Preparation of Large Transparent Silica Monoliths with Embedded Photoluminescent CdSe@ZnS Core/Shell Quantum Dots

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Highly photoluminescent CdSe quantum dots (QDs) and their core/shell structures have been attracting a great attention as potential optical materials because of their high photostability, good luminescence efficiency, and emission tunability in the visible region.[1] Due to the potential advantages of the QDs over organic dye molecules, there have been intense research activities in incorporating the QDs as a chromophore in various host materials such as polymers and inorganic oxides.[2−12] Particularly, the composites of quantum dots with silica and titania have attracted considerable interests because of their nonlinear optical properties and thermal stability of the host materials.[3−12] However, the reported QD-silica (and QD-titania for that matter) composites have been limited to the form of thin films or nanocomposites, and to our knowledge, none of the previous efforts has produced "free-standing" QD-silica composite monoliths in the "centimeter size" range. This is quite in contrast to the research area on dye-containing silica composites in which such large dye-silica composite monoliths can be routinely prepared and mechanically modified for their utilization in current glass-based nonlinear optical devices and color filters.[13−15] In this communication, we describe a successful preparation of large free-standing transparent silica monoliths with embedded highly fluorescent CdSe@ZnS QDs, based on a straightforward application of inorganic−organic hybrid approach in room temperature sol−gel synthesis.

The inorganic−organic hybrid approach employed in this work is indeed a direct synthetic route to the introduction of organic functional groups into silica network in sol−gel chemistry,[16] and it usually involves the co-condensation of alkoxysilane and organoalkoxysilane that allows an organic moiety to become a part of the covalent network. This co-condensation ensures a homogeneous distribution of the organic groups throughout the silica matrix under mild reaction conditions.[16] A straightforward application of the inorganic−organic hybrid sol−gel method is easily envisaged upon replacement of the organoalkoxysilane by using alkoxysilane-capped semiconducting QDs. The commonly employed basic pH condition is well suitable for the semiconducting QDs because they are otherwise sensitive to strong acids, such as HCl and HNO_3, the common catalysts in sol−gel synthesis.[17] Despite the previous relevant efforts, however, the successful realization of the direct sol−gel method has not been reported so far for large-size QD-silica composite monoliths in the literature, probably due to the degradation or phase separation of the QDs during the synthetic process.[9]

In our experiments, we employed 3-mercaptopropyltrimethoxysilane (MPS) as the capping agent because of the high affinity of the thiol ligand on the surface of the semiconducting II−VI QDs. The MPS-capped CdSe@ZnS core/shell structures were first prepared in two steps based on the original low-temperature synthetic method reported by us.[18] The new method achieves ligand exchange and the core/shell formation "simultaneously" in a single step[19] and thus avoids the possible decrease of quantum yield (QY) during the ligand exchange process.[3b]

Three kinds of oleylamine-capped CdSe QDs were obtained with green, yellow, and red photoluminescence (PL)

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colors. Handling of the chemicals and solutions was carried out in a nitrogen-filled glovebox except during the post-synthesis processes. In a typical synthetic process, 0.2 mmol of B_2Se_3 and 0.6 mmol of $CdCl_2$ were loaded into 3 mL of oleylamine in separate sealed vials and dissolved by heating at 110 °C for 20 min. After the solutions were cooled, they were mixed together and divided into three 15-mL crimp-top microwave-reaction vials. The vials were tightly sealed using an aluminum crimp cap with Teflon-lined rubber septum before taken out from the glovebox. Each mixture solution was heated at 70, 120, or 190 °C for 60 s in a CEM microwave reactor, and the different reaction temperatures provided products of different PL emission wavelengths (λ_{max} = 525, 574, and 618 nm; QY= 3.4%, 2.7%, and 2.3%,[20] respectively).

The CdSe@ZnS core/shell QDs with MPS as a capping agent were prepared by coating the core CdSe QDs with a ZnS shell, as MPS replaced oleylamine, the original capping ligand, at the same time.[19] In a typical reaction, 0.1 mmol of P_2S_5 and 1.2 g of MPS were heated at 110 °C for 20 min in 10 mL of 1-methyl-2-pyrrolidinone (NMP) in a sealed vial that also contained 0.5 mL of butylamine to dissolve the sulfide. In a separate vial, 0.5 mmol of $ZnCl_2$, 1.2 g of MPS, and 0.5 mL of butylamine were dissolved in 10 mL of NMP and heated in the same way. After cooling to room temperature, the $ZnCl_2$ solution was divided into five crimp-top vials. 0.01 g of oleylamine-capped CdSe core particles was dissolved in the P_2S_5 solution, and the whole solution was divided into five portions. Each portion of the CdSe/P_2S_5 solution was injected into one $ZnCl_2$ solution preheated at 70 °C, and the solution was kept at the same temperature for 30 s in the microwave reactor, which provided MPS-capped CdSe@ZnS core/shell products. The success of the reaction could be easily checked from the enhancement of PL intensity and solubility difference of QDs capped with different capping molecules. For example, oleylamine-capped QDs are freely soluble in hexane but insoluble in methanol. MPS-capped QDs behave in the opposite way. The as-prepared CdSe@ZnS core/shell QDs were concentrated by extracting the solvent mixture with hexane 3−5 times, and the concentrate was re-dispersed in 10 mL of methanol.

Figure 1 shows the absorption spectra and PL spectra under a 365 nm excitation wavelength of the three different core/shell samples. The optical spectra were measured with Shimadzu UV-2100U spectrophotometer and JobinYvon Fluoromax-3 spectrofluorometer, respectively. QYs of the green-, yellow-, and red-emitting CdSe@ZnS QDs are 64.2%, 47.7%, and 28.3% with PL λ_{max} of 524, 574, and 619 nm, respectively.

The silica monoliths embedded with the CdSe@ZnS QDs were prepared by using sol−gel method with TMOS as a silica precursor and with ammonia as a catalyst. In a typical process, 3 mL of the concentrated CdSe@ZnS solution was mixed with 2 mL of *N,N*-dimethylformamide (DMF) while magnetically stirred. DMF works as a drying control chemical additive (DCCA) to prevent the crack formation in the
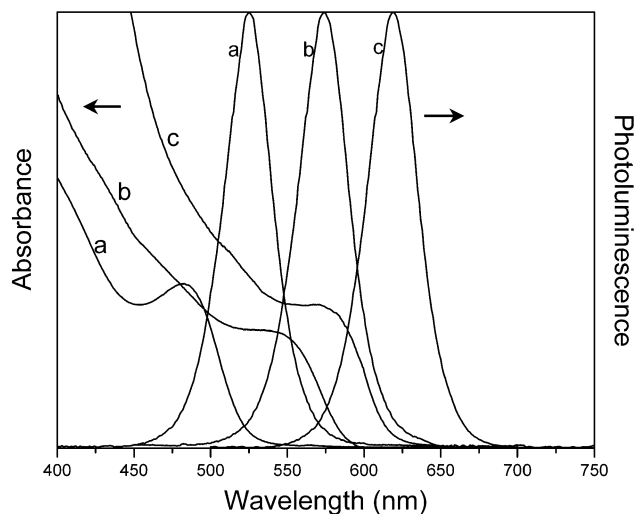
Figure 1. Absorption and PL spectra of the MPS-capped CdSe@ZnS QDs in methanol. The core particles for the samples a−c were prepared at 70, 120, and 190 °C, respectively. A 365 nm UV light was used for the excitation of the samples.

monoliths during the evaporation of the solvents.[21,22] Subsequently, 4 mL of TMOS was added into the mixture, followed by addition of 1 mL of ammonia solution (pH = 11). The whole solution was kept stirred for 10 min, and then it was transferred to a plastic mold. The gelation took place within 20−30 min under the basic reaction condition. The gel was dried in a solvent-saturated environment at room temperature over 3 d, which provided ca. 5 mm thick free-standing monoliths. Figure 2 shows three monolith samples with different emission wavelengths under a room light (top) or a UV light (bottom). The samples were transparent without apparent inhomogeneity in color and showed strong PL emissions.

The chemical stability of CdSe@ZnS QDs during the gelation and drying processes in the silica gel was examined by monitoring the PL of the gel kept in a plastic cuvette over 7 d with a 24-h interval. The typical change of PL spectra shown in Figure 3a indicates that the QDs maintain the same average size and size distribution during the gelation and drying processes. A slight decrease of the PL intensity over several days is noticed in Figure 3a, but at a decreasing rate. Its origin is not clear because the shrinkage and condensation of the gel do not allow us a direct comparison of the PL spectra obtained after different gelation/drying periods. In any event, the overall slowdown of the decrease in the relative PL peak area suggests a high stability of CdSe@ZnS QDs during the gelation/drying periods (Figure 3b). Furthermore, the silica monoliths kept their PL even after several months without any visible decrease in their PL intensity. The observed high chemical stability indicates that the surfaces of CdSe nanocrystals were well passivated with the ZnS shell layer and the MPS capping molecules and that the mild sol−gel condition kept the CdSe@ZnS QDs surfaces intact during the reaction.

In summary, we have shown that highly transparent and highly fluorescent silica monoliths could be prepared with

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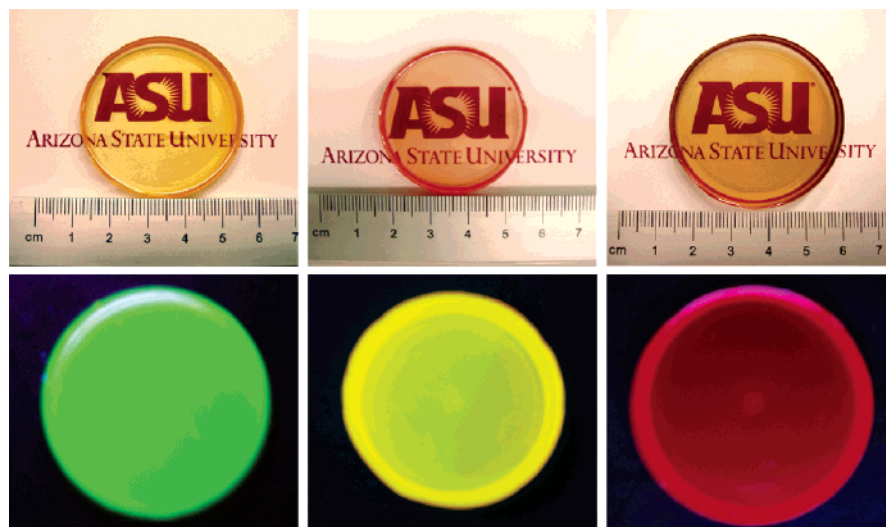
Figure 2. Silica monoliths embedded with the three different CdSe@ZnS QD products under a room light (top) and a 365 nm UV light (bottom).
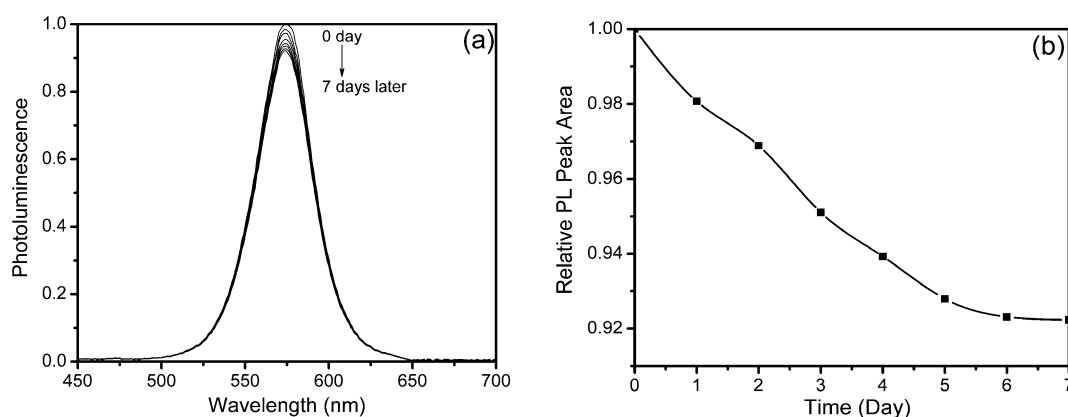
Figure 3. (a) PL spectra of a silica gel containing MPS-capped CdSe@ZnS QDs in a cuvette taken every 24 h consecutively for 7 d. (b) The relative PL peak area of the PL curves in panel (a) after different gelation/drying periods.

embedded CdSe@ZnS QDs by employing the inorganic−organic hybrid approach based on the sol−gel chemistry. The room-temperature reaction condition with a basic catalyst avoids chemical degradation of the QDs during the sol−gel process. The apparent homogeneity in the color and PL intensity of the silica monoliths indicates that co-condensation was successfully achieved between the MPS-capped QDs and TMOS precursor molecules. It is suspected that this method can be applied for other semiconducting QDs and can be extended to prepare various types of QD composites that are based on sol−gel chemistry.

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