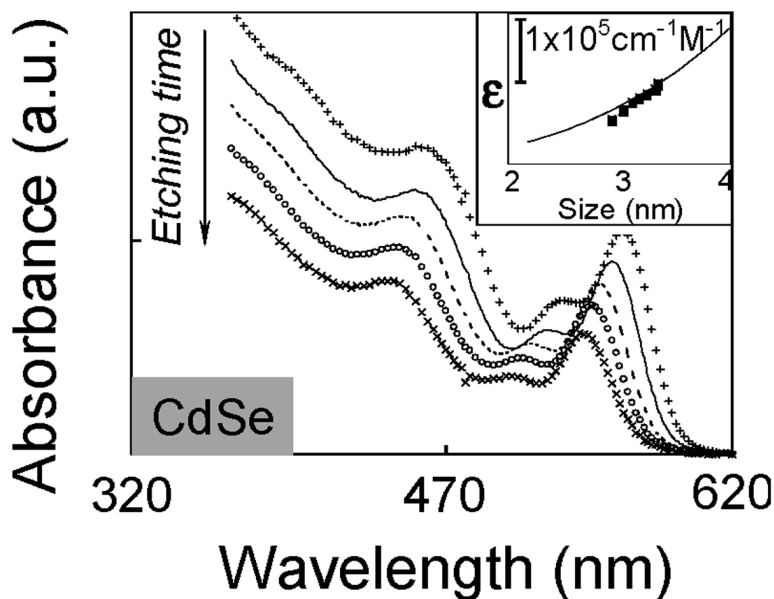


Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals

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Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals

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The extinction coefficient per mole of nanocrystals at the first excitonic absorption peak, ϵ , for high-quality CdTe, CdSe, and CdS nanocrystals was found to be strongly dependent on the size of the nanocrystals, between a square and a cubic dependence. The measurements were carried out using either nanocrystals purified with monitored purification procedures or nanocrystals prepared through controlled etching methods. The nature of the surface ligands, the refractive index of the solvents, the PL quantum yield of the nanocrystals, the methods used for the synthesis of the nanocrystals, and the temperature for the measurements all did not show detectable influence on the extinction coefficient for a given sized nanocrystal within experimental error.

Introduction

Quantum confinement plays a key role for the determination of the size-dependent properties of semiconductor nanocrystals. In general, there are two major effects associated with quantum confinement.^{1–4} The first one is the size-dependent band gaps of the nanocrystals, which is well documented both experimentally and theoretically.^{1–4} The well-known size-dependent transmission and emission colors of semiconductor nanocrystals are the direct results of this first effect. However, the second major effect, size-dependent extinction coefficient, is much less understood, especially experimentally. Experimental determination of the extinction coefficient of given sized nanocrystals is not a trivial task. The accessibility to desired quality nanocrystal samples, reliable and well-examined purification procedures, and independent determination of the concentration of nanocrystals in solution are all obvious obstacles.

Determination of the extinction coefficient of semiconductor nanocrystals is of importance for convenient and accurate measurements of the concentrations of nanocrystals. For example, semiconductor nanocrystals have been explored for various applications, such as LEDs,^{5–7} lasers,⁸ solar cells,⁹ and bio-medical

labeling.^{10–12} For many of those, it is essential to determine the actual concentration of the semiconductor nanocrystals in solution or in a given medium. In addition to those research activities toward technical applications, it is also essential to determine the particle concentration in solution for the study of the nucleation and growth mechanisms of colloidal nanocrystals.^{13–16} If the extinction coefficient of those nanocrystals was known, it would be easy to obtain the concentrations of the nanocrystals by simply taking an absorption spectrum of the sample. Unlike conventional organic and inorganic compounds, the concentration of colloidal nanocrystals is difficult to determine by gravimetric methods. Because the number of ligands on the surface of nanocrystals is quite difficult to identify, and may also vary significantly under different conditions,¹⁷ measurements solely based on gravimetric methods using ligands-coated nanocrystals are accurate only when the interactions between nanocrystals and ligands are sufficiently strong to withstand necessary purification procedures.¹⁸ Therefore, the absorption spectrum method in many cases is the most practical and convenient way to determine the particle concentrations, if it is not the only possible way.

There are some reports in the literature regarding experimental determination of the extinction coefficient

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- (1) Efros, A. L.; Efros, A. L. *Sov. Phys. Semicond.* **1982**, *16*, 772.
- (2) Brus, L. J. *Phys. Chem.* **1986**, *90*, 2555.
- (3) Wang, Y.; Herron, N. J. *Phys. Chem.* **1991**, *95*, 525.
- (4) Alivisatos, A. P. *Science* **1996**, *271*, 933.
- (5) Schlamp, M. C.; Peng, X. G.; Alivisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837.
- (6) Mattoussi, H.; Radzilowski, L. H.; Dabbousi, B. O.; Thomas, E. L.; Bawendi, M. G.; Rubner, M. F. *J. Appl. Phys.* **1998**, *83*, 7965.
- (7) Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S.; Banin, U. *Science* **2002**, *295*, 1506.
- (8) Klimov, V. I.; Mikhailovsky, A. A.; Xu, S.; Malko, A.; Hollingsworth, J. A.; Leatherdale, C. A.; Eisler, H. J.; Bawendi, M. G. *Science* **2000**, *290*, 314.
- (9) Greenham, N. C.; Peng, X. G.; Alivisatos, A. P. *Phys. Rev. B* **1996**, *54*, 17628.

- (10) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013.
- (11) Chan, W. C. W.; Nie, S. M. *Science* **1998**, *281*, 2016.
- (12) Han, M.; Gao, X.; Su, J. Z.; Nie, S. *Nat. Biotechnol.* **2001**, *19*, 631.
- (13) Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343.
- (14) Peng, X.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. *Nature* **2000**, *404*, 59.
- (15) Peng, Z. A.; Peng, X. J. *Am. Chem. Soc.* **2001**, *123*, 1389.
- (16) Peng, Z. A.; Peng, X. J. *Am. Chem. Soc.* **2002**, *124*, 3343.
- (17) Striolo, A.; Ward, J.; Prausnitz, J. M.; Parak, W. J.; Zanchet, D.; Gerion, D.; Milliron, D.; Alivisatos, A. P. *J. Phys. Chem. B* **2002**, *106*, 5500.
- (18) Guo, W.; Li, J. J.; Wang, Y. A.; Peng, X. J. *Am. Chem. Soc.* **2003**, *125* (13), 3901–3909.

of the first excitonic absorption peak of semiconductor nanocrystals. Because of the experimental difficulties mentioned above, significant discrepancies exist in the literature. For example, the extinction coefficient per particle of CdTe¹⁹ and CdS²⁰ nanocrystals were reported to be independent of the particle size in the strong confinement size regime, which seemed to be consistent with the prediction of the current theoretical models.^{2,3} In both cases, the results rely on, at least partially, the assumption that all monomers added for the growth of the nanocrystals were all converted to nanocrystals. Until very recently, CdSe nanocrystals possessed the best size and shape control in comparison to any other semiconductor nanocrystal system. Unfortunately, this best system did not really simplify the difficulties for the experimental determination of the extinction coefficient. The experimental results reported by different groups differed considerably from each other. Schemelz et al.²¹ reported that the extinction coefficient per particle in the size range between 1.5 and 4.5 nm increases as the size of the nanocrystals increases, roughly with a cubic function. Their method was based on atomic absorption of the digested nanocrystals. As pointed out by the authors, the data points substantially deviate from the cubic function in the large size range likely due to the size and shape distribution of the nanocrystals. Using an osmotic method, Striolo et al.¹⁷ recently reported that the extinction coefficient of CdSe nanocrystals in the size range between 2.5 and 6 nm qualitatively matched the cubic size dependence observed by Schemelz et al., with some noticeable disagreement in the small size range. Bawendi's group²² determined the integrated extinction coefficient per particle of CdSe nanocrystals by using the absorption cross section of the nanocrystals. Their results, however, imply a linear increase of the integrated extinction coefficient per particle as the size of the nanocrystals increases.

In this work, two independent approaches were used in the determination of the extinction coefficient of nearly monodisperse CdTe, CdSe, and CdS dot-shaped nanocrystals in a wide size range. For the first approach, the nearly monodisperse nanocrystals were purified by efficient and monitored purification procedures, and then the concentrations of the nanocrystals were determined by standard atomic absorption (AA) measurements. The results of the first approach were further confirmed by the second approach — controlled etching of the nanocrystals in solution with a defined volume. In the second approach, the concentration of the nanocrystals and the size distribution of the nanocrystals were both defined by the initial samples, which yields reliable relative ϵ values in a certain size range. Our experimental results (to be described below) indicate that for CdTe, CdSe, and CdS nanocrystals, the extinction coefficient per mole of nanocrystals in the strong quantum confinement size regime increases as their size

increases approximately in a square to a cubic function. The integrated ϵ of the first absorption peak seemed to be independent of temperature, which was confirmed for CdSe nanocrystals at 25 and 250 °C. The extinction coefficient of the nanocrystals seemed also independent of the nature of the surface capping groups, the refractive index of the solvents, the photoluminescence (PL) quantum yield of the nanocrystals, and the methods employed for the synthesis of the nanocrystals.

Experimental Section

Chemicals. *n*-Tetradecylphosphonic acid (TDPA; 98%) was purchased from Alfa Aesar. Oleic acid, 1-octadecene (ODE; tech. 90%), trioctylphosphine (TOPO; both 90% and 98%), tributylphosphine (TBP; 97%), cadmium oxide (99.99+%), sulfur (99.998%), selenium (100 mesh, 99.999%), tellurium (200 mesh, 99.8%), mercaptoundecanoic acid (MUA; 95%), pyridine, benzoyl peroxide, and tetramethylammonium hydroxide pentahydrate were obtained from Aldrich. Acetone, hexane, chloroform, toluene, concentrated HCl, concentrated HNO₃, and methanol were ordered from VWR.

Synthesis of High-Quality Nanocrystals. Synthesis of CdSe^{23–26} and CdS²³ nanocrystals was performed following recently reported methods. CdTe nanocrystals were synthesized in ODE, and the details will be reported later. A typical synthesis of CdTe nanocrystals is as follows. A mixture of CdO (0.0128 g, 0.10 mmol), TDPA (0.0570 g, 0.205 mmol), and technological-grade ODE (3.9302 g) was heated to 300 °C to get a clear solution. A 2-g solution of tellurium (0.025 g, 0.2 mmol), dissolved in 0.475 g of TBP and diluted by 1.500 g of ODE) was quickly injected into this hot solution, and then the reaction mixture was allowed to cool to 250 °C for the growth of CdTe nanocrystals. Aliquots were taken out at different reaction times to monitor the reaction process by measuring the UV–vis absorbance. The reaction was stopped when the desired nanocrystal size was reached. The synthesis was carried out under argon. To avoid oxidation, the aliquots taken for the ϵ measurements were added into anhydrous hexanes and stored under Ar before the purification and measurements.

Extraction and Precipitation Procedures. Separation of unreacted cadmium precursors from the nanocrystals was performed by repeated extraction (twice for most cases) of the reaction mixtures dissolved in hexanes. An equal volume mixture of CHCl₃/CH₃OH (1:1) was used as the extraction solvent. After extraction, the hexanes/ODE phase containing nanocrystals was precipitated with acetone. The precipitate was isolated by centrifugation and decantation. The final product was redissolved in a desired solvent for the following measurements. The complete removal of cadmium precursors from the final solution was confirmed by UV–vis spectroscopy (see Results and Discussion).

Surface Ligands Exchange. To obtain the pyridine-coated nanocrystals,^{27,28} CdSe nanocrystals powder (about 10 mg) coated with TOPO was put in 5 mL of pyridine and heated at 50 °C under argon flow until the nanocrystals were totally dispersed in pyridine to get a clear solution. A large amount of hexanes was added to precipitate the nanocrystals, and the precipitate was isolated by centrifugation. After two repetitions of dissolution/precipitation with pyridine/hexanes, the surface-capping ligands were replaced by pyridine. For the ϵ measurements, methanol was used as the solvent.

For the thiol-coated nanocrystals,²⁹ MUA (20 mg) and 15 mL of methanol were placed in a reaction flask, and the pH of

(19) Rajh, T.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* **1993**, *97*, 11999.

(20) Vossmeier, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmüller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665.

(21) Schemelz, O.; Mews, A.; Basche, T.; Herrmann, A.; Mullen, K. *Langmuir* **2001**, *17*, 2861.

(22) Leatherdale, C. A.; Woo, W. K.; Mikulec, F. V.; Bawendi, M. G. *J. Phys. Chem. B* **2002**, *106*, 7619.

(23) Yu, W. W.; Peng, X. *Angew. Chem., Int. Ed.* **2002**, *41*, 2368.

(24) Qu, L.; Peng, X. *J. Am. Chem. Soc.* **2002**, *124*, 2049.

(25) Qu, L.; Peng, Z. A.; Peng, X. *Nano Lett.* **2001**, *1*, 333.

(26) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 183.

(27) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1997**, *119*, 7019.

(28) Mikulec, F. V.; Kuno, M.; Bennati, M.; Hall, D. A.; Griffin, R. G.; Bawendi, M. G. *J. Am. Chem. Soc.* **2000**, *122* (11), 2532–2540.

(29) Aldana, J.; Wang, Y.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 8844.

the solution was adjusted to 10.3 with tetramethylammonium hydroxide pentahydrate. CdSe nanocrystals, 20 mg, were added. The originally TOPO-coated nanocrystals became gradually dissolved in methanol by magnetic stirring. The solution was refluxed overnight with argon flow under dark. The obtained nanocrystal solution was precipitated with ethyl acetate and ether. After the solution was centrifuged, methanol was added to dissolve the precipitate. After two more repetitions of precipitation and dissolution, MUA-coated nanocrystals were obtained. The ϵ measurements of those nanocrystals were performed with water as the solvent.

UV-vis Measurements. The purified nanocrystals were dispersed in a suitable amount of desired solvent to obtain a clear solution with UV-vis absorbance at about 0.15–0.25 at room temperature (HP 8453 UV-visible spectrometer). The absorbance values (A_m) were used to calculate the molar particle extinction coefficients at room temperature. For high-temperature measurements, the absorption spectra of nanocrystals at 250 °C were recorded in situ during the growth of the nanocrystals using an Ocean Optics USB2000 UV-visible spectrometer equipped with a dip probe. When a spectrum was recorded at 250 °C, aliquots with a certain amount of reaction mixture, typically around 100 mg, were taken at the same time and dissolved in a given amount of solvent. An absorption spectrum of the diluted solution was recorded. The particle size and concentration of the nanocrystals at 250 °C were determined using the room-temperature measurements as the calibration standards.

AA Measurements. A solution of 5 mL of purified nanocrystal sample with known absorbance was carefully dried by gentle heating in a fume hood, and then the residual was digested by ~2 mL of aqua regia. The digested sample was transferred into a volumetric flask to make an aqueous solution for the AA measurement. The cadmium concentration was determined using a GBC 932 atomic absorption spectrometer. The obtained Cd concentration was converted into the nanocrystal particle concentration by dividing it by the number of Cd atoms in one nanocrystal, assuming that the nanocrystal particle has the same density as its bulk material.

Controlled Etching. Two etching methods were employed. For CdTe nanocrystals, benzoyl peroxide dissolved in chloroform with a saturated concentration of TDPA was used. CdSe nanocrystals sealed in dendron boxes (box nanocrystals)¹⁸ were etched using a concentrated HCl DMSO/H₂O solution. Upon mixing a nanocrystal solution and the desired etching solution, the mixture was sealed inside a cell to prevent any possible evaporation of the solvent, and the UV-vis absorption spectrum of the mixture was recorded at different reaction time intervals.

Results and Discussions

Synthesis of Nanocrystals. The nanocrystals used for the experiments were all synthesized through the recently developed alternative approaches of the traditional organometallic methods.^{13,30} CdTe, CdSe, and CdS nanocrystals were synthesized in a noncoordinating solvent,²³ octadecene, which provided us the best quality nanocrystals with nearly monodisperse size and shape. TEM measurements of the nanocrystals revealed that they are approximately a dot shape (one example in Figure 1). The structural information about CdSe and CdS nanocrystals was published previously.^{23,24} CdSe nanocrystals were also synthesized via several other established alternative approaches developed by us, which can controllably produce dot-shaped nanocrystals.^{23–25} This should exclude possible errors caused by the shape distribution encountered by Schemelz et al.²¹

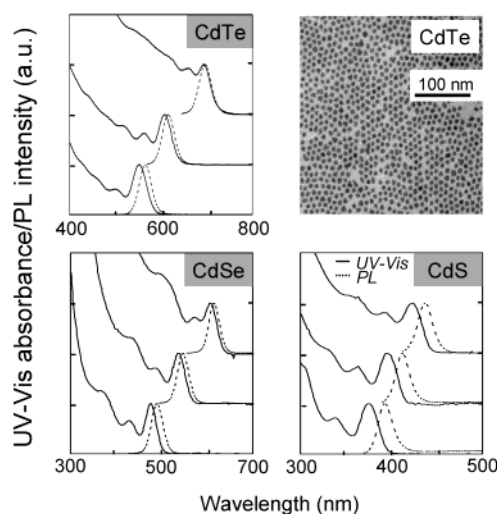


Figure 1. UV-Vis and PL spectra of the representative nanocrystal samples. TEM image (top right) of a CdTe nanocrystal sample. The nanocrystals shown in this figure are all as-prepared.

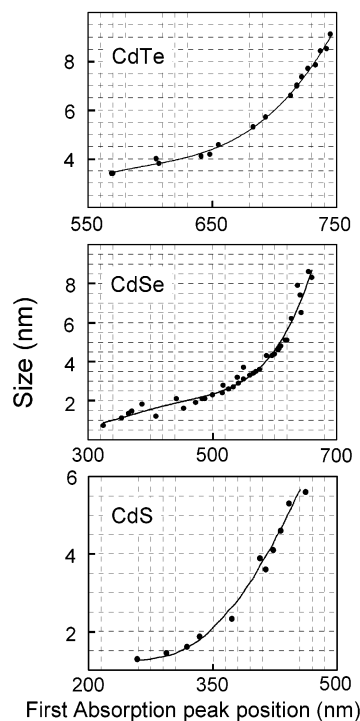


Figure 2. Sizing curves for CdTe, CdSe, and CdS nanocrystals.

Figure 1 illustrates the absorption and photoluminescence (PL) spectra of some representative samples of the as-prepared nanocrystals, which are very sharp. Typically, the full width at half-maximum (fwhm) of the PL spectra of the different sized CdTe, CdSe, and CdS nanocrystals used for the measurements were 29 ± 2 nm, 25 ± 2 nm, and 18 ± 2 nm, respectively. For the absorption spectra, it is very difficult to determine the fwhm. Instead, we measured the half width at the half-maximum (hwhm) on the low energy side of the first exciton absorption peak for each sample. Typically, the hwhm values were 18 ± 1 nm, 14 ± 1 nm, and 11 ± 1 nm for CdTe, CdSe, and CdS, respectively. Size dependence of the peak widths was not observed within the experimental limit.

(30) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

The sizes of the nanocrystals were determined either by TEM measurements or the sizing curves using their first absorption peak positions. The sizing curves shown in Figure 2 combined the literature values and our experimental measurements. The data shown in Figure 2 were all originally determined by TEM measurements, except the very small CdSe³¹ and CdS²⁰ nanoclusters which were examined by XRD. For CdTe, the sizes of the nanocrystals were mostly determined by us, as related information is scarce in the literature. For CdSe nanocrystals, there is a rich literature published by several groups,^{13,30,31} and all those literature values are included in Figure 2. For CdS nanocrystals, values of small sizes are mostly from Vossmeier et al.²⁰ and the big ones are largely based on our own results.²³

Upon the suggestion of a reviewer of the first version of the manuscript, the empirical fitting functions of the curves shown in Figure 2 are provided as follows.

$$\text{CdTe: } D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84)$$

$$\text{CdSe: } D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57)$$

$$\text{CdS: } D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + (13.29)$$

In the above equations, D (nm) is the size of a given nanocrystal sample, and λ (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample. It must be pointed out that the functions provided above are only polynomial fitting functions of the experimental data, which may become invalid in the size ranges not covered by the data shown in Figure 2.

Purification of Nanocrystal Samples. The nanocrystal samples were purified in several different ways. In this work, the concentration of the nanocrystals in a given sample was determined by the number of cadmium atoms contained in the sample and the size of the nearly monodisperse particles. Therefore, it was critical to remove any unreacted cadmium precursors in the sample. The main scheme was an extraction method.²³ The typical dissolution/precipitation methods and replacement of the surface ligands were also examined.

The extraction method is based on the fact that the solubilities of the unreacted cadmium precursors used in the synthesis and the resulting nanocrystals were significantly different in a two-phase system, methanol, and octadecene. Evidently, the cadmium precursors, either a cadmium-fatty acid salt or a cadmium-phosphonic acid salt, were very soluble in the methanol phase and barely soluble in octadecene at room temperature. In contrast, the nanocrystals were insoluble in methanol and stayed in the octadecene phase. In some cases, chloroform and hexanes were added into the system to improve the separation efficiency. Conveniently, the completion of the separation was monitored by UV-vis absorption (Figure 3).

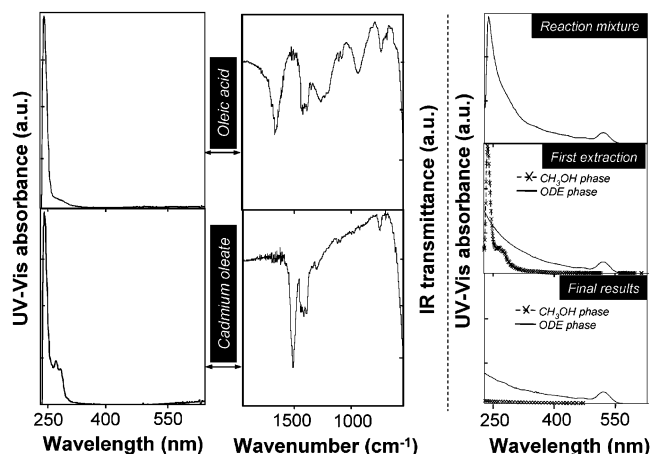


Figure 3. Left: UV-Vis and FTIR spectra of oleic acid and cadmium oleate. Right: UV-vis measurements confirmed the separation of unreacted cadmium oleate from the CdTe nanocrystals to be used for the AA measurements.

The conversion factor of the cadmium precursors to the cadmium atoms in the form of nanocrystals generally varied dramatically, from about 10 to 90%. Typically, the conversion factor increased with the increase of the size of the nanocrystals if the synthetic conditions were similar.

Extinction Coefficient of Particles. The extinction coefficient per mole of particles (ϵ) described below will be the values at the first absorption peak position. They were calculated using Lambert-Beer's law.

$$A = \epsilon CL \quad (1)$$

In eq 1, A is the absorbance at the peak position of the first exciton absorption peak for a given sample. C is the molar concentration (mol/L) of the nanocrystals of the same sample. L is the path length (cm) of the radiation beam used for recording the absorption spectrum. In our experiments, L was fixed at 1 cm. ϵ is the extinction coefficient per mole of nanocrystals (L/mol cm). Equation 1 was confirmed in the entire dynamic range of the two spectrophotometers for the semiconductor nanocrystals used in this work. The confirmation was completed by analysis of a series of the nanocrystal solutions which were prepared by the dilution of a common stock solution.

Because the extinction coefficient of semiconductor nanocrystals is of great practical importance, it is appropriate to report the peak value, even though the integrated value of the entire absorption peak carries more physical meaning. For future theoretical considerations, we also report the peak width of the standard samples (see above). It should be reasonably easy to calculate integrated values based on the peak values and the peak widths.

Figure 4 illustrates the extinction coefficient per mole of particles for CdTe, CdSe, and CdS nanocrystals. It is clear that the theoretical prediction,^{2,3,32} a size independent constant, is not the case for all three systems. In fact, each case can be fitted into a power function with fitting correlation coefficients ranging from 0.96 to 0.98. Two different sets of fitting curves were plotted in Figure 4. For the solid lines, the fitting functions are

(31) Soloviev, V. N.; Eichhofer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2000**, *122*, 2673.

(32) Kayanuma, Y. *Phys. Rev. B* **1988**, *38*, 9797.

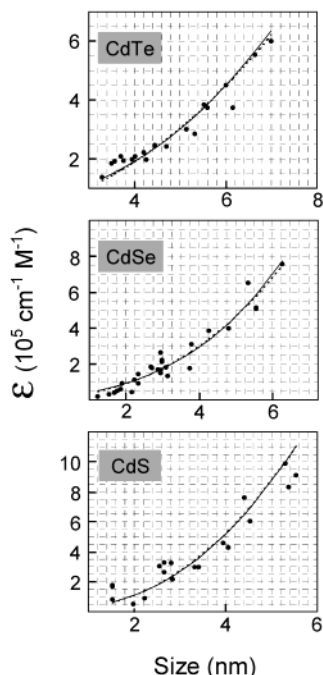


Figure 4. Size-dependent extinction coefficient per mole of nanocrystals at the first excitonic absorption, ϵ , of CdTe, CdSe, and CdS nanocrystals. Solid lines are the fitting curves shown by eqs 2–4. Dashed lines are the fitting results of eqs 5–7.

exhibited as follows.

$$\text{For CdTe: } \epsilon = 3450 \Delta E (D)^{2.4} \quad (2)$$

$$\text{For CdSe: } \epsilon = 1600 \Delta E (D)^3 \quad (3)$$

$$\text{For CdS: } \epsilon = 5500 \Delta E (D)^{2.5} \quad (4)$$

Here, ΔE is the transition energy corresponding to the first absorption peak and the unit is in eV. D is the diameter or size of the nanocrystals. The format of the fitting functions was chosen according to an existing equation discussed by Brus² and by Wang et al.³

The experimental ϵ values shown in Figure 4 can also be fitted into an empirical function of the size of the nanocrystals without considering the energy of the absorption peak, the dashed lines with correlation coefficients ranging between 0.96 and 0.98. The fitting results are as follows.

$$\text{For CdTe: } \epsilon = 10043 (D)^{2.12} \quad (5)$$

$$\text{For CdSe: } \epsilon = 5857 (D)^{2.65} \quad (6)$$

$$\text{For CdS: } \epsilon = 21536 (D)^{2.3} \quad (7)$$

When those values in Figure 4 were used for the determination of the concentration of the nanocrystals using eq 1, it would be necessary to calibrate the absorbance if the size distribution of the nanocrystals was significantly broader than that of the standard samples used, which could be estimated by comparing the peak width of the absorption or PL spectra of the given sample and the corresponding standard samples. If the emission spectrum — measured with a low particle concentration to avoid reabsorption and excited with high-energy photoradiation to ensure the excitation of the ensemble — was symmetric, the following equation

is sufficient for the calibration.

$$A = A_m (\text{hwhm})_{\text{UV}} / K \quad (8)$$

A and A_m are the calibrated absorbance and the measured absorbance, respectively. $(\text{hwhm})_{\text{UV}}$ is the half width at the half-maximum on the long wavelength side of the first absorption peak. K is the average $(\text{hwhm})_{\text{UV}}$ of the standard samples used for the measurements. For CdTe, CdSe, and CdS nanocrystals, the average $(\text{hwhm})_{\text{UV}}$ values of the standard samples are 18, 14, and 11, respectively.

Alternatively, the calibration can be performed with the fwhm of the PL spectrum using eq 9.

$$A = A_m (\text{fwhm})_{\text{PL}} / K' \quad (9)$$

Here, A and A_m are the calibrated absorbance and the measured absorbance, respectively. $(\text{fwhm})_{\text{PL}}$ is the full width at the half-maximum of the PL spectrum. K' is the average $(\text{fwhm})_{\text{PL}}$ of the standard samples used for the measurements. For CdTe, CdSe, and CdS nanocrystals, the average $(\text{fwhm})_{\text{PL}}$ values of the standard samples are 29, 25, and 18 nm, respectively. If the PL spectrum was significantly asymmetric, eq 9 should provide a better calibration.

Influence of Synthetic Methods, Surface Ligands, and Solvents. There was no detectable influence of the synthetic methods, the surface ligands, or the solvents on the ϵ values of the nanocrystals. For example, the ϵ values of the CdSe nanocrystals coated with TOPO,²⁹ pyridine,^{27,28} or hydrophilic thiols²⁹ prepared by the standard surface modification techniques from the same batch of CdSe nanocrystals, 3.0 nm average size, were found to be the same within the experimental errors. The set of experiments also confirmed that nanocrystals dissolved in nonpolar organic solvents, polar organic solvents, and water all possess the same ϵ value within the experimental errors as long as the size and composition of the inorganic nanocrystals were the same. In addition, influence of the PL quantum yield of the nanocrystals on their ϵ values was also not detectable.

Mikulec et al. reported that by replacing the surface ligands it is possible to remove the reaction precursors possibly trapped inside the ligands monolayer on the surface of the nanocrystals.²⁸ The results mentioned in the last paragraph confirmed that the purification procedure adopted in this work was sufficient for removing the cadmium precursors, as the ϵ values of the nanocrystals were found to be the same after a variety of surface ligands replacement treatments.

The ϵ values of nanocrystals with the same size and inorganic composition synthesized by different methods seemed indistinguishable experimentally. For instance, differences in the ϵ values of the CdTe nanocrystals synthesized in ODE using either TDPA or oleic acid as the ligands were found to be not detectable, provided that the size and size distribution of the nanocrystals were similar.

Controlled Etching Methods. Controlled etching methods were established to further confirm the results shown in Figure 4. Ideally, the concentration of the nanocrystals in the solution should not change if the etching process was well controlled and proceeded in a homogeneous manner. The indication of such a con-

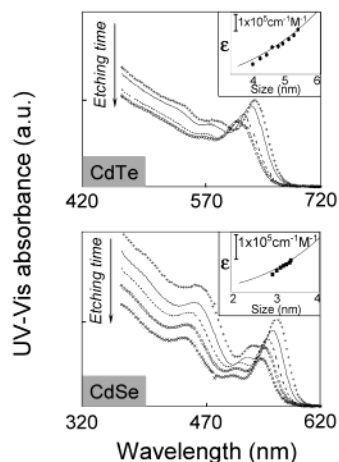


Figure 5. UV-Vis absorbance decreased dramatically as the nanocrystals were being controllably etched. See text for details. Insets: The ϵ values obtained by the etching methods (dots for CdTe and squares for CdSe nanocrystals) in comparison to the fitting values shown in Figure 4 (solid line in both cases).

trolled etching is that the size distribution of the nanocrystals should not change significantly, although the size of the nanocrystals decreases with time. Experimentally, a controlled etching process should gradually shift the absorption spectrum to higher energy and maintain the contour and the peak width of the UV-vis spectrum of the original nanocrystals.

Benzoyl peroxide was found to controllably etch CdTe nanocrystals with a large excess of TDPA existing in the solution. As shown in Figure 5 (top), the first absorption peak of the UV-vis spectrum of the CdTe nanocrystals shifted continuously to blue, but the contour and the peak width of the absorption spectrum were well maintained until the average size of the nanocrystals shrank from about 5.5 to 4 nm for this particular sample.

The etching of CdSe nanocrystals was carried out by concentrated HCl after the nanocrystals were "sealed" in dendron boxes.¹⁸ As shown in Figure 5 (bottom), the spectroscopic signatures of a controlled etching of nanocrystals were also observed in this case.

Considering the concentration of the nanocrystals in the solution did not change in the controlled etching experiments, the peak intensity shown in Figure 5 should directly reflect the relative extinction coefficient per mole of particles. Therefore, the significant intensity drop of the spectra shown in Figure 5 as etching proceeded clearly indicate that the extinction coefficient per mole of particles decreased dramatically. The absolute values of ϵ of the nanocrystals generated by the controlled etching experiments nicely agreed with the fitting curves from Figure 4 (see the insets in Figure 5).

Etching of CdS nanocrystals through either oxidation or dissolution was very difficult to control. The qualitative experimental results indicate that the ϵ values of the CdS nanocrystals are also size dependent although it was not yet possible to obtain quantitative confirmation.

ϵ Values of CdSe Nanocrystals at 250 °C. Figure 6 shows the plotted ϵ values of CdSe nanocrystals at 250 °C. Because the thermal expansion coefficient of the

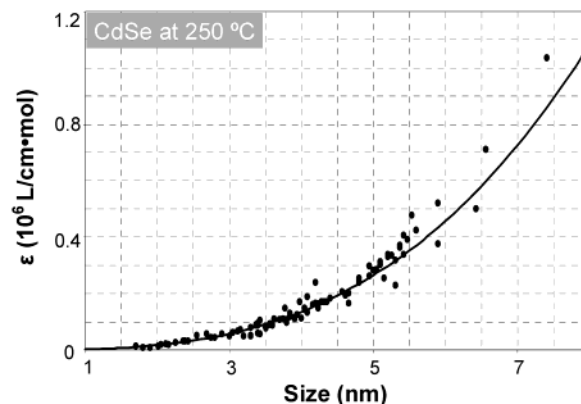


Figure 6. Extinction coefficients per mole of CdSe nanocrystals at 250 °C. Solid line is the fitting curve of the experimental data using a function similar to that shown in eq 4 but with a different proportional constant. No peak-width calibration applied.

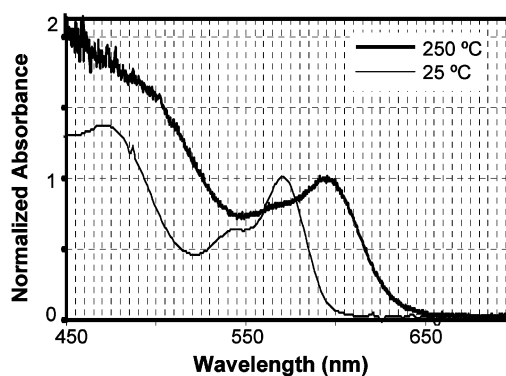


Figure 7. UV-Vis spectra of the same batch of CdSe nanocrystals taken at different temperatures.

nanocrystals is not known, we plotted the ϵ values against the size of the nanocrystals at room temperature. The experimental data can be fitted to a cubic function with a form similar to eq 3. It should be pointed out that, at high temperatures, the absorption spectrum of the nanocrystals shifts to red significantly as shown in Figure 7.

In comparison to the ϵ values at room temperature, the absolute value for a given sized CdSe nanocrystal at 250 °C is about 30% lower. Evidently, this decrease is due to the thermal broadening of the absorption spectrum. As shown in Figure 7, the (hwhm)_{UV} of the first excitonic absorption at the high temperature is about 30% larger than that at room temperature of the corresponding sample. This implies that the integrated ϵ values are not strongly dependent on the temperatures.

Experimental Errors. The key factor for reliable determination of ϵ is the purification procedure, besides the inhomogeneous broadening of the spectra caused by the size distribution. As mentioned above, the conversion factor of the cadmium precursors to the cadmium atoms in the form of nanocrystals varied significantly and typically increased with increasing the size of the nanocrystals. This is probably why the data reported in the case of CdTe¹⁹ and CdS²⁰ nanocrystals did not show a size dependence of the ϵ values since they assumed that the conversion of cadmium precursors was unity.

A nonunity and size-dependent conversion factor is actually consistent with the principles of the growth of monodisperse nanocrystals through “focusing of size distribution” and the size-dependent solubility of the nanocrystals.¹³ In the course of “focusing of size distribution”, it is required to incorporate more monomers originally in the solution onto the nanocrystals when the crystals grow in size, and the conversion factor should thus increase as the nanocrystals grow in size.

The experimental errors of the measurements reported in this work should mainly come from the determination of the size and size distribution of the nanocrystals. In principle, the sizes of the nanocrystals were all determined by TEM measurements except those in very small nanoclusters. It is well-known that the edge of a nanocrystal determined by TEM can be accurate only to approximately one lattice plane. For example, the sizes of CdSe nanocrystals with the same absorption peak position reported by Bawendi's group³³

and Alivisatos' group¹³ were noticeably different from each other. In addition to this size inaccuracy, most samples — except those magic-sized nanoclusters — used in this work all have a finite size distribution, around 5–10% standard deviation. The combination of these two errors will likely bring about 20–30%, or ± 10 –15%, standard deviation for the ϵ values shown in Figure 4.

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Note Added after ASAP Posting

Due to a production error, this article was released ASAP on 6/7/2003 with an incorrect value in the CdSe empirical curve fitting function. The correct version was posted on 6/18/2003.

(33) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, 545.