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## Composition-Tunable Properties of CdS<sub>x</sub>Te<sub>1-x</sub> Alloy Nanocrystals

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Ternary CdS<sub>x</sub>Te<sub>1-x</sub> semiconductor quantum dots with both homogeneous and gradient composition have been fabricated via pyrolysis of organometallic precursors. The nanocrystal structure, size, and composition were characterized by UV–visible absorption and fluorescence spectroscopy, transmission electron microscopy, energy-dispersive X-ray elemental analysis, and X-ray diffractometry. It was found that the band gap of homogeneously alloyed CdS<sub>x</sub>Te<sub>1-x</sub> is highly nonlinear with the crystalline composition, which was evidenced by a significant red-shift in the fluorescence of these nanocrystals with respect to the emission wavelength of their CdS and CdTe binary compounds. This effect, also known as optical bowing, seems to be enhanced in CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals because of large differences in atomic radii and electronegativities of S and Te chalcogens. Properties of gradient ternary alloys were found to be markedly different from those of homogeneous CdS<sub>x</sub>Te<sub>1-x</sub>. Their absorption and emission profiles, for instance, had a relatively low spectral overlap leading to large Stokes shifts of up to 150 nm. Other properties of fabricated CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals and their significance to applications in areas of biomedical imaging, solar cells, and quantum dot-based LEDs are discussed.

### Introduction

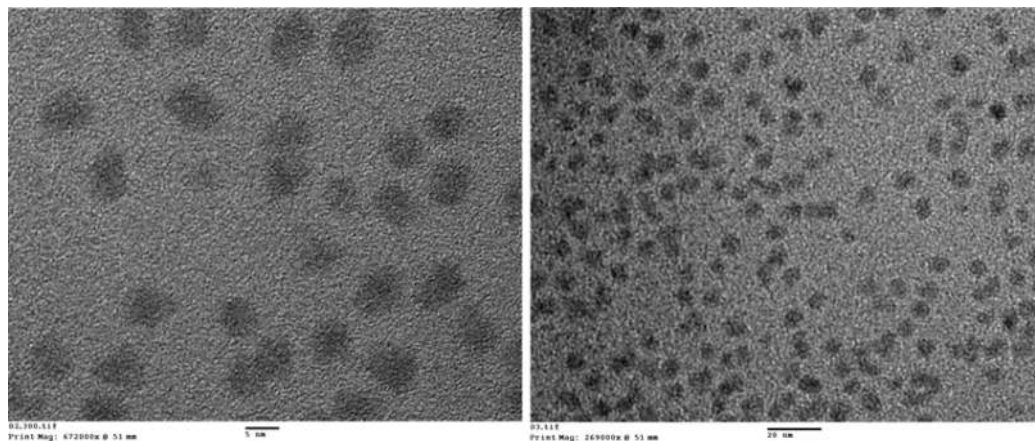
Semiconductor alloy nanocrystals (AB<sub>x</sub>C<sub>1-x</sub>)<sup>1–5</sup> are becoming increasingly important in many areas of nanoscale engineering because of the continuous tunability of their physical and optical properties through gradual variation of the composition variable  $x$ . This added degree of freedom allows tuning an exciton energy of alloy nanoparticles independently of their size, which can be used to extend the nanocrystal (NC) emission range into parts of the spectrum that are not easily accessible with binary quantum dots (QDs) or to achieve a wide range of fluorescence colors from nanoparticles of the same diameter. Further optimization of nanocrystal properties is also possible by varying the ratio of alloying elements throughout the quantum dot, such that either homogeneous or gradient nanocrystal composition, often with distinctly different properties, can be formed. Owing to their superior luminescent properties that are on par with binary nanocrystals, ternary alloys are now well suited for many practical realizations, including quantum dot-based LEDs,<sup>6</sup> where emission at a specific wavelength is often required; in vivo imaging,<sup>7–10</sup> where small diameter infrared fluorescence labels are preferred; and solar cells,<sup>11,12</sup> where a wide range of absorption and the small size of NC sensitizers are an advantage.

To date, several II–IV semiconductor alloy nanocrystals have been synthesized: CdS<sub>x</sub>Se<sub>1-x</sub>,<sup>1</sup> Cd<sub>x</sub>Zn<sub>1-x</sub>S,<sup>13</sup> Cd<sub>x</sub>Zn<sub>1-x</sub>Se,<sup>4,14</sup> CdSe<sub>x</sub>Te<sub>1-x</sub>,<sup>2</sup> and HgSe<sub>x</sub>S<sub>1-x</sub>.<sup>5</sup> These compounds can be classified into two groups according to the type of the two elements, whose stoichiometric ratio is varied in the resulting ternary alloy, such that nanocrystals of the first group consist of two chalcogen atoms and one transition-metal element (CdS<sub>x</sub>Se<sub>1-x</sub>, CdSe<sub>x</sub>Te<sub>1-x</sub>, and HgSe<sub>x</sub>S<sub>1-x</sub>), and nanocrystals of the second type are made of two transition-metal elements and one chalcogen atom (Cd<sub>x</sub>Zn<sub>1-x</sub>S, Cd<sub>x</sub>Zn<sub>1-x</sub>Se). Recent works<sup>1,15</sup> demonstrated that, in contrast to the second group alloys, whose properties change

quasi-linearly with their composition, properties of nanocrystals in the first group have a pronounced nonlinear dependence on the ratio of two chalcogens in the alloy and thus could be difficult to predict. For instance, it was found<sup>2</sup> that emission energies of CdSe<sub>x</sub>Te<sub>1-x</sub> NCs are well outside the range of transition energies of contributing CdSe and CdTe binary QDs, such that  $E(\text{CdSe}_x\text{Te}_{1-x}) < xE(\text{CdSe}) + (1-x)E(\text{CdTe})$ . These nonlinear effects, also known as “optical bowing”, have been observed previously in bulk semiconductors and were subsequently explained in a work by Bernard and Zunger<sup>16</sup> that identified three structural and electronic factors leading to nonlinearity of ternary compounds: (i) different ions in the alloy have different atomic sizes, (ii) these ions have different electronegativity values, and (iii) the binary structures have different lattice constants. Thus far, bowing effect has been confirmed for ternary quantum dots that were based on S/Se and Se/Te combinations of chalcogen atoms. Meanwhile, no reports of S/Te composed ternary nanocrystals have been made, which according to Bernard and Zunger should exhibit more extensive nonlinearity, resulting from large differences in S and Te atomic radii and their electronegativities. In this work, we thus aim to explore such combination of chalcogens by studying optoelectronic properties of CdS<sub>x</sub>Te<sub>1-x</sub> alloy nanocrystals. The use of Cd as a transition metal was inspired by a substantial lattice mismatch (11%) between the binary semiconductor quantum dots CdS and CdTe, which should further enhance nonlinear effects.

In this work, both homogeneous and gradient ternary CdS<sub>x</sub>Te<sub>1-x</sub> semiconductor nanocrystals were synthesized via a traditional pyrolysis of organometallic precursors. Strong optical bowing was verified for the case of homogeneous alloy NCs, where the emission peak was red-shifted with respect to those of CdS and CdTe binary subcompounds, extending into near-infrared region. In contrast to homogeneous CdS<sub>x</sub>Te<sub>1-x</sub> alloy NCs, nanoparticles with the gradient composition of S and Te ions did not exhibit significant nonlinear effects. Nonetheless,

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**Figure 1.** High-resolution TEM images of  $\text{CdS}_x\text{Te}_{1-x}$  nanocrystals with homogeneous composition of S and Te chalcogens. The scale bars for the two images are 5 and 20 nm, respectively.

their optical properties were found to be different from those of binary or core/shell nanocrystals and to a certain extent from those reported for other ternary heterostructures. For instance, the observed Stokes shifts were in the range of 80–100 nm, which is considerably larger than that for most semiconductor nanocrystals. This property of gradient ternary  $\text{CdS}_x\text{Te}_{1-x}$  NCs can be of interest in applications that require a small degree of spectral overlap between emission and absorption profiles such as in Förster resonance energy transfer-based sensors<sup>17,18</sup> or when reduced self-absorption of colloids is an advantage.

### Experimental Section

**Synthesis of  $\text{CdS}_x\text{Te}_{1-x}$  NCs with Homogeneous Composition.** All reactions were conducted under argon atmosphere using standard Schlenk techniques. Cadmium solution was prepared by dissolving 0.0128 g of cadmium oxide in 0.2 mL of oleic acid and 4 mL of 1-octadecene (ODE) in a 25-mL flask while heating the mixture to 300 °C. The sulfur injection stock solution was prepared by mixing 0.0016 g of sulfur in 1.5 mL of ODE and heating to 180 °C followed by cooling of final (clear) solution to room temperature. Tellurium solution was prepared by dissolving 0.0095 g of tellurium in 0.5 mL of tributylphosphine and then further diluting the mixture with 2 mL of ODE. To ensure a simultaneous injection of precursors during the synthesis of homogeneous alloy NCs, epimolar amounts of tellurium and sulfur solutions were mixed together. The mixture was then injected into the cadmium solution at a rate of 0.02–0.05 mL/min while being stirred. The reaction was stopped after 20 min by removing the flask from the heating mantle.

**Synthesis of  $\text{CdS}_x\text{Te}_{1-x}$  NCs with Gradient Composition.** The same procedure was carried out to prepare the cadmium, sulfur, and tellurium stock solutions. During the synthesis, the sulfur solution was injected into the reaction flask where a dissolved cadmium solution was kept at 300 °C. The temperature was then lowered to 250 °C, and 0.01–0.04 mL of tellurium was added to the mixture 1–6 min following the S injection. The reaction was stopped after 30–40 min by removing the flask from heating mantle.

**Purification of CdS/CdTe QDs.** After the reaction mixtures were allowed to cool to 50 °C, 3–5 mL of hexane was added to the solution to prevent solidification. The subsequent cleaning of nanocrystals was done by hexane/methanol extraction. Typically, 6–7 mL of methanol was slowly added to the reaction mixture in hexane, which was then centrifuged for 10 min at 3500 rpm. The upper hexane layer containing QDs was

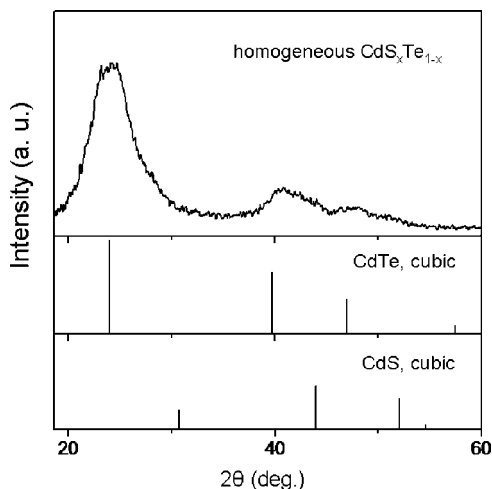
taken out with a syringe for further purification. We found that at least 3–4 extraction cycles were necessary to ensure that the quantum yield of NC colloids was maximized.

**Characterization.** UV–vis absorption and photoluminescence (PL) spectra were recorded using a CARY 50 scan spectrometer and a Jobin Yvon Fluorolog FL3-11 fluorescence spectrophotometer. PL quantum yield of sufficiently dilute nanocrystal suspensions was determined relative to that of quinine sulfate, Cy3, and Cy5 dyes that were excited at 360–420 nm. For energy-dispersive X-ray (EDX) measurements, purified nanocrystals were deposited onto carbon substrates and loaded into a Hitachi (S-2700) scanning electron microscope (SEM) equipped with EDAX detector. High-resolution transmission electron microscopy (TEM) measurements were carried out using JEOL 311UHR operated at 300 kV. Specimens were prepared by depositing a drop of nanocrystal hexane solution onto a Formvar-coated copper grid and letting it dry in air. X-ray powder diffraction (XPD) measurements were carried out on Scintag XDS-2000 X-ray powder diffractometer.

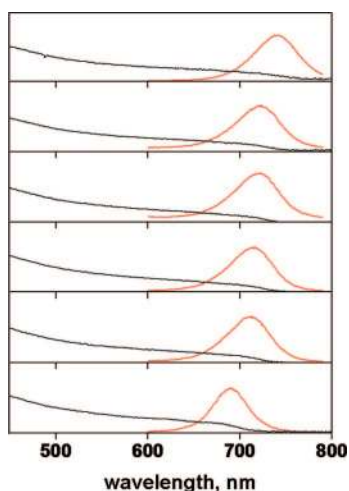
### Results and Discussion

**Homogeneous  $\text{CdS}_x\text{Te}_{1-x}$  Alloy Nanocrystals.** Previous work on the synthesis of alloy NCs showed that highly homogeneous spatial distribution of elements within a quantum dot can be achieved if the amount of both precursors is in large excess of the amount of the transition metal.<sup>19,20</sup> This approach minimizes the influence of uneven reactivities of participating chalcogens, such as in the case of S and Te elements, which can lead to a gradient-like composition. Accordingly, homogeneous  $\text{CdS}_x\text{Te}_{1-x}$  nanocrystals were synthesized under Cd-limited conditions by gradual injection of S/Te precursors with a carefully controlled molar ratio. The as-synthesized nanocrystals were investigated by means of transmission electron microscopy and X-ray powder diffraction to collect statistically reliable data for the nanocrystal size, shape, and crystallinity. Typical TEM images of large-diameter  $\text{CdS}_x\text{Te}_{1-x}$  nanocrystals are shown in Figure 1. The shape of most nanoparticles appeared to be elongated, indicating a faster nanocrystal growth along one of its axes. By examining 30–40 isolated specimens under high magnification (up to  $\times 600$  K), we estimated the average width and the length of nanoparticles to be  $5.1 \pm 0.2$  and  $6.3 \pm 0.4$ , respectively. Considering the size of nanoparticles, the distribution of their diameters was relatively narrow (SD: 7%).

The crystal structure of homogeneous  $\text{CdS}_x\text{Te}_{1-x}$  nanocrystals with 1:1 stoichiometric ratio of S and Te precursors was investigated using X-ray powder diffraction. By comparing the



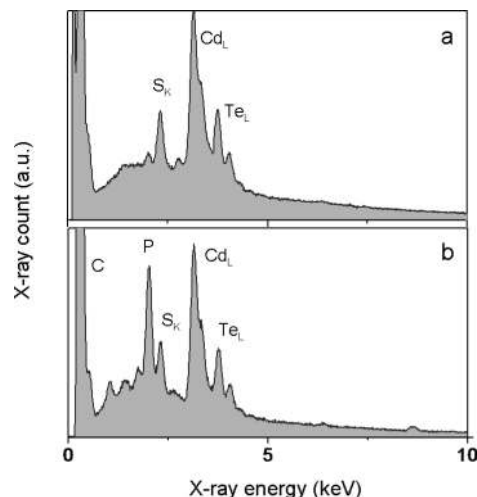
**Figure 2.** X-ray powder diffraction spectra of homogeneous CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals along with XPD patterns of CdTe and CdS bulk cubic phases. Broadening of reflection peaks is attributed to an alloying effect, which alters binary lattice parameters.



**Figure 3.** Evolution of the UV-vis absorption and room-temperature fluorescence spectra of homogeneous CdS<sub>x</sub>Te<sub>1-x</sub> alloy NCs. During nanoparticle growth, the FL peak gradually shifts from 690 nm (1 min) to 745 nm (45 min).

experimental pattern, shown in Figure 2, with peak positions expected from cubic phases of bulk CdS and CdTe crystals, we conclude that the lattice structure is predominantly cubic sphalerite with no evidence of the hexagonal phase. The two reflection peaks (220) and (311) at 42 and 48° appear to incorporate the diffraction patterns of both CdS and CdTe bulk crystals structure, which is consistent with a linear dependence of the lattice spacing of the homogeneous alloy structure on its composition. The mixture of the CdS and CdTe phases is skewed toward the CdTe, as can be evidenced by asymmetric intensity profiles of the (220) and (311) Bragg peaks, which indicates that ternary alloys prepared with an equal amount of chalcogen precursors contain more Te than S ions. This result is also consistent with EDX analysis (given further) showing that the final ratio of Te to S in homogeneous alloy NCs was 1.5.

The growth kinetics of the reaction mixture is summarized in Figure 3, where the evolution of fluorescence (FL) and absorption spectra measured at different times after the injection of S and Te precursors is shown. Because of a considerable mismatch of band gap energies between CdS and CdTe binary nanocrystals, the resulting absorption profile of CdS<sub>x</sub>Te<sub>1-x</sub> is

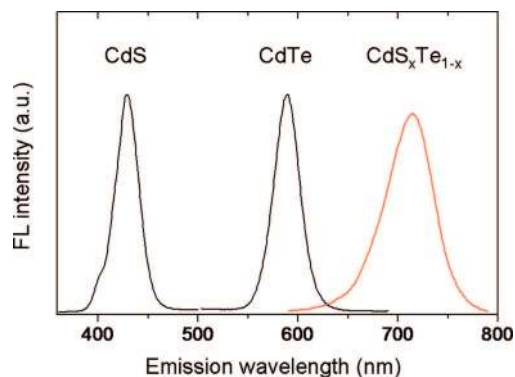


**Figure 4.** Energy dispersive X-ray emission spectrum of homogeneous (a) and gradient (b) CdS<sub>x</sub>Te<sub>1-x</sub> alloy nanocrystals.

relatively broad with no clear indication of the band edge peak. Such a wide absorption spectrum seems to be unique to S/Te combination of elements as it is largely different from the spectral shapes observed in previously studied CdS<sub>x</sub>Se<sub>1-x</sub> and CdSe<sub>x</sub>Te<sub>1-x</sub> nanocrystals, where distinct absorption features centered near band edge energies were reported. The possibility of inhomogeneous broadening of the CdS<sub>x</sub>Te<sub>1-x</sub> absorption profile caused by large variations in nanocrystal diameters should be discarded because of relatively narrow widths of the observed fluorescence emission, which indicates quasi-monodispersity of nanoparticles. We therefore believe that a monotonous absorption spectrum is an intrinsic feature of the fabricated CdS<sub>x</sub>Te<sub>1-x</sub> alloys. As shown in Figure 3, the nanocrystal growth is accompanied by a steady evolution of the fluorescence peak in the spectral window of 690–745 nm, corresponding to nanoparticle sizes of 2.8–6 nm. Quantum yield of as-fabricated samples in chloroform was steadily increasing during nanocrystal growth, reaching 6–7%, and was further improved to 14% after coating purified nanoparticles with a thin ZnS shell in a separate procedure.

Energy dispersive X-ray emission spectra were measured to study the elemental composition of fabricated alloys. For this purpose, hexane suspension of purified CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals (FL peak at 745 nm) was evaporated onto a carbon substrate and loaded into SEM equipped with an X-ray detector. Figure 4a shows a typical X-ray spectrum obtained at 20 kV, along with peak assignments for Cd, S, and Te elements. After integrating the peak area, we converted the X-ray count into the elemental weight percentages using quantification software (EDAX Genesis). The resulting stoichiometric ratio of elements Cd/S/Te was found to be 29:11:17, respectively. The amount of Cd in the sample was approximately balanced by the combined amounts of S and Te, which indicates that most of the unreacted ions were removed during purification. From the ratio of S to Te, we determine the stoichiometry of the homogeneous alloy NCs, fabricated by using equal portions of chalcogens precursors, to be CdS<sub>0.4</sub>Te<sub>0.6</sub>.

To understand how the observed emission energies of CdS<sub>x</sub>Te<sub>1-x</sub> alloy NCs relate to the emission range of CdS and CdTe binary QDs, we measured the fluorescence of ca. 3.9-nm-diameter CdS and CdTe QDs and compared their spectra to the emission of 3.9-nm CdS<sub>x</sub>Te<sub>1-x</sub> NCs. As can be seen from the positions of the three peaks in Figure 5, the FL peak of the alloy NC is well outside the wavelength range defined by binary



**Figure 5.** Normalized emission of 3.9-nm CdS, CdTe, and CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals. Because of a nonlinear relation between the composition of homogeneous CdS<sub>x</sub>Te<sub>1-x</sub> NCs and their band gap energy, the FL peak in CdS<sub>x</sub>Te<sub>1-x</sub> (red line) is shifted outside the spectral range of FL in CdS and CdTe QDs.

**TABLE 1: Comparison of the Bowing Constants for Ternary Nanocrystals**

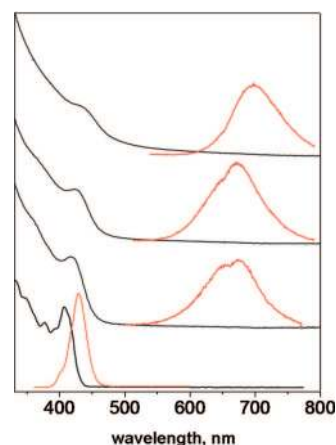
ternary nanocrystal	bowing constant, <i>b</i>	reference
CdS <sub>0.53</sub> Se <sub>0.47</sub>	0.3	ref 1
CdSe <sub>0.34</sub> Te <sub>0.66</sub>	1.19	calculated from ref 2
CdS <sub>0.50</sub> Te <sub>0.50</sub>	3.17	present work

CdS and CdTe QDs, with a corresponding interval between CdTe and CdS<sub>x</sub>Te<sub>1-x</sub> peaks of 125 nm, which indicates that the band gap of a ternary CdS<sub>x</sub>Te<sub>1-x</sub> NC is smaller than that of CdS or CdTe QDs. This result is consistent with Végard's Law<sup>21</sup> for bulk semiconductors, stating that, while the lattice constant changes linearly with composition, other properties, such as band gap, have a more complex dependence on the stoichiometric ratio of binary subcompounds. In the quadratic approximation, the value of the band gap becomes:

$$E_g(\text{CdS}_x\text{Te}_{1-x}) = xE_g(\text{CdS}) + (1-x)E_g(\text{CdTe}) - bx(1-x) \quad (1)$$

where *b* is the bowing constant that describes the extent of nonlinearity and  $0 < x < 1$ . To estimate *b* for CdS<sub>x</sub>Te<sub>1-x</sub> alloys fabricated here, we substituted band gap values of bulk semiconductor materials, *E<sub>g</sub>*, in eq 1, with the measured emission energies of equal-sized CdS, CdTe, and CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals. Strongest nonlinear effects were realized for 3.9-nm-diameter nanoparticles (shown in Figure 5), corresponding to a bowing constant of 3.17. This result is somewhat greater than previously reported values of *b* for other ternary compounds (Table 1), which is not surprising if we consider the main factors that contribute to nonlinear behavior in alloys. According to a model proposed in ref 16, bowing effect is associated with a large lattice mismatch between binary subcompounds, and differences in atomic radii and electronegativities of alloying elements. For CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals, all of these factors are substantial. First, the lattice mismatch between CdS and CdTe quantum dots (11% for zinc blende structure) is the largest among the possible combinations of binary nanocrystals that form previously reported alloys. Second, the difference in electronegativities and atomic radii (bond length) of S and Te chalcogens is the greatest in group IV elements.

**Gradient CdS<sub>x</sub>Te<sub>1-x</sub> Alloy Nanocrystals.** In contrast to homogeneous alloys, gradient ternary nanocrystals have a continuously changing composition in the form of CdS<sub>x</sub>Te<sub>1-x</sub>, where *x* can vary from 0 to 1 within a single quantum dot. These compounds were grown by creating a 1–6 min delay between

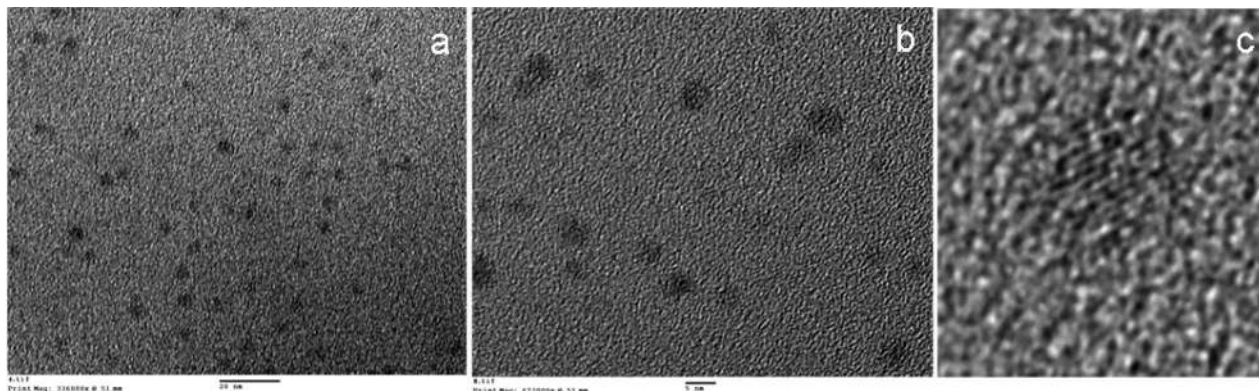


**Figure 6.** Evolution of emission (red) and absorption (black) spectra for gradient CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals during their synthesis. The bottom panel shows spectral features of CdS QDs that form in the reaction flask before the injection of Te precursor.

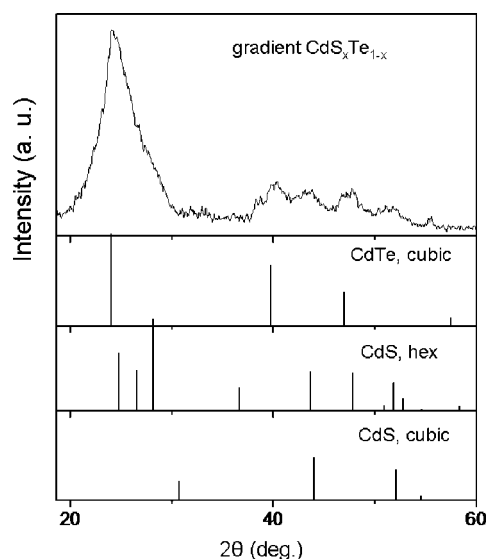
consecutive injections of the two chalcogen precursors into the Cd solution. In this work, we mainly focus on the synthesis of gradient alloys containing a CdS core, which was motivated by earlier reported<sup>2</sup> difficulties in the fabrication of fluorescent CdS/CdTe core/shells nanocrystals, via a traditional two-step overcoating procedure. We hope that a gradual change of the composition at the CdS/CdTe interface can help minimize the lattice stress, which is partially responsible for the absence of FL emission in CdS/CdTe core/shell NCs. The evolution of optical spectra during nanocrystal growth is shown in Figure 6. The initial formation of the CdS core is seen in the bottom spectrum, which shows optical characteristics of the sample that was taken 4 min after the sulfur injection. Upon the first addition of Te precursor to the reaction flask, the growth solution turned dark red, which was accompanied by appearance of the FL feature near 670 nm. During the subsequent growth, this peak gradually red-shifted until reaching a “saturation” value of 695 nm. The quantum yield of as-prepared nanocrystals was somewhat lower than that of homogeneous alloys, reaching the maximum value of only 4%. Yet this is the first evidence of CdS/CdTe-like arrangement with a nonzero emission yield.

Figure 7 shows several TEM images of gradient CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals fabricated by introducing a 6 min delay between the injection of S and Te precursors into the reaction flask. A nearly spherical shape was observed for most of the examined nanoparticles. The average diameter, determined by studying several specimens under 300 000 magnification (Figure 7b), was found to be 5.2 nm, with a somewhat wider distribution of sizes than was observed for homogeneous alloys. The inferior monodispersity of gradient nanocrystals is also reflected in their emission spectra, where the values of the corresponding FL peak widths are almost twice as large as those obtained for homogeneous nanocrystals.

Elemental composition of gradient CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals was investigated using EDX. A typical X-ray scan of purified samples is shown in Figure 4b. After converting the integrated peak area into the elemental weight percentages, we found the stoichiometric ratio for the three elements Cd, S, and Te to be 1.00:0.35:0.47, respectively. X-ray powder diffraction analysis was conducted to further investigate the structure of gradient CdS<sub>x</sub>Te<sub>1-x</sub> alloy NCs. Figure 8 shows an experimental diffraction pattern of nanoparticles that were fabricated by introducing a 4 min delay between the injection of S and Te solutions. In comparison with peak positions of bulk CdTe and CdS, we



**Figure 7.** High-resolution TEM images of  $\text{CdS}_x\text{Te}_{1-x}$  nanocrystals with the gradient composition of S and Te. The scale bars are (a) 20 and (b) 5 nm. (c) Ultrahigh resolution image of the 5.0-nm nanoparticle showing the crystal lattice planes.

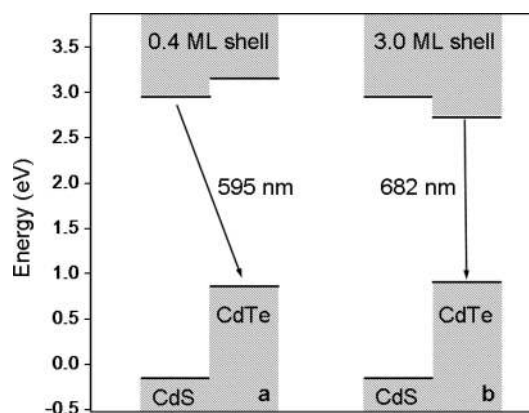


**Figure 8.** XPD spectra of gradient  $\text{CdS}_x\text{Te}_{1-x}$  alloy NCs along with XPD patterns of relevant bulk phases. Major reflection peaks associated with CdTe and CdS crystal structure are well separated, which is consistent with a core/shell arrangement.

identify both cubic and wurtzite structure lattice structure in our samples. In contrast to broad spectral features that were observed for homogeneous  $\text{CdS}_x\text{Te}_{1-x}$ , the major reflection peaks associated with CdTe and CdS phases in gradient alloy NCs are easily distinguishable, indicating the formation of separate CdTe and CdS lattice structures. Such a pattern cannot be produced by a pure alloy crystal structure, where unique ternary lattice is formed, indicating that the composition of gradient  $\text{CdS}_x\text{Te}_{1-x}$  nanoparticles is more comparable to a core/shell arrangement. In this case, nonlinear effects that arise in homogeneously alloyed  $\text{CdS}_x\text{Te}_{1-x}$  NCs may not be as strong in gradient NCs because of a lower volume of the ternary crystalline phase.

To understand if optical bowing is significant in gradient alloys, we calculated the positions of  $1S_c$  and  $1S_h$  energy levels for a CdS/CdTe core/shell nanoparticle, where a sharp interface between the two semiconductor materials was assumed. The size of the core CdS nanocrystals in our calculations was set to be equal to that of CdS seeds that form in the growth solution before the Te injection. It was estimated from the known relation between the FL peak and nanocrystal diameter<sup>22</sup> to be 3.9 nm.

Figure 9 shows a relative alignment of zero-angular momentum states for the two different thicknesses ( $H$ ) of the CdTe shell. When  $H = 0.4$  ML (Figure 9a), the conduction band edge



**Figure 9.** Energy diagram showing positions of the zero-angular momentum states in CdS and CdTe binary NCs. Expected optical transitions for a CdS/CdTe core/shell NC containing 0.4 monolayers (a) and three monolayers (b) of CdTe in the shell.

of the CdS is situated lower than that of CdTe, causing an electron to localize primarily in the core of the heterocrystal, whereas the higher positioned valence band edge in CdTe results in a shell localization of an excited hole. For this type II interfacial band alignment, the recombination of carriers occurs via a spatially indirect transition, characterized by emission energies that are lower than the ones corresponding to carrier recombination in isolated CdS and CdTe QDs. As shown by an energy diagram in Figure 9a, the transition wavelength for this case is expected to be around 595 nm. The experimental value of the FL peak, measured for a sample of thin-shell CdS/ $\text{CdS}_x\text{Te}_{1-x}$  nanocrystals, was 670 nm (Figure 6). While this difference indicates that some degree of optical bowing could be present, the exact value of  $b$  cannot be determined for this case because of insufficient data on the composition of gradient alloy. For instance, it is not certain if the shell itself is a gradient mix of S and Te or if it is primarily formed by Te ions as should follow from the stoichiometric ratio of precursors. For larger gradient nanocrystals such composition analysis, however, it becomes possible through a combination of UHR TEM and EDX measurements, which determine an approximate percentage of Te in the shell. By comparing an average diameter of quasi-spherical ternary nanocrystals obtained from TEM study with the size of CdS seeds that are formed in the flask by the time of Te injection, we can estimate the thickness of the  $\text{CdS}_x\text{Te}_{1-x}$  shell. For 5.2-nm alloy nanoparticles shown in Figure 7, the diameter of CdS QDs, determined from their emission spectra, was 4 nm, which corresponds to a 2-nm-thick layer of the overgrown  $\text{CdS}_x\text{Te}_{1-x}$  material. According to the EDX scan of these nanocrystals, the ratio of tellurium to sulfur in a gradient

alloy is 1.5. If we assume that the penetration of Te into the CdS core is negligible, then the average ratio of Te to S in the shell of 5.2-nm-diameter gradient  $\text{CdS}_x\text{Te}_{1-x}$  NC is approximately 10. This provides an additional support to our conclusion that the composition of gradient alloy NCs is very similar to the CdS/CdTe core/shell arrangement.

We now would like to address whether any degree of optical bowing is present in large-diameter gradient alloys by comparing their experimental emission energies with that of the CdS/CdTe core/shell structure shown in Figure 9b. We first consider the CdTe shell, where physical properties are linearly dependent on the composition, such that the positions of its zero-angular momentum energy levels,  $1S_c$  and  $1S_h$ , are defined by the  $x$  to  $1 - x$  ratio of corresponding levels in CdS and CdTe nanocrystals. For this arrangement, an excited e-h pair in a 5.2-nm nanocrystal shown (Figure 9b) is expected to localize entirely within the shell, which should lead to a transition wavelength of 682 nm. An experimentally observed value for this transition (698 nm, Figure 5, top panel) is slightly red-shifted, indicating that some extent of bowing could be present. Even if the actual portion of Te in the shell is different from the estimated value of 90%, the transition wavelength in CdS/CdS<sub>x</sub>Te<sub>1-x</sub> nanocrystals with linear composition dependence would still be less than the experimental value of  $\lambda = 698$  nm. We therefore conclude that, for gradient CdS<sub>x</sub>Te<sub>1-x</sub> NCs,  $b$  is greater than zero. It is also apparent that the bowing effect in gradient alloys is less extensive than that in homogeneous nanocrystals, where red-shifting in the range of 100–130 nm was observed.

## Conclusions

In conclusion, we report on a colloidal synthesis of novel CdS<sub>x</sub>Te<sub>1-x</sub> alloy NCs with both homogeneous and gradient composition of S and Te chalcogens. Our results demonstrate the existence of strong nonlinear effects in homogeneously alloyed nanoparticles, evidenced by a significant red-shift of the emission of ternary compounds relative to FL peaks of binary CdS and CdTe quantum dots, which corresponded to a bowing constant of 3.17. Optical spectra of gradient CdS<sub>x</sub>Te<sub>1-x</sub> alloy nanocrystals, fabricated by overcoating small CdS seeds with CdTe-rich shell in a one-pot synthesis, differed from those of homogeneous ternary alloys. In addition to a smaller extent of optical bowing observed for these nanoparticles, their absorption profile was dominated by a CdS  $1S_c-1S_h$  peak with almost vanishing absorbance for lower photon energies, which gave rise to large Stokes shifts with value of up to 150 nm.

Overall, optical properties of fabricated CdS<sub>x</sub>Te<sub>1-x</sub> were found to be markedly different from those of binary or core/shell

nanocrystals and to a certain extent from those reported for other ternary heterostructures, making these materials of potential interest in biomedical imaging and photovoltaics.

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## References and Notes

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