Water-Soluble, Cyclodextrin-Modified CdSe−CdS Core−Shell Structured Quantum Dots

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β-Cyclodextrin (β-CD)-modified CdSe (β-CD/CdSe) and CdSe−CdS core−shell structured (β-CD/CdSe−CdS) quantum dots (QDs) were synthesized by a single-phase approach in aqueous solutions. These receptor-modified QDs are very soluble and stable in water over a wide range of pH values and ionic strengths. Coating a CdS shell on the CdSe core greatly increased the quantum yield (QY) of original CdSe QDs. Photoactivation of these particles by the room light results in 46% QY for β-CD/CdSe−CdS in water. The surface-anchored β-CD still retains its host capability for the complexation of different organic species in aqueous solutions. More interestingly, the fluorescence sensitivity of these QDs to the same substrate is ten times higher than that of their counterparts reported in our previous work. Furthermore, the fluorescence of these receptor-modified QDs could be reversibly tuned in two directions, enhancement or quenching, by selectively introducing different redox-active substrates in aqueous media.

Introduction

Semiconductor quantum dots (QDs) are currently an active subject of research[1] in nanoscience and nanotechnology because of the fast development of their synthetic methods. In particular, ligand-protected QDs have been increasingly explored as analytical tools in many biological fields[2] since the seminar works[3] from Alivisatos et al. and Chan and Nie. Introduction of organic ligand on nanoparticle surfaces provides not only the stability of these nanoentities in different solvents but also the desired surface functionality.[4] Within this scheme, artificial receptor-modified nanoparticles[5] are one of the interesting research topics. Cyclodextrins (CDs)[6] are well-known molecular hosts capable of including small hydrophobic molecules inside their cavities in aqueous media. It was observed that self-assembly of CDs on nanoparticles would bring these nanoscale entities with the ability to hold hydrophobic molecules on their surfaces,[7] which led to several interesting studies.[8]

In this work, we report the preparation of the first water-soluble, monothiolated β-cyclodextrin[9] (mSH-β-CD, Chart 1)-modified CdSe−CdS core−shell structured QDs by using a one-pot approach in aqueous media. These receptor-modified QDs are very soluble and stable over a wide range of pH values and ionic strengths. In addition, the quantum yield (QY) of these particles could reach ∼40% upon photoactivation under the room light. More interestingly, the fluorescence of these QDs could be reversibly tuned through complexation induced interactions between these QDs and selected molecular species in aqueous solutions. Thus, these receptor-modified QDs may serve as a good model system

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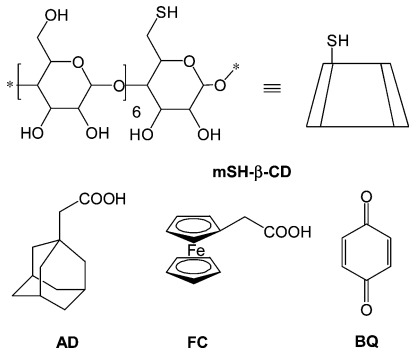
Chart 1. Molecular Structures of Host and Guests in This Study



in the investigation of noncovalent interactions between chemical or biological species and QDs in aqueous media.

Experimental Section

Materials. All chemicals and solvents used in the work are commercial products (from Aldrich or Acros) with the highest quality available unless noted in the following text. Deionized and doubly distilled water was used throughout all experiments. Deuterated solvents for NMR study were obtained from Cambridge Isotope. Carbon-coated copper grids (400 mesh) for transmission electron microscopy (TEM) measurement were from Ted Pella. mSH-β-CD (Chart 1) was synthesized and fully characterized according to the reported procedure.[9]

Preparation of CdSe QDs Modified with mSH-β-CD (β-CD/CdSe). Synthesis of mSH-β-CD-modified CdSe QDs (β-CD/CdSe) followed a procedure similar to the one reported by Kotov et al.[10] In a typical preparation, 50 mg of sodium citrate was added to 45 mL of deionized water containing 2 mL of 0.04 M cadmium perchlorate at pH 9. This mixture was purged with N_2 for 10 min, and 2 mL of 0.01 M *N*,*N*-dimethylselenourea was then added. The reaction was taking place under the reflux condition in the N_2 atmosphere. After 30 min, 50 mg of mSH-β-CD was added, and the reaction was carried out for another 6 h. During this course, the solution became a clear orange color indicating the formation of CdSe QDs. The reaction was then naturally cooled to room temperature and kept stirring under N_2 overnight.

Preparation of CdSe−CdS Core−Shell Structured QDs Modified with mSH-β-CD (β-CD/CdSe−CdS). A total of 50 mg of sodium citrate was added to 45 mL of deionized water containing 2 mL of 0.04 M cadmium perchlorate at pH 9. This mixture was purged with N_2 for 10 min, and 2 mL of 0.01 M *N*,*N*-dimethylselenourea was then added. The reaction took place under the reflux condition in the N_2 atmosphere for 6 h. Thioacetamide (0.04 M) was then introduced into the reaction mixture. The molar ratio between Se and S was controlled to be 1:1. A total of 50 mg of mSH-β-CD was also introduced at this stage. The solution turned red within minutes at 75 °C. The reaction mixture was stirred for 24 h under N_2 and then naturally cooled to the room temperature.

Purification of β-CD/CdSe and β-CD/CdSe−CdS. Purification of β-CD/CdSe and β-CD/CdSe−CdS essentially followed our reported procedure.[11] In a typical workup, the volume of the reaction mixture was reduced to 10 mL under the reduced pressure. This sample was centrifuged at 10 000 rpm for 8 min to remove any aggregates. The supernatant was dialyzed against a basic aqueous solution (pH ∼ 12) three times and then pure water four times. A solid powder was obtained by freeze-drying this sample.

Photoactivation of Receptor-Modified QDs in Aqueous Solutions. A desired amount of β-CD/CdSe or β-CD/CdSe−CdS was dissolved in deionized water. The solution was kept sealed in a glass vial on the lab bench. The photoactivation was carried out under room light. No additional light source was used. The optical properties of this sample were monitored everyday by UV−vis and florescence measurements.

TEM Measurements. The TEM and energy-dispersive spectrometry (EDS) measurements were carried out on a JEOL4000FX instrument. A few drops of either β-CD/CdSe or β-CD/CdSe−CdS aqueous solution were transferred onto a carbon-coated copper grid. The water was naturally evaporated at room temperature. The TEM images were obtained at 200 keV acceleration voltages.

Photon Correlation Spectroscopic (PCS) Measurements. PCS experiments were carried out on a Coulter N4-Plus instrument. The stability of β-CD-modified QDs in aqueous solutions was monitored at room temperature. The scattered light was detected at 90 °C from the incident beam. The viscosity and refractive index of QD solutions were taken as identical to the values of the pure water.

NMR Measurements. NMR spectra (400 MHz) were recorded on a Varian UI400 NMR spectrometer. ^{1}H NMR spectra of free β-CD and surface-anchored β-CD on QDs were obtained in D_2O.

Fluorescence Measurements. The fluorescence of β-CD/CdSe and β-CD/CdSe−CdS in aqueous media was recorded by using a Spex Fluorolog 1681 fluorophotometer. QYs of these surface-modified QDs were calculated by using Rhodamine B as a reference.[12] Optical densities were kept within 0.2 at the excitation wavelength.

UV−Vis Measurements. UV−vis spectra of β-CD/CdSe and β-CD/CdSe−CdS in aqueous media were recorded on a HP8452A diode array spectrophotometer at room temperature.

Results and Discussion

Preparation and Characterization of Water-Soluble, β-CD/CdSe and β-CD/CdSe−CdS. Water solubility is very important to QDs for their chemical[13] and biological applications. A popular approach for the preparation of high-quality water-soluble CdSe QDs is to synthesize these particles in trioctylphosphine oxide at high temperature[14] and then to perform the ligand exchange for the introduction of water solubility of these nanoentities. Several other approaches[15] have been reported to prepare water-soluble QDs.

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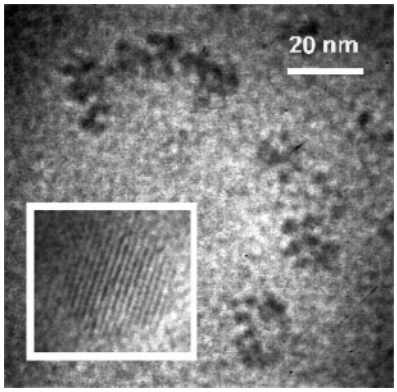

Figure 1. TEM and high-resulution TEM (inset) images of β-CD/CdSe−CdS.

Adapted from a Kotov et al.'s report,[10] a one-pot approach has been developed in this work for the preparation of β-CD/CdSe and β-CD/CdSe−CdS QDs in aqueous solutions. Briefly, to prepare β-CD/CdSe, a basic aqueous solution (pH = 9) containing cadmium perchlorate and *N*,*N*-dimethylselenourea in the presence of sodium citrate and mSH-β-CD was refluxed for several hours in a N_2 atmosphere. The formation of QDs was evidenced by the appearance of an orange color in the reaction mixture. To prepare core−shell structured β-CD/CdSe−CdS, thioacetamide (as the sulfur source) was introduced in the reaction containing the CdSe core which was temporarily stabilized by sodium citrate. mSH-β-CD was also introduced at this moment. The formation of core−shell structured QDs after overnight reaction at an elevated temperature (75 °C) was envisioned by the appearance of an orange/red color in the solution. The purification of these particles was achieved by using a dialysis approach reported from our previous work.[11] The final products are orange (β-CD/CdSe) and orange/red (β-CD/CdSe−CdS) powders.

Figure 1 shows the typical TEM images of β-CD/CdSe−CdS. By counting over 100 individual particles from their TEM images, the average particle sizes for β-CD/CdSe and β-CD/CdSe−CdS are 4.0 ± 0.7 nm and 4.3 ± 0.8 nm, respectively (Supporting Information). It is important to note that the deposition of the CdS shells on the CdSe cores resulted in a uniform increase in their diameters. Every examined particle revealed EDS signals both from S and from Se. The continuity of the CdS shell was difficult to establish from microscopy data because of the closeness of the CdS and CdSe lattice constants.

The optical properties of these as-prepared QDs have been investigated. While the absorption onset of β-CD/CdSe in water is 522 nm, coating a shell of CdS on these particles renders β-CD/CdSe−CdS, which exhibits an absorption onset at 550 nm (Figure 2A). Irradiation (400 nm) of β-CD/CdSe generated two fluorescence bands, a band-edge emission (550 nm) and a broad trap-state emission (Figure 2B). These typical two-band emissions were also observed in other QD systems.[16] In comparison with that of rhodamine B, the QY of the room-temperature excitonic emission of as-prepared β-CD/CdSe is weak, about 0.65%. Upon deposition of a CdS shell over the CdSe cores, the luminescence intensity increases by six times, reaching to a 3.7% QY for as-prepared β-CD/CdSe−CdS. A red shift in the band-edge emission peak (579 nm, Figure 2B) is also observed in these core−shell structured QDs. The red shift in both the absorption and the fluorescence emission of CdSe after CdS coating is probably resulted from the expansion of volume for the exciton originally available only inside the CdSe core to the CdS shell.[17] Deposition of a CdS shell over the CdSe QDs passivates their surface defects, thus leading to the localization of photoexcited charge carriers in the CdSe core.[18] The strategy of growing an inorganic shell of material with a larger band gap around each semiconductor core has also been shown to improve the luminescence QY dramatically in other CdSe systems.[19]

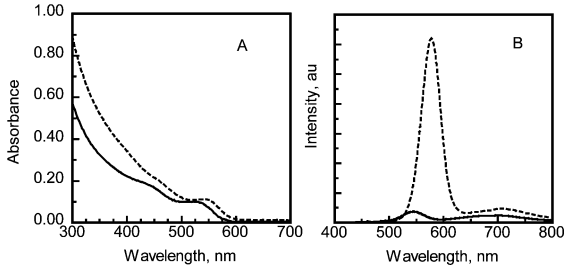

Figure 2. Electronic absorption spectra (A) and fluorescence (B) of as-prepared β-CD/CdSe (solid line) and β-CD/CdSe−CdS (dotted line) QDs in aqueous media.

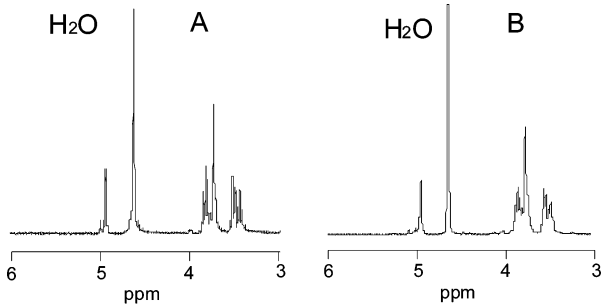

Figure 3. ^{1}H NMR of (A) free β-CD and (B) β-CD on CdSe−CdS QDs in D_2O.

As expected, these particles were very soluble in water which is believed to be attributed to the presence of β-CD on the particle surfaces. Figure 3 shows the proton signals of β-CD before (Figure 3A) and after (Figure 3B) they attached to the surface of CdSe−CdS QDs in D_2O. The result obtained in this study is very similar with our previous study.[11] A noticeable difference is that the extent of broadening of proton signals of β-CD is less in the current case as compared with the ones from perthiolated β-CD on CdS QDs. This discrepancy is believed to be the result of a

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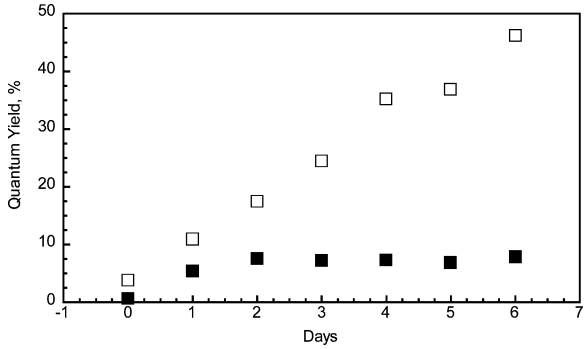
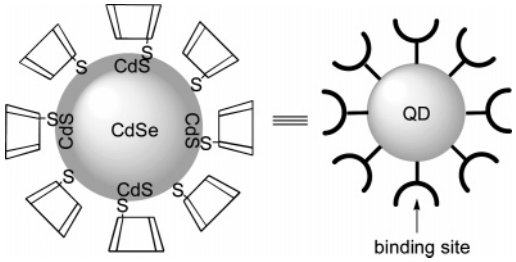


Figure 4. Enhancement of QY of β-CD/CdSe (filled square) and β-CD/CdSe−CdS (empty square) under room light in pure water.

difference in the nature of the surface attachment of β-CD. While perthiolated β-CD has seven thiol groups on each molecule, only one thiol group exists on mSH-β-CD. Attachment of perthiolated β-CD on CdS QDs fixes not only this molecule on the particle surface but also its own geometry. As a result, the surface-attached perthiolated β-CD is more rigid as compared with its free form in solutions which leads to the broadening of its proton signals. In the current study, attachment of mSH-β-CD on the particle surface does prevents neither the free rotation of the molecule along the SH group nor the flexibility of its structure. Consequently, the broadening of proton signals is not significant.

A common problem encountered in using water-soluble, ligand-protected QDs for practical applications is their low QY.[11] Thus, we performed a photoactivation process[20] on these as-prepared QDs. Exposing either β-CD/CdSe or β-CD/CdSe−CdS water solutions to the room light over 1 week under a sealed condition greatly enhanced the quantum efficiency of these particles (Figure 4), from the original 0.65% and 3.7% to 7.8% and 46.2% for β-CD/CdSe and β-CD/CdSe−CdS, respectively. The enhancement of exciton emission of these QDs probably results from the water−[21] and oxygen[10]−QD interactions during the course of phototreatment. The further phototreatment led to the decrease in the fluorescence effeciency which might be due to the photoionization of these QDs.[34] Thus, we monitored the electronic absorption of these particles during this treatment. It was observed that the optical densities of all samples noticeably decreased during the illumination (Supporting Information). It was also noticed that light treatment promoted spectral shifts toward shorter wavelengths in both the absorption and the luminescence spectra. This result is possibly due to the decrease in particle size during illumination. Photooxidation of the thiol ligand and, consequently, destabilization of ligand-protected QDs during the light treatment are also a concern.[22] PCS measurements evidenced that there was no aggregation in these solutions after 1 week of phototreatment. The ^{1}H NMR study further demonstrated that β-CD still existed on the particle surface (Supporting Information). To prevent the destabilization of these particles after phototreatment,[23] the photoactivated QDs were obtained in the solid form by re-collecting these particles from their solutions under the reduced pressure.

Scheme 1. Ideal Model of β-CD/CdSe−CdS



Many water-soluble QDs have been prepared by introducing a variety of organic species, from small charged molecules[24] to peptides,[25] to their surfaces. A unique feature of these β-CD-modified QDs is that the high solubility of these particles in the water is not due to the presence of charged ligand on particle surfaces. Instead, the existence of many hydroxyl groups of surface-attached β-CD on each particle is the major contribution to its water solubility. The PCS measurements indicated that there is no aggregation observed in these receptor-modified QDs at pH values from 5 to 9 as well as at high ionic strength, for example, 0.2 M during the fluorescence study. Thus, the covalent attachment of β-CD on these QDs leads to a robust and isolable nanomaterial which can be dissolved and then re-collected from water without losing its stability (Scheme 1).

Although ligand-protected QDs have been used extensively as optical probes/tags for various biological species, such as cells,[26] proteins,[27] and DNA,[28] reversible mediation of fluorescence properties of QDs with small, neutral molecular species has not been fully explored. Major approaches used to alter the fluorescence of QDs in previous reports were

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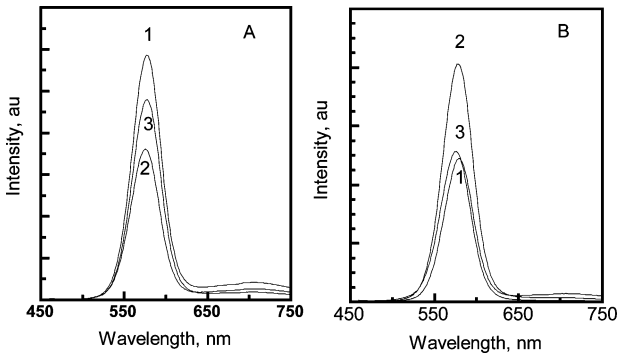

Figure 5. (lines A1 and B1) Fluorescence of β-CD/CdSe−CdS (0.5 mg/mL) in the aqueous solution; (line A2) β-CD/CdSe−CdS + FC (0.24 mM); (line A3) β-CD/CdSe−CdS + FC + AD (1 mM); (line B2) β-CD/CdSe−CdS + BQ (0.1 mM); (line B3) β-CD/CdSe−CdS + BQ (0.1 mM) + FC (0.23 mM).

the direct physical adsorption or chelation of metal ions on their surfaces.[13b,29] In these studies, fluorescence of these QDs are usually quenched in the presence of these ionic species. Addition of amine derivatives in QD solutions enhanced the fluorescence emission of these particles.[30] But, these investigations were performed in the organic media. Physical adsorption of these electron donors on particle surfaces is believed to be the major mechanism for the increase in the fluorescence QY.

In this work, we report, for the first time, that the fluorescence of these receptor-modified QDs can be reversibly tuned in two directions, either enhancement or quenching, depending on the selection of the substrate. In a previous work, we reported that ferrocene derivatives were the efficient quencher after they were complexed with β-CD on β-CD-modified CdS QDs in aqueous media.[11] We concluded that the fluorescence quench in this study was not due to the direct physical adsorption of these substrates with a specific functional group. Instead, the nature of the ferrocene, being a redox-active moiety in three ferrocene derivatives, could play a key role in the interaction with CdS QDs leading to the fluorescence quenching. Such phenomenon was also observed in the current study. Addition of 0.23 mM of FC (Chart 1) in the β-CD/CdSe−CdS aqueous solution resulted in the decrease in the fluorescence of these particle to the half of their original one (Figure 5). But, introduction of 1 mM AD (Chart 1), being an excellent guest for β-CD, in this solution led to the partial recovery of the fluorescence emission of β-CD/CdSe−CdS. As such, complexation induced mediation of the fluorescence change of the QDs was also demonstrated in this system. It should be noted that the QDs prepared in this work are more sensitive in their fluorescence change toward the same substrate, such as ferrocene derivatives, as compared with those from our previous report.[11] For example, β-CD/CdSe−CdS is 10 times more sensitive than β-CD/CdS prepared in the last report to the same analyte, FC, under identical conditions. Such enhancement in the sensitivity is attributed to the higher QY of these QDs and is very valuable for the development of QD-based fluorescence sensors. Thus, the major goal of this work has been reached.

Then, we extended our investigation to other redox-active species. Quinones are a class of compounds that have widespread importance in biology and chemistry. Quinone derivatives are active in cellular respiration,[31] photosynthesis,[32] and blood coagulation.[33] In this sense, probing these redox-active species in aqueous media is of great importance. In this work we found that, in contrast to the ferrocene derivatives, benzoquinone (BQ, Chart 1) acted as a fluorescence enhancer (Figure 5B). The fluorescence emission of β-CD/CdSe−CdS increased almost onefold (Figure 5B, line 1 to line 2) in the presence of 0.1 mM of BQ. Introduction of 0.23 mM FC reduced the fluorescence intensity back to its original one. The effective competition of FC with BQ for the availability of β-CD on the QD surfaces replaced some BQ in the cavity of surface-anchored β-CD with this molecule. Consequently, the resulted fluorescence of these QDs was balanced between the enhancing and the quenching process exerted by two different species.

The nature of such enhancement of these water-soluble QDs by the presence of BQ is not very clear at this moment. Considering that BQ is a redox-active species, the relationship between the redox potential of this molecule and the valence band edge of CdSe may play a crucial role in this process.[27a] In this sense, tuning the valence band of CdSe by changing its particle size for the investigation of the BQ−CdSe interaction may provide some useful information to answer this question.

Conclusion

In this paper, we report the preparation and characterization of the first water-soluble, CD-modified CdSe−CdS core−shell structured QDs. Up to 46% QY of these particles in aqueous media has been achieved upon the photoactivation under room light. In addition, these receptor-modified nanoentities are very stable in a wide pH range and at high ionic strength. The surface-attached β-CD still retains its capability of engaging host−guest complexation on QDs. More interestingly, the fluorescence of these CD-modified QDs can be tuned in two directions, either quenching or enhancing, by introducing selected organic species in their aqueous solutions. In addition to quinone reported in this work, we are currently studying other molecular cofactors, such as reduced nicotinamide adenine dinucleotide and adenosine 5′-triphosphate by using these QDs in aqueous media. We hope that these highly quantum efficient, water-

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soluble receptor-modified QDs can serve as an active component in the construction of QD-based hybrid nanomaterials for practical applications, such as clinical diagnosis and solar energy conversion.

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Supporting Information Available: Size distribution of β-CD/CdSe and β-CD/CdSe−CdS QDs, ^{1}H NMR of β-CD/CdSe−CdS after photoactivation, and electronic absorption spectra of β-CD/CdSe and β-CD/CdSe−CdS during the photoactivation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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