# Synthesis and Characterization of Surface-Modified Colloidal CdTe Quantum Dots

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The controlled synthesis of quantized colloidal CdTe nanocrystals (in aqueous solutions) with narrow size distributions and stabilized against rapid oxidation was achieved by capping the quantum dot particles with 3-mercapto-1,2-propanediol. Nanocrystals (i.e., quantum dots) with mean diameters of 20, 25, 35, and 40 Å were produced. Optical absorption spectra showed strong excitonic peaks at the smallest size; the absorption coefficient was shown to follow an inverse cube dependence on particle diameter, while the extinction coefficient per particle remained constant. The quantum yield for photoluminescence increased with decreasing particle size and reached 20% at 20 Å. The valence band edges of the CdTe quantum dots were determined by pulse radiolysis experiments (hole injection from oxidizing radicals); the bandgaps were estimated from pulse radiolysis data (redox potentials of hole and electron injecting radicals) and from the optical spectra. The dependence of the CdTe bandgap on quantum dot size was found to be much weaker than predicted by the effective mass approximation; this result is consistent with recently published theoretical calculations by several groups.

### Introduction

Ultrasmall semiconductor crystallites which are in the strong quantum confinement regime have aroused considerable interest because of their unique size-dependent properties.<sup>1-7</sup> As the diameter of the semiconductor crystallite is decreased into the nanometer range, its properties undergo a transition from bulk behavior to molecular behavior; such particles are called nanocrystals or quantum dots. This transition region exhibits many interesting and important size quantization effects. Of particular interest are the effects of size quantization on linear and nonlinear optical properties, electronic structure and transport, and photocatalytic and photoelectrochemical properties.

Major problems occurring with the study and applications of nanocrystals include (1) difficulties in producing sufficiently narrow size distributions to fully resolve and utilize the quantization effects, (2) the fact that nanocrystals have a large fraction of their atomic constituents at the surface, which frequently results in nonradiative surface recombination processes that quench luminescence, and (3) surface defect structures that may profoundly affect the electronic structure of the entire nanocrystal.

In the present study we report the synthesis of a series of CdTe quantum dots with narrow size distributions that produce a sharp excitonic absorption peak at the smallest particle size (20 Å). When these CdTe nanocrystals are capped with thiols, we observe very high quantum yields for photoluminescent emission. The dependence of the bandgap and oscillator strength on the CdTe particle size is also determined for the first time, and compared to theoretical predictions.

## **Experimental Section**

**Preparation of 20–40-Å CdTe Colloids.** All chemicals were of the highest purity commercially available and were used without further purification. Triply distilled water was used throughout, and all solutions were thoroughly deaerated by bubbling with argon or  $N_2O$ , depending upon the experiment.

Fifty milliliters of solution containing  $1 \times 10^{-3}$  M CdSO<sub>4</sub>, 8  $\times 10^{-4}$  M 3-mercapto-1,2-propane-diol (RSH), and  $2 \times 10^{-4}$  M

hexametaphosphate (HMP) at pH  $\geq$ 7.5 was placed in a threenecked vessel fitted with septum and valves and cooled to 0 °C. Oxygen was removed with Ar bubbling for 30 min. Then, 50 mL of an oxygen-free solution containing 2 × 10<sup>-4</sup> M NaHTe, cooled to 0 °C, was added into the solution and vigorously stirred. The CdTe concentration was calculated from the known concentration of NaHTe added to Cd<sup>2+</sup> solution assuming that the reaction yield is 100%; this is reasonable since all colloidal preparations were carried out with a large excess of Cd<sup>2+</sup> ions (see Table I).

Fresh solutions of  $2 \times 10^{-4}$  M NaHTe were always prepared before use in the following way: a solution of  $2 \times 10^{-4}$  M NaOH at 0 °C was titrated with H<sub>2</sub>Te (generated by the reaction of Al<sub>2</sub>Te<sub>3</sub> with 2 N H<sub>2</sub>SO<sub>4</sub> at 0 °C) under argon atmosphere, and the pH was monitored directly during titration. The titration is completed when the pH reaches 7-6 (for H<sub>2</sub>Te, pK<sub>2</sub> = 10.79 and pK<sub>1</sub> = 2.64). After titration, the solution was bubbled with Ar for 30 min to remove any trace of H<sub>2</sub>Te present in the solution. The NaHTe solution was spectroscopically checked for the presence of identifiable polytellurides, namely, Na<sub>2</sub>Te<sub>2</sub>, Na<sub>2</sub>Te<sub>3</sub>, or colloidal tellurium.<sup>8</sup>

The yellow colloid of  $2 \times 10^{-4}$  M CdTe that formed was thoroughly dialyzed against water at pH  $\geq$ 7.5 in a nitrogen atmosphere. The colloid was then concentrated in a rotary evaporator. The particle size of the colloid could be controlled by changing the initial concentration of the reactants or the pH of the solution (see Table I). The concentration of CdTe particles could be obtained knowing the molar concentration of CdTe in the sample and the CdTe particle size.

Apparatus. Spectrophotometric analyses were carried out at room temperature with a Perkin-Elmer Lambda 5 UV-vis spectrophotometer. The extinction coefficient per particle and the molar extinction coefficient were calculated from the absorbance, the CdTe concentration, and the particle concentration. Fluorescence spectra were obtained at room temperature using a Perkin-Elmer L-5 spectrofluorimeter. The quantum yields for PL emission were determined by comparing the integrated emission intensity to that of  $Ru(byp)_3^{2+}$ , knowing that the quantum yield for the latter complex is 0.042. The wavelengths for excitation of the CdTe colloid and the  $Ru(byy)_3^{2+}$  solutions were selected such that the absorbance of both systems was the same.

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Figure 1. Absorption spectra of colloidal  $1 \times 10^{-4}$  M CdTe (total concentration) with different particle sizes (optical path 1 cm). Insert shows the dependence of extinction coefficient of CdTe on the particle size of the quantum dots: (--) molar extinction coefficient; (--) extinction coefficient per particle concentration.

The size distribution and crystal structure were determined with a Philips EM 400 T electron microscope in transmission mode. X-ray powder analyses were carried out using a Siemens Crystaloflex 4 diffractometer. The total concentration of the  $Cd^{2+}$  ions present as colloidal particles was obtained by dissolving the colloidal particles in 1 M HNO<sub>3</sub> and measuring the absorption.

Pulse radiolysis employed a Febetron 707 (Field Emission Corp.) electron accelerator with a pulse duration of 20 ns; the operating conditions were similar to those described previously.<sup>9</sup> The total light path through the cell was 5.1 cm. The absorbed doses were in the range 1–130 Gy/pulse, measured using a ferrocyanide dosimeter, and taking  $\epsilon_{420}$ [Fe(CN)<sub>6</sub><sup>3-</sup>] as 1000 M<sup>-1</sup> cm<sup>-1</sup> and G[Fe(CN)<sub>6</sub><sup>3-</sup> = 5.6.

#### **Results and Discussion**

**Optical Properties of CdTe Nanocrystals.** CdTe is a direct bangap semiconductor with an absorption onset at 826 nm ( $E_g = 1.56 \text{ eV}$  at 300 K);<sup>10</sup> the bulk material is black. In this work, small colloidal particles of CdTe with diameters 20, 30, 35, and 40 Å were prepared in aqueous solution. These sizes were determined from TEM images and from the broadening of the lines in X-ray diffractograms. The absorption spectra of these CdTe colloids are presented in Figure 1.

All of the prepared nanocrystallites are in the strong confinement regime since the Bohr radius of CdTe is 73 Å.<sup>6</sup> The effective bandgaps (i.e., fundamental absorption edge) of the CdTe particles as a function of their size were estimated from the positions of the peaks or shoulders in Figure 1; the results are summarized in Table I and plotted in Figure 2. Also plotted in Figure 2 is the bandgap dependence on particle size that is predicted by the effective mass approximation.<sup>11</sup> It is seen that the blue shift of the bandgap for CdTe quantum dots with decreasing size is much less than expected from the effective mass approximation. This result is discussed below in the section on energy levels in CdTe quantum dots.

From Figure 1 it is also seen that the absorption coefficient,  $\alpha$ , increases sharply with decreasing particle size (at constant CdTe molar concentration). The molar extinction coefficient,  $\epsilon$ (related linearly to the absorption coefficient,  $\alpha$ ), was calculated for each particle size at the peak absorbance or at the shoulder in the spectra. A plot of  $\epsilon$  versus particle size is shown in the insert in Figure 1; also plotted in the insert is the extinction coefficient *per particle* versus particle size. A fit of these data show that  $\epsilon$  (or  $\alpha$ ) increases with the inverse cube of the Bohr radius divided by the particle radius  $(a_B/R)^3$ ), while the extinction coefficient or oscillator strength *per particle* is independent of particle size. The particle size distribution of each colloidal preparation is reasonably narrow as evidenced by TEM. We assume that differences in size distribution among the differentsized colloids will not seriously affect the relative absorbance values assigned to each mean particle size. Based on this assumption, our results are consistent with theoretical predictions of the dependence of oscillator strength on particle size<sup>4,12-14</sup> and are the first measurements confirming the inverse cube dependence of  $\alpha$  on quantum dot size. Earlier measurements<sup>15</sup> of the dependence of  $\alpha$  on quantum well thickness in GaAs quantum film structures (1-dimensional quantization) confirmed an (( $a_B$ )-L)<sup>1</sup> dependence, where L is the quantum well width.

CdTe colloidal particles with 20-Å diameters and exhibiting a very sharp excitonic peak at 412 nm were prepared in the presence of thiols (RSH), which are complexing agents for Cd<sup>2+</sup> ions. These colloids are composed of spherical particles with a very narrow particle size distribution, as observed by electron microscopy. The formation of very small and uniform particles of CdTe in the presence of thiols is the consequence of the previously reported fact that Cd<sup>2+</sup> ions form polynuclear complexes with RSH in alkaline solution;<sup>16</sup> these complexes consist of polymers of cadmium dithiolate ( $\{Cd(RS_5CD_3)_n\}^{(n+2)+}$ ). Under our experimental conditions, there is essentially no free Cd<sup>2+</sup> ions present in the solution at pH > 8. Several authors have examined the Cd<sub>n</sub> thiolate clusters (n = 1, 4, 10) as a molecular model for semiconductor growth<sup>17,18</sup> and have found that the idealized symmetry of the Cd cluster core is  $T_d(43m)$ ,<sup>18</sup> which has cubic zinc blende symmetry. Different types of RSH species were reported to modify and stabilize the surface of CdS colloids.<sup>19-23</sup> It was also previously reported that hexametaphosphate (HMP) added to these solutions competes with RSH for complexation with the  $Cd^{2+}$  ions.<sup>20</sup> Thus, by adjusting the relative concentration of RSH and HMP and the pH of the solution, different polynuclear species of cadmium thiolate could be formed, which subsequently react with Te<sup>2-</sup> ions to form CdTe colloids. During particle formation, the Cd surface atoms remain bound to RS-. The linkage of surface cadmium atoms to RS- significantly improves the CdTe stability toward oxidation (24 h in air); it also affects the surface such that the photoluminescence from CdTe nanocrystals is not quenched.

Excitation of the different-sized CdTe quantum dots with blue light gives a photoluminescence (PL) emission peak that is redshifted from the exciton absorption (Figure 3). The quantum yield of emission increases when the particles are treated with thiols and OH<sup>-</sup>. Thus, for example, the PL from the 40-Å CdTe colloid prepared in the presence of HMP was found to be negligible, while 2 h after addition of RS<sup>-</sup> into this colloidal solution at pH 9, a PL quantum yield of 0.005 was detected. The PL after addition of RS<sup>-</sup> was blue-shifted compared to the PL before RS<sup>-</sup> addition. For the 20-Å CdTe nanocrystals, the PL quantum yield reached 0.2 after a similar treatment; thus PL was also blue-shifted.

The red shift of the PL spectra with respect to the absorption spectra indicates that the emission is from radiative recombination in shallow surface states. The enhanced quantum yield for the blue-shifted emission after treatment with thiols in basic solution suggests that (1) strong nonradiative surface recombination is present in the initially prepared nanocrystals and (2) these nonradiative surface states lie deeper in the bandgap but can be passivated with basic thiols to yield relatively efficient PL emission. This model is similar to that suggested by Dannhauser et al.<sup>24</sup> where amines bound to CdS and Cd<sub>3</sub>As<sub>2</sub> quantum dots also produce large blue-shifted increases in the intensity of the subbandgap PL emission.

The quantum yield for PL emission increases with decreasing particle size (Figure 3). It is not clear whether this effect is

TABLE I: Relevant Data of CdTe Colloids with Different Particle Sizes

CdTe [M] (color)	stabilizer (before dialysis)	<i>Д</i> ем [Å]	absorbance					
			onset [nm]	peak or shoulder [nm]	emission peak [nm]	bandgap <sup>a</sup> [eV]	$E_{vb}^{b}$ [eV]	$E_{cb}^{b}$ [eV]
bulk (black) bulk (black)	S <sup>2-</sup> /S <sub>2</sub> <sup>2-</sup>					1.5° 1.5°	-0.6 <sup>c</sup> -1.47 <sup>d</sup>	0.9° 0.03 <sup>d</sup>
$1 \times 10^{-4}$ M, pH 10.5 (green-yellow)	8 × 10 <sup>-4</sup> M RS <sup>-</sup> , 2 × 10 <sup>-4</sup> M HMP, 1 × 10 <sup>-3</sup> M Cd <sup>2+</sup>	20	450	412	450 (2.76 eV)	3.01	0.12	-1.9 to -2.7
2 × 10 <sup>-4</sup> M, pH 10 (yellow)	4 × 10 <sup>-4</sup> M RS <sup>-</sup> , 1 × 10 <sup>-4</sup> M HMP, 5 × 10 <sup>-4</sup> M Cd <sup>2+</sup>	25	480	440	495 (2.50 eV)	2.81	0.10	-1.9 to -2.7
2 × 10 <sup>-4</sup> M, pH 9 (orange)	$1 \times 10^{-4} \text{ M RS}^-, 3 \times 10^{-4} \text{ M HMP},$ $5 \times 10^{-4} \text{ M Cd}^{2+} \text{ or } 3 \times 10^{-4} \text{ M HMP},$ $5 \times 10^{-4} \text{ M Cd}^{2+}$	35	560	506	575 (2.16 eV)	2.41	0.09	-1.9 to -2.7
$2 \times 10^{-4}$ M, pH 7.5 (red)	$3 \times 10^{-4}$ M HMP, $2 \times 10^{-4}$ M Cd <sup>2+</sup>	40	630	565	650 (1.91 eV)	2.19	0.06	>-1.9

<sup>a</sup> Based on optical spectra. <sup>b</sup> Based on pulse radiolysis data. <sup>c</sup> From ref 10. <sup>d</sup> From ref 26.



Particle diameter (Å)

Figure 2. Bandgap of CdTe quantum dots as a function of particle diameter: solid line, effective mass approximation; circles; experimental data.



Figure 3. Emission spectra of colloidal  $2 \times 10^{-4}$  M CdTe with different particle sizes. The excitation wavelength was 380 nm for 20- and 25-Å CdTe, 450 nm for 35-Å CdTe, and 500 nm for 40-Å CdTe colloids. Insert: dependence of the quantum yield of luminescence on the particle size of the quantum dot.

caused by enhanced radiative recombination rates at the trap sites arising from size quantization effects or is caused by the higher surface-to-volume ratio as the particle size is reduced. Further work is required to sort this out.

Hole Injection into CdTe Colloids. Radiation chemical processes provide a method for determining the redox potentials of colloids.<sup>25</sup> Injection of holes or electrons into the CdTe particles can be achieved using pulse radiolysis techniques; strong oxidizing and/or reducing radicals are created that produce charge-transfer reactions between the radical species and the colloidal particles. The highest occupied energy level (HOMO or valence band edge) in the CdTe particles with different particle sizes was determined by their reaction with the monovalent radical cation TMPD<sup>++</sup> (TMPD  $\equiv N, N, N', N'$ -tetramethyl-1,2-phenylenediamine); its standard redox potential is  $E^{\circ}$ [TMPD<sup>++</sup>/TMPD] = +0.27 V vs NHE.<sup>26</sup>

The monovalent radical cation TMPD<sup>•+</sup> has an absorption maximum at 610 nm ( $\epsilon_{610} = 1.2 \times 10^4 \, M^{-1} \, cm^{-1}$ ) that is sufficiently distinguished from that of the CdTe particles. TMPD<sup>•+</sup> is formed by radiolysis in a N<sub>2</sub>O-saturated aqueous solution of  $5 \times 10^{-4} \, M$ TMPD. The first step involves the formation of solvated electrons, which in N<sub>2</sub>O-saturated solutions are then converted into OH<sup>•</sup> radicals:

$$H_2O \rightarrow OH^{\bullet}, e_{aq}, H^{\bullet}, H_2O_2, H_2$$
 (1)

$$e_{ag}^{-} + N_2 O \rightarrow OH^{\bullet} + OH^{-} + N_2$$
 (2)

$$k_3 = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \text{ (ref 30)}$$

This method has been used previously to study excess charge effects in quantum dots of CdS,<sup>27</sup> CdSe,<sup>28</sup> and  $Cd_3P_2$ .<sup>29</sup> Then

$$TMPD + OH^{\bullet} \rightarrow TMPD \bullet OH$$
(3)

 $k_4 \approx 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ (ref 30)}$ TMPD•OH  $\rightarrow$  TMPD\*+ + OH<sup>-</sup> (4)

$$k_5 = 8 \times 10^4 \, \mathrm{s}^{-1} \, (\mathrm{ref} \, 31)^{-1}$$

$$CdTe + TMPD^{*+} \Rightarrow CdTe(h^{+}) + TMPD$$
 (5)

We found that all CdTe colloids with diameters in the range of 20-40 Å and capped with RS<sup>-</sup> react very slowly with TMPD<sup>++</sup> (rate constant  $k = 6 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>), while 40-Å CdTe colloids capped only with HMP react about 3 orders of magnitude faster ( $k = 5 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>). This indicates that the hydrophobic TMPD migrates slowly through the dense layer of hydrophilic RS<sup>-</sup> bound to the colloidal surface.

At equilibrium, the redox potential of the highest occupied energy level in CdTe equilibrates with the redox potential of the redox couple in solution; these potentials were found to be 0.12, 0.10, 0.09, and 0.06 V vs NHE for 20, 25, 35, and 40 Å quantum dots respectively (see Table I). The potential of the highest occupied energy level increases slightly with increasing concentration of holes injected into the particle (see Figure 4). All of these values are much more negative than the potential of the valence band of bulk CdTe in 5 M NaOH solution<sup>32</sup> ( $E_{vb} = 0.85$ V vs NHE); the reason for this is discussed below.



Figure 4. Redox potential of  $2 \times 10^{-4}$  M CdTe colloids determined from the equilibrium concentration of TMPD<sup>++</sup> (total concentration  $2 \times 10^{-4}$ M) as a function of number of injected holes per particle: (•) particle diameter 25 Å, stabilized with HMP and RS<sup>-</sup>; (O) particle diameter 35 Å, stabilized with HMP and RS; (×) particle diameter 40 Å stabilized with HMP and RS<sup>-</sup> absorbed on particle surface after preparation of the colloid. Pulse radiolysis experiments were performed at pH 8 in N<sub>2</sub>O atmosphere.

It has been reported previously that adsorption cf chalcogenide ions on the surface of bulk CdTe modifies the position of the conduction and valence bands;<sup>10,32</sup> for example, in the presence of the  $S^{2-}/S_n^{2-}$  redox couple the valence band of CdTe is located at  $E_{vb} = 0.10$  V vs NHE. It was also reported that this and dithio compounds shift the flatband potential of semiconductor electrodes up to 1 eV in the cathodic direction.<sup>33</sup> These effects are due to negative charging of the semiconductor surface by electrons donated by the reducing redox couples in solution. Thus, we expect that the energy bands of the thiol-modified surface of CdTe particles would also be strongly shifted to negative potentials, which was indeed found for the 20-40-Å CdTe colloids (Table I). We found that the energy bands of CdTe particles stabilized with just HMP are also shifted to negative values, and that subsequent addition of RS- to this colloidal solution did not modify the effective potential of the highest occupied level. These results suggest that negative surface charging of CdTe can also occur upon complexation of Cd<sup>2+</sup> ions with HMP and that this effect is similar to that occurring with RS- adsorption.

Electron Injection into the CdTe Particles. The position of the lowest unoccupied energy level (LUMO or conduction band) in CdTe was determined by electron-transfer reactions between CdTe particles and reducing radicals produced by pulse radiolysis. All the examined colloids of CdTe (20–40 Å) reacted with solvated electrons at the diffusion-controlled rate ( $k = 7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ); this was based on the decay kinetics of  $e_{aq}^{-}$  at 600 nm ( $k_{diff} = 4\pi NDR/1000 = 6.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ). However, we also found that only the 40-Å CdTe colloid reacts at a diffusion-controlled rate with the  $\dot{C}O_2^{-}$  radical, whose standard redox potential is  $E^{\circ}(CO_2|\dot{C}O_2^{-}) = -1.9 \text{ V vs NHE}$ 

$$CdTe(40 \text{ Å}) + \dot{C}O_{2}^{-} \rightarrow CdTe(e^{-}) + CO_{2}$$
(6)

After electron injection into 40-Å CdTe, a broad transient absorption,  $\tau_{1/2} = 350 \ \mu$ s, at about 480 nm was detected; this peak is attributed to the formation of Cd atoms.<sup>20,34</sup> The formation of Cd atoms indicates that the conduction band edge of 40-Å CdTe is more positive than -1.9 V vs NHE and that the injected electrons cause cathodic corrosion of the CdTe particles. The smaller particle sizes of CdTe (20-35 Å) do not react with CO<sub>2</sub>radicals and react only with hydrated electrons ( $E^{\circ} = -2.7$  V). This means that the effective conduction band potential of the 20-35-Å particles is in the range -1.9 to -2.7 vs NHE. This value is again more negative than that for bulk CdTe and reflects the negative shift of the band edges of CdTe modified with HMP or thiols, as discussed above.



Figure 5. Energy level diagram of CdTe with different particle sizes. The position of the highest occupied energy level was determined from the equilibrated concentration of TMPD<sup>+</sup>/TMPD; the first unoccupied energy level of 40-Å CdTe was determined from reaction with  $CO_2^-/CO_2$ .

Energy Level of Quantized CdTe Particles. An energy level diagram for the CdTe nanocrystals studied here can be derived from our optical and pulse radiolysis data (see Figure 5). The energy difference between the HOMO (valence band) and LUMO (conduction band) of the 40-Å CdTe colloid determined by pulse radiolysis compares favorably with the energy of the optical absorption peak (see Table I). This result supports the assignments of the positions of the conduction band edges of all of the CdTe colloids determined here from the pulse radiolysis experiments. Knowing the valence band edges for the CdTe quantum dots and the energy of the fundamental absorption transition, the conduction band position can be determined by their difference (see Table I). Only a range (-1.9 to -2.7 V) for the conduction band positions of the 35-, 25-, and 20-Å CdTe colloids can be established directly from pulse radiolysis experiments because electrons could not be injected into their conduction bands from  $\dot{C}O_2$ , while electron injection into all size particles was possible from hydrated electrons, as discussed above.

The blue shift of the CdTe nanocrystal bandgap, and the related cathodic shift of the conduction band edge with decreasing particle size, is much less than predicted using the effective mass approximation.<sup>11</sup> However, recent calculations based on pseudopotentials<sup>35</sup> or a tight-binding model<sup>36</sup> have shown that the effective mass approximation greatly overestimates the blue shift with decreasing size when nanocrystals are in the very strong confinement regime; results for CdS, 35, 36 ZnS, 36 GaAs, 35 and GaP<sup>35</sup> show that the error becomes significant at particles diameters less than 60, 50, 150, and 130 Å, respectively. At a particle diameter of 20 Å, the errors in the bandgaps predicted from the effective mass model for CdS, ZnS, GaAs, and GaP are 1.6, 0.7, 0.8, and 0.9 eV, respectively. For our 20-Å CdTe sample, the corresponding bandgap error appears to be about 2.2 eV. Calculations using pseudopotentials or tight-binding models have not yet been done on CdTe, so we cannot compare our observed increase in the CdTe bandgap as a function of decreasing diameter with theoretical expectations.

#### Conclusion

Colloidal nanocrystals of CdTe with a narrow size distribution, stability toward rapid oxidation, and low surface recombination velocity can be prepared in aqueous solutions by capping the quantum dot particles with 3-mercapto-1,2-propanediol, a strong

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complexing agent. The bandgaps of CdTe quantum dots over the range 20-40 Å were estimated from their optical spectra, which showed a strong excitonic peak at the smallest diameter. The dependence of the CdTe bandgap on quantum dot size exhibited a much weaker dependence on diameter than predicted from the effective mass approximation: at 20 Å the bandgap predicted from the effective mass model was larger than the experimental value by 2.2 eV. The optical data also showed that the absorption coefficient of the excitionic transition increases as  $(a_{\rm B}/R)^3$ , where  $a_{\rm B}$  is the Bohr radius and R is the quantum dot radius; the extinction coefficient per particle was independent of particle size. These results represent an experimental verification of theoretical predictions of the dependence of oscillator strength on quantum dot size.

The PL emission of the CdTe quantum data was red-shifted with respect to their absorption edge. Treatment with thiols in basic solution resulted in a blue shift of the PL emission and a greatly enhanced quantum yield. This is attributed to the presence of both radiative and nonradiative surface states, the latter lying deeper in the bandgap but passivated by adsorption of thiols from basic solutions.

Pulse radiolysis was shown to be a good technique to obtain the band edge positions, or the flatband potential, of CdTe quantum dots; this technique can also be used to obtain the bandgap when both electron injecting and hole injecting radicals can equilibrate (in separate experiments) with the respective band edges. A large negative shift of the flatband potential or the band edges is attributed to the negative charge produced on the surface after reaction with the thiol.

Note Added in Proof. A referee has correctly pointed out that calculating and comparing the extinction coefficients for the various quantum dot particles sizes from the absorbance values at the peak or shoulder in the respective spectra introduces an error because of variable inhomogeneous and homogeneous line broadening as a function of particle size. However, we believe that this error is not sufficiently large to affect the important conclusion that the absorption coefficient follows an inverse cube dependence on particle size and the extinction coefficient per particle is constant with size.

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