

Aqueous Synthesis of CdTe Quantum Dots and Optical Characterization Under High Voltage

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This paper reviews the synthesis process of water-soluble CdTe quantum dots using mercaptopropionic acid. The state-of-art synthesis of CdTe nanocrystals was carried out under special conditions, and quantum dots with varying sizes were successfully produced. The optical properties were investigated in the synthesis process. The effect of electromodulation on the CdTe nanoparticles was also researched to optimize electro-optical properties with spectroscopic techniques under high voltage. The results clearly showed that as the heat treatment time increases, the absorption wavelength of the CdTe nanoparticles increases, and the applied voltage causes the band gap of all nanoparticles to decrease.

topics: CdTe quantum dots, optical characterization, aqueous synthesis, electro modulation

1. Introduction

Since nanocrystals have size-dependent electrical, optical, physical, and chemical properties, it is thus important to seek out processes that control the physical dimensions of nanoparticles.

In recent years, scientific studies on nanotechnology have been met with a growing trend and great interest worldwide. Research on this subject requires multidisciplinary work in the fields of physics, chemistry, biology, medicine, genetics, and engineering. Nanoscale particles are very interesting due to their unique tunable optical and electronic properties. Quantum dots (QDs) are known as artificial atoms and were first discovered in the 1980s by A. Ekimov in a glass matrix [1] and L.E. Brus in aqueous solutions [2, 3]. These nanoscale particles' diameter changes in the range of 1–100 nm and they have broad application areas, such as photovoltaics, data storage devices, fluorescence labels, and DNA nanosensors. Due to the small size, quantum dots lie between the atomic and molecular limit, causing their energy levels to be quantized. The energies for an electron in the quantum dot are all discrete, so the QD system is closer to an atom than a bulk material, as shown in Fig. 1.

Free electrons in the conduction band of a 3D bulk semiconductor experience a boundless periodic electric potential within the crystal lattice. When electrons in the conduction band recombine radiatively with holes in the valence band, photons are emitted with energies close to the band gap E_g [4]. Electrons and holes may be weakly attracted here and behave as a single entity called an exciton. The

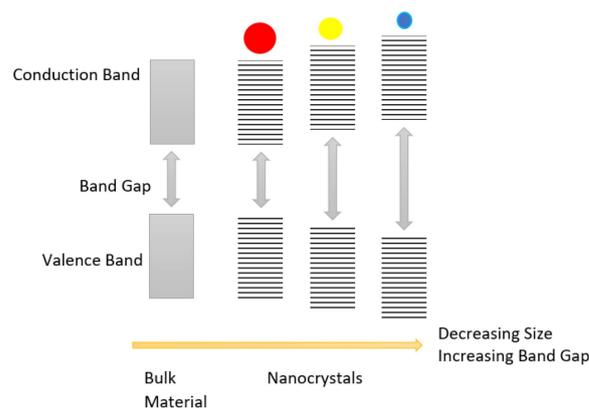


Fig. 1. Energy levels and band gaps of a semiconductor from bulk crystals to nanosized crystals.

behavior is analogous to the hydrogen atomic system of an electron orbiting a proton, and the exciton is said to have a bulk “Bohr” radius, α_B , within its crystal. If the radius of the semiconductor sphere is of the nanometer scale, it is called a semiconductor nanocrystal or quantum dot, but if the quantum dot radius is smaller than the bulk-exciton Bohr radius, size-dependent quantum confinement effects develop and radically change the chemical, physical, optical and electrical properties of the system. This is because the electron and hole wave functions are confined on all sides by the crystal boundaries where the electric potential is higher. Constrained electron-hole pairs can only have discrete energies, and the transition energy between the first two energy states is higher than the band gap energy, E_g ,

by a size-dependent energy shift, $\Delta E_{n,l}$ [5, 6]. As a result of this strong confinement, the band gap energy of QDs will increase. Various theories are used to explain and estimate the magnitude of this energy shift, but in this study, we use the effective mass approximation first derived by Brus [3] to calculate the physical size of quantum dots based on their energy shift from the bulk state. In this approximation, an exciton is confined to a spherical volume of a semiconductor nanocrystal and the masses of electrons and holes is replaced with effective masses (m_e and m_h) to solve the Schrödinger equation and define the wave function. In this study, the transition energies can be explained as a “particle” in a box; here, it is a displaced electron particle and a nanocrystal box. Since nanocrystals have size-dependent electrical, optical, physical, and chemical properties, thus it is important to seek out processes that control the physical dimensions of nanoparticles. Efforts in the literature have concentrated on controlling nanocrystal physical dimensions via a range of chemical parameters, such as annealing temperatures and times, pH of a solution, and reagent types [8, 9]. There are many state-of-the-art methods for synthesizing QDs, such as sol-gel, colloidal, electro-deposition, and solution phase reduction methods. Synthesis of nanoparticles (NPs) in a solution colloidal method was chosen due to ease of production, ease of implementation, and cost effectiveness. Colloidal QDs have been widely studied in both basic and practical research, and significant advances have been made in their synthesis. This chosen method enables quantum dots to be used in light-emitting diodes (LEDs), gas, pressure, and temperature sensing detectors, two- or three-dimensional imaging, and solar cells, as well as in biotechnology and medicine. Quantum dots present an energy level system that changes their optical properties according to external influences (such as electric field, magnetic field) in their state. The modification of the nonlinear optical properties of nanoparticles during the application of an external electric field is unique and provides an effective method to control their optical properties. The literature discusses the theoretical effect of applied electric fields on CdTe nanoparticle systems for a spherical quantum dot state exposed to the presence of an electric field [10–13]. Applying an electric field to isolated atoms disrupts the atom’s energy levels, causing a shift in the absorption wavelength. In semiconductor nanoparticles that exhibit atom-like properties, they degrade in the presence of electric fields. This leads to an electro-optical modulation of the absorption spectra, called the quantum confined Stark effect (QCSE) [14–16]. In QCSE, electrons and holes are pushed in opposite directions by this applied electric field, resulting in a decreased wavefunction overlap and hence absorption peaks. A red shift of the energy band gap also occurs. In this study, the effects of the electric field on the absorption coefficients and band gap energies

of CdTe nanoparticles in solution were investigated and the red shifts were observed along with a decrease in the absorption magnitude that is characteristic of QCSE.

2. Experiment

2.1. Materials

The production and testing of CdTe quantum dots require many chemicals and equipment. Chemicals were obtained from Sigma-Aldrich: tellurium powder (purity 99.999 % size: about 200 mesh), sodium borohydride (purity $\geq 96\%$), cadmium chloride ($\geq 99.99\%$), sodium hydroxide, mercaptopropionic acid (MPA) (purity $\geq 99.0\%$ (HPLC)). The required equipment was: glass and plastic standard laboratory equipment (beaker, pipette, cuvettes, volumetric flask, tubes, etc.), centrifuge, HPLC water machine, pH meter, mass balance measuring tool, UV-Vis spectrophotometer, and Raman spectrometer.

2.2. Synthesis of CdTe QDs

Since most published scientific studies involve complex processes and in-depth theoretical knowledge, the colloidal synthesis of aqueous CdTe — a simple, fast, and relatively safe method — was preferred [17, 18]. The aim was to synthesize different sizes of cadmium telluride (CdTe) quantum dots and characterize their optical properties. CdTe contains heavy metals and some hazardous chemicals; for this reason, a risk assessment of all chemicals used in the synthesis was performed before the study, allowing the necessary precautions to be taken. It is very important to wear gloves, protective clothing, and goggles throughout the synthesis. All the preparations and syntheses should be executed in a well-ventilated fume chamber.

CdTe QDs were synthesized in an aqueous system by mixing tellurium and cadmium precursors in the presence of a thiolate capping agent mercaptopropionic acid (MPA) under a vacuum.

This process takes place in two steps, i.e., synthesis of NaHTe precursor solution and cadmium ion solution. For the NaHTe precursor solution, 0.4 g Te powder and 1.6 g NaBH₄ were combined in a glass vial, and this mixture dissolved in 5 ml HPLC water. The most important step in the preparation of the precursor solution is to subject it to a rapid cooling process; it should be kept in the refrigerator for a few hours. After the cooling process, the mixture takes on a bright light and purple color, as shown in Fig. 2. Then, 1 mmol cadmium chloride is dissolved in 150 ml HPLC water in a three-necked flask.

The pH of this mixture is important and should be adjusted to three different pH values of 7.0, 7.4, and 8.5 by adding sodium hydroxide. It has been observed that quantum dots grow faster when the pH value is increased, so the preferred pH value is 7



Fig. 2. The NaHTe precursor solution.

for a controlled and slow growth rate of nanoparticles. Exactly 0.2 ml of MPA is added into the mentioned mixture, and 3 ml of Te precursor solution (0.3 mmol) is swiftly injected into the reaction mixture. The reaction mixture will turn a reddish color, indicating the formation of CdTe nuclei in solution. The mixture should then be refluxed at 95°C until the desired CdTe QD size is achieved. The solution is usually lightened in the first 10 or 15 min of growth, starting with a golden yellow and becoming red, as shown in Fig. 3. A sample taken between the first 10–15 min during the growth stage is yellow and represents the particles with the smallest radius obtained.

The growth of QDs takes a few hours. During the experiment, six different samples were taken at half an hour intervals. The color of the quantum dot solution changed from yellow to various tones of orange within a few hours, as shown in Fig. 4.

2.3. Optical characterization

The techniques of UV-Visible and Raman spectroscopy were used to characterize the optical properties of semiconductor nanoparticles. Longer synthesis times allow the formation of larger quantum dots. In the early stages of the synthesis, the extracted samples were quantum dots of smaller size. At the same time, the color of the quantum dots started changing from yellow to red.

The band gap energy of QDs or NPs increases with particle size, which changes the optical properties such as the absorption spectra of QDs. The absorption spectra method is one of the methods used to find E_g . Optical absorption is used to measure the absorption of inter-band transition energies in semiconductors. The Gaussian peak in each absorption spectrum results from the lowest electron-hole pair transitions in CdTe nanocrystals in an aqueous solution. Quantum dots absorption spectra reveal the position and energy associated with the first excitonic transition. The band gap of the material can be measured using this technique. The method is a fast and effective technique for short-term synthesis. Data from this method can be obtained from information about the absorbance, the band gap energy that particles have, and the radii of particles. Optical absorption measurements were recorded on PerkinElmer Lambda

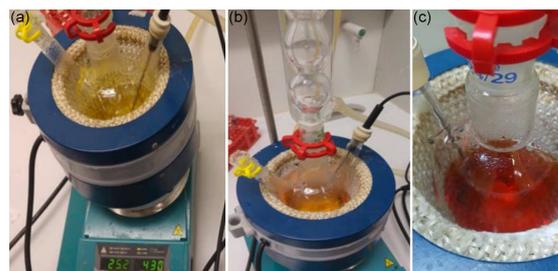


Fig. 3. Flasks contain different color samples because each sample has different-sized CdTe nanoparticles. The samples were prepared under different reflux times at constant temperature.



Fig. 4. CdTe QDs in aqueous solution with different sizes.

25 UV/Visible absorption spectrophotometer between 300–700 nm. Raman spectrometer is used to investigate phonon modes (vibration, rotation, and other low-frequency transitions in molecules) with a Renishaw InVia Raman system. Raman spectra measurements were performed using a 532 nm emission line of the 30 mW helium–neon laser at room temperature. The Raman spectra peaks were analysed by “peak fit” software program. The preferred method when preparing samples for Raman measurements is the spin coating method. Liquid CdTe quantum dots were layered onto a glass substrate, with 7 layers at 500 rpm. Before the measurements, the phonon peak of the Si substrate was used as a reference for the calibration of the phonon frequencies of the CdTe quantum dots.

A suitable system was designed to perform high DC voltage measurements for solution samples, as shown in Fig. 5. Absorption spectra of QDs in the solution under the influence of electrical field strength were studied at 1 kV.

3. Results and discussion

For CdTe QD synthesis to be carried out in a successful way, some of the critical conditions in the synthesis phase are the capping agent, the synthesis temperature, and the pH value. The results show that temperature affects the size of the particles — the higher the temperature, the smaller the quantum dots.

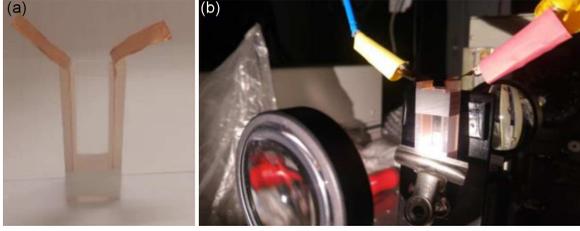


Fig. 5. Electro-absorption experimental setup for aqueous solution.

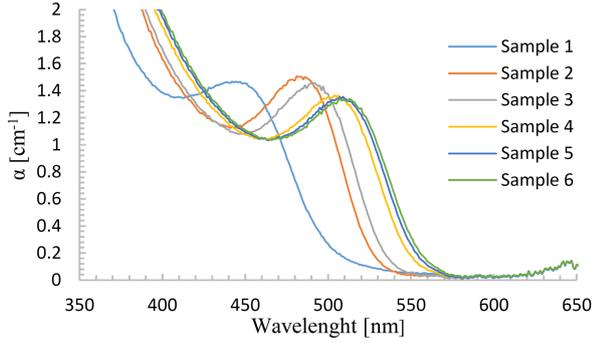


Fig. 6. The absorption spectra of CdTe solution semiconductor nanocrystals at (sample 1) 10 min, (sample 2) 45 min, (sample 3) 70 min, (sample 4) 140 min, (sample 5) 175 min, (sample 6) 190 min heat treatment time.

For each sample, the absorption wavelength plot of the data from absorption spectrometer measurements was drawn. At the lowest pH 7, the absorption spectrum of the nanoparticles was sharper and a narrower spectrum was obtained in the wavelength range of 450–510 nm given in Fig. 6. From this result, we can clearly see that the exciton absorption peaks shift red with the time of heat treatment.

The obtained results were used to determine the band gap energies of each sample. The value of the direct band gap was evaluated from a Tauc plot (the method of determining the optical band gap in semiconductors from absorption spectra measurements), with the use of the equation given below [19–22]

$$\alpha E = A(E - E_g)^n, \quad (1)$$

where A is a constant, E is photon energy ($h\nu$), and E_g is the optical band gap; $n = 1/2$ for direct band gap semiconductor, such as in the case of CdTe.

The equation (1) can be linearised accordingly

$$(\alpha h\nu)^2 = A h\nu - A E_g. \quad (2)$$

A Tauc graph was then plotted and extrapolation from the point of the inflexion through the x -axis enabled the band gap of the sample to be extracted from the absorption data. An example of one such plot is shown in Fig. 7.

One expects that the energetic position of the exciton band in the optical absorption spectra and the energetic position of the photoluminescence (PL)

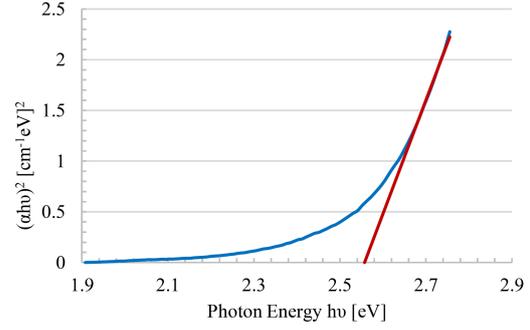


Fig. 7. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for a representative CdTe sample 1.

TABLE I

Quantum dot absorption peak wavelengths λ , band gaps E_g , and radii for all samples r .

Sample	λ [nm]	E_g [eV]	r [nm]
1	492	2.520	1.93
2	524	2.366	2.08
3	541	2.291	2.16
4	568	2.182	2.30
5	579	2.140	2.40
6	584	2.122	2.41

band in the PL spectra overlaps since absorption is the inverse of emission. However, in real crystal structures, and especially in nanometer-size structures, the emission occurs through the defect levels within the band gap, which is why the PL emission energy is red-shifted relative to the excitonic absorption band.

To determine the size of the particle the Brus equation (effective mass approximation) was used [23, 24]. According to the effective mass model, the first term is the band gap energy of QD, the second term is the band gap energy of bulk semiconductor, the third term is equal to the energy due to quantum confinement, and the last term is the Coulomb interaction energy of an exciton. The radius of the CdTe QD sample is approximated by

$$E = E_g^{\text{bulk}} + \frac{\hbar^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1}{4\pi\epsilon\epsilon_0} \frac{1.786 e^2}{r}, \quad (3)$$

where E_g^{bulk} is the bulk energy gap, r is the particle radius, m_e is the effective mass of electrons, m_h is the effective mass of holes, ϵ is the relative permittivity, ϵ_0 is the permittivity of free space, \hbar is Planck's constant divided by 2π , and e is the charge of an electron.

The band gaps (E_g) of all samples were determined from the absorption spectra. The radii (R) of the nanoparticles were calculated for increasing annealing times. All data are given in Table I. It is understood that the dimensions of CdTe quantum dots increase with time in the synthesis process.

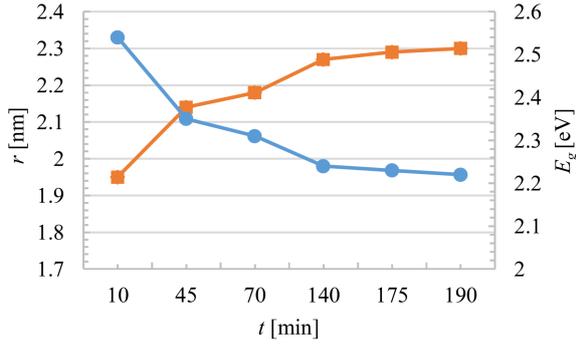


Fig. 8. Variation of the band gap E_g (●) and the radius r (■) with time (t).

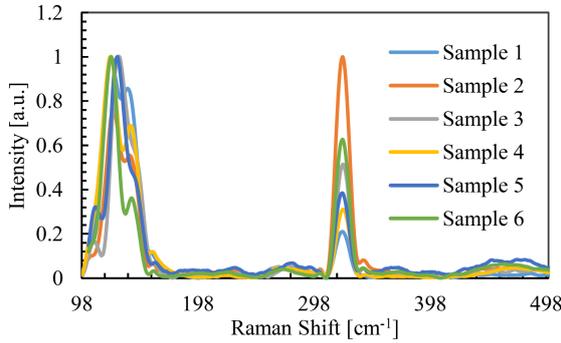


Fig. 9. Resonant Raman spectra of a series of the CdTe studied samples of different size at 300 K.

Particle radius and band gap energy is calculated using (2) and (3). The radius vs band gap energy plot is shown in Fig. 8, which indicates that the particle size increases with time and the band gap energy decreases with time.

Raman spectrum measurements of CdTe nanoparticles were analyzed from 100 to 500 cm^{-1} at room temperature, and the results are given in Fig. 9. Raman peaks and broadening were obtained by analyzing the measurement results with the Lorentzian line shape curve fitting program. The low Raman shift regime was investigated and the peaks were observed at approximately 120, 140, and 160 cm^{-1} , apart from the peak marked as longitudinal optic overtone predominantly observed at 320 cm^{-1} . The Raman peak observed in the 110 cm^{-1} region is commonly taken as a disorder activated phonon (DAP) [25–27]. The Raman peaks for bulk CdTe were compared with the values determined in the measurements and it was seen that the values in the literature were higher [28]. The next peak was around 120 cm^{-1} due to the zone center longitudinal acoustic (LA) phonons located at the X critical point. Other peaks, 140 cm^{-1} and 160 cm^{-1} represent the transverse optical (TO) (Γ -critical-point) and longitudinal optical (LO) (X-critical-point) phonon modes, respectively, compatible with the literature.

TABLE II

Band gap energies and size of the samples without field and under electric field.

Applied voltage	0 V		1000 V		Stark shift [meV]
	Band gap [eV]	Radius [nm]	Band gap [eV]	Radius [nm]	
Sample 1	2.520	1.93	2.514	1.94	6
2	2.366	2.08	2.355	2.09	11
3	2.291	2.16	2.280	2.17	11
4	2.182	2.30	2.165	2.33	17
5	2.140	2.40	2.124	2.37	16
6	2.122	2.41	2.106	2.43	16

In the CdTe samples, the LO mode is shifted to the upper wavenumber of about 10 cm^{-1} . This extra signal may be related to the ligand used molecule (e.g., MPA) on the CdTe quantum dot.

The second part of this study is the application of high DC voltage to CdTe nanoparticles in solutions. Finally, an ideal experimental setup was developed for electric field applications, and a voltage of 1 kV was successfully applied to all samples. As observed in the experimental study and in the literature, as the electron and hole wave functions are separated by the an increasing applied electric field, there is a decrease in the band [29]. The situation before and after the electric field application was compared and a blue shift was observed in the optical absorption spectrum given in Table II. The electro-optical measurement results clearly demonstrated that the increased electric field causes a reduction in the band gap energy due to the Stark effect causing red shift. It was observed that the CdTe nanoparticles in aqueous solution exhibited around 1% Stark shift.

4. Conclusions

This study focused on a simple and economical one-pot method to synthesize high-quality water-soluble CdTe QDs. The most important aspects of this study are that the synthesis method is fast and the shelf life of the resulting nanoparticles is long.

One of the advantages of this study is that the precursor solution, which is the first step of the synthesis, is more practical than the methods presented in the literature.

When the temperature was kept constant during the synthesis, and the heat treatment time was extended, the band gap energy of the particle decreased linearly. The effect of the heat treatment duration on the band energy is analyzed from absorption spectroscopy measurements. These results show evidence that the absorption wavelength gradually increases with increasing growth time, which is explained in terms of a red shift. In the samples with

increased time of heat treatment, the first exciton peak exhibits a red shift, and the broadening of the excitons peak may be related to the size dispersion of the quantum dots. For samples of an aqueous solution, the annealing time changed between 15 min and 3 h. Also, the band gap changed from 2.52 to 2.12 eV, which equals a 16% increase in the band gap.

This is the evidence that the Brus equation infers that the size of the particle becomes smaller. Thus optimal heat treatment time and temperatures of the synthesis may allow particle radius to be tunable.

The particle radii were successfully calculated from the effective mass model by Brus. Nanoparticle size for aqueous samples was changed between 1.93 and 2.40 nm with heat treatment of 3 h — this corresponds to a 18% increase in the particle size. The results show that the growth rate of the particles decreases as the reaction continues.

It is seen that the change in the dimensions of the quantum dots is not large. One of the reasons for this is that the study takes place in a limited time. These results were reached in an experimental period of about 3 h. It is thought that as the experiment time increases, the quantum dots will get larger. Since the dimensions are very small, the band energy calculations were compared, taking values from different parts of the graph in order to minimize error, and it was seen that the values did not affect the size calculation.

The results indicate that the size dependence of absorption spectra at various QD dimensions provides evidence for the quantum confinement effect. Furthermore, bandwidth expansion is compatible with the theoretical radius calculation based on the effective mass model.

The high electric field induced a red shift of CdTe QDs band gap in an aqueous solution with the rates of radius changing from 0.06 nm/kV to slightly less than 0.17 nm/kV. Since the electron and hole wave functions are separated by applying an electric field, the decrease in band gap is expected due to QCSE. This decreases the absorption peak height since the electrons and holes move closer together in energy, increasing the wavelength of the absorption.

Compared to bulk CdTe, the LO and TO absorption peaks in the Raman spectrum showed a blue shift of 5 and 10 cm^{-1} , which is due to the quantum confinement effect. For the range analyzed in the Raman spectrum, three Raman peaks centered near 125, 139, and 159 cm^{-1} confirmed the formation of CdTe QDs.

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