{θ}) of 39° and 49.5°, which can be indexed to diffraction from (1 1 0) and (1 1 2) planes of hexagonal crystal lattice, respectively. This matches quite well with the international centre for diffraction data (JCPDS card card no. 19-193).

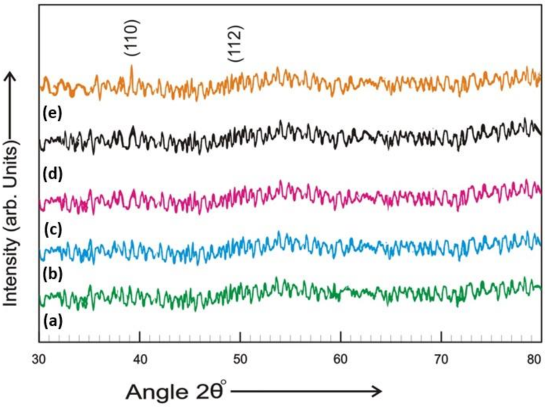


Fig. 1 X-ray diffraction patterns of CdTe nanoparticles refluxed at (a) 15 min (b) 30 min (c) 45 min (d) 60 min (e) 120 min

Lattice constants a= 4.58Å and c=7.50Å are calculated by the following equation which are in close agreement with the standard data.

$$1/d_{hkl}^2 = 4/3a^2\ (h^2 + hk + K^2) + l^2/c^2 \qquad (1)$$

From the XRD pattern it can be concluded that as the reflux time increases the crytsallinity of the particles increases, and the sample refluxed for 2 hours shows a sharp peak at (1 1 0) plane which confirms the hexagonal structure of CdTe nanoparticles. Crystallite size is found to be in range of 11 – 19nm, calculated by Scherer equation stated below:

$$D = K\lambda/B\cos\theta \qquad (2)$$

Where K is a constant that is equal to 0.94, lambda is the X-ray wavelength λ = 1.5405Å and B is the full width at half maximum (FWHM) of the XRD selected diffraction peak on the 2θ scale, θ is the diffraction angle.

FWHM initially increases with the reflux time; as the reflux time increases from 15min to 30min the FWHM increases from 0.2° to 0.44°, a slight decrease in 0.4° was found for sample refluxed at 45min and then FWHM remains almost constant for rest of the reflux times [Fig. 2a]. Crystallite size is inversely related to the FWHM of the individual peak i.e. the more narrow the peak the larger the crystallite size. Fig. 2(b) shows a graph of crystallite size values (nm) (calculated from Scherer equation) and reflux time (minutes). Crystallite size decreases significantly when the reflux time increases from 15 min to 30 min. However, an increasing trend in crystallite's size was observed for rest of the reflux times.

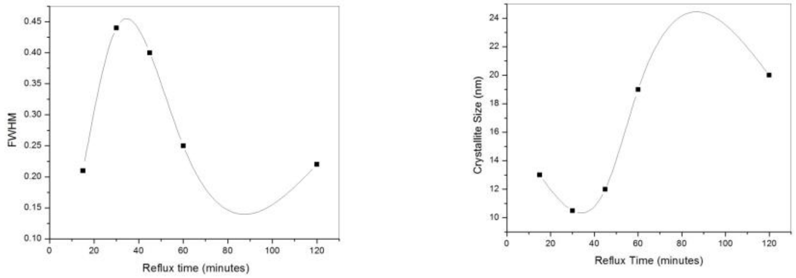


Fig. 1 (a) FWHM and (b) crystallite size of CdTe nanoparticles at different reflux times

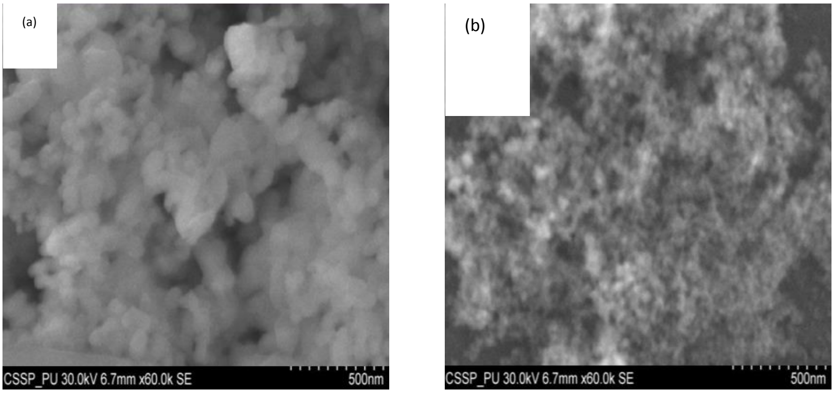
The dissimilarity in growth of crystallites can be referred to the stresses and relaxations produced in the films. The stress/strain ratio varies notably as a function of crystallite growth since the films provide accommodation to the high temperature stresses in the grains. Crystallite growth is driven by neighboring crystals that possess different energies due to the curvature of energetic grain boundaries and different amounts of accumulated strain energy. By differentiating the Bragg's law the micro strains are calculated as:

$$b = \Delta 2\theta = -2\frac{\Delta d}{d}\tan\theta \qquad (3)$$

The uniform strain is observed in the films and this fact is evident from the shapes and shifts of the peaks of reflection planes when compared with the standard shapes. (Cullity 1978).

3.2. Surface properties

SEM results of the CdTe nanoparticles are shown in Fig. 3. SEM images of sample refluxed for 15 min (S1) shows the particles with average diameter size of ~50 nm. However, a remarkable decrease in the size of nanoparticles, ~ 11 nm, was observed for the reflux time of 30 min (S2). By further increasing the reflux time to 45 min an increase in particle diameter was observed, with an average value of ~25 nm. Size of nanoparticles kept growing with the increase in reflux time for 60 (~50nm) and 120 min (~100nm). The increase in particle size for samples (S3-S5) with increased refluxing time is found to be in correlation with the results reported earlier, where the EMA sizes of the particles were found to increase with the increased in reflux duration (Abd El-sadek 2011). This suggests that nanoparticles' size keeps on growing with the increase in reaction time. Such growth of particles suggests that mechanism of growth is "Ostwald ripening", where a large number of colloidal particles fight for a finite number of monomers. The high surface energy of smaller particles promotes their dissolution and larger particles will continue to grow as more and more material adds to the existing nuclei and slowly there is a reduction in total number of particles.



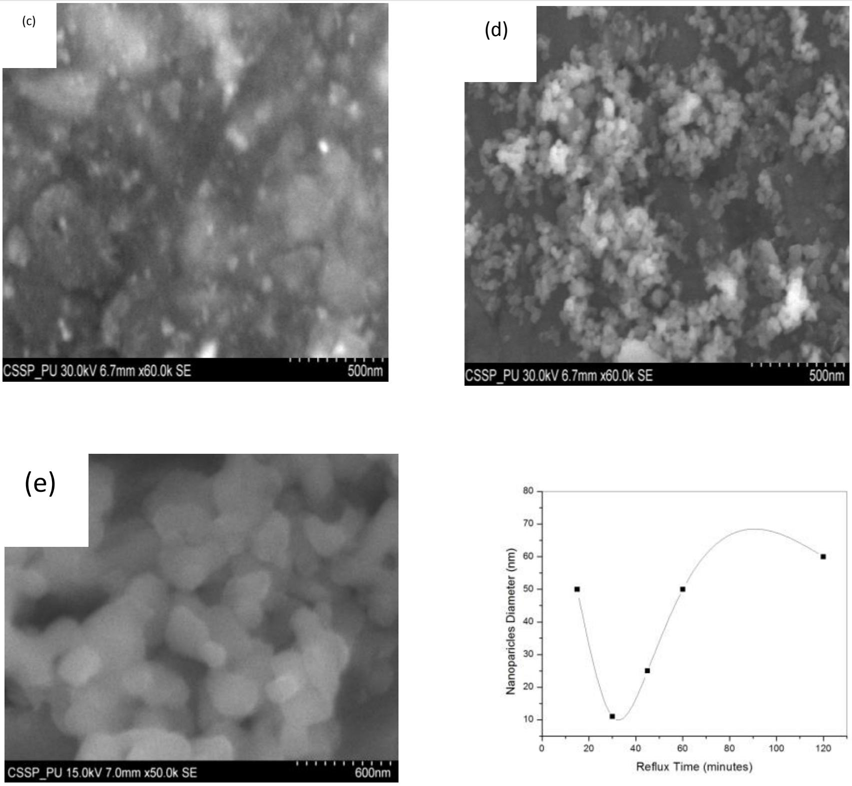


Fig. 3 SEM micrographs of CdTe nanoparticles refluxed for (a) 15 min, (b) 30 min, (c) 45 min, (d) 60 min (e) 120 min and (f) Plot between nanoparticles' diameter and reflux time.

Fig. 4(f) shows a plot of nanoparticle diameter against reflux time. A sharp decrease in particle size was observed when the reflux time was changed from 15 min to 30 min and after that a steady increase in particle size was observed. The trend is similar to that of "crystallite size versus reflux time", calculated from XRD pattern.

3.3. Optical Properties

Absorption spectra of CdTe nanoparticles are plotted in Fig. 4. Pure CdTe has a high absorption coefficient in the visible and near infrared region; the same was observed in this research work [Fig. 4]. It can be seen through the absorption plot that by increasing the reflux time absorption of CdTe nanoparticles also increases. However, band edge energies are not shifting linearly. The band edge shifts towards high energy side, i.e. blue shift, for CdTe nanoparticles prepared at 15, 30 and 120 minutes reflux time. Relatively larger band shift was observed for 30 minutes reflux time which might have had happened because of the quantum confinement effect on the electronic band structure (Rastogi 2000) for CdTe nanopaticles' diameter ~ 11 nm [Fig. 3b].

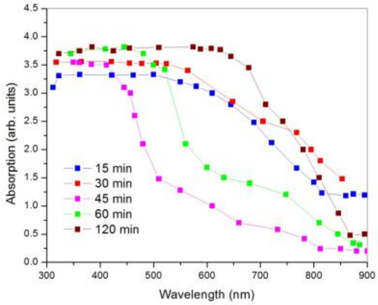


Fig. 4 Absorption spectra of CdTe nanoparticles refluxed for different time

Effect of refluxing time on the band gap energies of different samples was also investigated. Optical band gap energies of cadmium telluride (CdTe) nanoparticles was calculated from absorption spectra through plotting photon energy (hυ) versus $(\alpha)^2$ [Fig. 5].

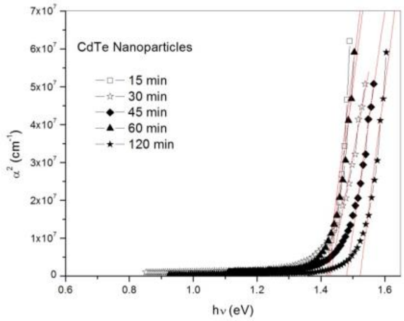


Fig. 5 Variation in band gap energies of CdTe nanoparticles refluxed for different time

Band gap of CdTe (1.42 eV) makes it the most suitable material for photovoltaic conversion (Rastogi 2000). However, the absolute value of band gap energy would slightly depend upon the deposition process and conditions in case of a thin film.

It can be seen from Fig. 5 that band gap energy in the range of 1.41 – 1.51eV is observed for these CdTe nanoparticles prepared under 30 and 60 refluxed times. Band gap energies, with respect to particle size and shape, is given in Table - I. The sharp increase in band gap energies indicates the direct band gap of chemically synthesized CdTe nanoparticles.

Table - I Effect of reflux time on CdTe nanoparticles' size, shape and band gap energy

Sample	Reflux Time (minutes)	Nanoparticles' Diameter (nm)	Nanoparticles' Shape	Band Gap (eV)
S1	15	50	Spherical	1.41
S2	30	11	Spherical	1.42
S3	45	25	Spherical	1.47
S4	60	50	Spherical	1.42
S5	120	100	Spherical	1.51

Conclusion

We have successfully synthesized CdTe nanoparticles, without using any capping agent, via simple and environmental friendly route. Particle size was monitored with respect to refluxing time, and their size ranging from ~11nm to ~50nm was observed after refluxing for 15 to 60 minutes. All particles were found to be spherical in shape. XRD patterns confirmed the formation of hexagonal cadmium telluride for all the refluxed times. High absorption values along with a direct band gap of 1.42 eV was observed for the nanoparticles prepared at 30 and

60 refluxed time. Whereas, a small increase in band gap energies was found for reflux time 45 min (1.47eV) and 120min (1.51eV).

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