

Research Article

Aqueous Synthesis of CdTe Quantum Dot Using Dithiol-Functionalized Ionic Liquid

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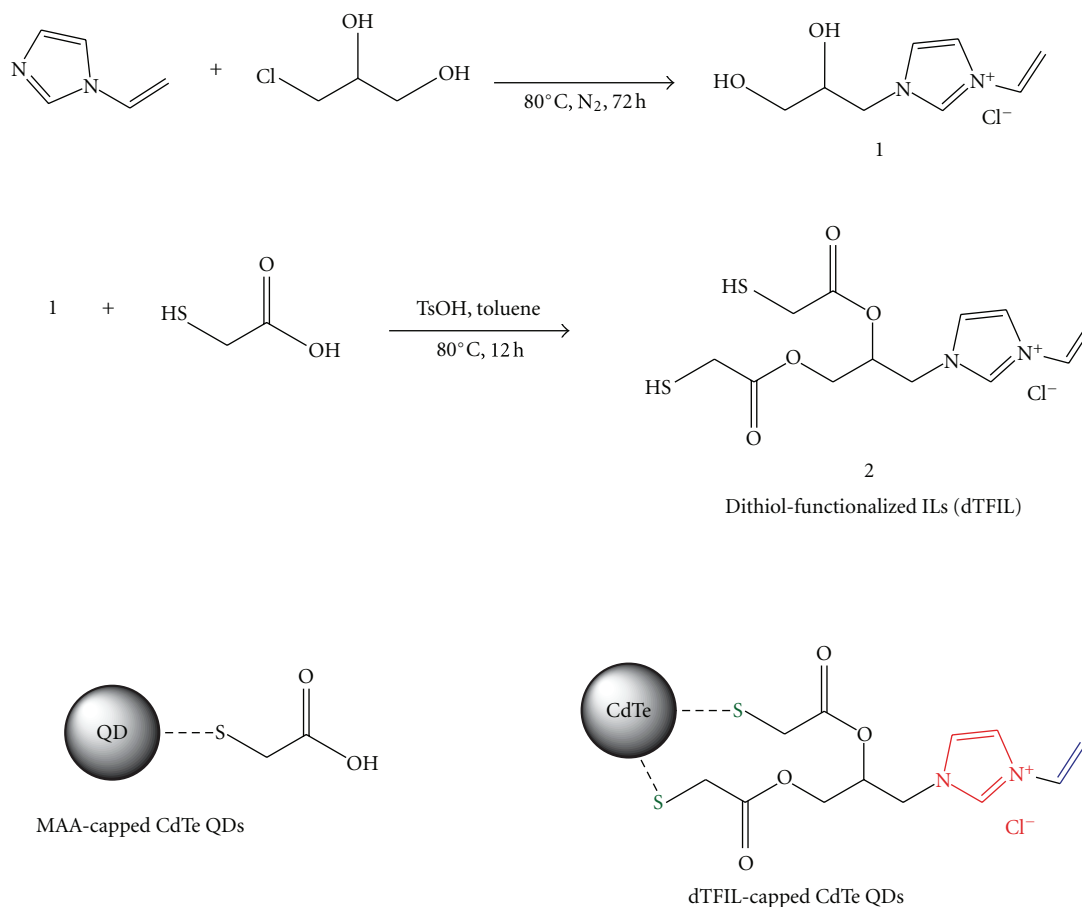
We report on an aqueous synthesis of cadmium telluride (CdTe) nanocrystals by using dithiol-functionalized ionic liquids (dTFILs). The dTFILs were designed to have dithiol and vinylimidazolium functional groups and used as a ligand molecule of CdTe quantum dot (QD) to utilize the bidentate chelate interaction afforded by the dithiol groups of dTFILs. The photoluminescence quantum yield of dTFIL-capped CdTe QDs reached up to ~40%, and their luminescent property was maintained for 8 weeks, suggesting an improved stability in water phase. This approach will provide a new synthetic route to the water soluble QDs.

1. Introduction

Quantum dots (QDs) have been a topic of intense theoretical and experimental investigation owing to their size-tunable luminescence, narrow photoluminescence (PL) bands, and broad absorption spectra [1–4]. QDs are often prepared from organometallic precursors via high-temperature solution routes, in which their inorganic core is capped with organic ligand mixtures consisting of trioctylphosphine/trioctylphosphine oxide (TOP/TOPO) and/or long-chain alkylamines [5–8]. Substitution of these organic ligands with polar-terminated groups permits tailoring of QDs for efficient dispersal in aqueous solution, which makes them compatible with biological manipulation [9–12]. The QDs in an aqueous environment have been achieved with various methods including silica shelling [13–16], micelle formation around the external organic capping layer [17, 18], and formation of polymer coatings [19–21]. While many of the reported schemes render aqueous solubility of QDs, they often have several limitations which include short-term stability and increased nanoparticle diameter from 2–5 nm to 20–100 nm [22–24]. These limitations underscore the need for developing new approaches for surface functionalization of QDs to improve their stability in water phase without increasing its size drastically.

In this regard, the direct synthesis of QDs in water phase provides an attractive alternative because of its simplicity and use of relatively soft condition [25–27]. Prior reports showed that cadmium telluride (CdTe) QDs with moderately high photoluminescence quantum efficiency (QE) have been produced via aqueous synthetic route with a thiol capping ligands such as mercaptocarbonic acid, 2-aminoethanethiol, and dihydrolipoic acid [28–30]. However, the environmental instability of QDs prepared by aqueous synthetic method was also reported. Therefore, an improvement of the stability of CdTe QDs in water is a task of special interest.

In parallel, ionic liquids (ILs) have recently led to a growing interest in the preparation of organic or inorganic nanomaterials because of their unique properties that can be tuned by selecting appropriate combination of cations and anions [31–33]. ILs have been reported to effectively stabilize a range of colloidal nanocrystals in solutions with controlled hydrophilic or hydrophobic surface properties. Therefore, the QD-ionic liquid hybrids are expected to be one of the most promising materials [34, 35]. This study intends to provide a direct aqueous synthetic route to the CdTe QDs capped with ionic liquid. The role of the ILs on the stability and emission properties of QDs in the aqueous solution is also investigated. To this end, we designed a dithiol-functionalized ionic liquid consisting of dithiol and



SCHEME 1: Synthetic route to the dithiol-functionalized ionic liquid (dTFIL).

vinylimidazolium coupled with chloride, as illustrated in Scheme 1. This approach utilizes the bidentate chelate interaction afforded by the dithiol groups of IL, while the hydrophilic vinylimidazolium groups provide solubility in water as well as possible postpolymerization reaction. This new ligand allows for the design of QDs that are water compatible, stable, and multifunctional.

2. Experimental

CdTe QDs were synthesized via aqueous synthetic route in which Cd^{2+} ions and NaHTe were reacted in the presence of dithiol-functionalized ionic liquid (dTFIL). The control experiment with the use of mercaptoacetic acid (MAA) as a capping ligand was also conducted for comparison.

2.1. Synthesis of Dithiol-Functionalized Ionic Liquid (dTFIL).

The preparation of thiol-functionalized ionic liquid was as follows: 1-(2',3'-dihydroxypropyl)-3-vinylimidazolium chloride (1) was prepared from the reaction of 1-vinylimidazole and 3-chloro-1,2-propanediol at 80°C for 72 h under N_2 atmosphere. A mixture containing 0.1 mol of 1-(2',3'-dihydroxypropyl)-3-vinylimidazolium chloride (1) and

0.3 mol of mercaptoacetic acid (MAA) was refluxed with 0.03 mol of *p*-toluenesulfonic acid in toluene. After the solvent was evaporated in a rotary evaporator, 1,3-di(2',3'-dithioacetoxypopyl)vinylimidazolium chloride (dTFIL) (2) was obtained by washing with CH_2Cl_2 .

2.2. Aqueous Synthesis of dTFIL-Capped CdTe QD. CdTe QDs were synthesized by the reaction of oxygen-free NaHTe with N_2 -saturated $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of dTFIL or MAA. The NaHTe solution was prepared by reducing metallic tellurium powder (0.383 g, 3 mmol in 10 mL water) with sodium borohydride (0.227 g, 6 mmol in 5 mL water) at 0°C . A solution of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.97 g, 4.7 mmol) and dTFILs (or MAA) (7 mmol) in 250 mL of demineralized water was adjusted to pH 11 with 1 M NaOH. The solution was placed in a three-necked flask and deaerated with N_2 bubbling for 30 min. After NaHTe solution was injected, the reaction mixture was refluxed for 24 hours and then cooled down to room temperature.

2.3. Characterization. UV-vis absorption spectra were recorded at room temperature using a Shimadzu UV-3101PC spectrophotometer, and photoluminescence measurements were performed at room temperature using an AMINCO

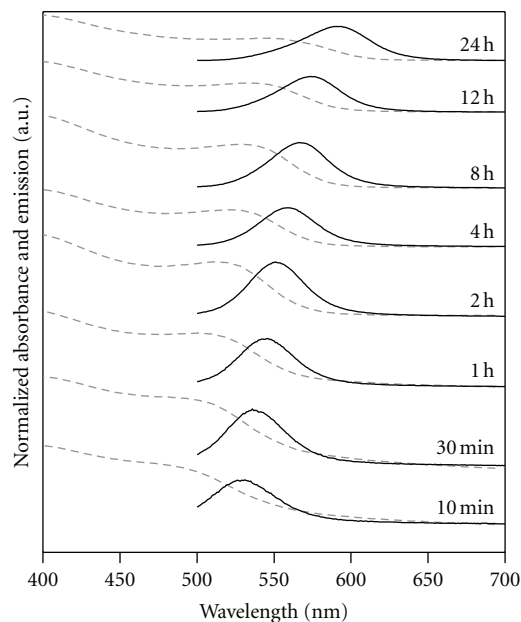


FIGURE 1: Absorption and photoluminescence spectra of IL-capped CdTe QDs with respect to the reaction time. PL spectra were recorded with an excitation at 470 nm.

BOWMAN II Luminescence spectrometer. Quantum efficiencies (QEs) of all samples were estimated by using Rhodamine 6G as a reference. The QE was obtained by comparing the integrated PL intensities of the CdTe QDs to Rhodamine 6G, while optical densities of sample and reference were set to the same value (< 0.15) to avoid significant reabsorption. High-resolution transmission electron microscope (HRTEM) images were obtained on a JEOL JEM-2000EX operated at 200 kV. The samples for TEM studies were prepared by dropping diluted aqueous solution of CdTe QDs onto 400 mesh carbon-coated copper grids. The size distribution of QDs in aqueous solution was measured by a dynamic light scattering (DLS) instrument (Microtrac NPA252) equipped with a 780 nm laser.

3. Result and Discussion

Figure 1 shows the absorption and PL spectra of the dTFIL-capped CdTe QDs in aqueous solution. As expected for quantum-sized particles, the position of the first electronic transition was shifted to higher photon energies in accordance with the size quantization effect. The PL emission peak position of QDs shifts from 529 nm (green) to 593 nm (orange) with an increase of the QD size. The whole spectra between these two wavelengths is covered by the intermediate sizes of CdTe QDs. The full width at half maximum (FWHM) is about 35 nm at the emission wavelength of 529 nm, which is close to the previously reported values [25–27]. The values of FWHM increase from 35 to 55 nm with increasing QD size and this is ascribed to the effect of Ostwald ripening and the wider size distribution of CdTe QDs in the aqueous solution [28–30].

The photoemission quantum yields were calculated using Rhodamine 6G (in ethanol, $QY = 0.95$). For the measurement, concentration was adjusted in a way that both reference and QD samples showed same optical densities at the excitation wavelength, and solvent refractive indexes were taken into account. The photoluminescence quantum yield of dTFIL-capped CdTe QD ranged up to 40%, comparable to the value reported in previous literatures [25–30].

Figure 2 shows the typical photographs of the dTFIL-capped CdTe QDs in aqueous solution, which were obtained from the same sample at different reaction times. The well-resolved lattice fringes for the as-synthesized QD were observed with high-resolution transmission electron microscope (HRTEM), indicating a formation of crystalline structure of CdTe QD. The TEM studies also reveal that the size of dTFIL-QD (at 12 h reaction time) is 5 ± 0.5 nm, while the hydrodynamic size of dTFIL-QD was measured as ~ 7 nm by dynamic light scattering (DLS). This result implies that dTFIL molecules bind to the surface of CdTe QDs with a capping thickness of ~ 1 nm, which is close to the estimated value from molecular simulation of dTFIL.

On the other hand, the stability of CdTe QD in aqueous solution is strongly dependent on the nature of the capped ligands. The dTFIL-capped QDs were stable in aqueous solution for at least 8 weeks, whereas MAA-capped QD were stable only for 2–3 weeks. Figure 3 gives a comparison of PL spectra for MAA-capped and IL-capped QDs in water after the 15 days of standing at room temperature. While the MAA-capped QDs undergo a significant decrease in emission peak maxima with a slight redshift in the peak position, dTFIL-capped QDs maintain their initial PL intensities. This is indicative of the capability of dTFIL ligand to effectively stabilize the QDs in the water phase and thus prevent their uncontrolled growth. Moreover, a slight enhancement in emission intensity was also observed for dTFIL-capped QDs, which is attributed to the specific suppression of quenching process by dTFILs. For MAA-capped QDs, MAAs are likely to dissociate from the QD surface as thiol group is converted into disulfide with the formation of localized electronic surface states and gradual precipitation of the QDs [28, 36]. In contrast, bidentate thiol groups of dTFILs lead to the efficient protection of QD, because they have the stronger coordinative ability with CdTe QD surface due to the multiple binding sites. These effects may contribute to the enhanced stability and the relatively high quantum yield of CdTe QD in water.

4. Conclusion

In summary, we have demonstrated an effective method for aqueous synthesis of highly luminescent and stable CdTe nanocrystal by using thiol-functionalized ionic liquid as ligand molecules. The photoluminescence quantum yield of dTFIL-capped CdTe nanocrystals reached up to $\sim 40\%$. The luminescent property was maintained for 8 weeks with an improved stability. This approach will provide a new synthetic route to the functionalized QDs in water phase.

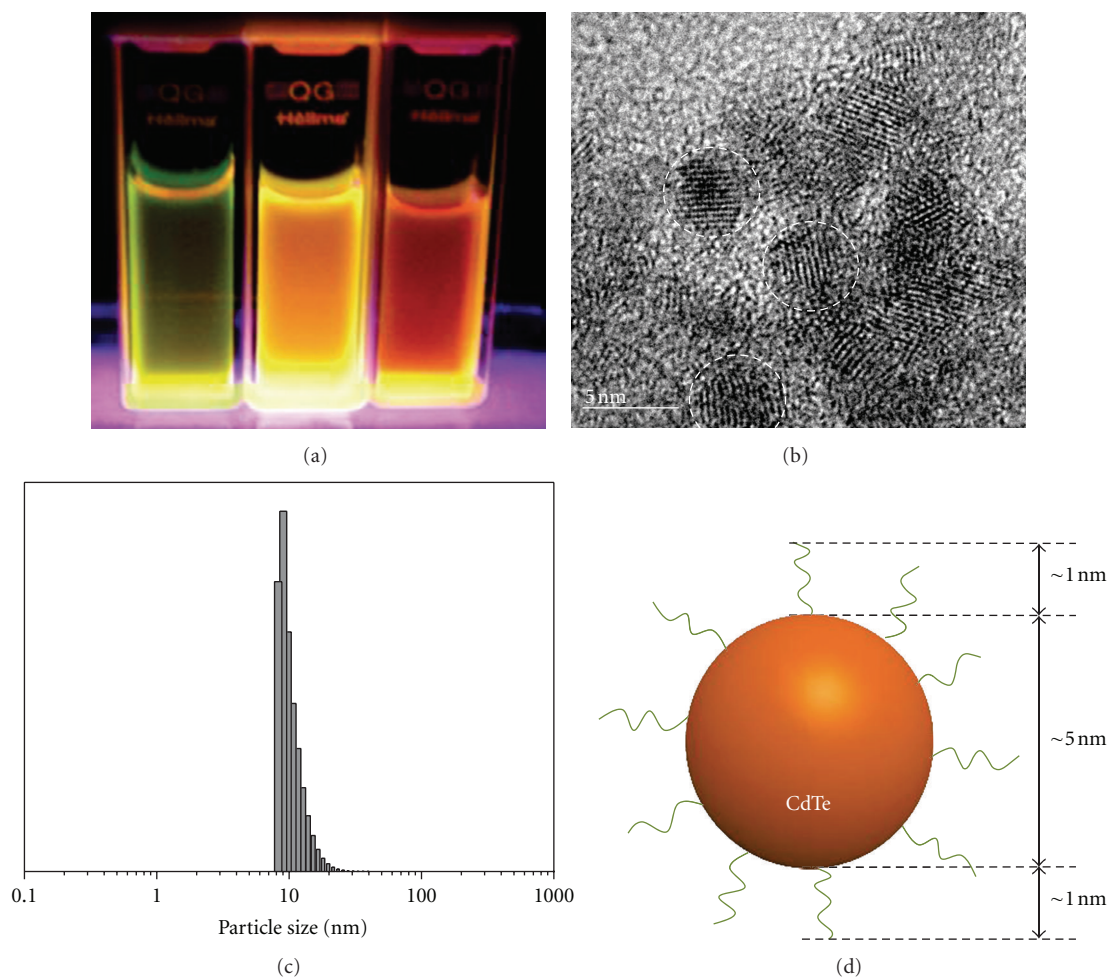


FIGURE 2: (a) Fluorescence images of dTFIL-capped CdTe QDs at different reaction times. All solutions were excited with a hand-held UV lamp. (b) TEM images of the dTFIL-capped QDs, taken from the aliquots at the reaction time of 12 h. (c) DLS results of the dTFIL-capped QD in aqueous solution, indicating a hydrodynamic size of ~ 7 nm, and (d) illustration of dTFIL-capped CdTe QD with estimated dimensions.

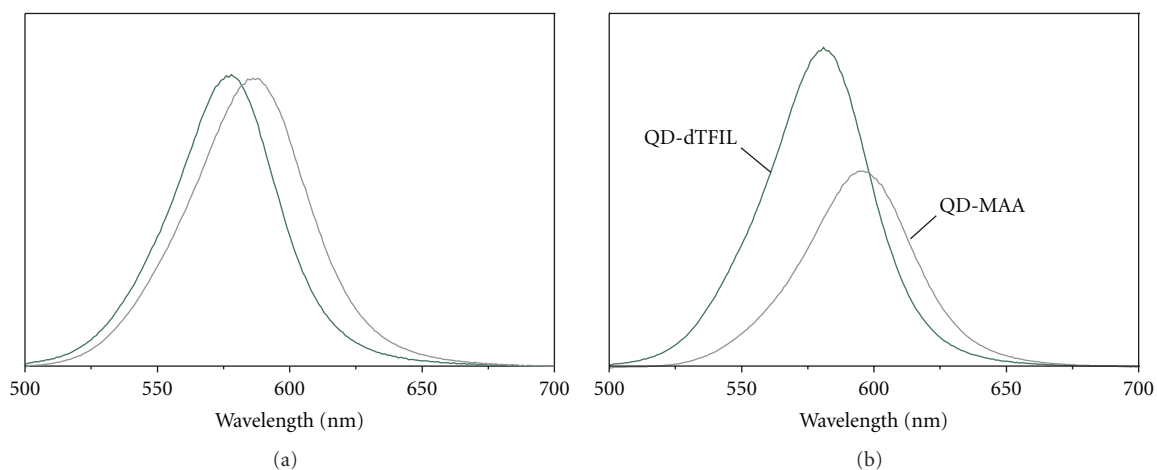


FIGURE 3: PL intensity of aqueous CdTe QDs (dTFIL- and MAA-capped QDs) as a function of the exposure time in ambient environment: (a) as-synthesized and (b) after 15 days.

Acknowledgments

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