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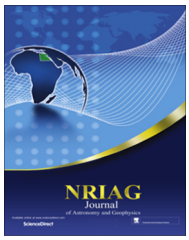

Characterization of CdSe-nanocrystals used in semiconductors for aerospace applications: Production and optical properties

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Abstract Semiconductor nanocrystals (NC's) are the materials with dimensions less than 10 nm. When the dimensions of nanocrystals are reduced the bulk bohr diameter, the photo generated electron-hole pair becomes confined and nanocrystal exhibits size dependent upon optical properties. This work is focused on the studying of CdSe semiconductor nanocrystals. These nanocrystals are considered as one of the most widely studies semiconductors because of their size – tunable optical properties from the visible spectrum. CdSe-nanocrystals are produced and obtained throughout the experimental setup initiated at **Nano-NRIAG Unit (NNU)**, which has been constructed and assembled at NRIAG institute. This unit has a specific characterization for preparing chemical compositions, which may be used for solar cell fabrications and space science technology. The materials prepared included cadmium oxide and selinid have sizes ranging between 2.27 nm and 3.75 nm. CdSe-nanocrystals are synthesized in "TOP/TOPO (tri–octyl phosphine/tri–octyl phosphine oxide). Diagnostic tools, include UV analysis, TEM microscope, and X-ray diffraction, which are considered for the analytical studies of the obtained materials. The results show that, in this size regime, the generated particles have unique optical properties, which is achieved from the UV analysis. Also, the TEM image analysis shows the size and shape of the produced particles. These studies are carried out to optimize the photoluminescent efficiency of these nanoparticles. Moreover, the data revealed that, the grain size of nanocrystals is dependent upon the growth time in turn, it leads to a change in the energy gap. Some applications of this class of materials are outlined.

1. Introduction

Nanocrystal materials are one of the most interesting branches of today's nanoscience and nanotechnology. Semiconductor nanocrystals exhibit unique size and shape-dependent optical properties due to the quantum confinement effects and thus may find a wide range of applications in optoelectronic

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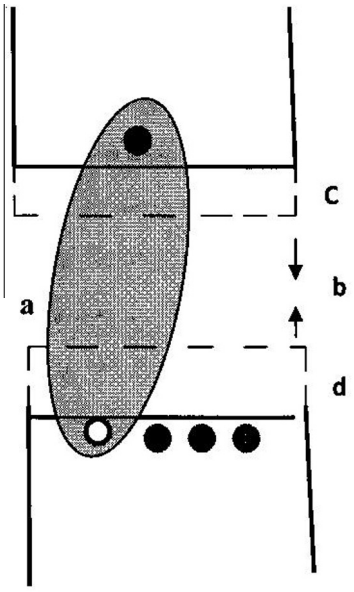

Fig. 1 Illustration of the effect of quantum confinement on the formation of an exciton (coupled electron-hole pair); the symbols (a) Exciton; (b) Band gap; (c) Confinement energy of the excited electron; and (d) Confinement energy of the excited hole.

devices, photocatalysis, solar energy conversion and biological imaging (Acharya et al., 2011, and Chin, 2008). A prerequisite for successful attempts in this direction is the availability of nanoparticles of superior quality. "Quality" in this respect is expressed in terms of mono dispersity, surface control, and stability. Thiol-stabilized II-VI semiconductor particles have proven to fulfill these requirements to a large extent. Nanoparticles of different materials, such as CdSe, have been prepared with several different thiols giving the opportunity to vary the functional groups at the surfaces (Chin, 2008; Rogach et al., 1999, and Eychmüller and Rogach, 2000). This opens the field of doing chemistry with the preformed particles. This could be the built-up of larger structures consisting of nanocrystals of one kind, "hetero-atomic" structures made from different semiconductor materials (Seo et al., 2006).

This work concerns the experimental studies of the CdSe nanoparticles in terms of its production, and the optical properties. We present the production of the nanomaterials with the processing of "TOP/TOPO (tri–octyl phosphine/tri–octyl phosphine oxide) and discuss its optical properties. UV analysis, TEM, and X-ray diffractions are taken in our consideration to investigate and analyze the obtained results.

1.1. Quantum confinement

Quantum dots (QD's) are nanoparticles of semiconductor materials ranging from 2 nm to 10 nm in diameter. Like CdSe, their electronic characterizations are closely related to the size and shape of the individual crystal. If the size of the crystal is small, then, the band gap between the higher valance band and the lowest conduction band becomes high and more energy is required for exciting the dot and consequently, more energy is released when the crystal returns to its resting state. A principle advantage with quantum dots is that by controlling the size of crystals. The conductive properties by the material are controlled because of their small size (Seo et al., 2006, and http://voh.chem.ucla.edu/vohtar/spring05/classes/185/pdf/CdSe_nanocrystal_lab_guide.pdf).

Quantum dots (QD's) display unique optical and electrical properties. The wavelength of the photon emission depends not only on the material from which the quantum dots is made, but also on its size. The ability to control the size of quantum dots enables the manufacturer to determine the wavelength of emission which in turn determines the color of light which the human eye perceives. The smaller the dots, the closer the blue end of the spectrum and the larger the dot, the closer the red end of the color spectrum (Yu et al., 1997) (Fig. 1).

Different sizes of CdSe quantum dots (QD's) are shown in the image of Fig. 2 taken in our laboratory at **Nano-NRIAG Unit (NNU)**.

If the size of the quantum dot is smaller than the critical characteristic length, called the excitation in Bohr radius, the

Fig. 2 Different size CdSe quantum dots (QD's), taken at NRIAG laboratory.

electron crowding leads to splitting of the original energy levels into smaller ones with smaller gaps between each successive levels. On the other hand, for the quantum dots that have radii longer than the excitation Bohr radius, are said to be in the weak confinement regime, and the ones that have radii smaller than the excitation Bohr radius, are said to be in the strong confinement regime

2. Experimental procedure

Fig. 3 illustrates the structure of **Nano-NRIAG Unit (NNU)**, which has been constructed and assembled at NRIAG institute. The experimental studies for CdSe nanoparticles, produced from this unit, are demonstrated in the following sections.

2.1. Materials

The materials considered in this work are of the purest quality available and used as received;

- Se powder, (Aldrich, 99% purity)
- Cadmium Oxide (CdO) powder (Aldrich, 99.99% purity),
- N-Trioctyl phosphine oxide Topo, (Merck), 97% purity),
- Triostyl phosphine Top (Fluka, 90% purity).
- Hexodecyl amine (HDA), (Fluka 97%);
- Stearic acid (SA) ($CH_3(CH_2)_{16}$ COOH), Aldrich 98%)
- Toluene, (Aldrich)

2.2. Synthesis and characterization

2.2.1. Production of CdSe

CdSe-nanocrystals in our laboratory have been synthesized using the procedure developed by Peng et al. (1998). This is detailed as follows;

The CdO was dissolved in stearic acid in a tri-neck flask at 180 °C with stirring. The red color of CdO disappears and the solution becomes colorless. The Se powder was dissolved in TOP and injected into Tri-neck flask at 210 °C to 280 °C. After injection we work on 11 samples from the reaction mixture for a time taken at a constant rate (15 s). All samples were cooled with toluene to stop particle growth. .

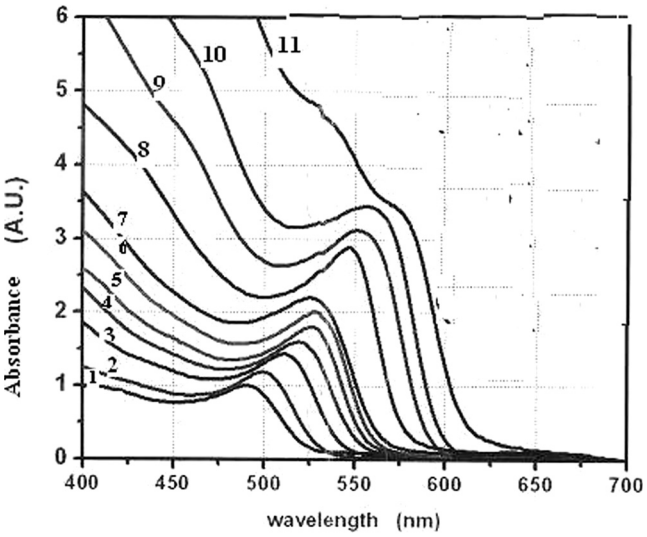

Fig. 4 UV–vis absorption spectra of CdSe nanocrystals at different particle size TOPO/HDA capped and different energy gaps.

3. Experimental results and discussions

3.1. Optical characterization of CdSe quantum dots (QD's) by UV–vis spectrometer

The nanocrystals discussed here are considered to be in a spherical shape. The optical absorption spectra of CdSe QD that are in toluene give information on the size of the nanocrystals. This is shown in Fig. 4. The data were taken from 11-samples and at different reaction times. The figure shows a series of peaks for all samples. A peak shifted toward a larger

Fig. 3 Nano unit (NU) at NRIAG.

Table 1 Calculated values of the different size CdSe quantum dots (QD's) obtained from UV-analysis.

Sample	Time of generated nanoparticles (Sec)	First peak of wavelength (nm)	Size of CdSe (nm)	Energy band gap (eV)
1	15	492	2.27	2.52
2	30	500	2.34	2.48
3	45	512	2.47	2.42
4	60	520	2.56	2.38
5	75	524	2.61	2.36
6	90	526	2.64	2.35
7	105	526	2.64	2.35
8	120	546	2.96	2.27
9	135	552	3.08	2.24
10	150	558	3.09	2.201
11	165	578	3.75	2.14

wavelength with an increase in growth time, which should result from an increase in particle size with time. The position of a peak is related to the size of the absorbing nanocrystal, this result points toward the sequential appearance of different sizes. These behaviors confirmed the results obtained in the work of Zhu et al., 2014.

Moreover, Table 1 shows the obtained results described in Fig. 4. The data presented in this table show that, the absorption maximum (peak values) is varying from 492 nm to 578 nm (for 11 samples), which was derived from Fig. 4. These values are corresponding to a particle size for each wavelength, which can be obtained using Eq. (1), and presented in column (4). Also, the energy band gap in this table column (5), is given using the formula of energy band gap, considered in Eq. (2). In this table, we found the same values of the energy band gap and particle size for the samples 6 and 7 (2.35 eV). This is because these samples have the same peaks wavelengths in spite of these samples differ in broaden far from the peak.

The proportional relationship between the absorption of the nanocrystals and the size (D in nm) can be obtained from the following relation that is given by Yu et al. (2003) in the form;

$$\textbf{CdSe}: \quad D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57) \tag{1}$$

where λ (nm) is the first exciton peak of CdSe spectrum.

The particle size changes the corresponding band gap of the quantum dot. Then, this energy gap can be described in the following relation written in the formula;

$$E_g = hv = \frac{hc}{\lambda} \tag{2}$$

where the parameter E_g, is the energy band gap of the quantum dot, h is the Planck's constant, and c is the speed of light. Our findings are consistent with the results obtained by Yu et al. (2003), in describing the relationship between the particle size and the corresponding band gap.

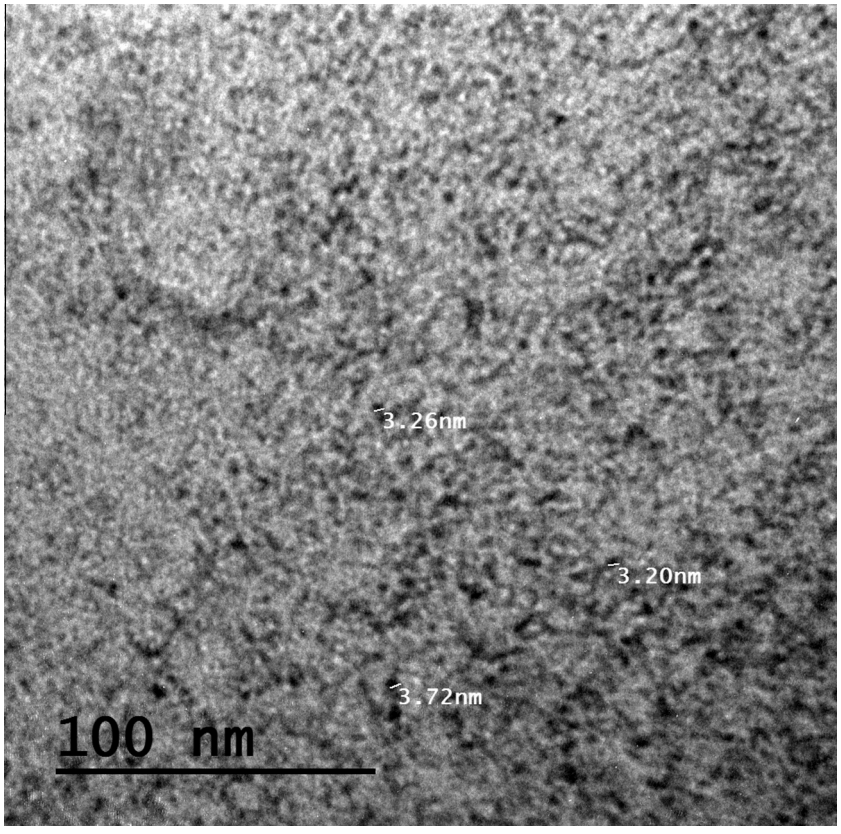

Fig. 5 Transmission Electron Microscope (TEM) of CdSe quantum dots [sample (11)].

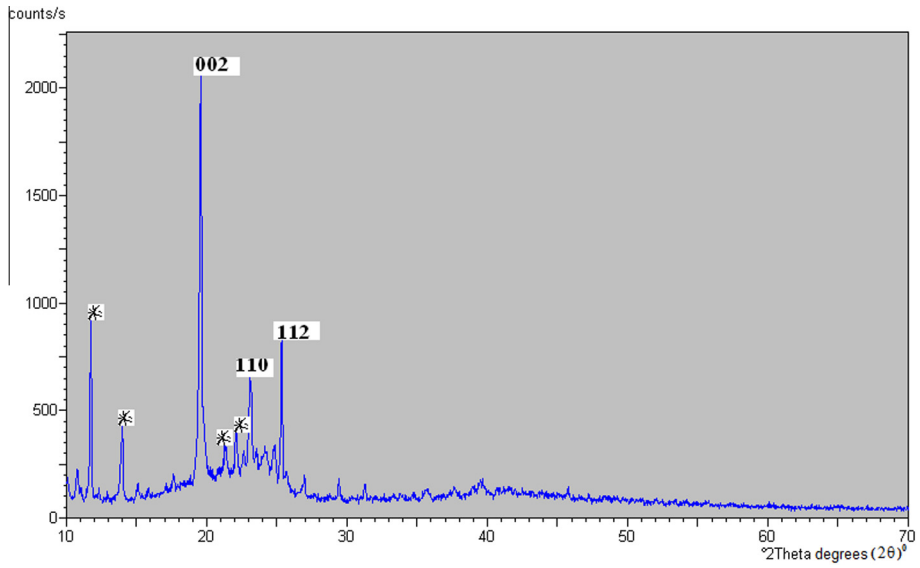

Fig. 6 XRD pattern of synthesized CdSe.

3.2. Transmission Electron Microscope (TEM)

Now, we analyze the image of spherical morphology of sample (11) obtained from the Transmission Electron Microscope (TEM). This sample is taken as an example to discuss the shape and the size of the nanoparticles. It is measured by GEM 2100 (GEOL) Japan instrument. This image is shown in Fig. 5.

It is seen from the above figure that, the dots on the TEM images of sample 11 show different sizes 3.26 nm, 3.72 nm, and 3.20 nm at different regions of this sample. From the UV-analysis, seen in Fig. 4, the size of this sample is found to be 3.75 nm, which was considerably in the range of that obtained from TEM analysis.

3.3. X-ray diffraction pattern

X-Pert Philips Holand X-ray diffraction (XRD) with $cu–k_{\alpha}$ radiation was used to characterize our sample. Fig. 6 shows the X-ray diffraction pattern of the prepared CdSe sample. The 2Theta (2θ) range was taken from (10)° degrees to (70)° degrees in the step of (10)° degrees. The XRD measurements of CdSe nanoparticles reveal the position of several different peaks. These points are obtained due to the diffraction form {002}, {110}, and {112}. The peaks marked by (*) correspond to impure phase of CdSe.

The XRD data clearly demonstrate the growth of nanocrystals as the thermal treatment temperature increases. The behavior represented in the above figure confirms the results obtained by Acharya et al. (2011).

4. Conclusion

From this study we conclude that our experiments successfully have demonstrated the synthesis of CdSe nanocrystals by the hot injection method. Nanoparticles with varying sizes and band gaps emerge in the process and produced in spherical shape. The coloration of the nanoparticle is directly linked to the band gap. The color of the light depends on the size of the quantum dots. The results showed that, CdSe quantum dots with sizes ranging from 2.27 nm to 3.75 nm, enabled the control of the optical properties. A TOP-TOPO – HAD been used to synthesize the high quality CdSe quantum dots.

The size dependent optical properties of nanoparticles have many applications from solar cell technology to chemical sensing. In the field of nano electronics, the size of the quantum dots can be tuned to be comparable to the scattering lights, reducing the scattering rote and hence, the signal to noise ratio. The band gap of the particles can be tuned so as to absorb energy over a large range of the solar spectrum.

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