Kinetic Controlled -Growth Synthesis of Cadmium Selenide Nanocrystal Quantum Dots

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Abstract

A kinetic controlled-growth method has been used to synthesize cadmium selenide, CdSe, nanocrystals. Nanocrystal structures are consistent with that of a quantum dot. Ligand passivation on the surface of the micelle is best carried out using trioctylphosphine, TOP. This allows one to tune the particle surface chemistry. Quantum dots intersperse as colloids within the 1-octadecene solvent matrix. The color gradient observed among the samples is indicative of its dependence on particle size which is consistent with the "particle-in-a-box" theory. Results also indicate that the particle size of these nanocrystals is dependent on reaction time and may be dependent on reaction temperature. Our method presents a greener and faster approach to the synthesis of these important photoactive materials.

Introduction

Development of nanoscale materials with photophysical properties that depend on particle size is important in fabricating optoelectronic devices. Among others, cadmium selenide, CdSe, is known for its novel photophysical and electrochemical properties. The quantum nature of this type of nanocrystal can be explained *via* "particle-in-a-box" theory[1-3]. CdSe nanoparticles are quantum dots (QDs), and are often employed as photosensitizer dyes in photovoltaic cells (PVCs, see Figure 1). In this paper, we present a greener, faster and efficient, kinetic controlled-growth synthesis of CdSe QDs passivated with trioctylphosphine, TOP, ligands

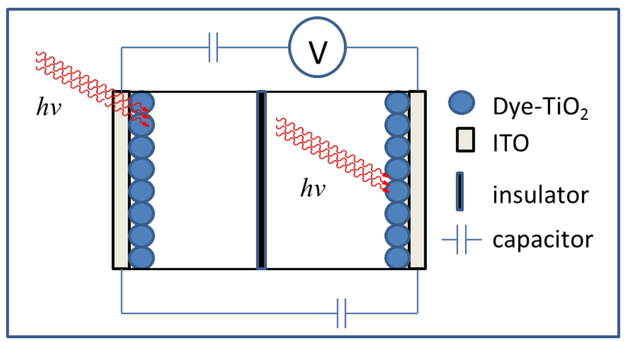

Figure 1. Light-harvesting mechanism of proposed PVC

Figure 2 shows the three dimensional matrix in a CdSe nanocrystal. Historically, the density of TOPs are known to influence that surface chemistry allowing one to tune the conductivity, stacking and physical properties of a crystal suspended as colloidal particles in various types of solvents of varying dielectric constants and proticity.

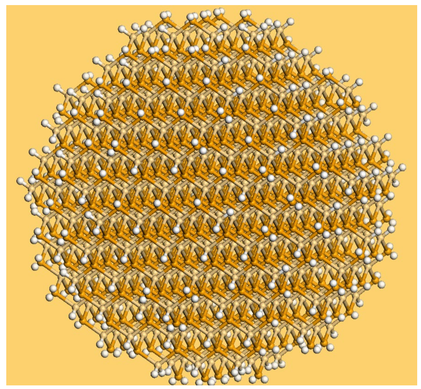

Figure 2. Non-passivated core structure of a CdSe Quantum Dot

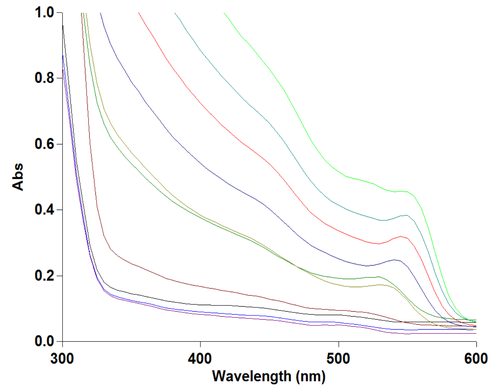

Figure 3. Overlayed UV/Visible Absorption Spectra of CdSe Quantum Dots synthesized at 225°C

Methodology

Cadmium selenide, CdSe, nanocrystals have been synthesized using a one pot method. A separate trioctylphosphine-selenide precursor, Precursor A, was prepared by mixing 30.0mg selenium with 0.40ml trioctylphosphine, TOP and 5.0ml 1-octadecene in a single-neck 25-ml round bottom flask. Precursor A was stirred and lightly heated to homogenize the solution and allowed to cool slowly to room temperature (~23.0° C). One batch of precursor A contains enough precursor for five runs and excess was sealed and stored at room temperature in a fume hood. A separate cadmium oleate solution, Precursor B, was prepared by mixing 13.0mg of cadmium oxide, CdO, and 0.60ml oleic acid with 10.0ml 1-octadecene in a 50-ml, three-neck round bottom flask. Precursor B was heated and soon as it reached 225.0° C. A1.0ml of Precursor A was injected into the Precursor B solution. Approximately 0.75ml aliquot samples were immediately withdrawn from the reaction mixture and were delivered to individual test tubes in rapid succession (see Figure 3). Sample test tubes were sealed and stored in a freezer.

References

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Results and Discussion

Figure 3 shows the overlayed UV/Visible absorption spectra of a series of CdSe quantum dots synthesized at 225° C. Synthesis of these nanoparticles are temperature dependent and we are still exploring the chemistry associated with this dependence.

Figure 4 shows different CdSe QDs that were synthesized in the lab. Each CdSe sample is passivated by trioctylphosphine, TOP. Passivation is the process of preventing the surface of a particle from chemical degradation within its environment. Variability in colors of each CdSe quantum dot in the visible region is dependent on particle size. It is apparent that the larger the particle size, the lower is the energy of absorption of the particle. This is indicated by the observed red-shift, *a.k.a.* bathochromic shift, in the absorbance.

It is important to note that each type CdSe nanoparticles is suspended in 1-octadecene solvent. Typical quantum dot size ranges from 2.0 – 4.0 nm. Surface chemistry indicates that each quantum dot is made up of CdSe core and a ligand-based outer shell. The core nanocrystal adopts a wurtzite (hexagonal closed-pack, hcp) crystal structure (see Figure 1). The ligand shell gives rise to a property called 'particle confinement' in which the electrons within the crystal are confined to a very small volume. Also, the chemical property of the ligand influences the solubility, stability and suspendability of quantum dots in various solvents. Overall, each particle is micellar in nature.

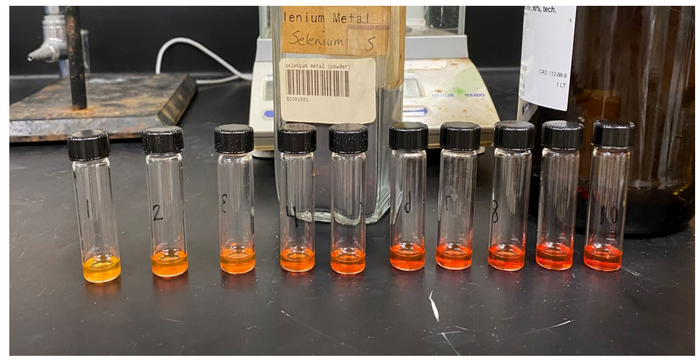

Figure 4. Synthesized CdSe Quantum Dots passivated with trioctylphosphine, TOP

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