Fluorescent Nanocrystal−Polymer Composites from Aqueous Nanocrystals: Methods without Ligand Exchange

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Fluorescent nanocrystal−polymer composites were prepared from aqueous CdTe nanocrystals via two related routes. Route 1 was summarized as CFP (coating followed by polymerization), coating CdTe nanocrystals with polymerizable surfactant of octadecyl-*p*-vinylbenzyldimethylammonium chloride (OVDAC), followed by the copolymerization of OVDAC-coated CdTe with radical monomers to achieve nanocrystal−polymer bulk composites. Route 2 was summarized as PFC (polymerization followed by coating), coating CdTe directly with the copolymers of OVDAC and styrene to achieve processable nanocrystal−polymer composites. Both of these two methods avoided the exchange of surface ligands of nanocrystals. Photoluminescence (PL) quenching from free radicals was observed in the CFP method, which depended strongly on both the size of the nanocrystals and the species of the thiol stabilizers. We attributed it to the distinct surface composition of each nanocrystal sample. With control of the surface composition of the nanocrystals, this PL quenching could be effectively avoided. The PFC method obviated handling nanocrystals in the polymerization process and thus the maximum PL was retained.

Introduction

Incorporation of fluorescent semiconductor nanocrystals with polymers has attracted great interest mainly due to the wide potentials of nanocrystal−polymer composites in optical displays, nonlinear optical devices, and biological encoding.[1−4] Based on the nature of nanocrystals, some incorporating methods have been successfully established.[1−8] The key to the incorporation is the ability to preserve the size monodispersity and the high photoluminescence (PL) of nanocrystals.[8] Superficially, the nanocrystals prepared by organometallic routes and their derivatives could be directly mixed with organic monomer for polymerization, but the resultant composites usually show bad transparency and poor fluorescence.[9] The barrier of this approach was the aggregation of nanocrystals in polymer matrixes resulting from the lack of covalent attachment. Functional groups have settled on the nanocrystal surface via ligand exchange for the subsequent copolymerization with monomers;[7−9] however, PL quenching was observed in the exchange process.[10] Besides the low cost of the preparation of nanocrystals in aqueous solutions,[11] functional groups, such as carboxyl, amido, and hydroxyl, could be directly modified on the nanocrystal surface during the preparation process that provided anchor points to achieve various hybrid structures.[12−15] This advantage also provided the opportunity for the preparation of nanocrystal−polymer composites from aqueous nanocrystals.[5]

It has been found that free radicals induced the PL quenching of semiconductor nanocrystals during the polymerization process.[16] This quenching was disadvantageous to obtain fluorescent composites with high PL intensity, especially for the microfabricated samples. This problem might be solved when aqueous nanocrystals were used to prepare nanocrystal−polymer composites. Previous reports have proved the presence of the complexes of cadmium ions and mercaptocarboxylic acids around CdTe nanocrystals and a thick shell of these complexes formed in the proper conditions.[17,18] This structure improved both the PL intensity and the PL stability

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of aqueous nanocrystals.[19] In this paper, fluorescent nanocrystal−polymer composites were prepared from aqueous CdTe nanocrystals via two related methods summarized as CFP and PFC. Although PL quenching was observed in CFP preparation, it could be effectively avoided by tuning the surface composition of CdTe. Maximum PL was retained by PFC preparation since handling nanocrystals in the polymerization process was obviated. With use of either of these two methods, aqueous nanocrystals were proved to be a good choice for the preparation of nanocrystal−polymer composites.

Experimental Section

Materials. *N*,*N*-Dimethyloctadecylamine, 4-vinylbenzyl chloride, styrene, azobisisobutyronitrile (AIBN), 3-mercaptopropionic acid (MPA), thioglycolic acid (TGA), thiolactic acid (TLA), mercaptosuccinic acid (MSA), $CdCl_2$, $NaBH_4$, and tellurium powder are commercially available products.

Preparation of Nanocrystals. Mercaptocarboxylic acid-stabilized CdTe nanocrystals were prepared in aqueous solution according to the previous reports.[18,20] Typically, freshly prepared NaHTe solution was added to N_2-saturated $CdCl_2$ solution at pH 9.0 in the presence of mercaptocarboxylic acids (TGA, MPA, TLA, or MSA) as stabilizing agents to achieve CdTe precursors. The precursor was maintained at the desired temperature either by reflux or by hydrothermal conditions that controlled the growth of nanocrystals.[18,20,21]

Synthesis of Polymerizable Surfactant and Alkylammonium-Functional Polymer (AFCP). Polymerizable surfactant of octadecyl-*p*-vinylbenzyldimethylammonium chloride (OVDAC) was prepared according to the following procedure: a mixture of *N*,*N*-dimethyloctadecylamine (4.2 mL, 10 mmol) and 4-vinylbenzyl chloride (1.87 g, 11 mmol) in acetone (5 mL) was refluxed at 40 °C for 2 h. The cold mixture was washed with acetone and the volatiles were removed in vacuo. The copolymerization of styrene and OVDAC was performed in the presence of AIBN in an oil bath at 72− 74 °C for 30 h.[22] Typically, 1 g of OVDAC was dissolved in 1 mL of styrene for bulk polymerization, and the concentration of OVDAC unit in the copolymer is around 20% ($M_W = 5000$).

CFP Preparation. OVDAC-coated CdTe nanocrystals and nanocrystal−polymer composites were prepared according to our previous method.[5] OVDAC was dissolved in styrene at a concentration of 2 mg mL^{-1}. Ten milliliters of OVDAC styrene solution was added to 20 mL of CdTe aqueous solution (0.00125 N according to Cd^{2+}) under vigorous stirring. The pH of parent CdTe aqueous solution was adjusted to the desired value before each OVDAC coating. The styrene phase was then separated and polymerized in a glass tube in an oil bath at 72−74 °C for 30 h using 20 mg of AIBN as initiator. Then, transparent CdTe−polystyrene composites were obtained. The concentration of the inorganic CdTe nanocrystals, embedded in polymer composites, was characterized by thermogravimetric analysis. The concentration in the composites could be up to 3 wt %.

PFC Preparation. AFCP was dissolved in dichloromethane solution at a concentration of 5 mg mL^{-1}. Ten milliliters of AFCP solution was added to 20 mL of CdTe aqueous solution (0.00125 N according to Cd^{2+}) under vigorous stirring. The organic phase was then separated to yield the solution of CdTe−AFCP composites that were used for the fabrication of macroscopic shapes, patterned structure, and microspheres.[23,24]

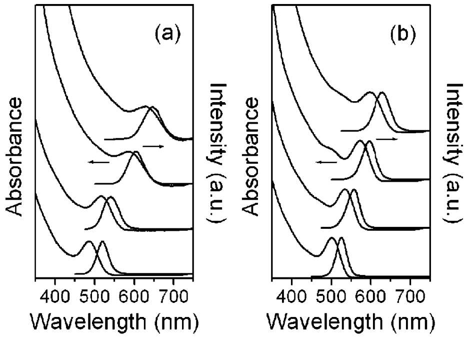

Figure 1. Temporal evolution of UV−vis absorption and PL spectra of CdTe nanocrystals stabilized by 3-mercaptopropionic acid (MPA) (a) and thioglycolic acid (TGA) (b).

Characterization. UV−visible transmission spectra were recorded by using a Shimadzu 3100 UV−Vis−near-IR spectrophotometer. Fluorescence experiments were performed with the help of a Shimadzu RF-5301 PC spectrofluorimeter. X-ray powder diffraction was carried out using a Siemens D5005 diffractometer. X-ray photoelectron spectroscopy was performed on a VG ESCALAB MK II spectrometer with Mg Kα excitation (1253.6 eV). FTIR spectra were performed with a Nicolet AVATAR 360 FTIR instrument. Thermogravimetric analysis was performed on a Mettler Netzsch STA 449C thermoanalysis instrument. Analyses were carried out under N_2 flow in the range of 30−800 °C with a heating rate of 20.0 °C/min. An Olympus BX-51 fluorescence microscope was used to examine the composite microspheres. Specimens were excited using ultraviolet source.

Results and Discussion

Evolution of Surface Composition of Aqueous CdTe Nanocrystals. Figure 1 presents the temporal evolution of UV−vis absorption and PL spectra of 3-mercaptopropionic acid (MPA) and thioglycolic acid (TGA)-stabilized CdTe nanocrystals. Both of them show quantum size effect.[25,26] With the prolonged thermal growth, the size of nanocrystals increased and respective green, yellow, orange, or red emission was obtained. Annulus complexes of cadmium ions and mercaptocarboxylic acids also formed around the CdTe core during nanocrystal growth.[17] The evolution of these complexes involved the following three stages: fast deposition, deposition balance, and thermal decomposition of the complexes. As shown in Figure 2, the size-dependent elementary composition of MPA-stabilized CdTe nanocrystals was analyzed by X-ray photoelectron spectroscopy. Since MPA was the only S source, the change of S/Te ratio would indicate the evolution of surface composition of nanocrystals.[17,18,27] At the initial stage of nanocrystal growth, a fast deposition rate of Cd−MPA complexes was observed. CdTe

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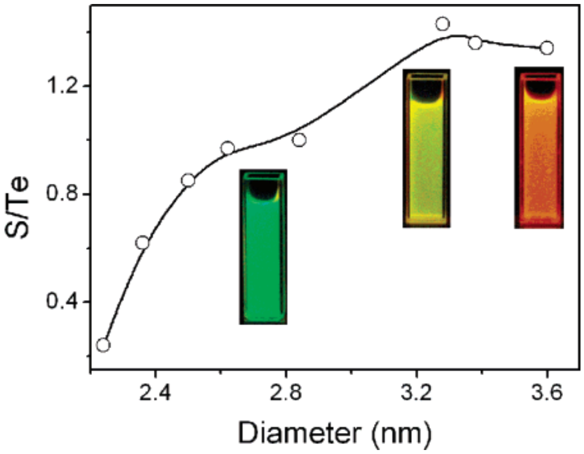

Figure 2. S/Te vs diameter curves of MPA-stabilized CdTe nanocrystals obtained by X-ray photoelectron spectroscopy characterization. The fluorescent images correspond to differently sized CdTe nanocrystals.

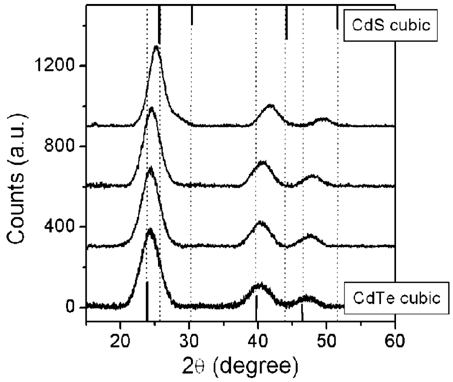

Figure 3. X-ray diffraction (XRD) patterns of differently sized CdTe nanocrystals stabilized by MPA. From lower to upper, the diameters of the nanocrystals are 2.5, 3.2, 3.6, and 4.0 nm, respectively.

nanocrystals only had a thin layer of the complexes and corresponded to nanocrystal samples with green emission. A nearly zero deposition rate was observed when the complexes reached a certain thickness that corresponded to nanocrystal samples with yellow or orange emission. Figure 3 presents the X-ray diffraction (XRD) patterns from MPA-stabilized CdTe nanocrystals with different diameter. The lattice parameters of CdTe nanocrystals that were prepared with a short growth time fitted well to the cubic zinc blende structure of bulk CdTe crystal.[26] However, a shift of XRD peak positions toward cubic CdS crystal was observed for the samples with prolonged growth time that indicated the decomposition of the annulus complexes and the incorporation of S element into the nanocrystals.[11]

From aforementioned results, it was understandable that differently sized CdTe nanocrystals also possessed different surface composition. CdTe nanocrystals with typical green emission (around 530 nm) were partially capped by Cd−MPA complexes, while yellow, orange, and especially red samples were well-capped. This difference would influence the PL stability of CdTe samples with different PL emission in the following polymerization process.

CdTe nanocrystal−polymer composites were prepared by two methods that were summarized as CFP (coating CdTe nanocrystals with polymerizable surfactant of OVDAC, followed by the copolymerization of OVDAC-coated CdTe with radical monomers) and PFC (coating CdTe directly with the copolymers of OVDAC and styrene). Instead of the exchange of surface ligands of nanocrystals, electrostatic interaction between negatively charged CdTe nanocrystals and a positively charged building block was the main driving force to achieve the desired structure. The preparation procedure of our strategies is summarized in Figure 4.

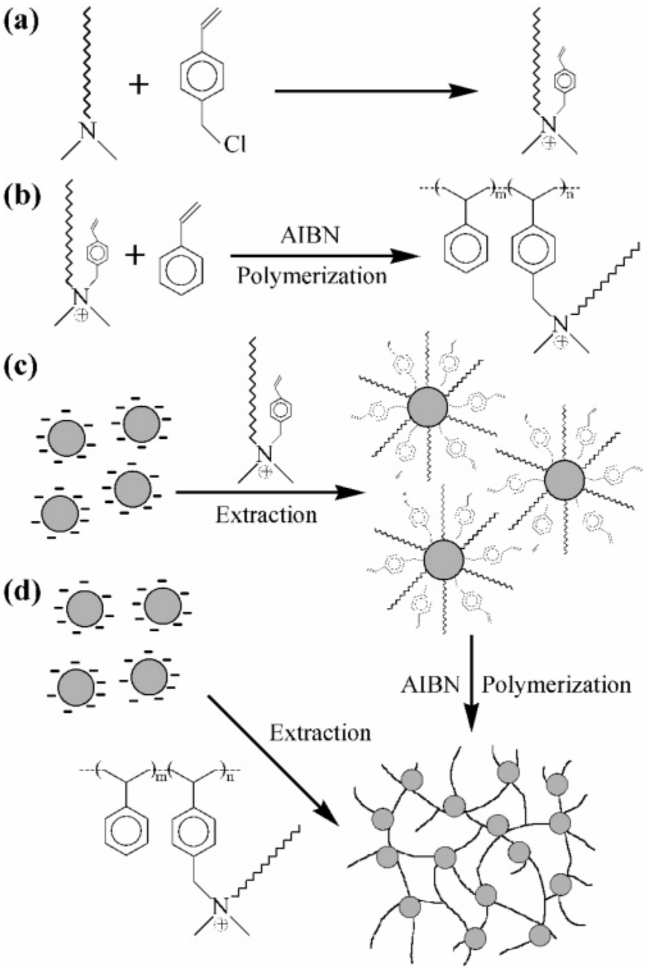

Figure 4. Schematic procedure for the preparation of CdTe nanocrystal−polymer composites: (a) Preparation of polymerizable surfactant of octadecyl-*p*-vinylbenzyldimethylammonium chloride (OVDAC); (b) preparation of alkylammonium-functional polymer (AFCP); (c) CFP method to nanocrystal−polymer composites, coating nanocrystals by OVDAC followed by copolymerization with styrene; (d) PFC method, coating nanocrystals directly using AFCP.

CFP Preparation. As shown in Figure 4a, polymerizable surfactant of OVDAC was prepared by the alkylation of *N*,*N*-dimethyloctadecylamine with 4-vinylbenzyl chloride. Negatively charged CdTe nanocrystals could be coated by positively charged OVDAC and transferred to organic monomers, such as styrene, for radical copolymerization to obtain nanocrystal−polymer composites (Figure 4c).

Figure 5 shows the FTIR spectra of OVDAC, MPA-stabilized CdTe nanocrystals, OVDAC-coated CdTe, and CdTe−polystyrene (PS) composites. For OVDAC, the strong absorption peaks at 2918, 2852, and 1475 cm^{-1} were assigned to the $-CH_2-$ vibration of alkyl chains in OVDAC. For MPA-stabilized CdTe nanocrystals, the weak absorption peaks at 2918 and 2852 cm^{-1} were also assigned to the $-CH_2-$ stretching vibration of MPA, while the absorption peaks at 1558 and 1394 cm^{-1} were assigned to the vibration

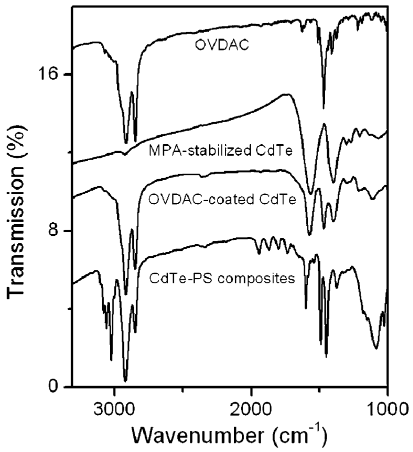

Figure 5. FTIR spectroscopy of OVDAC (a), MPA-stabilized CdTe nanocrystals (b), OVDAC-coated CdTe (c), and CdTe−PS composites (d).

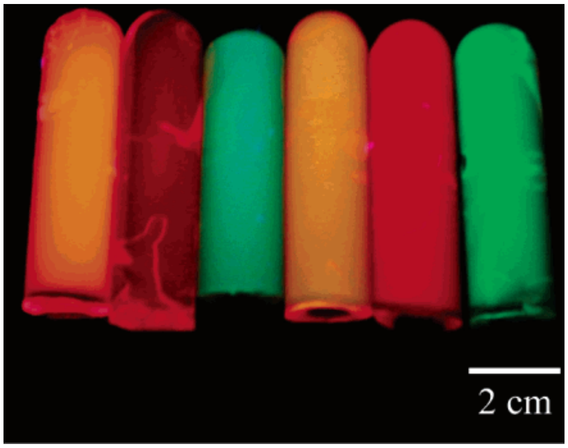

Figure 6. Fluorescent images of CdTe−PS composites excited by an ultraviolet lamp.

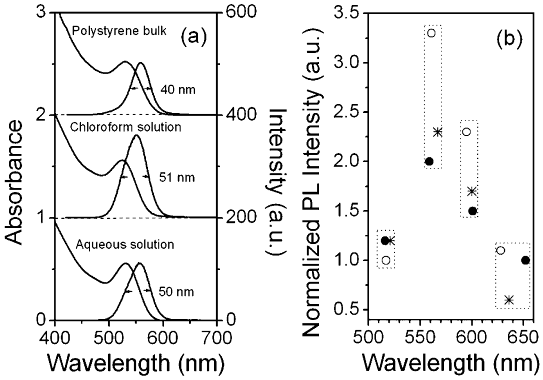

Figure 7. Typical change of the spectral properties of MPA-stabilized CdTe nanocrystals. (a) UV−vis absorption and normalized PL spectra of parent aqueous CdTe, OVDAC-coated CdTe in chloroform, and resultant polystyrene bulk. (b) The summary of PL intensity and PL peak positions of four CdTe samples with respectively green, yellow, orange, and red emission. PL intensity was normalized according to absorption spectra. The aqueous solution of green emitting CdTe was stored in the dark for more than 3 months before CFP preparation. (*) Parent aqueous CdTe, (○) OVDAC-coated CdTe in chloroform, and (●) CdTe−PS composites.

of carboxylate of MPA on the surface of CdTe. The surface-settled carboxylate groups provided an electrostatic interaction in the following OVDAC coating.[15] In this process, MPA-stabilized CdTe's were extracted from water to organic phase through OVDAC coating. After coating MPA-stabilized CdTe with OVDAC, the characteristic absorption peaks of both OVDAC (2918, 2852, and 1475 cm^{-1}) and MPA-stabilized CdTe (1558 and 1394 cm^{-1}) appeared in the spectrum that confirmed the successful coating of nanocrystals with OVDAC. Compared with pure PS, the CdTe−PS composites indicated an enhanced $-CH_2-$ vibration. This result suggested the existence of OVDAC-coated CdTe nanocrystals in the resultant composites. The fluorescent images and PL spectra of CdTe−PS composites firmly verified the existence of CdTe nanocrystals. As shown in Figure 6, CdTe nanocrystals with different emissions were successfully embedded in PS matrixes, and the resultant composites preserved the strong PL from parent nanocrystals.

The spectral change of CdTe nanocrystals in CFP preparation was monitored on a CdTe sample with an asymmetrical PL spectrum. As shown in Figure 7a, no obvious change of absorption spectra was found when CdTe nanocrystals were transferred from aqueous solution to chloroform. The increase of the apparent PL intensity of nanocrystals was attributed to the alteration of physicochemical environments that some disadvantageous effects of water were excluded.[28,29] The slight blue shift of PL peaks of CdTe in chloroform, compared with the corresponding peaks in water, resulted from the alteration of dielectric environments. The full-width at half-maximum (fwhm) of PL spectra for aqueous CdTe was 50 nm, and it was 51 nm for OVDAC-coated CdTe in chloroform. It meant the spectral properties of OVDAC-coated CdTe were mainly determined by the properties of aqueous nanocrystals. However, copolymerization of OVDAC-coated CdTe with styrene altered the PL spectra that could be apparently observed by the change of PL spectra from asymmetry to symmetry. Compared with OVDAC-coated CdTe, a drop of PL intensity was also observed in CdTe−PS composites that indicated the PL quenching occurred during the polymerization process (Figure 7a). The free radicals from initiator, generated in the polymerization process, should be the major cause of PL quenching.[16] Interestingly, this quenching was more serious for the nanocrystal fractions with extremely small and large sizes in the nanocrystal ensemble and made the fwhm more narrow (Figure 7a CdTe−PS bulk). It suggested the selective PL quenching must be related to the different surface quality of each nanocrystal fraction since it has been proven that the surface quality of each nanocrystal fraction within a nanocrystal ensemble was dramatically different.[30] The PL of nanocrystals was size-dependent and the apparent PL spectra were the collective of each nanocrystal fraction. This view was clearly exhibited in the current nanocrystal sample with the asymmetrical PL spectrum. Meanwhile, each fraction had respective surface quality resulting from the Ostwald ripening growth of the nanocrystal ensemble.[30,31] Good surface quality meant nanocrystals had ordered array of surface atoms, thick and continuous stabilizing shell of stabilizers. The nanocrystal fractions with nearly zero growth rate had relative perfect surface quality (middle size fractions in the ensemble), thus

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showing better PL stability toward free radical quenching, while others had only poor surface quality (fractions with extremely small and large sizes), thus showing poor PL stability. As a result, a more narrow and more symmetrical PL spectrum was observed for CdTe−PS composites than for parent nanocrystals.

Effects of Surface Composition. The dependence of PL stability on the surface quality of nanocrystals in the polymerization process was also proved by the fact that it was difficult to produce green emitting CdTe−PS composites using freshly prepared nanocrystals. As schemed in Figure 4c, the mixture of OVDAC-coated nanocrystals, styrene, and AIBN was heated at 72−74 °C to generate free radicals that initiated the copolymerization of OVDAC-coated nanocrystals and styrene. Free radicals could act as an efficient PL quencher. For the freshly prepared CdTe with green emission, only a thin layer of Cd−MPA complexes formed around CdTe (Figures 2 and 3) that could not efficiently protect nanocrystals from free radical quenching. Thus, the PL almost disappeared in the resultant composites. In comparison, it was easy to obtain CdTe−PS composites with yellow, orange, or red emission since the thick protecting layer of Cd−MPA complexes preserved most of their PL. Meaningfully, storing of CdTe nanocrystals with green emission for several months, however, thicker Cd−MPA complexes deposited spontaneously around CdTe, which improved the PL stability of nanocrystals.[19] No obvious PL quenching was found in using this stored sample to produce CdTe−PS composites (Figure 7b). This result proved the important function of Cd−MPA complexes around CdTe by protecting PL from free radical quenching.

Although MPA-stabilized CdTe nanocrystals retained strong PL in CdTe−PS composites (Figure 6), serious PL quenching occurred for other mercaptocarboxylic acid-stabilized CdTe. For instance, PL almost disappeared for the CdTe−PS composites from TGA or TLA-stabilized CdTe and fully disappeared for MSA-stabilized CdTe. It should be reasonable to attribute the different behavior of mercaptocarboxylic acid-stabilized CdTe to the distinction of thiol structure when settled on a nanocrystal surface. As mentioned in the previous reports,[32,33] the stability of mercaptocarboxylic acid-stabilized nanocrystals depended strongly on the hydrocarbon chain length and branch structure of thiol stabilizers. Aliphatic thiols with long hydrocarbon chain and without branch structure always show better stability. So MPA-stabilized CdTe's show better stability toward the free radical quenching than that of a short chain stabilizer of TGA and branch stabilizer of TLA or MSA. This result firmly proved that the annulus complexes of Cd−thiol play the most important role against free radical quenching. Although it could not fully exclude the protection from the OVDAC shell, such protection did not play a main role at least, because all nanocrystal samples were coated by OVDAC before being handled in CFP preparation.

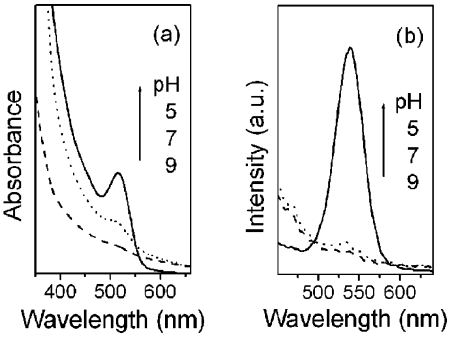

Figure 8. UV−vis absorption (a) and PL (b) spectra of CdTe−PS composites made from TGA-stabilized CdTe. The pH of parent CdTe was adjusted to 5, 7, and 9, respectively, by using TGA.

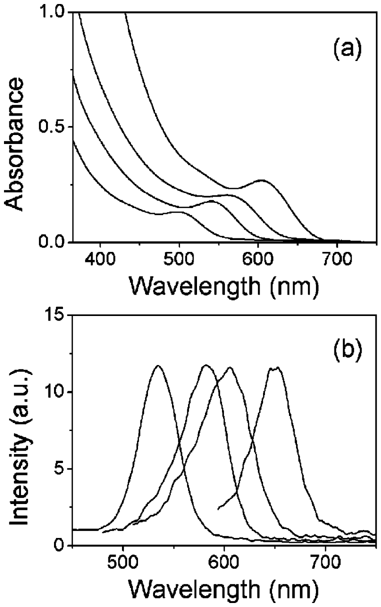

Figure 9. UV−vis absorption (a) and PL (b) spectra of CdTe−PS composites from TGA-stabilized CdTe that were successfully prepared by the deposition of a thick annulus of Cd−TGA complexes on nanocrystal surface before CFP preparation.

Our consideration was further verified by the experiment that adjusting the pH of aqueous nanocrystals before CFP preparation influenced the PL quenching (Figure 8). The pH of aqueous TGA-stabilized CdTe nanocrystals was adjusted to 9.0, 7.0, and 5.0, respectively, by using 0.1 M TGA aqueous solutions. Then, these nanocrystals were treated through CFP preparation to yield CdTe−PS composites. It was found that whereas the composites, prepared from pH 5.0 parent nanocrystals, showed relative strong PL, other composites almost did not show any fluorescence. As known from the previous work,[17−19] the formation of thicker annular Cd−TGA complexes on CdTe surface occurred only at pH 5.0. These complexes improved both the PL intensity and the PL stability of nanocrystals. Thus, PL quenching from free radicals was effectively avoided. Through the formation of such Cd−TGA complexes, different color CdTe−PS composites from TGA-stabilized nanocrystals were both prepared, though the PL spectra were still worse than those from MPA-stabilized nanocrystals (Figure 9).

PFC Preparation. To improve both the PL intensity and the processability of CdTe−polymer composites, an alternative method described as PFC was also indicated. Alkylammonium-functional polymer (AFCP) was prepared through the copolymerization of OVDAC and styrene. Then, nega-

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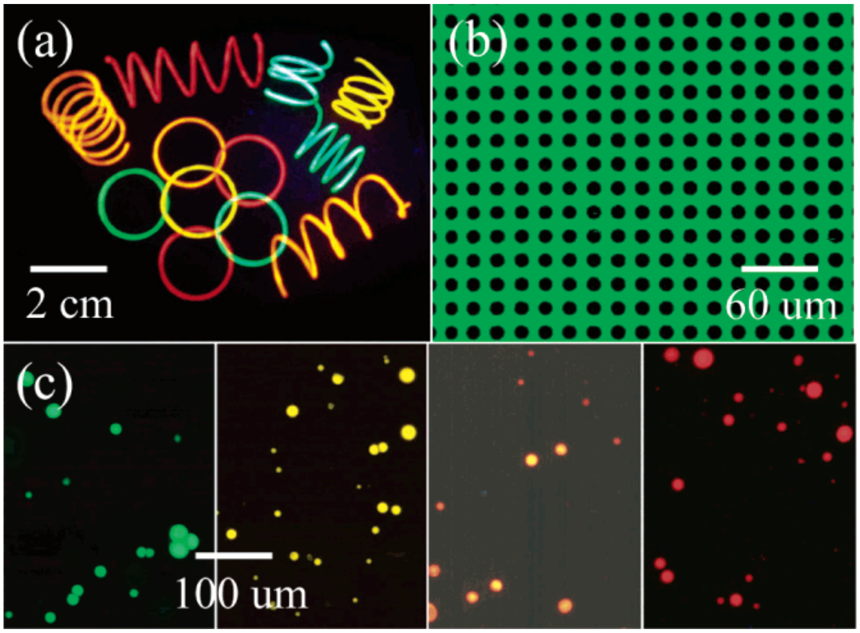

Figure 10. Fluorescent images of CdTe−AFCP composites. (a) In different macroscopic shapes, (b) patterned composites with green emission, and (c) microspheres with respectively green, yellow, orange, and red emission.

tively charged CdTe nanocrystals were simply coated by positively charged AFCP to achieve fluorescent composites (Figure 4b,d). This method was a shortcut to nanocrystal−polymer composites that fully avoided the PL quenching from free radicals. The strong PL emission of aqueous nanocrystals was retained in the resultant CdTe−AFCP composites with no regard to the fluorescence stability of aqueous nanocrystals. Thus, PFC preparation became a general method to achieve CdTe−polymer composites from negatively charged nanocrystals. A variety of CdTe nanocrystals, stabilized by MPA, TGA, TLA, and MSA, were practicable for this method. Besides, CdTe−AFCP composites exhibited an improved processability that was suitable for microfabrication. As shown in Figure 10, these composites have been facilely fabricated to patterned structures and microspheres.[23,24]

Conclusion

Preparation of fluorescent nanocrystal−polymer composites from aqueous CdTe nanocrystals without ligand exchange has been reported. Nanocrystal−polymer bulk composites were prepared through CFP preparation. Although obvious PL quenching from free radicals existed in the polymerization process, this quenching depended strongly on the species of thiol stabilizer and the thickness of Cd−thiol complexes around nanocrystals. By increasing the thickness of these complexes at proper conditions, nanocrystal−polymer composites with improved PL emission were prepared. Nanocrystal−polymer composites were also prepared by PFC preparation that obviated handling unstable nanocrystals in the polymerization process, and hence the maximum PL was retained. The PFC method also improved the processability of nanocrystal−polymer composites. Our strategy would also be extended to the preparation of fluorescent composites from aqueous nanocrystals and other functional polymers.

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