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Fabrication of Strongly Fluorescent Quantum Dot−Polymer Composite in Aqueous Solution

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For the first time, we report a simple method to fabricate a quantum dot (QD)−polymer composite completely via aqueous media from synthesis of QDs to formation of composite. A series of L-cysteine-capped CdTe QDs with tunable emission from green to red were prepared by using hydrothermal techniques, and the corresponding average particle sizes were estimated to be from 2.5 to 4.1 nm. After incorporating these CdTe QDs into the waterborne polyurethane (WPU) prepolymer aqueous suspension, we obtained a transparent nanocomposite film by casting and evaporating. The optical properties of the aqueous CdTe QDs solution and CdTe−WPU composites were investigated by UV−vis absorption and photoluminescence (PL). The results indicate that the quantum yield (QY) and the photochemical stability of the CdTe QDs in both CdTe−WPU aqueous complex and solid composite are enhanced significantly, because of a thicker and more compact passivating layer formed on the surface of CdTe QDs via the reaction between the groups of −NCO and −NH$_2$. In addition, the transmission electron microscopy (TEM) and laser scanning confocal fluorescence microscopy (LSCFM) images show that the CdTe QDs with excellent crystalline structure and strong florescence emission are well-dispersed in the WPU matrix without obvious aggregation or agglomeration. On the basis of the versatile properties of WPU and the photoluminescence originating from the CdTe QDs, these new fluorescent composite materials could have great potential applications. This approach provides a simple route for preparation of various fluorescent QD−polymer composite materials from aqueous QD solutions with neither ligand exchange nor phase transfer.

Introduction

Colloidal nanocrystals, often referred to as quantum dots (QDs), have attracted extensive scientific and industrial interests as a consequence of their strong size-dependent properties and unique optical and electronic features,[1] which give rise to their potential use in a variety of fields, including light-emitting devices,[2] photonic crystals,[3] nonlinear optical devices,[4] and biological labels.[5] However, most explorations of QD-based material in practical applications require the metastable nanoparticles to be stabilized in an appropriate matrix with retention of their initial photoluminescence (PL) efficiency, where aggregation and agglomeration should be suppressed.[6] On the basis of the excellent properties of polymer such as optical transparency, physical and chemical stability, tunable mechanical properties, and easy molding, incorporation of QDs into a polymer matrix is an efficient method to enhance the functions. Therefore, significant efforts have been devoted to fabricate the QD−polymer composites.[7]

More recently, the aqueous synthetic approach for preparation of QDs has been developed as an alternative route for the organometallic synthesis because it is simpler, less expensive, and easier to be scaled up than a conventional organometallic route.[8] Unfortunately, it is difficult to stabilize

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aqueous QDs into bulk polymer matrixes via a relatively simple route, especially when conventional hydrophobic polymers such as polystyrene are used.[9] A uniform dispersion of QDs in the solid polymer matrix is frequently hampered by phase separation and nanocrystal aggregation, which results in the luminescence diminishing or quenching of QDs. To improve the compatibility between QDs and polymer, introduction of covalent bonds between the QDs surface and the polymer is one of the most efficient methods, which could be achieved via the following three main approaches: (1) design and synthesis of polymers with functional groups, such as trioctylphosphine or trioctylphosphine oxide,[10] and thiol[7b,11] on their chains, thus allowing them to be attached on the QDs as a ligand via ligand exchange; (2) introduction of polymerizable ligands such as 4-thiomethylstyrene[12] on the surface of the QDs by ligand exchange and then copolymerization with an appropriate monomer to obtain QD−polymer composites; and (3) modification of the QDs using polymerizable surfactants, such as cetyl-*p*-vinyl-benzyldimethylammonium chloride,[13] cotadecyl-*p*-vinyl-benzyldimethylammonium chloride,[14] or didecyldimethyl-ammonium methacrylate,[15] and then transfer of these modified QDs into an organic solvent or monomer solution for incorporation into a polymer matrix via a radical polymerization or photopolymerization. However, the ligand-exchange and the addition of organic solvents could have negative or even fatal effects on the surface structure of QDs, which could adversely affect their PL properties.[16] The problem could be solved by preparation of QD−polymer composites in an aqueous solution directly. Some QD−polymer composites are prepared in aqueous solutions directly by electrostatically attracted layer-by-layer assembly of charged QDs and polyelectrolytes.[17]

In this paper, for the first time, we demonstrate a simple method to fabricate the QD−polymer composite completely via aqueous media from the synthesis of QDs to the formation of composites. Particularly, we describe herein the preparation of CdTe QD/waterborne polyurethane (WPU) composites via the reaction between the groups of −NH₂ on the QD surface and −NCO on the end of polymer chains in an aqueous solution and further report our investigation of their optical properties. In our experiments, CdTe is selected to be studied for the reason that it is one of the most promising materials for the fabrication of fluorescent composite, because of its ease of preparation, high quantum yield, and tunable emissions in the visible range, whereas waterborne polyurethane (WPU) is chosen as the polymer matrix because of its extensive applications, tunable physical properties, good biocompatibility, and biodegradability.[18] On the basis of the versatile properties of WPU and the PL originating from the QDs, it is envisioned that these materials could act as polymer coating, ink for the fabrication of ordered structures, envisaged optoelectronic devices, and so forth.

Experimental Section

Materials. Sodium telluride (−100 mesh, 99%), L-cysteine (nonanimal source), sodium borohydrate (99.995%), polycaprolactone diol (M_n = 1250), isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), triethylamine (TEA), ethylenediamine (EDA), Rhodamine 6G, and ethanol (anhydrous, ≥99.95%) were purchased from Sigma-Aldrich Corporation. Cadmium chloride hemipentahydrate was purchased from Acros Oganics. Sodium citrate tribasic dihydrate was obtained from Fluka. All of the chemicals were used as-received without further purification.

Synthesis of L-Cysteine-Capped CdTe QDs. A series of CdTe QDs were prepared in aqueous solution using sodium telluride as the Te source and L-cysteine as the ligands.[19] Briefly, 2 mL of cadmium chloride solution (0.08 mol L⁻¹) was diluted to 40 mL of deionized water, and then 100 mg of trisodium citrate dehydrate, 2 mL of sodium telluride solution (0.02 mol L⁻¹), 100 mg of sodium borohydride, and 35 mg of L-cysteine were added under vigorous stirring. The CdTe precursor solution was loaded into a Teflon-lined stainless steel autoclave with a volume of 50 mL. The autoclave was maintained at 180 °C for a desired time and then cooled down to room temperature with flowing water. No post-preparative treatment was performed on any of the CdTe samples for preparation of QD−polymer composites or optical characterization. During preparation, oxygen in the solution does not need to be removed, since the Te source, Na₂TeO₃, is stable in air.

Synthesis of WPU Prepolymer. WPU prepolymer aqueous suspension was prepared in a typical process.[20] Polycaprolactone diol (25.0 g) and DMPA (2.1 g) were introduced into a four-necked flask equipped with mechanical stirrer, condenser, and thermometer, and the mixture was heated up to 85 °C until the polycaprolactone diol was melted completely; then IPDI (12.0 g) was added dropwise, and the reaction was carried out for 2−3 h until the −NCO content reached a desired value, which was determined by using a standard dibutylamine titration method. After neutralization of carboxylic groups with TEA (1.6 g) for 30 min, the −NCO terminated WPU prepolymer aqueous suspension was prepared by dispersing with deionized water under vigorous stirring. For preparation of the EDA-extending WPU, coded as WPU(EDA), the stoichiometric EDA (chain extender) was added into a part of the WPU prepolymer suspension with stirring.

Preparation of CdTe−WPU Composite. These as-prepared CdTe QDs with tunable size-dependent emission from green to red, without any postpreparative treatment, were directly used to react with NCO-terminated WPU prepolymer in the aqueous solution. Scheme 1 shows the process for preparation of the CdTe−WPU composite, starting from the aqueous CdTe QDs. The NCO-

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Scheme 1. Preparative Process for the Fabrication of Fluroescent CdTe−WPU Composites
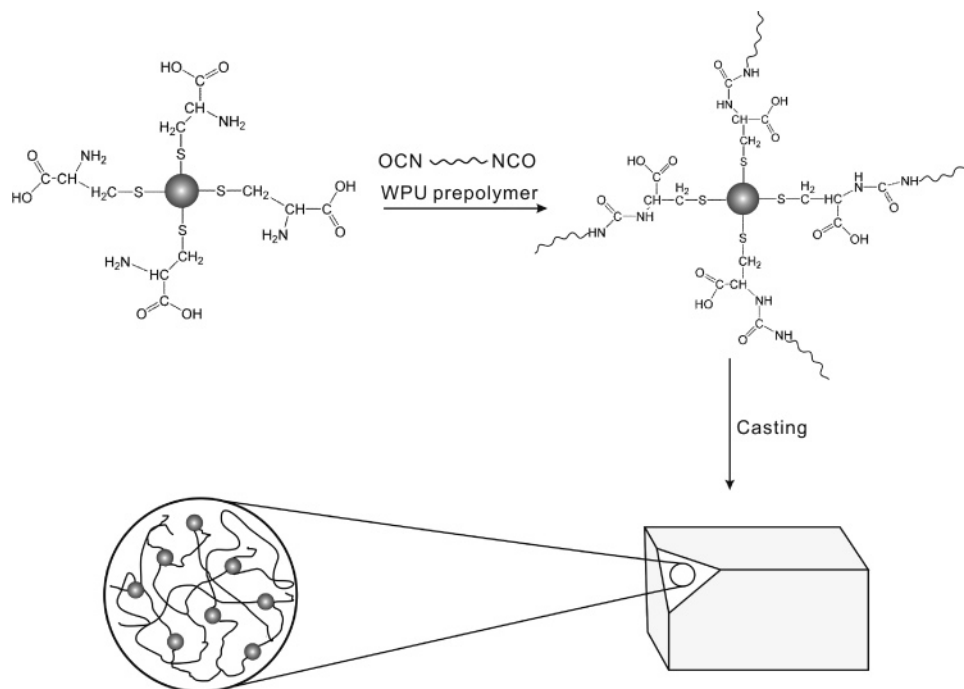
terminated WPU can be attached on the surface of QDs effectively via the reaction between the groups of −NH$_2$ and −NCO. It is noted that a fresh WPU prepolymer should be used here; otherwise, the −NCO groups are consumed by water slowly. As a control, CdTe−WPU(EDA) composite was also prepared using the same fabrication process except the EDA-extending WPU (without −NCO) was used instead. The concentration of CdTe QD in these composites is estimated to be about 0.3 wt %.

Characterizations. All of the optical measurements were performed at room temperature. Ultraviolet−visible (UV−vis) absorption spectra were obtained using a Hitachi U2800 spectrophotometer. Photoluminescence (PL) spectra were recorded with a Jobin-Yvon Horiba Fluorolog-3 spectrofluorimeter. The PL quantum yields (QYs) of all samples were estimated by using Rhodamine 6G as a PL reference (QY = 95%).[21,22] To measure PL QY of CdTe in WPU composites, CdTe−WPU composite films were fabricated on a quartz plate by casting. The optical densities (ODs) at excitation wavelength (400 nm) of Rhodamine 6G in ethanol and in the samples were set to the same value. The OD at either the first excitation absorption peak of QDs or the main absorption peak of Rhodamine 6G was set below 0.15 to avoid significant reabsorption. The PL QY was finally obtained by comparing the integrated PL intensities of the CdTe QDs in both aqueous solution and QD−polymer composite to Rhodamine 6G. Thus, the values of QY were calculated with the following equation

$$QY_s = [(A_r L_s n_s^2)/(A_s L_r n_r^2)]QY_r \qquad (1)$$

where A_s and A_r are the absorbances at the excitation wavelength of the sample and the reference, respectively; L_s and L_r are the integrated PL intensities of the sample and the reference, respectively; n_s and n_r are the refractive indexes of the sample and the reference, respectively; and QY_s and QY_r are the quantum yields of the sample and the reference, respectively.

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Laser scanning confocal fluorescence microscopy (LSCFM) measurement of CdTe−WPU composite was carried out with a Zeiss LSM 510 equipment with Ar/Kr laser. The sample was excited at 488 nm, and a long-pass 515 emission filter was used such that only light above 515 nm reached the photomultiplier tube (PMT). A Zeiss Plane-Aprochromat 63× oil-immersion objective lens was used for imaging, and the theoretical lateral resolution is 0.21 μm. The sample was prepared as follows: several drops of the CdTe−WPU aqueous solution were deposited on a glass cover slip and then dried overnight at ambient temperature.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained with JEM 2100 (JEOL, Japan) at an accelerating voltage of 200 kV. TEM samples were prepared by dropping aqueous complex of CdTe−WPU on copper grids and dried overnight at room temperature.

Results and Discussion

Figure 1 shows typical UV−vis absorption and PL spectra of a size series of as-prepared CdTe QDs in the aqueous solution. All samples demonstrate a well-resolved absorption maximum of the 1s−1s electronic transition, indicating a sufficiently narrow size distribution of the CdTe QDs prepared. The average particle size shown in Figure 1 is estimated in terms of the literature procedure,[23] which evolves from 2.5 to 4.1 nm within 85 min, and as a result, the excitonic peak position in absorption shifts from 507 to 633 nm because of the quantum confinement. Meanwhile, the PL emission peak position of QDs shifts from 528 (green emission) up to 665 nm (red emission) with an increase of the QD size, which indicates that the whole spectra between these two wavelengths is covered by the intermediate sizes of CdTe QDs. It is worthy of note that the full width at half-maximum (fwhm) is about 30 nm when λ_{em} is at ∼528 nm, which is about 5−10 nm narrower than the value reported before.[19] The narrower fwhm of the PL peak reflects the narrower particle size distribution, and thus, it can be
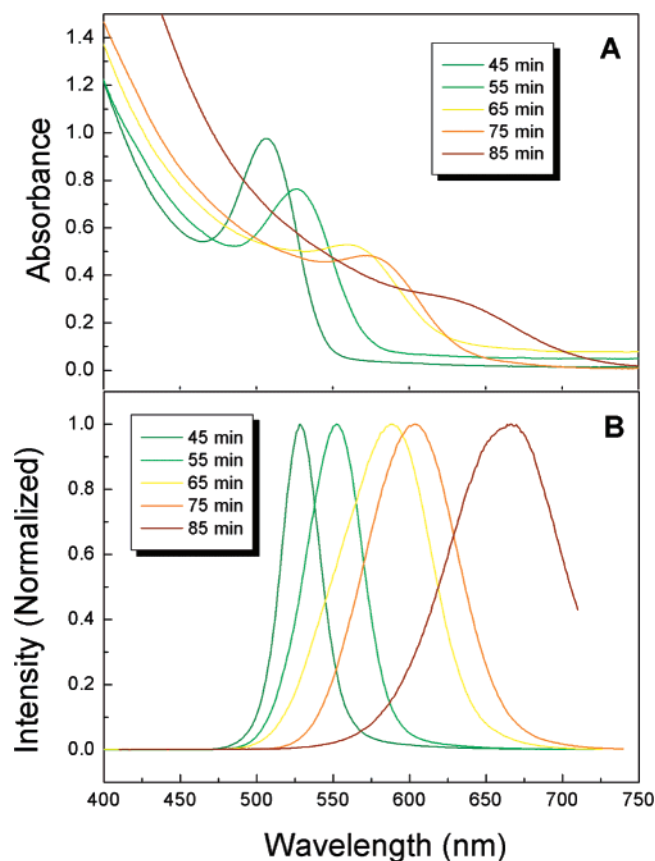
Figure 1. UV–vis absorption (A) and photoluminescence (PL) spectra (B) of L-cysteine-capped CdTe QDs grown at 180 °C for different times. PL spectra were recorded with an excitation at 373 nm. The average diameters of the QDs are 2.5, 2.9, 3.3, 3.5, and 4.1 nm, with the smallest particles showing absorption and PL at the shortest wavelengths. The sizes are estimated from the corresponding excitonic absorption peaks.

Figure 2. PL intensity (up) and emission peak position (bottom) of aqueous CdTe QD solution, CdTe–WPU, and CdTe–WPU(EDA) aqueous complexes as a function of the exposure time in ambient environment.

concluded that the higher growth temperature is favorable for a narrow size distribution.[24] In addition, the values of fwhm increase from 30 up to 85 nm with increasing the CdTe QD size (Table 1), which is ascribed to the effect of Ostwald ripening.[25]

In view of the effect of polymer environment on the photochemical stability of the CdTe QDs, the typical PL spectra of the CdTe QD aqueous solution and CdTe–WPU and CdTe–WPU(EDA) aqueous complexes were recorded (not shown), and the corresponding PL intensity at the peak position versus exposure time is shown in Figure 2 (up). After incorporation of the polymer aqueous suspension into the CdTe QD solution, a significant, though different, decrease in fluorescence is found for both CdTe–WPU and CdTe–WPU(EDA) aqueous complexes at the first moment. It can be explained by the disruption of the dynamic equilibrium between free and bound capping ligands, in which the
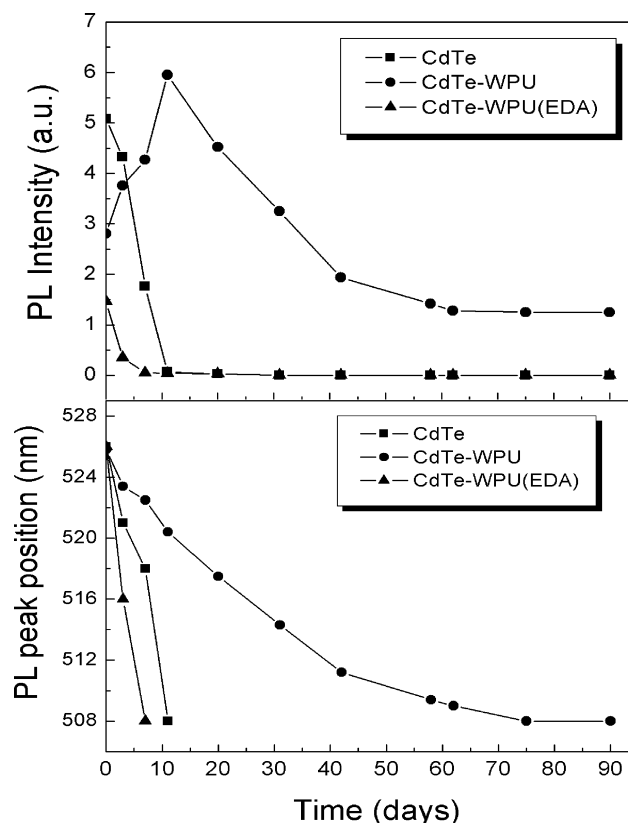
presence of the polymer molecules shifts the equilibrium in favor of free ligand and depassivated QDs. Meanwhile, the reduced absorbance resulted from the background scattering in the presence of polymer macromolecules also could lead to a slight decrease in the PL intensity of QDs.[26] Generally, the photochemical stability of CdTe QD aqueous solution is strongly dependent on the nature of the capped ligands. From Figure 2, we can see that the PL intensity of L-cysteine-capped CdTe QDs decreases with an increase of the exposure time and is quenched completely in two weeks. It is attributed to the fact that the L-cysteine is easily oxidized to be cystine and dissociates from the surface of QDs, leading to a rapid photochemical oxidation of the CdTe QDs. Additionally, the CdTe QDs in WPU(EDA) suspension are more instable and almost quenched in a week. For the CdTe–WPU aqueous complex, however, a contrary and very interesting phenomenon was observed. The PL intensity recovers slowly to a maximum value, which is higher than the initial value of the parent CdTe QD aqueous solution, and then decreases again to a plateau with a relatively strong fluorescence

Table 1. Ultraviolet–visible (UV–vis) Absorption and Photoluminescence (PL) Emission Peak Positions, the Full Width at Half-Maximum (fwhm), and the Relative Quantum Yield (QY) of Differently Sized CdTe QDs in Water and WPU Matrix

diameters of CdTe QDs	in CdTe QDs aqueous solutions				in CdTe–WPU composite films			
	absorption peak position (nm)	emission peak position (nm)	fwhm (nm)	QY (%)	absorption peak position (nm)	emission peak position (nm)	fwhm (nm)	QY (%)
2.5	507	528	30	12	505	529	57	18
2.9	525	552	42	14	525	552	63	17
3.3	560	589	70	8	564	591	82	12
3.5	576	603	71	9	582	609	87	14
4.1	633	665	87	3	635	678	105	6

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intensity even after 90 days. Compared to the CdTe−WPU-(EDA), it can be easily concluded that the enhancement of the PL intensity and photochemical stability is credited to the covalent bonding between WPU prepolymer and QD surface. In this case, CdTe QD acts as crosslinking centers, since each nanoparticle is capable of binding multiple WPU prepolymer molecules. After the reaction between the ligands and the WPU prepolymer, the WPU molecules can be attached on the surface of QD to form a thicker and more compact shell. Such a good passivating layer not only can reduce the nonradiative recombination on the QD surface but also is an effective diffusion barrier of oxygen from the bulk solution into the interface between the QD and the surface ligand.[27] This result is confirmed further from the relationship between the PL peak position and the exposure time in air, as shown in Figure 2 (bottom). The blue-shift, which correlates to the decrease in particle size, in the PL spectra for the CdTe−WPU is much slower than the other two cases, though the photooxidation is inevitable when the QDs are exposed to light in the presence of oxygen.[28] Such an improvement of PL intensity and photochemical stability in CdTe−WPU aqueous complex makes it feasible to prepare strong fluorescent CdTe−WPU solid composites.

Figure 3 shows the UV−vis absorption and PL spectra of the CdTe−WPU composites with different color emission prepared from the corresponding CdTe−WPU aqueous complexes by simple casting and evaporation. Compared with the as-prepared CdTe QDs in aqueous solution, a small red-shift (Table 1) and spectra broadening of the first electronic transition in the absorption is found. This can be attributed to the close-packed condition of CdTe QDs in the WPU matrix. A similar result was observed earlier and is considered as a possible precursor of the Anderson transition in a quantum dot ensemble, namely, a transition from localized electron states to states that are delocalized over a macroscopically large number of nanocrystals.[29] Along with the evolution of the absorption, a general red-shift and spectral broadening of PL emission peaks is also observed in Figure 3B. It can be understood by the resonance energy transfer from the small to the large QDs through dipole−dipole interaction.[30] The phenomenon of stronger red-shift and spectral broadening for the composites with larger CdTe QDs may be attributable to the wider size distribution of the parent CdTe QDs in an aqueous solution, as shown in Figure 1. Although the incorporation of CdTe QDs into the
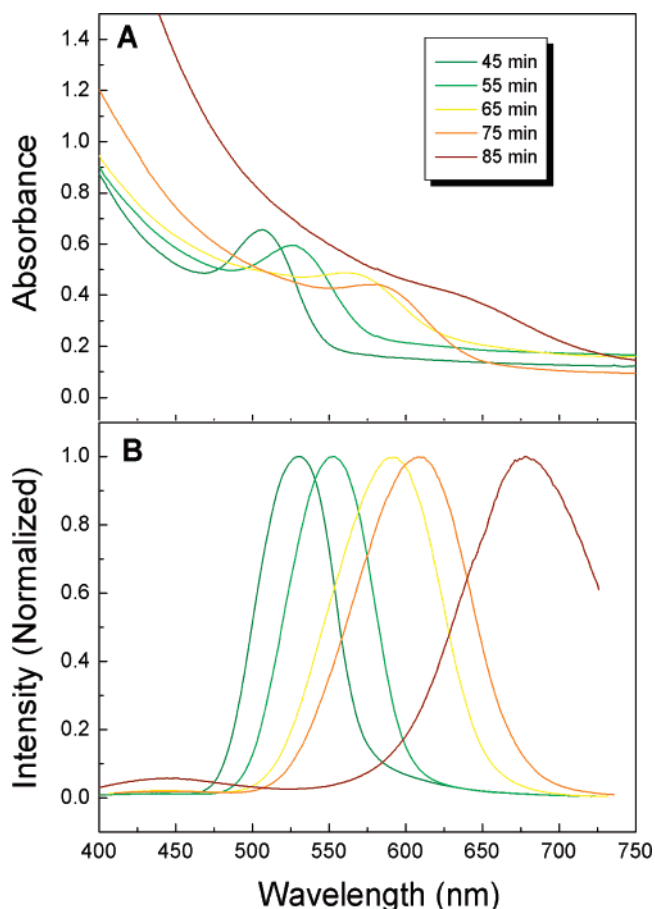

Figure 3. UV−vis absorption (A) and PL spectra (B) of CdTe−WPU composites containing CdTe QDs of different sizes. PL spectra were recorded with an excitation at 373 nm.

WPU matrix slightly changes their optical properties, the CdTe QDs still maintain their quantum size effects in these composites, and the optical properties of the composites are strongly dependent upon the properties of the parent CdTe QDs in an aqueous solution. Compared to the corresponding CdTe QD parent aqueous solutions, interestingly, the values of PL QY of the CdTe QDs are improved in composite films for all samples (Table 1). As discussed above, this also demonstrates that the WPU could further passivate the surface of the CdTe QDs and effectively diminish the contribution of the nonradiative channel for electron−hole recombination.[9]

Figure 4A shows the fluorescence images of the corresponding CdTe−WPU composite samples, for which PL spectra are given in Figure 3B. The surprisingly strong PL emission and nearly pure color emission from green to red exhibits that the composite is a novel fluorescent material. After extracting with water completely, the swollen composites still exhibit strong PL emission but the water does not, which further confirms the CdTe QDs are covalently bonded with the WPU molecular chains. Furthermore, after irradiation of the composites by UV light for >1 week, no significant decrease in PL intensity is observed, suggesting that the incorporation of CdTe QDs into the WPU matrix could well protect them from photochemical oxidation. On the contrary, the composite material dried from the CdTe−WPU(EDA) aqueous complex shows no electronic transition

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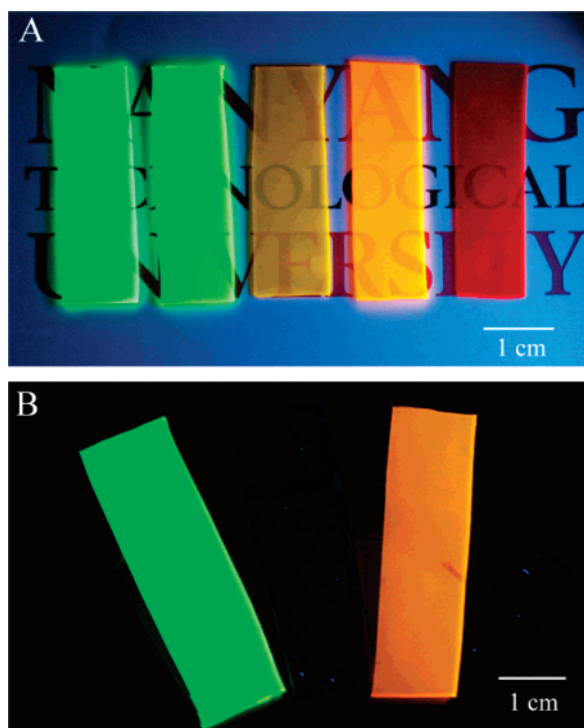
Figure 4. Fluorescence image of the CdTe−WPU composite films excited by a UV lamp at 363 nm: (A) the size of the CdTe QDs for fabricating these composites are estimated to be 2.5 nm (green), 2.9 nm (greenish-yellow), 3.3 nm (yellow), 3.5 nm (orange), and 4.1 nm (red), respectively; (B) the fluorescent films with greenish-yellow and orange emissions are the same samples in (A), while the black (middle) one was obtained in the same way but using ethylenediamine-extending WPU as the matrix instead of WPU prepolymer.

Figure 5. LSCFM image of the CdTe−WPU composite with green emission.

Figure 6. TEM image of the CdTe−WPU composite with green emission; inset = the HRTEM image of the CdTe QDs in the WPU matrix.

and PL emission peaks on the absorption and PL spectra, which demonstrates that the CdTe QDs are quenched completely during the process of water evaporation (Figure 4B, black sample). Therefore, we can concluded that the −NCO group on the WPU prepolymer plays a very important role in fabrication of the strongly fluorescent QD−WPU composite, because of the covalent bonds formed via the reaction between the groups of −NCO and −NH$_2$.

Figure 5 shows the LSCFM image of the CdTe−WPU composite. The well-dispersed bright dots in this image are provided by the emission from the CdTe QDs dispersed in the WPU matrix, which indicates a good compatibility between the components of CdTe QDs and WPU. It can be ascribed to the strong interaction between them by forming covalent bonds on the surface of CdTe QDs. More detailed information on the CdTe QDs dispersion in the WPU matrix can be gained from TEM, which is able to probe the spatial distribution of quantum dots well below optical length scales. The TEM image of the CdTe−WPU composite shown in Figure 6 further confirms the LSCFM results that the CdTe QDs are well-dispersed in the WPU matrix without obvious aggregation or agglomeration. The HRTEM image given in the inset was taken with a typical sample of CdTe QD in the CdTe−WPU composite. The well-resolved lattice fringes for the particle indicate that an excellent crystalline structure of CdTe QD (cubic zinc blended structure) is well-preserved during the reaction of the ligand on the QD surface and the WPU prepolymer.
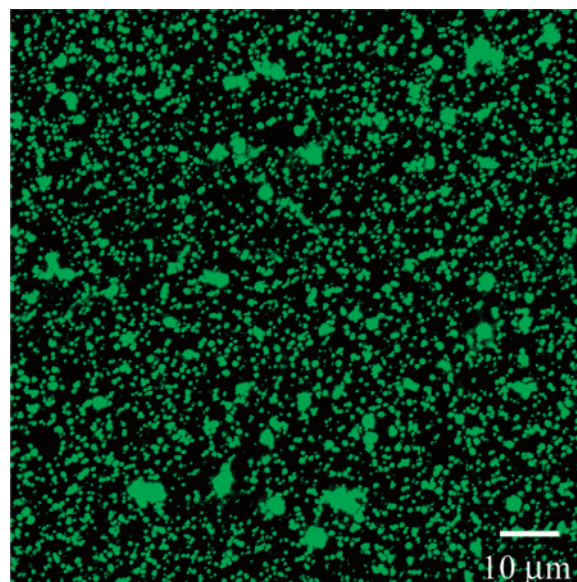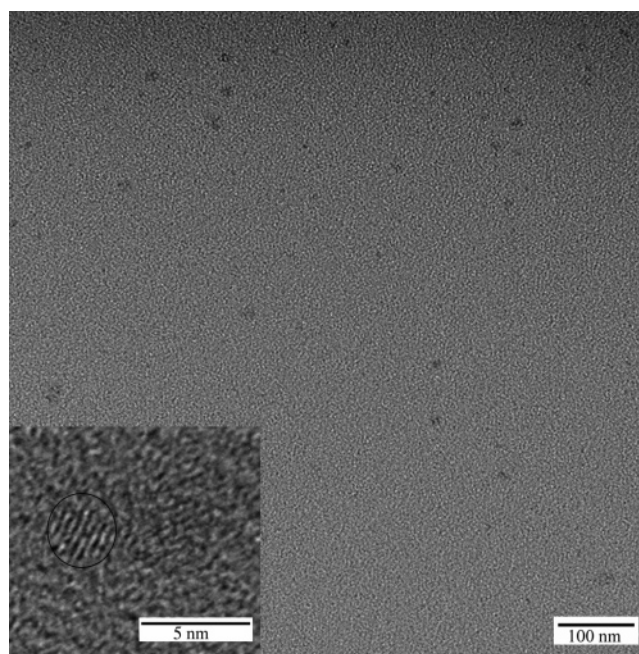
Conclusions

In summary, we have demonstrated a novel "green" way to prepare a fluorescent QD−polymer bulk composite in water by using the −NCO terminated WPU prepolymer as a matrix. The reaction between the ligand of L-cysteine on the QDs surface and the WPU prepolymer creates the CdTe nanocrystals as cross-linking centers, which could disperse uniformly in the matrix and enhance the QY and photochemical stability of the CdTe QDs in both aqueous complexes and solid composites significantly. Although the optical properties of the CdTe QDs are slightly changed after the incorporation in WPU matrix, the optical properties of the resulting CdTe−WPU composite are mainly determined by the initial CdTe QDs in aqueous solution. On the basis

of the versatile properties of WPU and the photoluminescence originating from the composites, it is envisioned that these materials could be used as polymer coating, inks for fabrication of ordered structures, envisaged optoelectronic devices, and biomaterials. Therefore, this work offers a novel approach to fabricate highly fluorescent QD−polymer composite from aqueous QDs without any postpreparative treatment.

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