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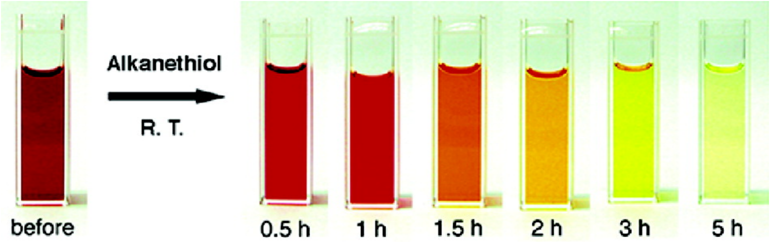

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Band Gap Engineering of CdTe Nanocrystals through Chemical Surface Modification

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The size-dependent optical properties of semiconductor nanocrystals have recently motivated attempts to use them as novel building blocks for optoelectronics and bioengineering applications.[1] To attain these ends, the ability to prepare semiconductor nanocrystals with controlled size and composition is of primary importance. A variety of methods are now accessible for preparing size-controlled II−VI semiconductor nanocrystals such as CdS,[2−4] CdSe,[3−5] and CdTe nanocrystals.[3,4,6,7] With the exception of size-selective photoetching of CdS nanocrystals,[8,9] control of the nanocrystal band gap has mostly been achieved via "growth" of nanocrystals during synthesis. Other approaches have modified the optical properties of the nanocrystals by creating inorganic shells or alloying[10−12] or by compensating surface defects with organic molecules.[13,14] However, the former processes usually require high-temperature treatment, and the latter process does not provide control of the optical properties over a wide spectral range.

The development of facile methods for controlling the optical properties of nanocrystals in mild conditions is an important challenge and could lead to a more powerful set of band gap engineering schemes. Herein, we describe a simple and convenient method that allows control of the optical absorption and fluorescence emission of CdTe nanocrystals over a relatively wide visible spectral range. Control is achieved through selective surface modification by thiolate ligands and can be performed in ambient conditions. The optical properties are controlled simply by altering either the concentration of ligands introduced to the nanocrystal surface or the reaction times, thus providing an alternative process to conventional synthetic strategies.

In a typical procedure, 3.3-nm CdTe nanocrystals stabilized by thioglicolic acid were prepared in water, as described previously.[7] The CdTe nanocrystals were then phase-transferred into a toluene phase using tetra-*n*-octylammonium bromide (TOAB), providing a clear red solution of CdTe nanocrystals stabilized with thioglicolic acid in the carboxylate form and complexed with the TOA cation.[15] To this dispersion was added a portion of 1-decanethiol (DT) in toluene, and the mixture was kept in the dark under mild stirring for several hours. During this period, the color of the solution gradually changed to orange or yellow (Figure 1) depending on the amount of DT added.

Figure 2A shows the time course of absorption and emission spectra after addition of DT (final concentration: 38.4 mM) to a toluene solution of CdTe nanocrystals (32 μM). Both the initial absorption edge and emission peak shift to higher energies; after mixing of DT for 15 min, 1 h, and 2 h these edges and peaks shifted to 550 and 575 nm, 520 and 545 nm, and 470 and 520 nm, respectively. For each sample, CdTe nanocrystals were precipitated by addition of acetonitrile, resulting in the removal of free thiolate molecules and TOAB. Surface modification of CdTe nanocrystals is clearly observed in FT-IR spectra of the purified nanocrystals (see Figure S1). The ratio of the intensity of the C−H stretching band to the C═O stretching band increases with reaction time, indicating ligand exchange of the initially surface-bound thiolates with DT.

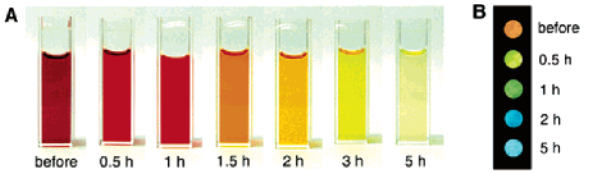

Figure 1. (A) Photographs of solutions containing CdTe nanocrystals before and after being mixed with DT for various times. (B) Fluorescence images of the purified nanocrystals (excited at 350 nm).

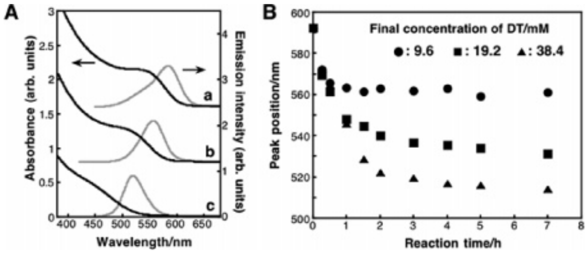

Figure 2. (A) Absorption and emission spectra of CdTe nanocrystals obtained after addition of DT to toluene at room temperature in air for (a) 15 min, (b) 1 h, and (c) 2 h. (B) Plots of emission peak position as a function of reaction time with DT.

The emission peak shifts remarkably at the early stages of reaction and then saturates (Figure 2B). The degree of blue shift depends on both the amount of DT added and the reaction time; adding a larger amount or increasing the reaction time leads to a greater blue shift, thereby providing kinetic control over the emission peak wavelength of the CdTe nanocrystals.[16]

Previous attempts using direct phase transfer of thioglicolic acid-stabilized CdTe nanocrystals from water to a dodecanethiol phase (without phase-transfer reagents) did not result in any distinct changes in solution color; rather, a slight red shift was observed in both absorption and emission spectra.[13] In contrast, the blue shift observed in the toluene phase clearly indicates a different mechanism of surface modification. One possible explanation is that the nanocrystals are becoming smaller during reaction. However, surprisingly, transmission electron microscopy of purified nanocrystals obtained 5 h after addition of DT reveals nanocrystals with a mean size of 3.2 nm, almost the same size as the initial nanocrystals (3.3 nm, Figure S2). To gain more insight into the reaction process, we conducted analytical experiments on the purified nanocrystals, and several important results were obtained. First, EDX analysis demonstrated that the reaction is accompanied by a decrease in Te content and an increase in S content (Table 1). Importantly, the sum of Te and S species, relative to Cd, is almost constant for these samples. Second, ICP analysis of the filtrate solution obtained after purification confirmed the dissociation of only Te species (no Cd signal was evident) from the nanocrystals (results not shown),

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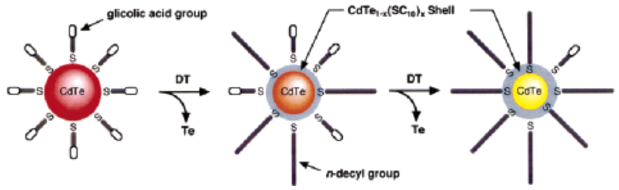

Figure 3. Schematic diagram of the proposed process for band gap engineering of CdTe nanocrystals.

Table 1. Atomic Contents of Purified Nanocrystals Obtained after Various Reaction Times[a]

reaction time/h	S (%)	Cd (%)	Te (%)	(S + Te)/Cd (–)
0	26.1	43.4	30.5	1.30
0.25	28.7	44.3	27.0	1.26
0.5	29.5	43.5	27.0	1.30
1.0	34.4	43.5	22.1	1.30
2.0	42.1	43.5	14.4	1.30
5.0	43.2	43.9	13.0	1.28

[a] The final concentrations in the reaction solution for these data were 32 μM and 38.4 mM for CdTe nanocrystals and DT, respectively.

which is consistent with the EDX results. Third, the S 2p XPS spectrum for the purified nanocrystals is similar in form to that of the initial nanocrystals (Figure S3) and indicates that S is in the form of decanethiolate (SC$_{10}$) rather than a metal sulfide such as CdS$_x$.

From the above results, we conclude that the process includes exchange of Te species with DT molecules in a 1:1 stoichiometric manner.[17] This selective exchange likely occurs at the nanocrystal surface, possibly generating thin CdTe$_{1-x}$(SC$_{10}$)$_x$ shells. The growth of this shell leads to a corresponding decrease in the size of the inner CdTe "core", as schematically shown in Figure 3. From these considerations, we propose that the observed blue shift arises from a decrease in the region that dictates the optical properties of the resulting nanocrystals, that is, the CdTe core within the nanocrystals, while the unknown CdTe$_{1-x}$(SC$_{10}$)$_x$ shell is generated to maintain the apparent nanocrystal size. Our proposed model is consistent with the aforementioned analytical results and is supported by basic calculations.[18]

Significantly, the reaction does not occur in an inert atmosphere. Moreover, after partial modification of the nanocrystals with DT (reaction time: 3 h) followed by purification using acetonitrile, a further blue shift was not observed when adding only DT or TOAB in air but was observed when adding both species (Figure S4), indicating that dissolved oxygen, TOAB, and DT are requisite in the reaction. Although it is not yet clear which components play the major roles in the reaction, the process could be mediated by cooperative behavior that includes selective dissociation of Te species, which can be oxidized by dissolved oxygen,[19] from nanocrystal surface and simultaneous attachment of DT at the defect site thus formed. The fact that the crystal structure of the cubic zinc blend and the mean diameter of the nanocrystals remained unchanged (Figure S2) supports this idea. This mechanism is also consistent with the process depicted in Figure 3, in which the key factors are shell formation and a corresponding decrease in the size of the "luminescent cores" of the nanocrystals. Significantly, a similar trend was observed for other alkanethiols (e.g., hexanethiol, octadecanethiol, and benzyl mercaptan; Figure S5) and for smaller nanocrystals (Figure S6), indicating the generality of the process. Further experimental study to explore the mechanism in detail is currently underway.

In conclusion, we achieved kinetic control of the optical properties of CdTe nanocrystals by simple chemical surface modification using alkanethiol molecules at room temperature. This process could offer an attractive alternative to conventional synthetic strategies, providing a new band gap engineering scheme for nanocrystals as well as unique opportunities in the design of ligand-stabilized semiconductor nanocrystals with tunable composition and optical properties.

Supporting Information Available: Experimental details, FT-IR spectra of purified nanocrystals, TEM images, XPS data, and results for partially surface-modified nanocrystals and reaction with alternative alkanethiols and smaller nanocrystals. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. *Nature* **1997**, *389*, 699−701. (b) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013−2016. (c) Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S.; Banin, U. *Science* **2002**, *295*, 1506−1508. (d) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425−2427. (e) Coe, S.; Woo, W.; Bawendi, M.; Bulovic, V. *Nature* **2002**, *420*, 800−803. (f) Pardo-Yissar, V.; Katz, E.; Wasserman, J.; Willner, I. *J. Am. Chem. Soc.* **2003**, *125*, 622−623. (g) Wang, Y.; Tang, Z.; Correa-Duarte, M. A.; Liz-Marzán, L. M.; Kotov, N. A. *J. Am. Chem. Soc.* **2003**, *125*, 2830−2831. (h) Pinaud, F.; King, D.; Moore, H.; Weiss, S. *J. Am. Chem. Soc.* **2004**, *126*, 6115−6123.

(2) Pradhan, N.; Efrima, S. *J. Am. Chem. Soc.* **2003**, *125*, 2050−2051.

(3) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−8715.

(4) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc*. **2001**, *123*, 183−184.

(5) Rogach, A. L.; Nagesha, D.; Ostrander, J. W.; Giersig, M.; Kotov, N. A. *Chem. Mater.* **2000**, *12*, 2676−2685.

(6) Rogach, A. L.; Katsikas, L.; Kornowski, A.; Su, D.; Eychmuller, A.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 1772−1778.

(7) Zhang, H.; Zhou, Z.; Yang, B.; Gao, M. *J. Phys. Chem. B* **2003**, *107*, 8−13.

(8) Torimoto, T.; Kontani, H.; Shibutani, Y.; Kuwabata, S.; Sakata, T.; Mori, H.; Yoneyama, H. *J. Phys. Chem. B* **2001**, *105*, 6838−6845.

(9) Torimoto, T.; Reyes, J. P.; Iwasaki, K.; Pal, B.; Shibayama, T.; Sugawara, K.; Takahashi, H.; Ohtani, B. *J. Am. Chem. Soc.* **2003**, *125*, 316−317.

(10) Reiss, P.; Bleuse, J.; Pron, A. *Nano Lett.* **2002**, *2*, 781−784.

(11) Manna, L.; Scher, E. C.; Li, L.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2002**, *124*, 7136−7145.

(12) Bailey, R. E.; Nie, S. *J. Am. Chem. Soc.* **2003**, *125*, 7100−7106.

(13) Gaponik, N.; Talapin, D. V.; Rogach, A. L.; Eychmuller, A.; Weller, H. *Nano Lett.* **2002**, *2*, 803−806.

(14) Wuister, S. F.; Swart, I.; Driel, F.; Hickey, S. G.; Donega, C. M. *Nano Lett.* **2003**, *3*, 503−507.

(15) Yao, H.; Momozawa, O.; Hamatani, T.; Kimura, K. *Chem. Mater.* **2001**, *13*, 4692−4697.

(16) Using a single-exponential function, we obtained a rate constant $k_{obs} = 1.0 \pm 0.1$ h^{-1} ($t_{1/2} = 0.69$ h) for nanocrystals with an initial size of 3.3 nm. Nanocrystals with an initial size of 2.8 nm gave effectively the same rate constant ($k_{obs} = 1.1 \pm 0.1$ h^{-1}, $t_{1/2} = 0.64$ h). These results imply that the reaction does not depend on initial nanocrystal size (and therefore relative surface area) because the reaction is performed with an excess of DT relative to CdTe nanocrystals in the solution.

(17) To characterize single nanocrystals, we performed nanobeam EDX analysis using a 3-nm electron beam spot for TEM observation. The composition of single nanocrystals was broadly consistent with the average composition obtained by EDX analysis in FESEM observation (Table 1). These results also gave direct evidence of Te dissociation from the nanocrystals and S incorporation into the nanocrystals.

(18) Assuming that our model is relevant, we roughly estimated the CdTe core size obtained after reaction with DT for 5 h using the data shown in Table 1 and the unit cell volume of cubic CdTe nanocrystals (0.27 nm^3). The initial 3.3-nm CdTe nanocrystal has ca. 276 Te atoms. EDX analysis reveals that ca. 57% Te is dissociated after reaction for 5 h (Table 1), which indicates that ca. 117 Te atoms remain in the CdTe core. This implies formation of CdTe cores with a diameter of 2.5 nm, which reasonably accounts for the emission peak wavelength of the nanocrystals obtained 5 h after reaction (520 nm). Since the estimated core size indicates a shell thickness of ca. 4 Å and the lattice constant of cubic CdTe is 6.5 Å, it is considered that only the outermost Te ions dissociate to achieve the final core size of 2.5 nm. When the outermost Te species are almost completely exchanged with DT, the DT layers thus formed may prevent further dissociation of Te from the core so that the reaction is terminated, resulting in saturation of the spectral blue shift.

(19) This reaction did not work for CdSe nanocrystals. This may be due to the relative stability of Se towards oxidation. We believe that the present process is due to the inherent instability of Te anions, which can be readily oxidized by dissolved oxygen (ref 6).

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