

# Synthesis and Optical Spectroscopy of Cadmium Chalcogenide Semiconductor Nanocrystals

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High optical quality Cd chalcogenide (Te, Se, and S) quantum dots with average size at the near Bohr radius were synthesized using a colloidal chemical reaction. The Cd chalcogenide (Te, Se, and S) nanocrystals exhibited strong blue shift and discrete energy states which were significantly modified from bulk crystals. The discrete structure of energy states leads to a discrete absorption spectrum of quantum dots, which is in contrast to the continuous absorption spectrum of a bulk semiconductor. Atomic-like discrete energy states of exciton indicate a quantum confinement effect. The energy spacing between the first and second peaks of exciton absorption is less than 50 meV for bigger than ~4 nm quantum dot size, and is more than several hundred meV for ~2 nm size of CdTe quantum dots. The emission of CdSe nanocrystals tuned from near-infrared to dark blue by a reduction in the dot radius from 8 to 0.8 nanometers. The quantum confinement modifies the optical absorption, the photoluminescence, the radiative decay time, and the nonlinear optical properties of nanocrystals. The optical properties of quantum dots are also sensitive to the dielectric effects of surrounding environment, which can be utilized for the detection of nanoscale crack on the spacecraft.

## 1. Introduction

Both space debris and intense cosmic rays pose serious threats to the structural integrity of the spacecraft. A better detection system for these problems is essential for the safety of space crews or for the successful continuation of NASA's mission in space. A nanophoto sensor with cadmium chalcogenide (Te, Se, and S) semiconductor nanocrystals is considered to be a best candidate to detect spacecraft cracks without increasing payload or changing the thermal properties of heat-shielding of spacecraft.

Synthesis and optical spectroscopy of cadmium chalcogenide (Te, Se, and S) semiconductor nanocrystals are proposed to develop high quality optical nanocrystals. The high quality optical nanocrystals are considered to have high luminescence efficiency, temperature stable emission, high color purity, and environmental stability without reduction in performance due to high temperature, or by exposure to oxygen, nitrogen, and moisture.

The semiconductor colloidal nanocrystals of cadmium (Cd) chalcogenide (Te, Se, and S) have unique properties of wide tunability of bandgap energy and emission color (~4.5 - ~1.7 eV) with their quantum confinements, radiative transitions from several nanoseconds down to picoseconds. The fundamental optical properties are directly related to morphology, distribution of size, and surface chemistry. This indicates that materials developments and optical spectroscopy of the nanocrystals play an important role in developing nanophoto sensors.

The performance of nanophoto sensors depends upon the emission properties of semiconductor nanocrystals. The emission properties of semiconductor nanocrystals include brightness, emission color, color purity, quantum yield, and emission temperature stability. Since the emission

color of semiconductor nanocrystals is strongly dependent on morphology, the color purity of emission is dependent on the distribution of size of colloidal nanocrystals. The quantum yield of semiconductor nanocrystals is strongly dependent on the surface chemistry.

The optical materials with nanoscale sizes are also sensitive to the surrounding environment, which can be utilized for the detection of nanoscale crack on the spacecraft. During the last decade, considerable theoretical and experimental efforts have been made in the fundamental aspects of quantum confinement effects, and optical properties of nanoscale materials. The term nanoscale particle refers to an intermediate in size, between isolated atoms and molecules and bulk materials, where the transitional properties between two limits can be controlled. As it is well known, a decrease of particle size will influence two of the most important contributions to the optical properties of nanoscale materials, which are quantum size effects, surface effects, and surrounding environments.<sup>1</sup>

## 2. Synthesis of semiconductor nanocrystals

High optical quality Cd chalcogenide (Te, Se, and S) nanocrystals with sizes near the Bohr radius ( $\alpha_B \sim 7$  nm (CdTe),  $\alpha_B \sim 5.6$  nm (CdSe), and  $\alpha_B \sim 1.8$  nm (CdS) were synthesized by the chemical colloidal reaction. Many synthesis techniques were developed for preparing Cd chalcogenide semiconductor nanocrystals, however, the following synthesis methods were mostly applied for our current research samples. For CdS nanocrystals synthesis, a mixture of CdO, oleic acid (OA), and technological-grade 1-octadecene (ODE) is heated to 300 °C. A solution of sulfur in ODE is swiftly injected into the heated solution, and the mixture is allowed to cool to 250 °C

for the growth of CdS nanocrystals. The synthesis can be carried out under argon or in open air. Aliquots are taken at different time intervals, and UV-Vis and PL spectra are recorded for each aliquot. For CdSe nanocrystal synthesis, CdO is mixed with Stearic Acid (SA), and heated until CdO is completely dissolved by the SA. The mixture of CdO and SA is optically clear at around 160 °C, while at room temperature the solution solidified as a waxy or a white substance. Hexadecylamine (HAD) and trioctylphosphine oxide (TOPO) are added in the mixture of CdO and SA, and heated to 320 °C. Then, the solution Se, tributylphosphine (TBP) and dioctylamine (DOA) are injected quickly. The growth temp is 290 °C. The first exciton absorption peaks after 90 seconds of growth are near 600 nm. For CdTe nanocrystal synthesis, CdO is mixed with tetradecyl phosphonic acid (TDPA), and ODE for the slow reaction, and is heated to 300 °C. Also, OA instead of TDPA can be used for the fast reaction. Then the mixture of Te, TBP, toluene and ODE is quickly injected into the solution. The growth temperature is around 245 °C. The first exciton absorption peaks are at ~600-630 nm after ~60 seconds for the slow reaction or after ~10 seconds for the fast reaction. The first absorption peak varies up to ~730 nm continuously adding Te and Cd precursors.

After nanocrystal synthesis, the size and size distributions of the nanocrystals are determined from the linear absorption spectra using calibration curves derived from a comparison of optical data with data of the TEM. The optical spectroscopy at room temperature is performed using an UV-VIS absorption spectrometer (Agilent Tech, 8453). Size quantization of nanocrystal quantum dots is carried out using an electron transmission microscopy (Hitachi, H-9000NAR).

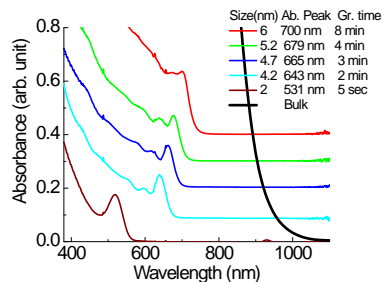
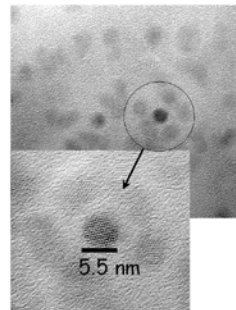
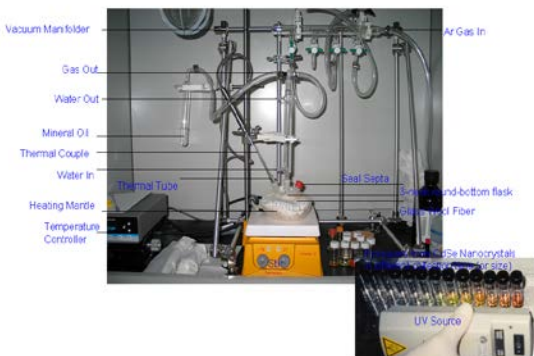


Figure 1. Experimental setup for colloidal-semiconductor nanocrystals, Transmission electron microscopy (Hitachi, H-9000NAR) and absorption spectra of cadmium telluride semiconductor nanocrystals.

### 3. Optical properties of semiconductor nanocrystals

One of the defining features of a semiconductor is the energy gap between the conduction and valence energy bands. The emission spectrum of semiconductor is determined by the energy bandgap. The energy bandgaps ( $E_g \sim 863$  nm), CdSe ( $E_g \sim 714$  nm), and CdS ( $E_g \sim 513$  nm)) of bulk semiconductors are a fixed parameter determined by the material's identity. The situation changes, however, in the case of nanoscale semiconductor particles with sizes near the Bohr radius ( $\alpha_B \sim 7$  nm (CdTe),  $\alpha_B \sim 5.6$  nm (CdSe), and  $\alpha_B \sim 1.8$  nm (CdS)). This size range corresponds to the regime of quantum confinement, for which the spatial extent of the electronic wave function is comparable with the dot size. As a result of these geometrical constraints, electrons feel the presence of the particle boundaries and respond to changes in particle size by adjusting their energy.<sup>2</sup> This phenomenon is known as the quantum-size effect, and it plays a very important role in quantum dots. For weak confinement ( $a \sim \alpha_B$ ), the energy of exciton in a spherical box potential model is expressed in the form of<sup>3</sup>

$$\Delta E = \frac{\hbar^2 x_{ml}^2}{2MR^2} - \frac{\mu e^4}{2\varepsilon^2 \hbar^2} \quad (1)$$

where,  $h$  is the Planck's constant  $\hbar = h/2\pi$ ,  $x_{ml}$  is the roots of the Bessel function,  $M$  is the exciton translation mass,  $R$  is the dot radius,  $\mu$  is the electron-hole reduced mass, and  $\varepsilon$  is the dielectric constant. For a spherical quantum dots with radius  $R$ , the equation (1) indicates that a size dependent contribution to the energy gap is simply proportional to  $1/R^2$ , implying that the gap increases as the nanocrystal size decreases.

Absorption spectra of CdTe nanocrystals have the strong blue-shift of optical bandage as shown in figure 2. Atomic-like discrete energy states of exciton indicate a quantum confinement effect, which is completely different with the bulk crystals. Plotting with the weak confinement equation, the energy spacing between the first and second peaks of exciton absorption is less than 50 meV for bigger than  $\sim 4$  nm quantum dot size, and is more than several hundred meV for  $\sim 2$  nm quantum dot size. The quantum confinement modifies the optical absorption, the photoluminescence, the radiative decay time, and the nonlinear refractive index of the nanocrystals.

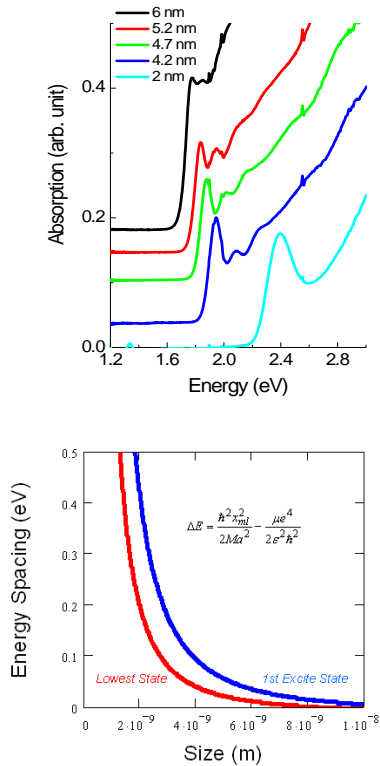


Figure 2. Absorption spectra of CdTe, confinement energy states at the conduction-band and energy transitions.

In addition, the quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels. The discrete structure of energy states leads to a discrete absorption spectrum of quantum dots, which is in contrast to the continuous absorption spectrum of a bulk semiconductor. Because of the quantum-size effect, this ability to tune the nanocrystal size translates into a means of controlling various nanocrystal properties, such as emission and absorption wavelengths. For example, the emission of CdSe nanocrystals can be tuned from near-infrared to dark blue by a reduction in the dot radius from 8 to 0.8 nanometers.

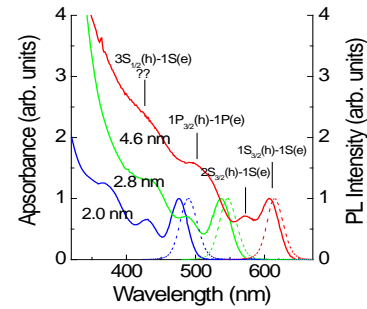


Figure 3. Absorption (solid lines) and photoluminescence (dot lines) spectra of TOPO-passivated CdSe nanocrystals.

Figure 3 shows typical absorption spectra of a series of TOPO-passivated colloidal NC's with mean radii from 2 to 4.6 nm. Because of the narrow NC size distribution, the absorption spectra clearly exhibit discrete features due to transitions coupling electron and hole quantized states. The electron quantized states are labeled using letter (l) to denote the angular momentum of the envelop wave function (S for  $l=0$ , P for  $l=1$ , D for  $l=2$ , etc) and a digit to denote the number of the state of the given symmetry. The three lowest electron states in the order of increasing energy are  $1S$ ,  $1P$ ,  $1D$ . A similar notation is used for hole states with an addition of a subscript which denotes the total hole angular momentum, which is the sum of the valence-band Bloch-function momentum and the momentum of the hole envelope wave function. For CdSe nanocrystals, the first three hole states in the order of increasing energy are  $1S_{3/2}$ ,  $1P_{3/2}$ ,  $2S_{3/2}$ .

The two lowest bands in the absorption spectra (solid lines) of figure 3 can be assigned to transitions involving the lowest electron state ( $1S$ ) and two different hole states ( $1S_{3/2}$  and  $2S_{3/2}$ ), or  $1S(e)-1S_{3/2}(h)$  and  $1S(e)-2S_{3/2}(h)$ . The absorption spectra of CdSe nanocrystals near the Bohr radius also exhibit a well-

resolved band associated with the transition coupling the  $1P$  electron state to the  $1P_{3/2}$  hole state ( $1P$  transition) and a higher-lying band associated with the transition involving the  $1S$  electron state and a hole state originating from the spin-orbit split-off band ( $3S_{1/2}$ ).

The photoluminescence (PL) spectra (dot lines) of CdSe nanocrystals are also shown in figure 3. The stark shifts ( $\Delta\lambda_S$ ) of CdSe nanocrystals are  $\Delta\lambda_S \sim 7.7$  nm for 4.6-nm size,  $\Delta\lambda_S \sim 9.9$  nm for 2.8-nm size, and  $\Delta\lambda_S \sim 13.7$  nm for 2.0-nm size. It implies that the nanocrystals have a wider stark shift with the smaller size. The change of stark shift can be expected even crystal structure dependent on ligand or shape of nanocrystals. Also, the emission and absorption spectra including bandgap energy of nanocrystals have wide tunability from near-infrared to dark blue by simply varying the size of the semiconductor nanocrystals.

#### 4. Conclusion

High optical quality Cd chalcogenide (Te, Se, and S) quantum dots with average size at the near Bohr radius were synthesized using a colloidal chemical reaction. The Cd chalcogenide (Te, Se, and S) nanocrystals exhibited strong blue shift and discrete energy states which were significantly modified from bulk crystals. The discrete structure of energy states leads to a discrete absorption spectrum of quantum dots, which is in contrast to the continuous absorption spectrum of a bulk semiconductor. Atomic-like discrete energy states of exciton indicate a quantum confinement effect. The energy spacing between the first and second peaks of exciton absorption is less than 50 meV for bigger than  $\sim 4$  nm quantum dot size, and is more than several hundred meV for  $\sim 2$  nm size of CdTe quantum dots. The emission of CdSe nanocrystals tuned from near-infrared to dark blue by a reduction in the dot radius from 8 to 0.8 nanometers. The quantum confinement modifies the optical absorption, the photoluminescence, the radiative decay time, and the nonlinear optical properties of nanocrystals. The optical properties of quantum dots are also sensitive to the dielectric effects of surrounding environment, which can be utilized for the detection of nanoscale crack on the spacecraft.

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