A simple biphasic route to water soluble dithiocarbamate functionalized quantum dots

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Hydrophobic trioctylphosphine oxide-functionalized CdSe quantum dots (CdSe-TOPO QDs) were transferred from organic solvent to aqueous solution *via* a simple yet novel biphasic ligand exchange process in *one step*, which involved the *in-situ* formation of hydrophilic dithiocarbamate moieties and subsequent ligand exchange with TOPO at the chloroform/water interface. The resulting water dispersible, dithiocarbamate functionalized CdSe QDs (*i.e.*, D-CdSe) exhibited an increased photoluminescence (PL) quantum yield as compared to the original CdSe-TOPO QDs, suggesting an effective passivation of dithiocarbamate ligands on the QD surface. The D-CdSe QDs were then mixed with hydroxyl terminated TiO₂ nanoparticles. A decrease in the PL of the mixture was observed, indicating a possible charge transfer from the D-CdSe QDs to the TiO₂ nanoparticles. The reaction of the carboxyl group on the D-CdSe surface with the hydroxyl group on the TiO₂, thereby facilitating the electronic interaction between them.

Introduction

Quantum dots (QDs) are highly emissive spherical nanoparticles with diameter of a few nanometers. They provide a functional platform for a new class of materials for use in solar cells,¹ LEDs,² tunable lasers,³ optical storage media,⁴ nonradiative energy transfer,⁵ biosensors,⁶ and bioimaging systems.⁷ For QDs such as cadmium selenide (CdSe), variation of particle size provides continuous and predictable changes in optical absorption and fluorescence due to their quantum-confined nature. Appropriate surface passivation with a monolayer of coordinating ligands is crucial to ensuring the solubility and miscibility of QDs with the host environment, and to retaining the spectroscopic properties of the materials by preventing QDs from aggregation. Ligand exchange permits derivatization with a broad range of functional groups.

QDs synthesized through a conventional organometallic high temperature growth procedure are functionalized with hydrophobic ligands (*e.g.*, trioctylphosphine oxide (TOPO)). However, on many occasions, it is desirable to prepare water soluble QDs for bioimaging, biosensor, and QD-sensitized TiO₂ nanocrystal solar cells (QDSSCs). In the latter context, due to the size-dependent optical properties and multiple exciton generation capability,⁸⁻¹² QDs can be exploited as the sensitizer in QDSSC. Placing the water soluble QDs in intimate contact with the hydrophilic TiO₂ nanocrystals is expected to facilitate efficient charge transfer from the QDs to the TiO₂. This can be realized by functionalizing both the QDs (*e.g.*, dithiocarbamate functionalized QDs with the carboxyl group on the surface) and the TiO₂ (*e.g.*, the hydroxyl group on the TiO₂ surface¹³⁻¹⁵) with

compatible functional groups, which allow them to react with each other under mild conditions.

Bifunctional molecules with thiol and carboxyl groups at each end (e.g., mercaptopropionic acid (MPA)^{15,16}) have been used as effective ligands to prepare water dispersible QDs. The thiol group provides the chemical affinity to QDs, while the carboxyl group imparts the water solubility. However, the use of monothiol ligands makes QDs susceptible to oxidation.¹⁷⁻¹⁹ This drawback was recently overcome by using dithiocarbamate moieties as ligands due to their strong chelate-type binding to metal atoms.^{20,21} The resulting dithiocarbamate functionalized QDs exhibited improved resistance to photooxidation. However, to obtain the dithiocarbamate ligand, a multi-step synthesis was needed. Later, a spontaneous assembly of dithiocarbamate on the gold surface was demonstrated by simply exposing gold to carbon disulfide (CS₂) and a secondary amine.²² This approach was then successfully extended to CdSe/ZnS core/shell QDs to tune the surface properties of QDs. Basically, TOPO functionalized CdSe/ZnS QDs were added to a solution containing equivalent amounts of CS2 and glycine (an amino acid based ligand), followed by stirring at room temperature for several hours to convert CdSe/ZnS-TOPO to dithiocarbamate functionalized CdSe/ZnS.17 Glycine, dissolved in a mixture of chloroform and methanol (1 : 1), provided both a source of amine groups for the formation of dithiocarbamate via its reaction with CS_2 and a source of carboxyl groups for aqueous solubility. It is noteworthy that only very dilute CdSe-TOPO QD dispersions $(i.e., 10^{-3} \text{ M})$ were used in the ligand exchange due to the limited solubility of glycine in the CHCl₃-MeOH mixture.¹⁷ Thus, the yield of dithiocarbamate functionalized CdSe (D-CdSe) QDs was rather low. However, for applications of water soluble QDs to bioimaging and QDSSCs, and also from cost considerations, a route to high yield (*i.e.*, large scale preparation) is desirable. Furthermore, dithiocarbamate functionalized CdSe/ZnS QDs were formed via ligand exchange in a single phase (i.e., in a 1:1

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CHCl₃–MeOH mixture). Thus additional steps (*i.e.*, precipitation and redissolution) were necessary to achieve the CdSe/ZnS QD aqueous solution.¹⁷

Here we describe a simple yet novel biphasic ligand exchange method to transfer original hydrophobic CdSe-TOPO QDs into hydrophilic dithiocarbamate functionalized CdSe (D-CdSe) QDs in one step. The D-CdSe QDs were produced with high yield (i.e., a very high concentration (for example, $c = 1 \text{ mg ml}^{-1}$ or higher) of CdSe-TOPO could be used in the reaction, which in turn led to the production of a large scale of D-CdSe QDs via ligand exchange). ³¹P NMR measurements confirmed the ligand exchange by detecting the existence of free TOPO in the chloroform-d phase after the exchange. The resulting water dispersible D-CdSe QDs exhibited an increased photoluminescence (PL) quantum yield as compared to the original CdSe-TOPO QDs, suggesting an effective passivation of dithiocarbamate ligands on the QD surface. The D-CdSe QDs were then mixed with the hydroxyl terminated TiO₂ nanoparticles. Photoluminescence (PL) measurements on the mixture showed a significant emission quenching of D-CdSe, indicating an efficient charge transfer from the D-CdSe QDs to the TiO2 nanoparticles. The reaction of the carboxyl group on the D-CdSe surface with the hydroxyl group on the TiO₂ rendered QDs in intimate contact with TiO₂, thereby facilitating the electronic interaction between them. The present *biphasic ligand exchange* method has several advantages over the previously reported ligand exchange processes. First, the reaction is simple and one-step. By mixing CS₂ and glycine in deionized (DI) water, and adding them into the CdSe-TOPO chloroform solution, the red-emitting CdSe QDs were *directly* transferred from the chloroform phase to the water phase after vigorous stirring at room temperature (i.e., interfacial reaction at the chloroform/water interface). Thus, no further precipitation and redissolution were needed to obtain the D-CdSe QD water solution. Second, glycine has excellent solubility in water (e.g., 25 g glycine can be readily dissolved in 100 ml water at room temperature) as compared to its limited solubility in CHCl₃-MeOH mixtures,¹⁷ thereby a large quantity of D-CdSe can ultimately be obtained by increasing the reaction volume and the concentration of CdSe-TOPO QDs. Finally, in comparison to monothiol counterparts, due to the strong chelate-type binding characteristic of dithiocarbamate, the resulting D-CdSe QDs exhibited improved resistance against photooxidation.

Experimental

Synthesis of CdSe-TOPO

TOPO-functionalized CdSe (CdSe-TOPO) QDs were synthesized *via* an organometallic high temperature growth approach described elsewhere.²³⁻²⁸ Briefly, 100 mg of cadmium oxide (CdO, Sigma-Aldrich) and 900 mg of stearic acid (Fisher Scientific) were loaded into an argon-protected 50 ml three neck flask. They were heated to 170 °C, resulting in a transparent liquid. The liquid was cooled to room temperature, followed by addition of 4 g trioctylphosphine oxide (TOPO, Sigma-Aldrich) and 4 g hexadecylamine (Sigma-Aldrich), and degassing under an argon flow for 30 min. The liquid was then heated to 290 °C, followed by the injection of a selenium stock solution containing 60 mg selenium (Sigma-Aldrich), 1.6 ml tributylphosphine (TBP,

Sigma-Aldrich), and 4 ml dioctylamine (Sigma-Aldrich). The size of CdSe QDs was readily controlled by altering the growth time. After the desired size was reached, 10 ml chloroform was injected into the reaction mixture to terminate the QD growth. This solution was finally collected and stored in the dark. All the chemicals were used as received without further purification.

Biphasic ligand exchange

As synthesized CdSe-TOPO chloroform solution (5 ml of 1 mg ml⁻¹ solution) was precipitated from methanol three times to remove the excess TOPO, and redissolved in 5 ml chloroform. Glycine (0.5 g) was dissolved in 5 ml DI water followed by addition of 0.4 ml CS₂. Glycine was chosen as the source for the amine group and the carboxyl group. The glycine–CS₂ DI water mixture was then added into the CdSe-TOPO chloroform solution. The resulting mixture was vigorously stirred at room temperature for 24 h. To purify the resulting dithiocarbamate functionalized CdSe (D-CdSe) QDs, the excess amount of free dithiocarbamate ligands was removed by either ultracentrifugation or dialysis against DI water with 3500 MWCO SnakeSkinTM Pleated Dialysis Tubing.

Synthesis of TiO₂ nanoparticles

TiO₂ nanoparticles were prepared according to the literature procedure.²⁹ Briefly, titanium isopropoxide was slowly dropped into ethanol and the solution was vigorously stirred for 2 h to hydrolyze titanium isopropoxide.

TiO₂ nanoparticle functionalization with D-CdSe QDs

Since TiO₂ nanoparticles were synthesized in ethanol, D-CdSe ethanol solution was prepared (*i.e.*, precipitation of D-CdSe QDs in DI water at pH = 7, followed by redissolution in ethanol) and mixed with TiO₂ nanoparticles at a 5 : 1 volume ratio. The mixture was allowed to react under vigorous stirring for different times. The use of larger amounts of D-CdSe ensures that each TiO₂ nanoparticle was linked by more than one QD (lower panel in Scheme 1), thereby resulting in a relatively intense PL.

Characterization

The diameter of the CdSe-TOPO QDs was determined by transmission electron microscopy (TEM; JEOL 1200EX scanning/TEM (STEM), operated at 80 kV). The absorption and emission spectra, the latter excited at 365 nm, were recorded with a home-made UV-vis spectrometer. The success of the biphasic ligand exchange process was verified by ³¹P NMR spectroscopy (Varian VXR-400). Glycine was dissolved in deuterium oxide (D₂O). Deuterochloroform (chloroform-d) was used in the ${}^{31}P$ NMR measurements to dissolve pure TOPO and CdSe-TOPO. The absolute PL quantum yield (PLQY) measurements on the CdSe-TOPO chloroform solution and the D-CdSe ethanol solution were carried out according to a well-established procedure,³⁰ using an integrating sphere and UV laser. The measurement involved three consecutive steps: first, the emission from the empty sphere; second, the emission with the sample in place and the laser beam directed towards the wall of the sphere; finally,



Scheme 1 Schematic illustrations of biphasic ligand exchange for the preparation of hydrophilic, dithiocarbamate functionalized CdSe QDs (*i.e.*, D-CdSe) by replacing the original ligand, TOPO, on the CdSe surface (upper panel), and of covalent linkage of dithiocarbamate functionalized CdSe QDs to native hydroxyl terminated TiO_2 nanoparticles (lower panel).

emission of the sample with the laser beam directed towards the sample.

Results and discussion

Fig. 1a shows the TEM image of 4 nm diameter CdSe-TOPO QDs. The absorption and PL spectra of the CdSe-TOPO chloroform solution are shown in Fig. 1b (solid curves). The absorption and PL maxima were at 599 nm and 612 nm, respectively. Subsequently, the glycine-CS₂ DI water mixture was added into the CdSe-TOPO chloroform solution. The resulting biphasic mixture was vigorously stirred at room temperature for 24 h. Glycine acted as a source of the carboxyl group and the amine group at each end. The carboxyl group offered aqueous solubility, while the amine group served as an anchoring moiety through its reaction with CS₂ (i.e., formation of the dithiocarbamate ligands, and subsequent attachment to the CdSe surface via biphasic ligand exchange with the original TOPO ligand at the CHCl₃/water interface as schematically illustrated in the upper panel in Scheme 1). The red-emitting CdSe QDs were found to be successfully transferred from the chloroform phase in the bottom (left image in Fig. 2) to the water phase on the top (right image in Fig. 2), as shown by the digital images of the strong emission excited at 365 nm. As a result, water soluble, dithiocarbamate functionalized CdSe QDs (D-CdSe) were obtained. Since glycine has excellent solubility in DI water (for example, 25 g glycine can easily be dissolved in 100 ml DI water at room temperature), a large quantity of D-CdSe can be obtained by using high concentration CdSe-TOPO chloroform solution ($c = 1 \text{ mg ml}^{-1}$) in the exchange as compared to $c = 10^{-3}$ M when glycine was dissolved in the CHCl₃–MeOH mixture.¹⁷ The shapes of the absorption and PL spectra of D-CdSe in water were the same as those of CdSe-TOPO in chloroform (Fig. 1b), signifying that the photophysical



Fig. 1 (a) TEM image of CdSe-TOPO. Scale bar = 40 nm. (b) The absorption and photoluminescence (PL) spectra of CdSe-TOPO in chloroform (solid curves), and the absorption and PL spectra of D-CdSe in water (dashed curves). The PL spectrum was obtained under UV excitation at 365 nm.



Fig. 2 Digital images of emission under UV excitation at 365 nm, demonstrating the transformation of hydrophobic CdSe-TOPO QDs from the chloroform phase (bottom layer in the left image) into hydrophilic D-CdSe QDs in water (top layer in the right image) after the biphasic ligand exchange at room temperature.

properties of the CdSe QDs were retained after the biphasic ligand exchange. The spectra of D-CdSe were slightly red-shifted. This may be due to the change of dielectric environment (*i.e.*, rather than chloroform, D-CdSe is dissolved in water) (Fig. 1b).

To verify the success of the biphasic ligand exchange process, ³¹P NMR measurements were carried out. Deuterochloroform (chloroform-d) and deuterium oxide were used in the biphasic ligand exchange process. For comparison, pure TOPO in chloroform-d was examined and showed a typical ³¹P NMR signal at \sim 50 ppm (Fig. 3a). In contrast, no obvious signals were observed for the CdSe-TOPO QDs in chloroform-d within the same scanning time (Fig. 3b). This can be attributed to the fact that most of the free TOPO was removed, and the broadening of the NMR signal due to the inhomogeneous distribution of magnetic environments.¹⁷ After the completion of the ligand exchange,



Fig. 3 ³¹P NMR of (a) pure TOPO in chloroform-d, (b) CdSe-TOPO in chloroform-d, and (c) free TOPO in chloroform-d phase; the free TOPO was released from original CdSe-TOPO as a result of the biphasic ligand exchange. All the ³¹P NMR measurements were performed in chloroform-d for the same period of time.

³¹P NMR on the chloroform-d phase showed a sharp peak at 52 ppm (Fig. 3c), indicating that TOPO was released from the original CdSe-TOPO surface during the ligand exchange with dithiocarbamate. It is worth noting that when either CS_2 or glycine solely was added to the CdSe-TOPO/chloroform/water system, no phase transfer as shown in Fig. 2 was observed.

The photoluminescence quantum yield (PLQY) was measured to be 2.4% for CdSe-TOPO in chloroform, and 15% for D-CdSe in ethanol, *i.e.*, over six times higher. The increase in the PLQY indicated improved passivation with the dithiocarbamate ligands on the CdSe QD surface. This is in sharp contrast to the decreased PLQY when monothiol ligands were used for ligand exchange to obtain water soluble QDs.31,32 We note that complete quenching or strong decrease in emission was recently reported when TOPO-functionalized CdSe QDs coated with a thin layer of ZnS in CHCl3-MeOH mixtures were ligandexchanged with dithiocarbamate in the same mixture of solvents (*i.e.*, single-phase ligand exchange).¹⁷ Hence, our method based on biphasic ligand exchange offers better surface passivation of dithiocarbamate, thereby resulting in a higher PLQY. In addition, the excellent solubility of glycine in DI water may also partially contribute to the increased PLQY. We note that an increase in PLQY in the water soluble QDs was also recently obtained by replacing the original TOPO with polyelectrolyte (i.e., polyallylamine),³³ which is consistent with our observation.

Compared to monothiol ligands, dithiocarbamates are bidentate chelating ligands and have stronger affinity for metal atoms.^{20,21} Thus, an increased photostability of the resulting QDs is expected. The D-CdSe QDs exhibit excellent stability under ambient conditions, as the strong emission is retained without any change in the absorbance for over 10 months (data not shown).

To explore the possibility of utilizing the D-CdSe QDs for use in photovoltaic devices (for example, QD-sensitized TiO₂ solar cells), PL studies were performed on a mixture of D-CdSe QD and TiO₂ nanoparticles in ethanol solution. The mixture was allowed to react under vigorous stirring for different periods. Compared to the PL of pure D-CdSe in ethanol (solid curve in Fig. 4; the emission peak was at 625 nm), a 65% reduction in emission after 2 h stirring was observed (dashed curve). It further dropped to 6% (*i.e.*, 94% reduction) after 24 h stirring, at which time the reaction between functionalized QDs and TiO₂ was expected to be complete. The decrease in the PL indicated a possible charge transfer from QDs to TiO₂. The reaction of the



Fig. 4 The PL spectra of a mixture of D-CdSe and TiO₂ nanoparticles during the different stirring periods. Compared to the original PL of D-CdSe in ethanol (solid curve), a 65% reduction in PL (dashed curve) after 2 h stirring and a 94% reduction in PL (dotted curve) after 24 h stirring were observed.

carboxyl group on the D-CdSe surface and the native hydroxyl group on the TiO₂ brought the QDs in direct contact with the TiO₂ nanoparticles as depicted in lower panel in Scheme 1, thereby facilitating the electronic interaction between them.²⁹ Furthermore, the polar solvent solubility of D-CdSe QDs enabled them to wet the hydrophilic TiO₂ nanoparticles easily, leading to a high adsorption efficiency of QDs on the TiO₂ nanoparticles. Taken together, the D-CdSe QDs can be exploited as intriguing sensitizers for use in QD-sensitized TiO₂ solar cells.^{29,34} Further investigations on the charge transfer using ultrafast transient absorption and fluorescence lifetime measurements are currently under way.

Conclusion

In summary, we have reported a simple yet novel route to hydrophilic dithiocarbamate-functionalized CdSe QDs (D-CdSe) via a biphasic ligand exchange process in one step. The resulting water-dispersible D-CdSe QDs exhibited an increased PLQY as compared to the original CdSe-TOPO QDs. The D-CdSe QDs also exhibited excellent stability under ambient conditions. The mixture of D-CdSe QDs and hydroxyl terminated TiO₂ nanoparticles showed almost complete quenching of the emission from D-CdSe, suggesting an efficient charge transfer from QDs to TiO₂. This was likely due to the reaction of the carboxyl group on the D-CdSe surface and the native hydroxyl group on the TiO₂, placing the QDs in direct contact with TiO₂ and thereby facilitating the electronic interaction between them. This opens up an avenue for use of D-CdSe in QD-sensitized TiO₂ solar cells. We envisage that, due to the presence of carboxyl groups on the D-CdSe QD surface, further control over the surface properties of QDs is possible. For example, positively charged QDs can be readily produced *via* the amidation of a diamine molecule with the carboxyl group of D-CdSe QDs.³⁵

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