Highly Luminescent CdTe Nanocrystal–Polymer Composites Based on Ionic Liquid

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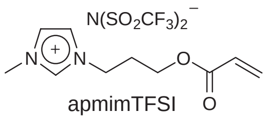
Water-soluble CdTe nanocrystals passivated with thiocholine bromide are efficiently incorporated into an acrylate-functionalized ionic liquid with the enhancement of photoluminescence, which gives an optically clear and highly luminescent polymer composite by polymerization of the ionic liquid.

Semiconductor nanocrystals, also referred to as quantum dots (QDs), have attracted much attention in the past few decades.[1] Recent progress in the chemical synthesis of highly luminescent QDs[2,3] explores their extensive uses for the biological probes[4,5] and makes their practical uses possible such as for light-emitting materials[6,7] as well as sensitizer in solar cells.[8,9] Considerable efforts have been made to embed the luminescent QDs into solid polymer matrices[10,11] for practical applications. In order to improve compatibility of QDs with polymeric matrices long-alkyl-chained lauryl methacrylate (LMA) which dissolves lipophilic QDs well have been employed as a monomer.[10] The hydrophobic (CdSe)ZnS QDs composites with PLMA after the polymerization showed relatively high photoluminescence (40% in quantum yield) in the presence of excess tri-*n*-octylphosphine (TOP). While these lipophilic QDs have been prepared by TOP/TOPO (tri-*n*-octylphosphine oxide) method, complicated procedure at high temperature,[2] water-soluble QDs are recently being prepared by simple and safer aqueous synthetic route.[3] Incorporation of the water-soluble CdTe QDs into conventional monomers such as styrene and methyl methacrylate was achieved by using vinyl-functionalized surfactants as a surface modifier.[11] Such surface-modifications may adversely affect QDs photophysical properties and there has been no report on the incorporation of water-soluble QDs into polymeric matrices without cost of luminescence properties.

We have recently reported the complete extraction of water-soluble CdTe nanocrystals into a hydrophobic ionic liquid and the remarkable enhancement of photoluminescence in the ionic liquid.[12] Hydrophobic nature of the ionic liquid is anticipated to suppress dissociation of thiolate anion from the QDs surface and to enhance emission efficiency. On the basis of these results, the polymers prepared from ionic liquid-based monomers are expected to be potential candidate as a matrix of luminescent QD-polymer materials. We describe herein the incorporation of cationic CdTe nanocrystals passivated with thiocholine bromide (TCB)[13,14] into polymer matrices by use of an acrylate-functionalized ionic liquid[15] for the first time.

Water-soluble TCB-capped cationic CdTe nanocrystals were synthesized by the aqueous synthetic method.[3] The photoluminescence quantum yields (ϕ_{PL}), which were determined by using rhodamine 6G as a reference ($\phi_f = 95\%$ in ethanol), ranged from 4 to 28% depending on the preparation condition and their sizes estimated from the excitonic absorption peaks.[3] We then investigated the optical properties of the CdTe nanocrystals in an ionic liquid-based monomer. 1-(3-acryloyloxypropyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (apmimTFSI, Scheme 1)[15] was employed as a polymerizable ionic liquid. Addition of an aqueous solution of the CdTe nanocrystals onto apmimTFSI of equivolume resulted in phase separation and the fluorescent aqueous layer covered over the colorless ionic layer. The TCB capped-CdTe nanocrystals were immediately extracted from water to apmimTFSI upon stirring. The degree of extraction was almost 100%. Figure 1 shows the typical absorption and photoluminescence spectra of the CdTe nanocrystals in water and in apmimTFSI before and after the extraction, respectively. The absorption spectrum of CdTe nanocrystals in apmimTFSI almost traced the original one in the water phase, while the photoluminescence intensity of CdTe nanocrystals remarkably increased in apmimTFSI. This result is consistents with the observations in the previous report.[12] Threfore the apmim$^+$ seems to hardly affect the extraction procedure. The ϕ_{PL} values in water and in apmimTFSI were 28 and 67%, respectively. The enhancement of photoluminescence in apmimTFSI was independent of their size (see Supporting Information).



Scheme 1.

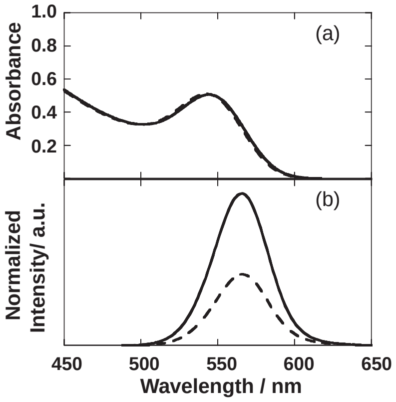


Figure 1. Typical absorption (a) and photoluminescence (b) spectra of CdTe nanocrystals in water (dashed lines) and in apmimTFSI (solid lines). (estimated size = 3.2 nm, λ_{ex} = 450 nm).

Because the both absorption and emission peak maxima almost unchanged in any samples, the marked enhancement in emission intensity should be attributed to the specific suppression of quenching process in apmimTFSI. In water, the dissociation of TCB from the QDs surface and efficient solvation of the thiolate anions would cause the insufficient protection of the nanocrystal and the formation of localized electronic surface states, which would lead to the relatively low ϕ_{PL} in water.[16] The electrostatic repulsion between the TCB molecules on a QD may also take a considerable place in the destabilization of protecting layer.[14] On the other hand, ionic liquids have extremely high salt concentration ($\approx$7 M in ions) which suppresses the Coulombic repulsion between the ammonium groups, resulting in the efficient protection of the QDs surface with TCB. In addition, the dissociation of thiolate anions from the nanocrystal surface seems to be much suppressed because they are less solvated and less stabilized in ionic liquids.[12] These effects should cooperatively contribute to the considerable improvement of CdTe nanocrystals photoluminescence in the ionic liquid.

The apmimTFSI-CdTe nanocrystal mixtures were then converted to the polymer composites by azobisisobutyronitrile (AIBN)-initiated radical polymerization with diethyleneglycol dimethacrylate as a cross-linker. Neither aggregation of nanocrystals nor phase separation was observed during the polymerization, providing optically clear materials (Figure 2a). Each solid sample in Figure 2b shows strong photoluminescence under the irradiation with a UV lamp. Since both the emission intensity and the peak position almost unchanged during the polymerization (Figure 3), the reaction little affected the luminescence properties of CdTe nanocrystals. Thus, the CdTe–polymer composites maintain the high emission efficiencies as high as 67%, which is the highest value for the polymer composites of II-VI type semiconductor QDs so far reported.[10,11] The present approach to prepare luminescent nanocrystal–polymer composites should be extendedly applicable to more conventional polymers such as poly(methyl methacrylate), since the CdTe nanocrystal–apmimTFSI composite was also dissolved into methyl methacrylate without any degradation.

In summary, we have demonstrated an effective method for the fabrication of highly luminescent nanocrystal–polymer composites from water soluble CdTe nanocrystals by use of a polymerizable ionic liquid. The photoluminescence of TCB-capped CdTe nanocrystals was significantly enhanced and the emission quantum yield reached up to as high as 67% in apmimTFSI, which is among the highest value for the CdTe nanocrystals prepared via aqueous synthetic approach.[3] The luminescent properties was still maintained after the polymerization, giving highly luminescent polymer composites. It gives a simple and general route to the design of the semiconductor or metal nanoparticle-functionalized polymer composites.

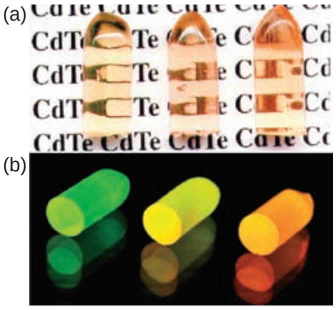


Figure 2. Color image of three transparent CdTe nanocrystal–polymer composites (a) and their luminescent image (b) excited by a UV lamp (365 nm). The concentration of nanocrystals was ca. 0.3 mg/mL.

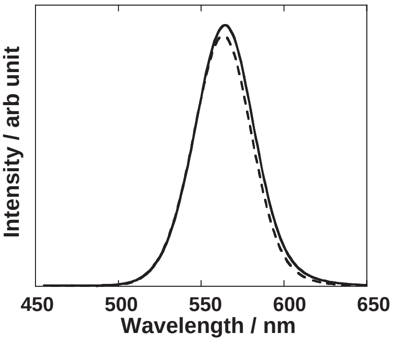


Figure 3. Spectral change in photoluminescence of the CdTe nanocrystal–apmimTFSI composite before (dashed line) and after (solid line) the polymerization. No marked change in the emission intensity was observed after the polymerization.

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References

1 A. P. Alivisatos, *Science*, **271**, 933 (1996); A. Eychmüller, *J. Phys. Chem. B*, **104**, 6514 (2000); K. Grieve, P. Mulvaney, and F. Grieser, *Curr. Opin. Colloid Interface Sci.*, **5**, 168 (2002).
2 C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.*, **115**, 8706 (1993); L. Qu and X. Peng, *J. Am. Chem. Soc.*, **124**, 2049 (2002).
3 T. Rajh, O. I. Mićić, and A. J. Nozik, *J. Phys. Chem.*, **97**, 11999 (1993); N. Gaponik, D. V. Talapin, A. L. Rogach, K. Hoppe, E. V. Shevchenko, A. Kornowski, A. Eychmüller, and H. Weller, *J. Phys. Chem. B*, **106**, 7177 (2002); H. Zhang, Z. Zhou, B. Yang, and M. Gao, *J. Phys. Chem. B*, **107**, 8 (2003); C. Li and N. Murase, *Chem. Lett.*, **34**, 92 (2005).
4 A. P. Alivisatos, *Nat. Biotechnol.*, **22**, 47 (2004).
5 W. C. W. Chan, D. J. Maxwell, X. Gao, R. E. Bailey, M. Han, and S. Nie, *Curr. Opin. Biotechnol.*, **13**, 40 (2002).
6 H. Mattoussi, L. H. Radzilowski, B. O. Dabbousi, E. L. Thomas, M. G. Bawendi, and M. F. Rubner, *J. Appl. Phys.*, **83**, 7965 (1998).
7 S. Coe, W.-K. Woo, M. G. Bawendi, and V. Bulovic, *Nature*, **420**, 800 (2002).
8 W. D. Huynh, J. J. Dittmer, and A. P. Alivisatos, *Science*, **295**, 2425 (2002).
9 R. Plass, S. Pelet, J. Krueger, M. Grätzel, and U. Bach, *J. Phys. Chem. B*, **106**, 7578 (2002).
10 J. Lee, V. C. Sundar, J. R. Heine, M. G. Bawendi, and K. F. Jensen, *Adv. Mater.*, **12**, 1102 (2000); N. Gaponik, D. V. Talapin, A. L. Rogach, A. Eychmüller, and H. Weller, *Nano Lett.*, **2**, 803 (2002).
11 B. H. Zhang, Z. Cui, Y. Wang, K. Zhang, X. Ji, C. Lü, B. Yang, and M. Gao, *Adv. Mater.*, **15**, 777 (2003); H. Zhang, C. Wang, M. Li, J. Zhang, G. Lu, and B. Yang, *Adv. Mater.*, **17**, 853 (2005).
12 T. Nakashima and T. Kawai, *Chem. Commun.*, **2005**, 1643.
13 T. Torimoto, M. Yamashita, S. Kuwabata, H. Mori, and H. Yoneyama, *J. Phys. Chem. B*, **103**, 8799 (1999).
14 T. Yonezawa, S. Onoue, and N. Kimizuka, *Chem. Lett.*, **2002**, 1172.
15 M. Yoshizawa and H. Ohno, *Electrochim. Acta*, **46**, 1723 (2001).
16 S. Hohng and T. Ha, *J. Am. Chem. Soc.*, **126**, 1324 (2004); J. Aldana, N. Lavelle, Y. Wang, and X. Peng, *J. Am. Chem. Soc.*, **127**, 2496 (2005).

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