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Simple Synthesis of Highly Luminescent Water-Soluble CdTe Quantum Dots with Controllable Surface Functionality

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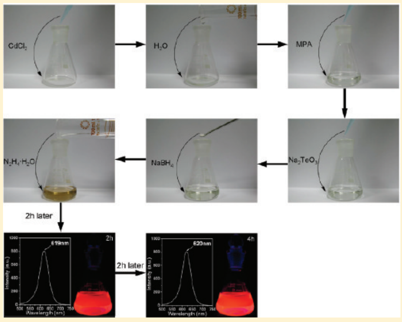
S *Supporting Information*

ABSTRACT: Highly luminescent quantum dots (QDs) could be synthesized in "conical flask" now. Through a room-temperature N_2H_4-promoted strategy, water-soluble CdTe QDs were facilely synthesized by a stepwise addition of raw materials in one pot. No prepreparation of precursors, pH adjustment, heating, and even N_2 protection were required. Just by adjusting the feed ratio of the reagents, different-sized QDs were easily obtained within a shortened time. More importantly, besides conventional thiol-ligands, such as thioglycolic acid (TGA), 3-mercaptopropionic acid (MPA), 1-thioglycerol (TG), 2-mercaptoethylamine (MA), glutathione (GSH), and L-cysteine (LCS), some special mercapto-compounds, for instance, 4-mercaptobenzoic acid (MBA), per-6-thio-α-cyclodextrin (α-CD-SH), and per-7-thio-β-cyclodextrin (β-CD-SH), were also practicable, which were impossible in the conventional reflux method because of the poor water-solubility of them. Furthermore, a spontaneous aggregation of MA-stabilized QDs was observed after synthesis, which facilitated the separation of QDs and recycle of N_2H_4-containing growth solution.



KEYWORDS: quantum dot, aqueous synthesis, CdTe, green chemistry

INTRODUCTION

Luminescent semiconductor nanoparticles, also known as quantum dots (QDs), are envisaged as important building blocks to fabricate advanced materials because of their unique dimensions and size-dependent physicochemical properties derived thereof.[1−4] In particular, the current efforts for developing intelligent materials and establishing new methodology to generate renewable energy sources greatly stimulate the academic interests in setting up QD-based device prototypes.[5−9] As a guarantee of various promising applications, the synthetic methodologies and surface engineering of QDs are rapidly developed in the past decade.[10−24] Colloid chemical protocol exhibits the advantages of manipulating the size and surface chemistry of QDs, thus becoming a robust method in supplying QDs for basic researches.[15,25−34] This method is also flexible for synthesizing QDs in the solvents with different polarity, ranging from water to nonpolar high-boiling-point solvents, endowing the products with distinct surface polarity and therefore the compatibility with different targets.[2,5,10,11,35,36] Despite significant progresses being achieved in QD synthesis, the procedure is still not facile as expected to be. For the synthesis in high-boiling-point solvents (organometallic route and the derivative methods), the most general strategy to obtain high quality QDs, high temperature over 250 °C is indispensable for generating nucleus and maintaining QD growth. Meanwhile, the reaction is operated in vacuum to avoid the oxidation of reagents and/or QDs.[11] Even for the simplified alternative to organometallic route, the synthesis of QDs in water still needs additional energy to promote QD growth simultaneously with N_2 protection.[15,17] Besides, accessorial precursor preparation is required before QD synthesis. In view of the commercial scale synthesis, establishing facile and feasible approaches are greatly welcome.

Because of utilizing environmentally friendly solvent of water, synthesis of QDs via aqueous route appears to close to "green chemistry" concept, which has supplied many highly luminescent QDs, such as CdTe, ZnSe, HgTe, CdHgTe, and so forth.[15,17] A typical synthesis includes three steps: preparation of hydrogen chalcogenide; preparation of precursors by injecting hydrogen chalcogenide into metal salt aqueous solution in the presence of thio-ligands, before which the pH of the solution was adjusted to proper range; and a thermal growth of precursors to produce QDs. To exert the advantages of simplicity, low cost, and high reproducibility of aqueous synthesis, in this article, we demonstrated a dramatically simple approach for synthesizing aqueous CdTe QDs. All materials were commercially available reagents and used as received; no prepreparation of precursors, pH adjustment, N_2 protection, and energy-promoted growth (such as heating, microwave, and ultrasonication) were required. Merely through a stepwise addition of raw materials in one pot at room temperature, highly luminescent QDs with tunable surface functionalities were synthesized.

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EXPERIMENTAL SECTION

Materials. Tellurium powder (−200 mesh, 99.8%), 3-mercaptopropionic acid (MPA, 99+%), thioglycolic acid (TGA, 98%), 1-thioglycerol (TG, 98%), 2-mercaptoethylamine (MA, 98%), glutathione (GSH, 99%), and L-cysteine (LCS, 97%) were purchased from Aldrich. 4-Mercaptobenzoic acid (MBA, 98%), $NaBH_4$ (96%), Na_2TeO_3 (98+%), $CdCl_2$ (99%), and $N_2H_4 \cdot H_2O$ (85%) were commercially available products and used as received. Per-6-thio-α-cyclodextrin (α-CD-SH), and per-7-thio-β-cyclodextrin (β-CD-SH) were synthesized according to a procedure described in previous papers.[37]

Preparation of MPA-Stabilized CdTe QDs. Aqueous CdTe QDs were prepared by directly adding the reagents in turn. Typically, 0.05 mL of 100 mmol/L $CdCl_2$ was placed in a conical flask first, and then 5.25 mL of water, 0.25 mL of 40 mmol/L MPA, 0.25 mL of 4 mmol/L Na_2TeO_3, 0.6 mg of $NaBH_4$, and 34.2 mL of 85% $N_2H_4 \cdot H_2O$ were added in turn. The concentration of QDs was 0.125 mmol/L referring to Cd^{2+}, and the molar ratio of $Cd^{2+}/MPA/TeO_3^{2-}/NaBH_4/N_2H_4 \cdot H_2O$ was 1:2.0:0.2:3.2:120 000. The mixture was stored at room temperature to maintain the growth of QDs. After 2 h storage, the QDs with red emission were obtained. By altering the ratio of reagents, QDs with different emission colors were prepared. Meanwhile, the precipitates of QDs could be gained by adding 2-propanol to QD solution and centrifugation. The collected precipitates were ready for XRD measurement. Following a similar procedure, except using different thio-ligands, CdTe QDs with desired surface functionalities could be prepared.

Characterization. UV−visible absorption spectra were obtained using a Lambda 800 UV−vis spectrophotometer. Fluorescence spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer. The excitation wavelength was 400 nm. All optical measurements were performed at room temperature under ambient conditions. The PLQYs of QDs were estimated at room temperature using quinine in aqueous 0.5 mol/L H_2SO_4 as PL reference.[21] Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera. X-ray powder diffraction (XRD) investigation was carried out by using Siemens D5005 diffractometer.

RESULTS AND DISCUSSION

Experimentally, $CdCl_2(s)$ was dissolved into water first, and then thio-ligands, such as MPA, $Na_2TeO_3(aq)$, $NaBH_4(s)$, and $N_2H_4 \cdot H_2O(aq)$ with specific stoichiometric ratio were added in turn (Figure 1). The resulting mixture was stored at room temperature to maintain the growth of CdTe QDs. After a short duration, luminescent QDs were achieved. The sequence of reagent addition was crucial for a success synthesis. After the addition of $CdCl_2$, MPA must be prior to Na_2TeO_3. Otherwise, the hydrolysis of Na_2TeO_3 would lead to the formation of $CdTeO_3$ and $Cd(OH)_2$ that were undissolved in water. Namely, MPA could coordinate with Cd^{2+} to avoid the deposition. In the following QD synthesis, $NaBH_4$ was added previous to $N_2H_4 \cdot H_2O$. This was attributed to the different reducibility of $NaBH_4$ and $N_2H_4 \cdot H_2O$ and the reaction rate of $NaBH_4$ under different pH values, which would greatly influence the nucleation of QDs (see Figure S1 in the Supporting Information).[38] The first addition of $N_2H_4 \cdot H_2O$ would only deoxidize TeO_3^{2-} to Te rather than Te^{2-} because of its weak reducibility, which made the apparent color of the solution turn to black (see Figure S1c1 in the Supporting Information). Meanwhile, the addition of $N_2H_4 \cdot H_2O$ increased the alkalinity of the solution. Under this condition, although the reducibility of $NaBH_4$ was thermodynamically enhanced, the reaction rate was decreased in kinetics (see Figure S1c1−c5 in the Supporting Information).[38,39] Thus the rapid nucleation of QDs, a prerequisite in QD synthesis, was suppressed. To further verify the effect of alkalinity on the reducibility of $NaBH_4$, before $NaBH_4$ addition, we adjusted the pH of the solution to 11.5 by 1 M NaOH. It was found that the rapid nucleation was nearly completely suppressed (see Figure S1d1−d6 in the Supporting Information). Therefore, $N_2H_4 \cdot H_2O$ must be introduced next to $NaBH_4$. Note that both $NaBH_4$ and N_2H_4 possessed reducibility. The former was a strong reductant, whereas the latter was a weak one. The unequal reducibility made them play different roles in the synthesis of CdTe QDs. $NaBH_4$ led to a fast reduction of Te^{4+} to Te^{2-} to supply the rapid nucleation of QDs, whereas N_2H_4 afforded a protective surrounding to avoid the oxidation of Te^{2-} during QD growth even without N_2 protection. Besides, N_2H_4 was a weak electrolyte, which permitted QD growth at room temperature by altering the electrostatic environment of growing QDs.[40] Consequently, the nucleation and growth of QDs were performed by simply storing the growing solution at room temperature for specific intervals.

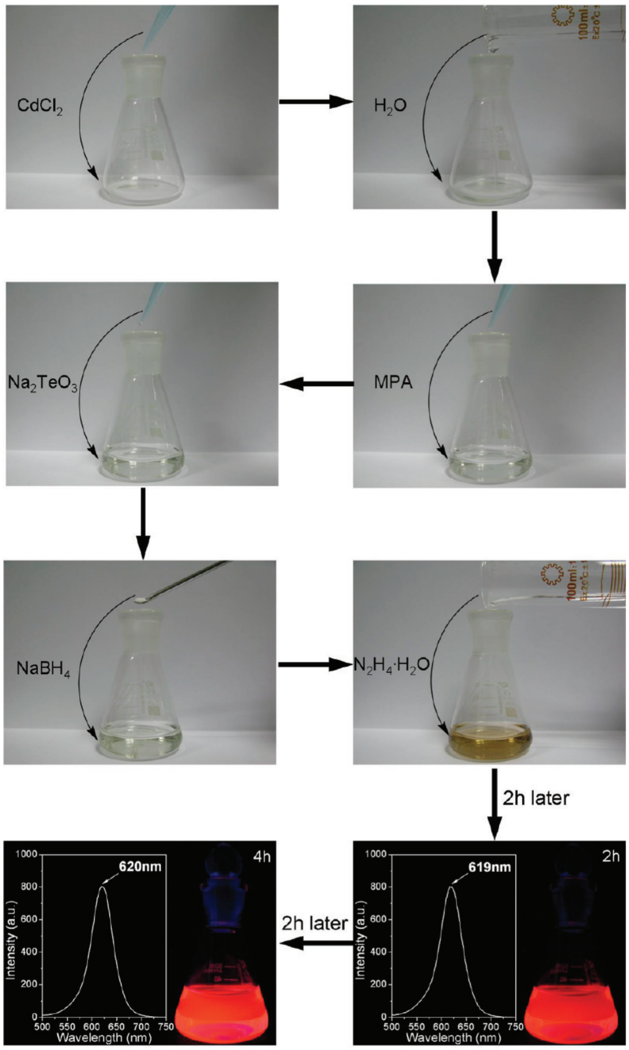


Figure 1. Photographic illustration of the procedure for synthesizing CdTe QDs with red emission.

CdTe QDs were further characterized by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) (Figure 2 and 3). Under TEM, the as-prepared QDs were

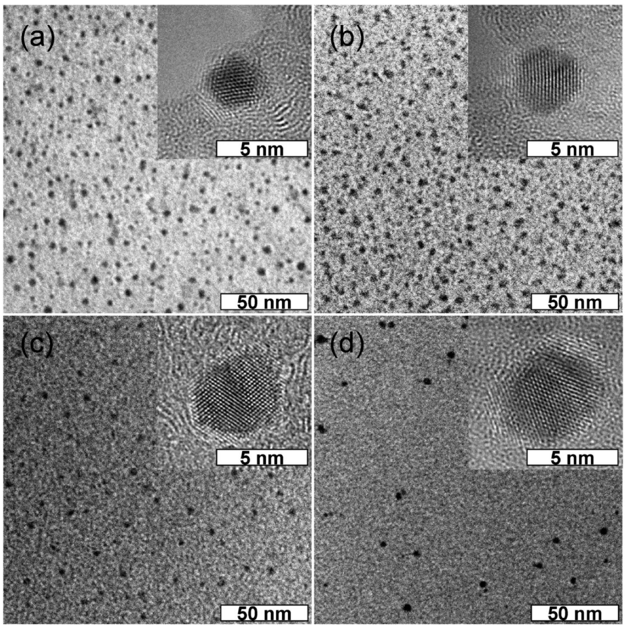


Figure 2. TEM and HRTEM images of the as-prepared CdTe QDs respectively with the emission at (a) 532, (b) 559, (c) 590, and (d) 620 nm.

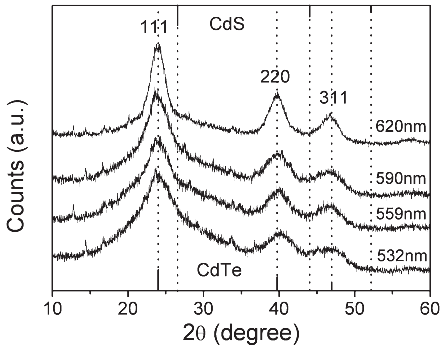
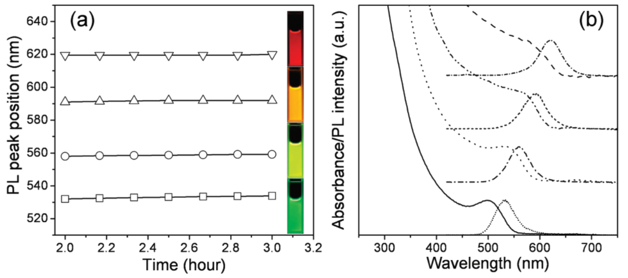


Figure 3. XRD patterns of the as-prepared CdTe QDs respectively with the emission at 532, 559, 590, and 620 nm.

quasi-spherical particles, consistent with the previously reported aqueous CdTe (Figure 2).[15] The high-resolution TEM (inset of Figure 2) and XRD patterns (Figure 3) indicated that the lattice parameters of CdTe QDs fitted well to the zinc blende structure of bulk CdTe crystal.[15] In comparison to the previous report,[15] nearly no shift in the XRD peaks toward cubic CdS was observed, which was attributed to two aspects. First, the shift of XRD peaks was resulted from the embedment of S into QDs through the decomposition of thio-ligands during the conventional thermal growth,[15] whereas the current synthesis at room temperature prevented the decomposition of thio-ligands. Second, both $NaBH_4$ and N_2H_4 possessed reducibility. The presence of them also avoided the oxidation and hence the decomposition of thio-ligands.

The sizes and hence the size-dependent emission of QDs were tunable by adjusting the feed ratio of the reagents. Within 2 h storage, CdTe QDs with different emission colors from green to red could be synthesized (Figure 4). Importantly, after a rapid size evolution at the initial stage, the growth of QDs almost terminated, represented by the less emission variation during the subsequent storage (Figure 1 and Figure 4a). This was attributed to the absence of a separated nucleation process in the current synthesis, which has been discussed in our previous report.[41] Thus, it was very convenient for commercially synthesizing QDs by the excellent reproducibility, because no strict time control was required in comparison to the previous synthesis of highly luminescent QDs. The full width at the maximum of the emission spectra was also narrower regarding to aqueous synthesized QDs, both of which was less than 50 nm (Figure 4b). This was



(c)

balanced PL peak (nm)	QD concentration (mmol/L)	amount of $NaBH_4$ (mg/mL)	N_2H_4 concentration (mol/L)
532	0.5	2.5	5
559	0.5	1.25	8.8
590	0.5	0.025	10
620	0.125	0.015	15

Figure 4. (a) Emission peak positions of different-sized CdTe QDs versus the prolonged storage in the growth solution. Insets: the corresponding PL images of CdTe QDs respectively with the emission at 532, 559, 590, and 620 nm. (b) UV−vis absorption and PL spectra and (c) the synthesis details of the four samples indicated in a.

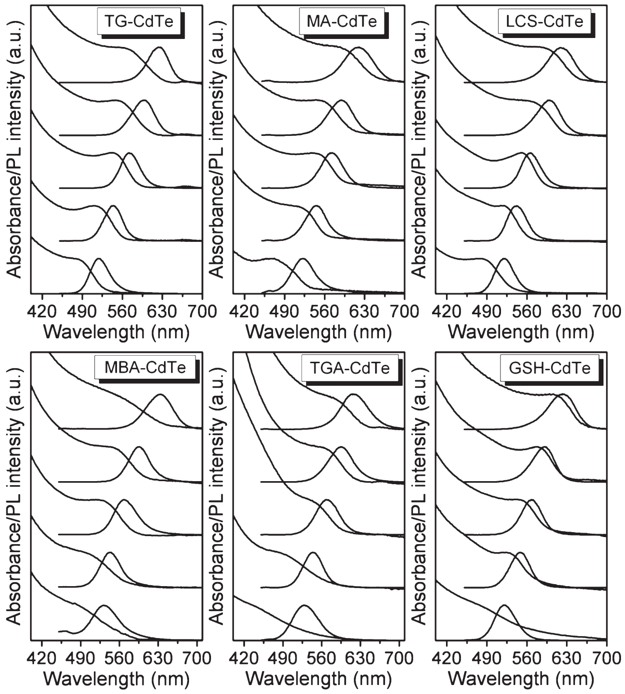


Figure 5. UV−vis absorption and PL spectra of different-sized CdTe QDs synthesized using different thio-ligands.

attributed to the small Stokes shift of the QDs synthesized in the presence of N_2H_4.[40]

The influence of feed ratio on the growth rate of QDs was dramatic. As shown in Figure 4c, high concentration of N_2H_4 was dominant to promote the growth of QDs by providing a favored electrostatic environment, which was consistent with the previous report.[40] The other key for controlling QD growth was the amount of $NaBH_4$. $NaBH_4$ greatly influenced the amount of CdTe nuclei, which in return governed the growth rate of CdTe QDs (Figure S2). Less $NaBH_4$ generated less CdTe nuclei, leaving more dissociative cadmium, tellurium, and thio-ligands in the growing solution, namely excessive monomers. These monomers facilitated the growth of QDs.[21] Consequently, a more rapid growth was observed with the addition of less $NaBH_4$.

Importantly, the current synthesis exhibited the facility in tuning the surface functionality of water-soluble QDs. Besides MPA, various commercial mercapto-compounds, for instance TGA, TG, MA, LCS, and GSH, and special mercapto-compounds, for instance MBA, α-CD-SH, and β-CD-SH were practicable, endowing QDs with surface carboxyl, hydroxyl, amine, cyclodextrin, and so forth (Figures 5 and 6). Note that regarding to the conventional thermal growth, the synthesis of TGA-, MA-, LCS-, and GSH-functionalized QDs was available only at high QD concentration (Table 1). For LCS, even the QD concentration was increased to 10 mmol/L, some deposits were still observed because of the oxidization of QDs. Because of the reducibility of N_2H_4, there was no ligand and concentration limitation in the current synthesis. Most meaningfully, through the conventional thermal growth, no luminescent CdTe QDs could be synthesized using MBA, α-CD-SH, or β-CD-SH as the ligands, resulting from the poor water-solubility of these mercapto-compounds. This inhibited the dynamic optimization of the surface structure of QDs and hence the poor luminescence. In comparison, CdTe QDs with strong luminescence were synthesized via room-temperature N_2H_4-promoted synthesis using the aforementioned ligands, because their water-solubility was greatly improved in the presence of N_2H_4.[42] Consequently, the current synthesis was versatile for synthesizing water-soluble luminescent QDs with enriched surface functionalities.

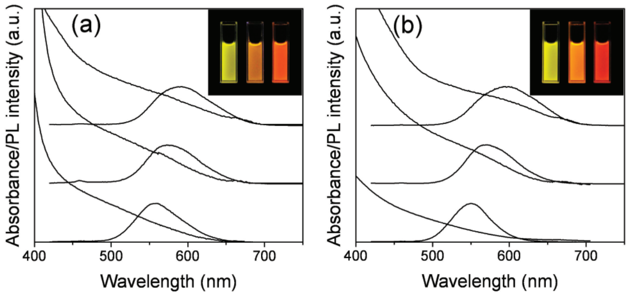


Figure 6. UV−vis absorption and PL spectra of different sized CdTe QDs synthesized using (a) α-CD-SH and (b) β-CD-SH as the ligands. Insets: the corresponding PL images. The CdTe QDs with the emission before 560 nm were prepared via room-temperature N_2H_4-promoted growth, whereas the other QDs were prepared with a moderate heating at 70 °C.

Moreover, there was another advantage in synthesizing MA-functionalized QDs. Because the growing solution possessed alkalinity, MA-functionalized QDs would spontaneously aggregate on bottom of the bottle, but the luminescence was well-preserved. The precipitate of QDs could be gained through centrifugation, and redissolved in a solution containing Cd^{2+} and MA (Figure 7). Meanwhile, the supernatant including a lot of N_2H_4 could be reused for synthesizing QDs. This was convenient for commercially synthesizing QDs by lowering the cost and waste, which was extending to other ligand-functionalized QDs for separation and recycle of N2H4. It should be mentioned that the stability of CdTe QDs via the current synthesis was the same as that via conventional reflux method. After the redispersion of the QDs into a solution containing Cd^{2+} and corresponding mercapto-ligands, the QDs could be stored for one year at least without obvious changes of the PL intensity and peak position.

The CdTe QDs synthesized by the current method possessed strong luminescence, which were not worse than those through conventional thermal growth. Table 1 compared the ligand-dependent photoluminescence quantum yields (PLQYs) of CdTe QDs synthesized through current method and conventional reflux. The PLQYs of all samples were measured without any postpreparation treatment.[21] The PLQYs of MPA- and TG-functionalized QDs was higher than conventional reflux, and in particular, the PLQY of TG-functionalized QDs increased from 5 to 13%. The PLQYs of LCS- and GSH-functionalized QDs were slightly lower than reflux, which was understandable according to the difference in QD composition. As mentioned in the previous reports,[15,26,29] CdTe QDs obtained from conventional reflux possessed quasi CdTe/CdS core/shell structure, whereas the QDs from the current synthesis were nearly pure CdTe (Figure 3). Therefore, current synthesis avoided the effect of CdS on the PLQYs of CdTe. On one aspect, the formation of CdS shell might lead to a disordered array of QD surface atoms, thus lowering the PLQYs, such as MPA- and TG-functionalized QDs. On the other aspect, the presence of CdS shell could passivate QD surface atoms, which improved the PLQYs, such as LCS- and GSH-functionalized QDs. Because there was less effect of CdS shell on the PLQYs, the ligand effect should be attributed to the capability of thiol-ligands to coordinate with QDs and hence the surface passivation of QDs.[43,44] For QDs, the PLQYs were essentially determined by the surface structure of QDs. Well-passivation of QD surface atoms contributed to high PLQYs. MPA and GSH well-passivated the surface atoms of QDs via strong coordination interaction, thus leading to high PLQYs. In comparison, MA led to poor surface passivation and therefore the low PLQYs.

Table 1. Comparison of the PLQYs of Different Ligand-Functionalized CdTe QDs Synthesized via Current Method and the Conventional Reflux

	thiol-ligand				
	MPA	TG	MA	LCS	GSH
current method (%)	18	13	3	10	13
conventional reflux (%)	14	5	3	13	15
the minimum concentration practicable by reflux (mmol/L)			5	10	5

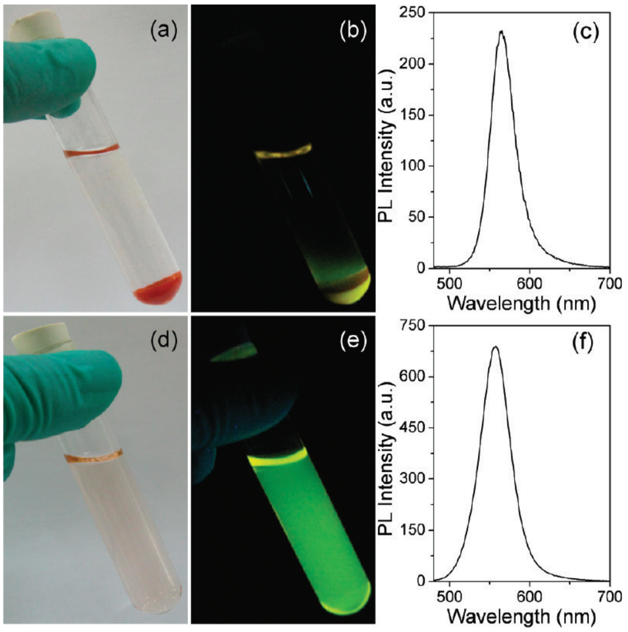


Figure 7. Photographic illustration of the self-aggregation of MA-stabilized QDs in growth solution under (a) visible light and (b) 365 nm ultraviolet, and (c) the PL spectrum. After separation from the growth solution, the aggregated QDs could be redispersed in water. (d) Under visible light, (e) under 365 nm ultraviolet, and (f) the corresponding PL spectrum.

CONCLUSION

In summary, we demonstrated a simplified route for room-temperature aqueous synthesis of highly luminescent CdTe QDs. Without precursor preparation, pH adjustment, N_2 protection, and energy promotion, CdTe QDs were synthesized through the stepwise addition of water, $CdCl_2$, thio-ligands, Na_2TeO_3, $NaBH_4$, and N_2H_4. By adjusting the amount of $NaBH_4$ and QDs to N_2H_4 ratio, luminescent QDs with different emission wavelength could be synthesized within a shortened time. The key of the current synthesis was the reducibility of N_2H_4, which afforded a protective surrounding to avoid the oxidation of QDs and thio-ligands, and therefore the subsequent effect on the growth rate and the PLQYs. Consequently, the previous limitations in synthesis condition and particularly the species of thio-ligands were overcome. Because the current synthesis was dramatically simple and highly reproducible, it would facilitate the commercial scale synthesis of highly luminescent water-soluble QDs with the surface functionalities tunable in broadened range.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** The influence of alkalinity and the addition sequence of $NaBH_4$ and $N_2H_4 \cdot H_2O$ on the nucleation process, influence of $NaBH_4$ amounts on the temporal evolution of the QD PL peak positions, and the PLQY of MBA-stabilized CdTe QDs. This material is available free of charge via the Internet at http://pubs.acs.org.

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