

# A Novel Organometallic Synthesis of Highly Luminescent CdTe Nanocrystals

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Highly luminescent CdTe nanocrystals were synthesized by reacting dimethylcadmium with different tellurium sources in mixtures of dodecylamine and trioctylphosphine as the coordinating and size-regulating solvent. Colloids of crystalline CdTe nanoparticles with zinc blende lattice displaying mean particle sizes between 2.5 and 7 nm were prepared at temperatures from 150 to 220 °C and were characterized by powder XRD, HRTEM, absorption, and luminescence spectroscopy. The particles show strong band-edge photoluminescence shifting from green to red with increasing particle size. The photoluminescence quantum yield was found to strongly depend on the tellurium source employed in the synthesis. The highest quantum yields were observed by using a suspension of tellurium powder in a mixture of dodecylamine and trioctylphosphine. These CdTe samples show a photoluminescence quantum yield up to 65% at room temperature without covering the surface of the nanoparticles with a passivating inorganic shell. If a solution of tellurium in TOP rather than tellurium powder is used, higher reaction yields but nanoparticles with lower quantum yields (about 35–50%) are the result. As-prepared colloids show rather narrow particle size distributions, although all reactants were mixed at low temperature. The size distributions can be further improved by standard size selective precipitation.

## Introduction

The chemical synthesis and the properties of highly luminescent II–VI semiconductor nanoparticles have been extensively investigated allowing a transition from pure basic research to the application of these nanomaterials in electrical and optoelectronic devices.<sup>1–5</sup> Most of the work involved cadmium chalcogenide nanocrystals, which can be prepared either in aqueous solutions using thiols as stabilizing agents<sup>6–10</sup> or in high-boiling coordinating solvents such as TOP-TOPO mixtures.<sup>11,12</sup> More recently, the synthesis of ZnSe nanocrystals in high-boiling amino alkanes has been reported which exhibit photoluminescence quantum yields as high as 20–50%.<sup>13</sup>

The high temperatures typically applied in nonaqueous synthesis methods lead to high crystallinity and to high luminescence quantum yields of the semiconductor nanocrystals. Radiationless recombination at surface traps can be further reduced by growing an inorganic shell heteroepitactically around the particles.<sup>14,15</sup> The latter drastically enhances the photoluminescence quantum yield, as has been shown recently for CdSe nanocrystals with a ZnS shell<sup>16,17</sup> or ZnSe shell<sup>18</sup> and for CdSe nanocrystals with a CdS shell.<sup>19</sup>

CdTe nanocrystals prepared in aqueous solution in the presence of thiols as the stabilizing agent<sup>9</sup> show a photoluminescence quantum yield up to 18% at room temperature. They were investigated as possible candidates for integration into light-emitting devices<sup>20,21</sup> and luminescent doping of photonic colloidal crystals.<sup>22</sup> Only few reports on nonaqueous chemical routes to CdTe nanoparticles have been published.<sup>11,23–26</sup> High quantum yields of about 50% have been reached if a special

tellurium compound was used in the synthesis.<sup>26</sup> In this communication, we report on the novel organometallic synthesis of CdTe nanocrystals using dodecylamine as a size-regulating and stabilizing agent. The synthesis allows obtaining a size series of highly luminescent CdTe nanoparticles whose emission colors cover the visible spectral range from green to red. If metallic tellurium is used as the tellurium source, the synthesis yields particles with a room-temperature quantum yield reaching 65%.

## Experimental Section

**Chemicals.** All chemicals used were of analytical grade or the highest purity available. Toluene, methanol, *n*-hexane (all anhydrous, Aldrich), and tellurium (99.999%, ChemPur, powder < 250 micron) were used as received. Dimethylcadmium (EpiChem) was filtered through a 0.2  $\mu$ m PTFE filter and stored at –35 °C in a glovebox. Tri-*n*-octylphosphine (Fluka) was purified by distillation. Dodecylamine (Merck) was purified and degassed in the reaction vessel by heating at 100 °C under vacuum for several hours. Rhodamin 6G (laser grade, Lambda Physik) and Perylene (Fluka) were used as standards for determining the quantum yields.

**Apparatus.** Photoluminescence (PL) and UV–vis absorption spectra were measured at room temperature with a FluoroMax-2 spectrofluorimeter (Instruments SA) and a Perkin-Elmer Lambda 40 UV–vis spectrophotometer, respectively. PL spectra were measured of colloidal solutions having an optical density of less than 0.2 at the excitation wavelength  $\lambda_{\text{exc}} = 400$  nm. Powder X-ray diffraction (P-XRD) spectra were taken on a Philips X'Pert diffractometer (Cu K $\alpha$ -radiation, variable entrance slit, Bragg–Brentano geometry, secondary monochromator). High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray analysis (EDX) were performed on a Phillips CM-300 microscope operating at 300 kV. TEM samples

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were prepared by dropping dilute solutions of isolated CdTe nanoparticles in toluene or hexane onto 400-mesh carbon-coated copper grids and immediately evaporating the solvent.

**Synthesis of CdTe Nanocrystals.** All synthetic work was performed inside a glovebox under dry nitrogen. Two different methods have been applied:

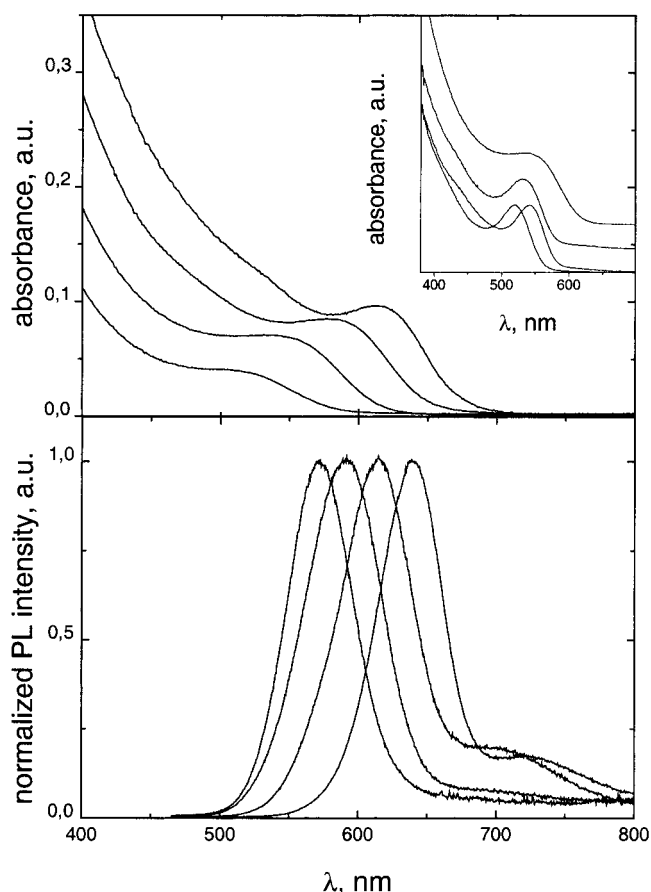
**Method A.** Five grams of dodecylamine (DDA) were dissolved in 7 mL of tri-*n*-octylphosphine (TOP) at 50 °C in a 50 mL two-neck flask with a reflux condenser attached. Subsequently, 0.11 mL (1.47 mmol) of dimethylcadmium and 0.128 g (1 mmol) of tellurium powder were added under stirring, and the temperature was slowly increased to 180 °C. After 30 min, the temperature was raised to 200 °C, and growth of the nanocrystals was allowed to proceed at this temperature for 20 h. Under these conditions, tellurium slowly dissolves in the reaction mixture, resulting in a very slow growth of CdTe nanocrystals at sufficiently high temperatures. Finally, toluene was added to the warm solution, and the mixture was left for 24 h at room temperature under stirring.

This method allowed obtaining CdTe nanocrystals in the size range of 4.0–6.0 nm, emitting from yellow to red with extremely high PL quantum yields exceeding 60%.

**Method B.** A 0.65 g sample of tellurium was dissolved in 10 mL of TOP by overnight heating at 220 °C. After cooling to room temperature, 1.96 mL of the resulting greenish-yellow solution was mixed with 0.11 mL (1.47 mmol) of dimethylcadmium and 3 mL of TOP. This mixture was loaded into a 5 mL syringe and injected into 10 g of DDA vigorously stirred at 150 °C in a 50 mL two-neck flask with attached reflux condenser. Directly before injection, the heater from the reaction flask was removed. The deep-yellow transparent solution obtained after injection slowly changed its color to bloody-red with time. Heating was resumed after approximately 10–15 min when the temperature of the reaction mixture had reached 90–100 °C. This initiated further slow growth of the particles, which was monitored by measuring the absorption and photoluminescence spectra of the reaction mixture at regular intervals of time.

The temperature and the duration of growth determine the final size of the particles. Yellow-emitting CdTe nanocrystals with an average size of ca. 3 nm, for instance, were obtained by heating the reaction mixture between 150 and 180 °C for a few hours only. The largest particles were prepared by overnight (10–12 h) heating at 200 °C. By this method, we obtained CdTe nanocrystals with mean sizes ranging from 2.5 to 5 nm. They show strong band-gap emission with quantum yields exceeding 30%. Depending on particle size, emission colors between green and red are observed. CdTe nanocrystals of larger size (up to app. 7.0 nm) were grown by the dropwise addition of mixed Cd and Te precursors (the same amounts as used for the synthesis itself). Before this additional injection, the reaction mixture was cooled to 70 °C. After injection, the temperature was raised to 100 °C for 3 h, with subsequent annealing at 180 °C. After completion of the particle growth and cooling the reaction mixture to ~50 °C, 20 mL of toluene was added to the solution, and the mixture was left for 24 h at room temperature under permanent stirring.

**Isolation of CdTe Nanocrystals.** Aliquots of 5 mL were removed from the reaction mixture, cooled to ~70–80 °C, and mixed with 10 mL of anhydrous toluene to prevent DDA from solidification. After byproducts and unreacted tellurium had been removed by passing the mixture through a 0.22  $\mu$ m membrane filter (Millipore), standard solvent/nonsolvent size-selective precipitation procedure<sup>11</sup> was carried out by adding small volumes of methanol to the mixture and collecting the precipitate

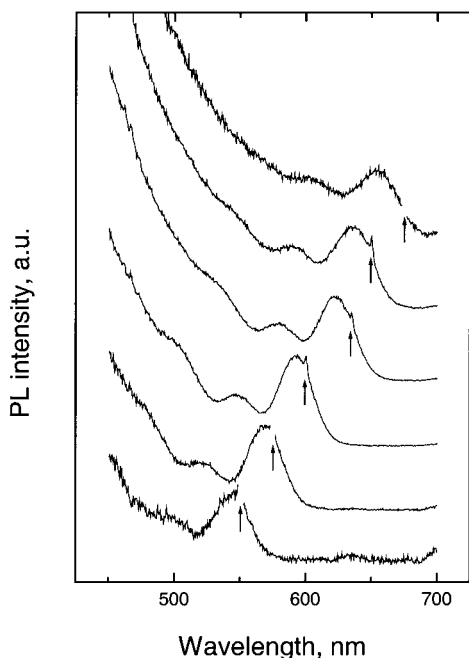


**Figure 1.** Absorption (top) and photoluminescence (bottom) spectra of CdTe nanocrystals. From left to right: immediately after injection of the dimethylcadmium/tri-*n*-octylphosphine telluride mixture into DDA at 150 °C; after heating for 1 h at 150 and 200 °C, respectively; after heating for 12 h at 200 °C. The insert shows the narrowing of the size distribution of CdTe nanocrystals by size-selective precipitation from toluene/methanol mixtures.

by filtration. Isolated fractions of CdTe nanocrystals were readily dispersible in a variety of organic solvents such as toluene, *n*-hexane, CH<sub>2</sub>Cl<sub>2</sub> etc. The luminescence efficiency was stable during the storage of the redispersed CdTe crystallites in the glovebox over months. The storage of the crude colloidal solution of CdTe nanoparticles inside the glovebox for several weeks resulted in a slight enhancement of their band-edge PL quantum yield.

## Results and Discussion

Figure 1 shows the absorption and the photoluminescence spectra of CdTe nanoparticles prepared according to method B at different stages of particles growth. The spectra shown are from samples taken from the reaction vessel without any further narrowing of their size distribution. They were diluted with toluene to provide the optical densities appropriate for PL measurements. A shift of the absorption edge and the PL maximum toward longer wavelengths indicates growth of CdTe nanocrystals during the heat treatment. The use of DDA as a size-regulating and stabilizing agent resulted in quite narrow particle size distributions, although we did not apply a hot injection method.<sup>27,28</sup> Prolonged heating (20 h) of the nanoparticles at temperatures between 180 and 210 °C significantly increased the quantum yield of the band-edge PL, presumably owing to annealing of defects and improvement of the crystallinity. Nanoparticles prepared by method A finally exhibit a quantum yield of up to 65% at room temperature.

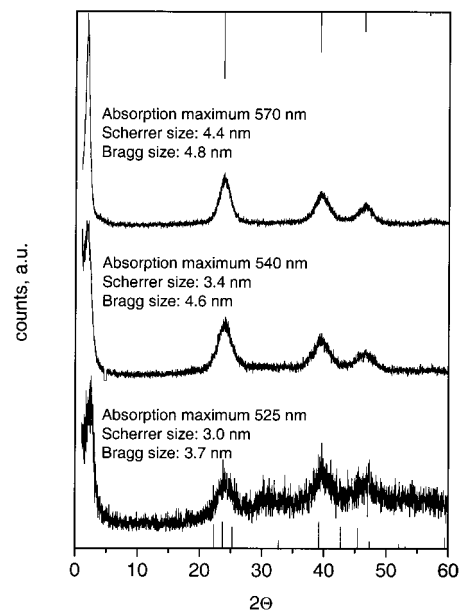


**Figure 2.** Photoluminescence excitation spectra of CdTe nanocrystals measured at different emission wavelengths as indicated by the arrows. The spectra correspond to different particle sizes in the sample.

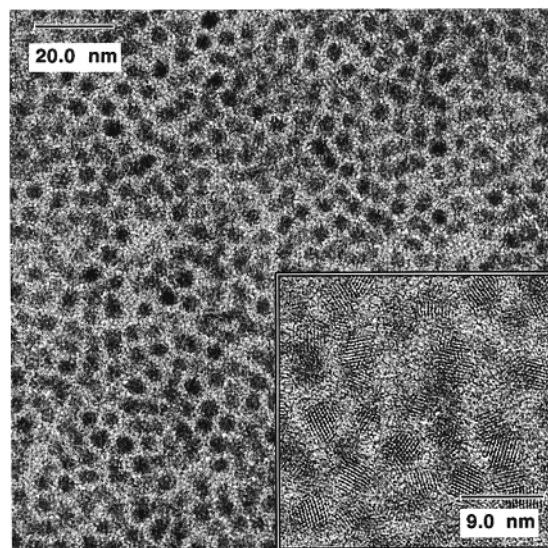
Similar to CdS and CdSe nanocrystals,<sup>1</sup> the CdTe colloids also show a relatively weak PL band red-shifted from the absorption edge (Figure 1), which originates from the radiative recombination of electrons and holes trapped in defect (surface) states. Its intensity is strongly influenced by the presence of TOP and DDA in the colloidal solutions, and complete suppression of the defect luminescence through surface modification of the nanocrystallites is currently investigated.

The insert in the Figure 1a shows the absorption spectra of size-selected samples of CdTe nanoparticles. The size distribution of the nanoparticles became narrower after size-selective precipitation, resulting in a better resolution of the first electronic transition in the absorption spectra (from top to bottom). However, residual inhomogeneities of the size-selected samples are evident from the photoluminescence excitation spectra (Figure 2). At a resolution of about 2 nm (emission and excitation monochromator), well-structured spectra are obtained displaying up to four transitions even at room temperature.

Figure 3 shows small- and wide-angle powder X-ray diffraction data of size-selected CdTe nanoparticles. The positions of the diffraction peaks at wide angles match those of the cubic modification of bulk CdTe (zinc blende phase). As expected, the width of the diffraction peaks is considerably broadened and decreases with increasing particle size. By using the Scherrer formula, we can calculate the mean sizes of the nanocrystals from the peak width at half-maximum. Particle sizes obtained from the width of the (111) reflection are depicted in the figure. As is often observed for samples with narrow particle size distribution, the XRD-pattern also shows a strong peak in the small-angle region, which is caused by some short-range ordering of particles in the powder. By using the Bragg equation, we can roughly calculate the distance between nearest neighbors from the peak position.<sup>8</sup> The calculated values given in Figure 3 are slightly larger than the particle sizes obtained from the Scherrer equation, indicating that the particles are separated from each other by a shell of organic ligands around them. The latter is in fact observed in transmission electron micrographs of the particles. An example is given in Figure 4, showing particles



**Figure 3.** Powder X-ray diffraction data of size-selected fractions of CdTe nanocrystals. The particle sizes decrease from top to bottom; particle sizes were calculated from the Bragg equation and the Scherrer equation. The line spectra indicate the reflections of bulk CdTe (top: zinc blende, cubic; bottom: wurzite, hexagonal).



**Figure 4.** TEM overview image of a monolayer of CdTe nanocrystals. The insert shows a high-resolution image of single CdTe nanocrystals.

with an absorption maximum at 605 nm. The image displays well-separated particles with a mean size of 4.0 nm, the latter being in accord with the size calculated from the Scherrer equation. The Fourier transform of the image in fact confirms short-range ordering in the powder, with a period of about 5.5 nm. The high-resolution image given as the inset shows lattice fringes for most particles indicating highly crystalline material. The EDX measurements indicate the presence of Cd, Te, and P in the samples, with the Cd:Te ratio being very close to 1:1.

Thus, the use of DDA as coordinating solvent allows synthesizing highly crystalline CdTe nanoparticles showing size-dependent and very strong band-edge PL. For the synthesis of these nanoparticles, dodecylamine was found to have several advantages over other amines. For instance, octylamine, with its relatively low boiling point, did not allow the use of temperatures higher than 160–170 °C, and the particles tend to precipitate after several hours of heating. The use of



dioctylamine as a solvent resulted in the immediate precipitation of the reaction products. Hexadecylamine provided good conditions for the growth of CdTe nanoparticles, but the particle size distribution obtained after prolonged heating was not as narrow as was achieved with DDA.

A proper choice of the tellurium source is another important point in the synthetic route developed. In method A, elemental tellurium slowly dissolves in the presence of TOP, providing a constant source of highly diluted tellurium precursor. The method allows growing CdTe nanocrystals at high temperatures but with extremely low rates controlled by the very slow dissolution of tellurium. This probably results in a very low defect density, which may be the reason for the very high room-temperature PL quantum yield of 65%.

## Summary

Highly luminescent CdTe nanocrystals were synthesized by the reaction of dimethylcadmium and metallic tellurium in a mixture of dodecylamine and trioctylphosphine. Fairly narrow particle size distributions have been obtained without using "hot injection" to separate nucleation and growth of the nanoparticles. A series of nearly monodisperse crystalline CdTe nanoparticles with zinc blende lattice and mean particle sizes between 2.5 and 7 nm was isolated by size-selective precipitation. The particles show strong band-edge photoluminescence tunable in the visible spectral range from green to red and have been characterized by powder XRD, HRTEM, absorption, and luminescence spectroscopy. A photoluminescence quantum yield of up to 65% is observed at room temperature without passivating the surface of the nanoparticles with an inorganic shell.

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