

The Facile Synthesis of Nanocrystalline Semiconductor Quantum Dots

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ABSTRACT

Current synthetic techniques to high-quality quantum dots (“QD’s”) involve organometallic precursors that are hazardous and expensive and require they be rapidly injected into an extremely hot solvent to form the QD’s. A new method for synthesizing high-quality CdSe QD’s while circumventing these problems has been developed. Different cadmium salts were studied as Cd precursors alternative to dimethylcadmium. High-quality CdSe QD’s were found possible with cadmium acetate as the Cd precursor. Changes in solvent temperature and reaction time had a systematic effect on QD particle sizes and the accompanying optical properties. These preliminary results point to a general method for producing high-quality QD’s that is safer and much more versatile.

INTRODUCTION

Quantum dots are crystalline semiconductor nanoparticles that exhibit unique optical properties derived from quantum confinement effects [1]. They luminesce with very sharp spectral resolution upon UV-vis irradiation, and the emission color of QD’s can be tuned with great precision, depending on their composition and particle size. Such properties make this class of optical materials very attractive in a variety of applications and devices, such as fluorescent biological labeling, lasers and electrochromic displays [2-4]. Among the many synthesis routes to QD’s, the high-temperature thermolysis route reported by Murray et al. led to QD’s with the best quality in terms of particle size distribution and optical properties [5]. Several aspects of the synthesis chemistry limits general use, though: the dimethylcadmium precursor is pyrophoric, moisture sensitive and expensive (cost ~20 times that of cadmium salts); the solvent is heated to temperatures in excess of its flash point (252 °C for “TOPO”); and large amounts of gas are released upon precursor injection into this solvent. In this work, a safer and more tractable synthesis route to CdSe QD’s using a cadmium salt precursor was found to give similar high-quality CdSe QD’s. Important synthesis parameters were probed for their effects on the QD optical properties via UV-vis spectroscopy and photoluminescence measurements.

EXPERIMENTAL METHODS

A cadmium salt (chloride, iodide or acetate) and 2 molar equivalents of trioctylphosphine oxide (“TOPO,” 90%, Aldrich) were placed in a flask and dried at 140 °C under reduced pressure ($\sim 3 \times 10^{-2}$ Torr) for 0.5 hr. A 0.4 M solution of trioctylphosphine selenide (“TOPSe”) was prepared by dissolving Se powder (99.95%, Cerac) in trioctylphosphine (“TOP,” 90%, Aldrich) under Ar purge. From these stock solutions, the Cd and Se precursors were combined under Ar purge at a Cd/Se molar ratio of 1.4 to give a clear solution. In a typical QD synthesis experiment, 5.5 g of TOPO (previously degassed at 140 °C and at $\sim 3 \times 10^{-2}$ Torr) was heated

slowly (~0.5 hr) under Ar atmosphere to an elevated temperature of 250-350 °C. When the desired temperature was reached, 1 ml of the Cd/TOPO/TOPSe solution was injected quickly with a syringe (<0.25 sec) into the stirring TOPO solvent. The reaction solution immediately became colored, with the solvent temperature dropping by 15 °C. Aliquots were withdrawn as a function of time and cleaned of excess TOPO by flocculating the CdSe QD's with methanol and recovering them through centrifugation. The QD's were re-dispersed in an organic solvent, such as dichloromethane or chloroform.

Optical characterization of the CdSe QD's was done via UV-vis spectroscopy and fluorospectroscopy. UV-Vis spectra were collected on a Shimadzu UV-Vis spectrophotometer (Model UV-1601) at a resolution of 0.5 nm, and photoluminescence (PL) spectra were collected on a SPEX FluoroMax fluorospectrometer at a resolution of 0.5 nm. Quantum yields were determined relative to rhodamine 6G and at optical densities in the range of 0.03-0.05. Transmission electron microscopy (TEM) was performed on a JEOL2010 equipped with a LaB₆ gun, operating at an accelerating voltage of 200 kV.

RESULTS AND DISCUSSION

Three different cadmium salt precursors were studied as possible substitutes for dimethylcadmium in the preparation of CdSe QD's. Cadmium acetate led to CdSe QD's, based on the UV-vis absorbance and fluorescence emission spectra (Figure 1). The presence of a steep absorbance edge and a well-defined peak centered at 567 nm which is attributed to the first exciton transition are characteristic of QD systems [1]. The band gap is estimated to be ~600 nm, or 2.1 eV, and is blue-shifted from the band gap value of bulk CdSe, 1.74 eV (712 nm), as a consequence of quantum confinement.

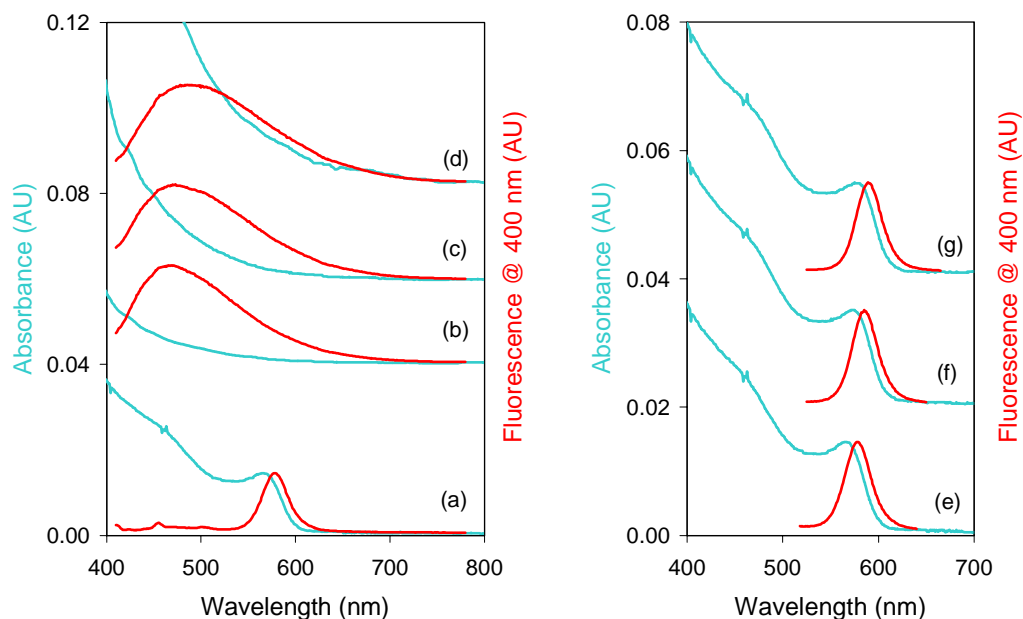


Figure 1. UV-vis absorption and fluorescence emission spectra for CdSe QD's prepared at a solvent temperature of 300 °C for 0.5 min using (a,e) Cd(ac)₂, (b) CdCl₂, (c) CdI₂, and (d) no Cd precursors; and for CdSe QD's prepared at a solvent temperature of 300 °C using Cd(ac)₂ precursor for (e) 0.5 min, (f) 1 min and (g) 2 min.

These CdSe QD's exhibited photoluminescence (PL) upon excitation at 400 nm, emitting a peak at 579 nm with a FWHM of 36nm. The emission peak did not shift when excited at other, higher wavelengths, indicating that the emission was due to a real electronic transition in the material. It is attributed to radiative relaxation of the band edge exciton [6].

Under the same synthesis conditions, the chloride and iodide salts of Cd did not lead to solutions that showed any fine structure in their absorbance spectra, indicating QD's were not formed. The product solutions did show fluorescence, but the emission spectra was broad (FWHM ~ 150 nm) and was similar to the product solution prepared without any Cd precursor, demonstrating the efficacy of the Cd(ac)₂/TOPO complex versus that of either CdCl₂/TOPO or CdI₂/TOPO complexes. Recently, it was shown that CdO/organophosphonic acid complex led to QD's but the CdCl₂/acid complex did not [7].

The reaction time was varied when preparing CdSe QD's with Cd(ac)₂ at 300 °C (Figure 1). At all times the optical spectra of the resultant QD's retained the general absorbance and PL features as those of the QD's prepared at 0.5 min. The optical features red-shifted with time, indicating an enlargement of the QD's with reaction time. There is a direct correlation of UV-vis (and PL) peak with particle size [1], and so particle sizes of the Cd(ac)₂-derived CdSe QD's can be estimated using a calibration curve for dimethylcadmium-derived CdSe QD's (Table I) [5,8]. The PL emission narrowed with reaction time, indicating a sharpening of the size distribution of the QD's [8].

Table I. Particle size and PL width of CdSe QD's prepared at 300 °C with reaction time.

Time (min)	Size (nm)	FWHM (nm)
0.5	3.50	35
1.0	3.55	33
2.0	3.60	33

The quantum yield (QY, the ratio of number of emitted photons to the number of absorbed photons) was 0.4% for the three samples when measured 1 day after their synthesis. QY's of CdSe QD's prepared with dimethylcadmium were reported to be higher (~10-15% [5,6]) but that may be a result of the higher reaction temperatures used. Indeed, increasing the reaction temperature from 300 °C to 350 °C raised the QY of the resulting CdSe QD's to 2.9%. The difference in Cd precursor type could be responsible for the difference in QY's. It was reported that dimethylcadmium-derived CdSe's were covered by TOPO and/or TOPSe molecules and that the QY's dropped from 10-15% to <1% after exchanging the surface molecules with thiol compounds [6]. This sensitivity to surface species suggests that the lower QY's of the Cd(ac)₂-derived QD's is due to non-TOPO/TOPSe molecules on the surface, e.g. residual acetate groups. Intriguingly, the QY of the Cd(ac)₂-derived QD's increased over a period of 30 days, to a three-fold value of 1.3%. It is further noted that QY's are very sensitive to the presence of water, which could be another factor in the observed QY increase [9].

TEM studies found the CdSe QD's to be fairly monodisperse, roughly spherical nanoparticles (Figure 2). Average particle sizes measured 3.5±5 nm, in the range of particle sizes estimated from the UV-vis peak positions (Table I).

CdSe QD's prepared at solvent temperatures of 300 °C were found to be of the highest quality in terms of narrowness of the particle size distribution and QY's (Table II). Lower temperatures (250 °C) gave smaller QD's with lower QY's (0.3-0.6%). They exhibited deep trap PL, a broad emission (FWHM ~ 200 nm) red-shifted from the band-edge emission peak. The

trap PL could be removed by growing the particles for longer than 0.5 min. Higher temperatures (350 °C) gave slightly smaller QD's rather than larger ones. It is postulated that, under these conditions, the precursors were depleted too rapidly upon injection into the solvent to form the expected larger particles. Indeed, while the QD's did grow in size with reaction time, the size distribution (as judged by the width of the PL emission) widened significantly, indicating Ostwald ripening of the particles occurred [8].

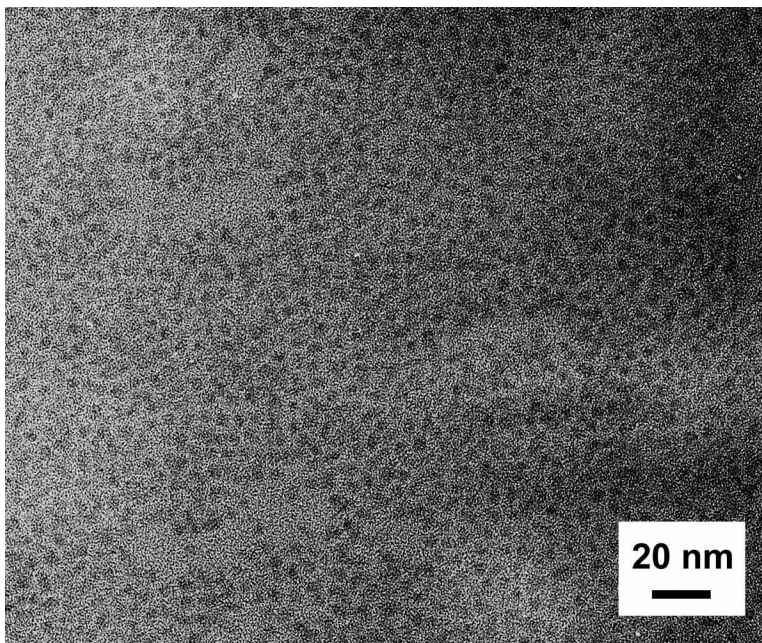


Figure 2. TEM image of CdSe QD's prepared at 300 °C for 0.5 min.

Table II. Particle size and PL width of CdSe QD's prepared at various solvent temperatures and heated for 0.5 min.

Temp (°C)	Size (nm)	FWHM (nm)
250	2.3	59
300	3.5	35
350	3.2	42

Preliminary work with QD's of other compositions (e.g. CdS, CdTe, ZnS, ZnSe, ZnTe, and (CdSe)ZnS core/shell) has proven successful, and current work is focussed on generalizing the chemistry of this QD synthesis method [10].

CONCLUSIONS

A new synthesis method to high-quality CdSe based on the use of cadmium acetate has been successfully developed. It is safer, easier to perform, and more cost-effective than the thermolysis route to CdSe QD's using dimethylcadmium. Particle size and emission spectra can be controlled with reaction time and solvent temperature, strongly suggesting that QD's prepared with cadmium salt underwent nucleation and growth processes similar to those prepared with dimethylcadmium. A general approach to synthesizing high-quality QD's based on metal salts appears possible.

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