Quantum dots–ionic liquid hybrids: efficient extraction of cationic CdTe nanocrystals into an ionic liquid†

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Water soluble CdTe nanocrystals covered with cationic thiol derivatives are efficiently transferred into a hydrophobic ionic liquid, in which they show enhanced photoluminescence.

Semiconductor nanocrystals,[1] also referred to as quantum dots (QDs), have attracted much attention as highly luminescent nanomaterials whose applications range from biological labels[2] to optoelectronics.[3] Luminescent QDs of metal chalcogenides are successfully prepared either in aqueous medium[4] or *via* organometallic routes.[5] While the former method gives water soluble QDs, the latter gives lipophilic ones. The solubility of QDs depends mainly on the nature of the organic protecting layer covering the QDs surface. Several approaches, such as encapsulation with surfactants or exchange of protecting molecules, have been used to make the water soluble QDs hydrophobic[6] and *vice versa*.[7] Such surface-modifications sometimes adversely affect their photophysical properties.

Room-temperature ionic liquids are receiving much interest as environmentally benign solvents for organic chemical reactions[8] and separations,[9] and recent developments include their use for materials chemistry.[10] Since ionic liquids have been also investigated as the electrolytes[11] for dye-sensitized solar cells and light-emitting electrochemical devices, the QD–ionic liquid hybrids are among the most promising materials for future optoelectronic applications. We describe herein an efficient extraction of cationic CdTe nanocrystals prepared by an aqueous synthetic approach into a hydrophobic ionic liquid. Characteristic enhancement in photoluminescence of CdTe nanocrystals in the ionic liquid are reported for the first time.

Water soluble cationic CdTe nanocrystals whose surface is passivated with 2-(dimethylamino)ethanethiol hydrochloride were synthesized by following the literature procedure.[4a] The size of the CdTe nanocrystals was *ca.* 2.5 nm as determined by TEM observation. 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide[11a] was employed as a water immiscible ionic liquid. Addition of an aqueous solution of cationic CdTe nanocrystals onto an ionic liquid of equivolume resulted in phase separation and the fluorescent aqueous layer was on top of the colorless ionic layer. The CdTe nanocrystals were immediately extracted from the water into the ionic liquid upon stirring for several minutes. The emission from the aqueous layer disappeared and the ionic phase became emissive after the extraction. The ionic phase was then subjected to spectroscopic measurements after separation from the mixture and drying *in vacuo*.

Fig. 1 shows the absorption and photoluminescence spectra of the aqueous and ionic liquid phases before and after the extraction. The absorption band at 520 nm observed in the water phase completely transferred to the ionic liquid and the distribution ratio of the CdTe nanocrystals is larger than 10^4. No noticeable change was observed between the absorption spectra of the nanocrystals in either phase (Fig. 1a). The size of CdTe nanocrystals therefore seems to be unchanged during the extraction. In addition, neither precipitation nor degradation of CdTe nanocrystals was observed in the ionic liquid even after centrifugation at 13,000 rpm, and the dispersion was stable for more than three months. These results clearly indicate that effective protection of the CdTe nanocrystal surface with cationic thiol derivatives is maintained in the ionic liquid. Since the extraction of nanocrystals presumably occurs *via* a simple cation-exchange process[9b] at the water–ionic liquid interface, the extraction process has little effect on the surface.

Interestingly, the photoluminescence intensity of CdTe nanocrystals was markedly enhanced in ionic liquid in comparison with that in aqueous solution. The photoluminescence quantum yields (ϕ_f) in water (n = 1.333) and that in the ionic liquid (n = 1.427) were estimated to be 16% and 27%, respectively. In these

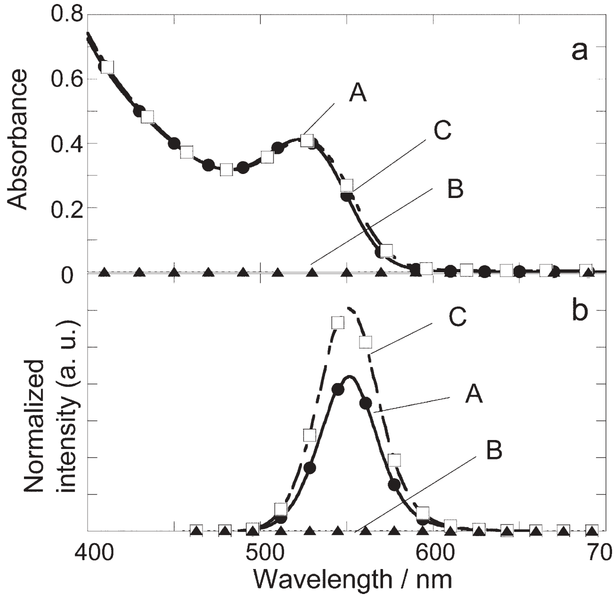

Fig. 1 Absorption (a) and emission (b) spectra of CdTe nanocrystals in water before (A) and after (B) extraction, and those in the ionic liquid after extraction (C) (λ_{ex} = 450 nm).

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† Electronic supplementary information (ESI) available: Photoluminescence spectra of three different sized CdTe nanocrystals in the ionic liquid. See http://www.rsc.org/suppdata/cc/b4/b418001a/

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evaluation, rhodamine 6G was used as the standard sample (ϕ_f = 95%) and the relative integrated emission intensity was corrected by the square of the refractive index of the medium. The emission properties of the CdTe nanocrystals were also studied with time-resolved photoluminescence measurements by using an ultra-short pulse laser (Δt = 80 fs, $\lambda \sim$ 400 nm). The numerical fitting of the emission decay profiles indicated dual exponential kinetics with time constants of τ_1 = 0.95 ns (A_1 = 0.41) and τ_2 = 7.5 ns (A_2 = 0.59) in the aqueous solution and those of τ_1 = 0.93 ns (A_1 = 0.42) and τ_2 = 9.3 ns (A_2 = 0.58) in the ionic liquid. Since the absorption spectra of CdTe nanocrystals in both media agreed well, rate constant of direct emission, k_{em}, might not be affected by the medium. Therefore, these changes in the emission properties are attributed to the suppression of quenching processes in the ionic liquid. On the basis of a simple two-state model, the photoluminescence quantum yield ϕ_f is expressed by the product of the emission rate constant and the photoluminescence lifetime, $\phi_f = \tau_{em} \times k_{em}$. This model seems to be oversimplified for the present case, since the change of ϕ_f upon extraction from the aqueous solution to the ionic liquid was considerably larger than that of the emission lifetime. Ha *et al.*[12] have recently proved that the dissociation of surface protecting thiolate from CdSe nanocrystals causes loss of emission quantum yield. Since thiolate anions cannot be hydrated in the ionic liquid and should be much more unstable than in aqueous solution, dissociation of thiolate anions seems to be much suppressed in the ionic liquid, resulting in improved photoluminescence properties.

We expected that the ionic liquid stabilizes the surface protecting layer and makes the CdTe nanocrystals fatigue resistive even under light irradiation. Fig. 2 shows the degradation behavior of the photoluminescence intensity of the CdTe nanocrystals upon UV light irradiation. In these measurements, the samples were irradiated with an ultra high pressure Hg lamp (150 W) through a UV pass filter (λ = 313–365 nm). The irradiation power was about 0.2 mW cm^{-2}. The photoluminescence intensity of the CdTe nanocrystals in the aqueous solution decreased gradually with irradiation time, while an almost constant intensity was observed in the ionic liquid under the same conditions. The decrease in photoluminescence intensity can be attributed to either a loss of CdTe nanocrystals or the generation of quenching centers such as surface defects formed by dissociation of thiolate groups. Cleary, in the ionic liquid, the organic layer effectively protects the CdTe-core from light-induced decomposition or the generation of surface defects.

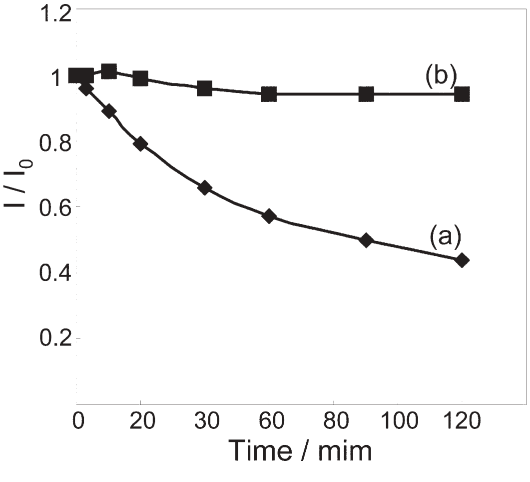

Fig. 2 Relative photoluminescence intensity (I/I_0) of CdTe nanocrystals as a function of irradiation time in water (a) and in the ionic liquid (b).

Although higher preparation temperatures of QDs is effective for enhancing photoluminescence intensity, the preparation temperature of water-soluble CdTe nanocrystals was limited by the boiling point of water.[4] We thus studied effects of heat treatment in the ionic liquid on the photoluminescence properties of CdTe nanocrystals, since ionic liquids are stable at much higher temperatures. Fig. 3a shows the changes in the absorption and emission spectra of CdTe nanocrystals in ionic liquid after heat-treatment. In these experiments, the nanocrystal–ionic liquid composite was heated at 120 °C for different periods. The heat-treatment resulted in marked red-shifts in the emission peaks, which suggests growth in the effective size of the nanocrystals though there was no Cd and Te source in the medium. The nanocrystal size can be evaluated from the absorption peak wavelength to be 1.7 nm and 2.4 nm in the A and C states in Fig. 3b, respectively. Moreover, the photoluminescence intensity significantly enhanced from ϕ_f = 11% (A) to ϕ_f = 43% (C) after heat-treatment for 4 h. It should be noted that the original CdTe nanocrystals showed relatively weaker photoluminescence emission at 520 nm with ϕ_f = 11% than the sample discussed in Fig. 1 whose emission wavelength was about 550 nm. Another sample also showed significant improvement in the emission properties, which exhibited a photoluminescence quantum yield as high as ϕ_f = 54% after heat treatment in the ionic liquid. It should be also noted that the full width at half maximum (FWHM) of the emission profile decreased after the heat-treatment as can be seen in Fig. 3a. Therefore, the average and the distribution of the size of the nanocrystals seem to be changed upon heat-treatment. Since the surface ordering and reconstruction of CdTe nanocrystals should take place at high temperature, heat treatment in the ionic liquid is regarded as being responsible for the partial growth of the nanocrystals and correction of the imperfections in the nanocrystal structure. Although a detailed mechanism is now under consideration, the present findings may provide a conventional but effective method for improving the photoluminescence properties of CdTe nanocrystals.

In conclusion, we have demonstrated an efficient introduction method of water soluble CdTe nanocrystals into an ionic liquid and their improved emission properties in the ionic liquid. The

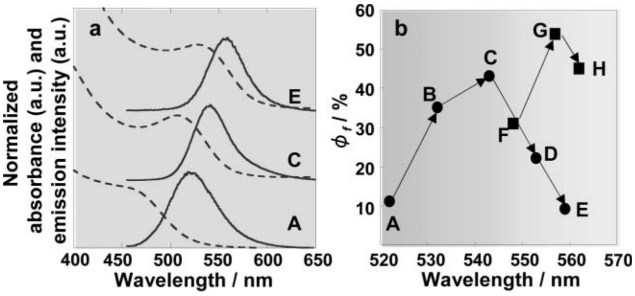

Fig. 3 Effects of heat treatment on the photoluminescence of two CdTe nanocrystal samples in the ionic liquid. (a) Absorption and photoluminescence spectra before and after heat treatment. (b) Temporal evolution of ϕ_f and emission peak wavelength. A, 0 h; B, 1 h; C, 4 h; D, 8 h; E, 10 h; F, 0 min; G, 15 min; H, 60 min.

phase transfer behavior of CdTe nanocrystals was independent of their size (see ESI †data). A remarkable enhancement in photoluminescence intensity was demonstrated by heat-treatment in the ionic liquid. Since ionic liquids are easily solidified by thermal polymerization[13] or by gelation,[10a,11b] the QD–ionic liquid hybrids seem to play a considerable part in future optoelectronic devices such as solar cells and light emitting devices.

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Notes and references

1 A. P. Alivisatos, *J. Phys. Chem.*, 1996, **100**, 13226.
2 A. P. Alivisatos, *Nature Biotechnol.*, 2004, **22**, 47.
3 (*a*) Y. I. Klimov, A. A. Mikhailovsky, S. Xu, A. Malko, J. A. Hollingsworth, C. A. Leatherdale, H.-J. Eisler and M. G. Bawendi, *Science*, 2000, **290**, 314; (*b*) S. Coe, W.-K. Woo, M. Bawendi and V. Bulovic, *Nature*, 2002, **420**, 800.
4 (*a*) N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmuller and H. Weller, *J. Phys. Chem. B*, 2002, **106**, 7177; (*b*) H. Zhang, L. Wang, H. Xiong, L. Hu, B. Yang and W. Li, *Adv. Mater.*, 2003, **15**, 1712; (*c*) S. Kuwabata, K. U. Sarson and T. Torimoto, *Chem. Lett.*, 2004, **33**, 1344.
5 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
6 (*a*) D. G. Kurth, P. Lehmann and C. Lesser, *Chem. Commun.*, 2000, 949; (*b*) H. Zhang, Z. Cui, Y. Wnag, K. Zhang, X. Ji, C. Lu, B. Yang and M. Gao, *Adv. Mater.*, 2003, **15**, 777; (*c*) N. Gaponik, D. V. Talapin, A. L. Rogach, A. Eychmuller and H. Weller, *Nano Lett.*, 2002, **2**, 803.
7 S. F. Wuister, I. Wart, F. van Driel, S. G. Hickey and C. de Mello Donega, *Nano Lett.*, 2003, **3**, 503.
8 R. Sheldon, *Chem. Commun.*, 2001, 2399.
9 (*a*) A. E. Visser, R. P. Swatloski and R. D. Rogers, *Green Chem.*, 2000, **2**, 1; (*b*) M. L. Dietz and J. A. Dzielawa, *Chem. Commun.*, 2001, 2124.
10 (*a*) N. Kimizuka and T. Nakashima, *Langmuir*, 2001, **17**, 6759; (*b*) T. Nakashima and N. Kimizuka, *J. Am. Chem. Soc.*, 2003, **125**, 6386; (*c*) M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem. Int. Ed.*, 2004, **43**, 4988.
11 (*a*) P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168; (*b*) P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar and M. Grätzel, *J. Am. Chem. Soc.*, 2003, **125**, 1166; (*c*) C. Yang, Q. Sun, J. Qiao and Y. Li, *J. Phys. Chem. B*, 2003, **107**, 12981.
12 S. Hohng and T. Ha, *J. Am. Chem. Soc.*, 2004, **126**, 1324.
13 M. Yoshizawa and H. Ohno, *Electrochim. Acta*, 2001, **46**, 1723.