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Reversible and Multisensitive Quantum Dot Gels

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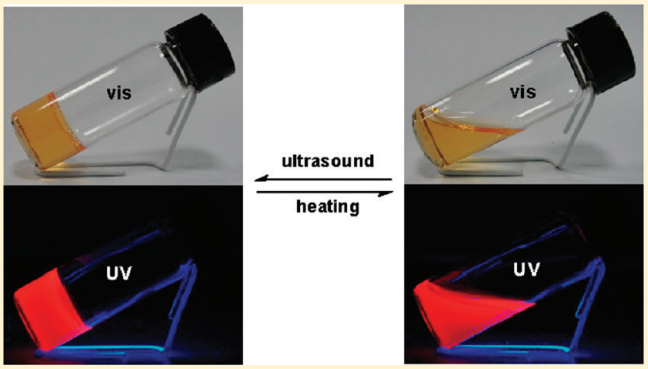
Supporting Information

ABSTRACT: Functional fluorescent semiconductor quantum dot (QD) based gels prepared via immobilizing QDs in organic matrices have shown promising properties, but the compatibility of QDs and organic matrix is not good, and the interactions of the ligands on the surface of QDs with organic matrix are weak, which lead to poor dispersion of QDs in the formed gel and decrease of photoluminescence after gelation in some cases. In this work, we report a hyperbranched macromolecule that can not only act as an excellent ligand to stabilize QD but also act as a good gelator that can gel QD solution to form a reversible and multiresponsive fluorescent gel. This hyperbranched macromolecule-capped QD is stable, and the sol−gel switching can be easily realized via heating and ultrasonicating. Most important, the formed QD gel shows stronger fluorescence than that of the corresponding solution. This novel QD-hyperbranched macromolecule inorganic/organic hybrid network shows great promise in fields such as imaging, sensors, drug release, and nanoscience.



INTRODUCTION

Reversible and stimuli-responsive (such as temperature and pH responsive) gels, exhibiting reversible changes in morphology and/or physical properties in response to various external stimuli, are drawing considerable attention because of their potential applications in gene and drug delivery systems,[1−5] sensors,[1,6,7] actuators,[7] shape memories,[8,9] and switches.[10−13] Among these reversible and stimuli-responsive gels, functional fluorescent gels are most promising.[14−19] Compared with organic fluorophores, semiconductor quantum dots (QDs) are nanometer-sized particles with unique optical and electronic properties and are currently under intensive research for a broad range of applications such as solar energy conversion and molecular imaging.[20,21] Although semiconductor QD based fluorescent stimuli-responsive gels are very promising, it is difficult to prepare these QD based gels. Recently, some reports on the preparation of QD based gels via immobilizing QDs in organic matrix have appeared: for examples, Bardelang et al. prepared photoluminescent gel by interfacing trioctylphosphine oxide (TOPO)-capped CdSe@ZnS quantum dots with supramolecular dipeptide gel;[22] Li et al. reported a highly photoluminescent gel by physically immobilizing CdTe quantum dots in poly(*N*-isopropylacrylamide) thermosensitive gel;[15] Leblanc et al. immobilized mercaptoacetic acid-capped QDs within a photo-cross-linked poly(ethylene glycol) (PEG) hydrogel through the utilization of physical trapping.[23] Although these methods are simple and useful, some problems remain; for examples, compatibility of QD and polymer matrix is not good, the interactions of the ligands on the surface of QD with organic matrix are weak, which results in poor dispersion of QDs in gel, most of the gels are irreversible and not stimuli-responsive, and the photoluminescence decreased after QDs being immobilized in organic matrix in some cases.[22] We are hoping to design special macromolecule that not only acts as excellent ligand to stabilize QD but also acts as a good gelator that can gel the semiconductor QD solution. Hyperbranched macromolecule is of three-dimensional structure and has multiple functionalities; some functionality in hyperbranched macromolecule may bind the QD surface to stabilize QD, and some others may bind each other via intermolecular interactions to gel QD solution. Here, we report a specially designed branched macromolecule with these functionalities.

RESULTS AND DISCUSSION

Functional poly(amido amine)s with different structure—PAA1 (linear poly(amido amine), MW = 29 200, PDI = 2.9); PAA3 (hyperbranched poly(amido amine), MW = 52 000, PDI = 1.5)—were first prepared as shown in Figure 1 since these polymers have different amine units (primary amine, secondary amine, and tertiary amine) in the backbone, and their topology (linear, branched, and hyperbranched) can be easily controlled

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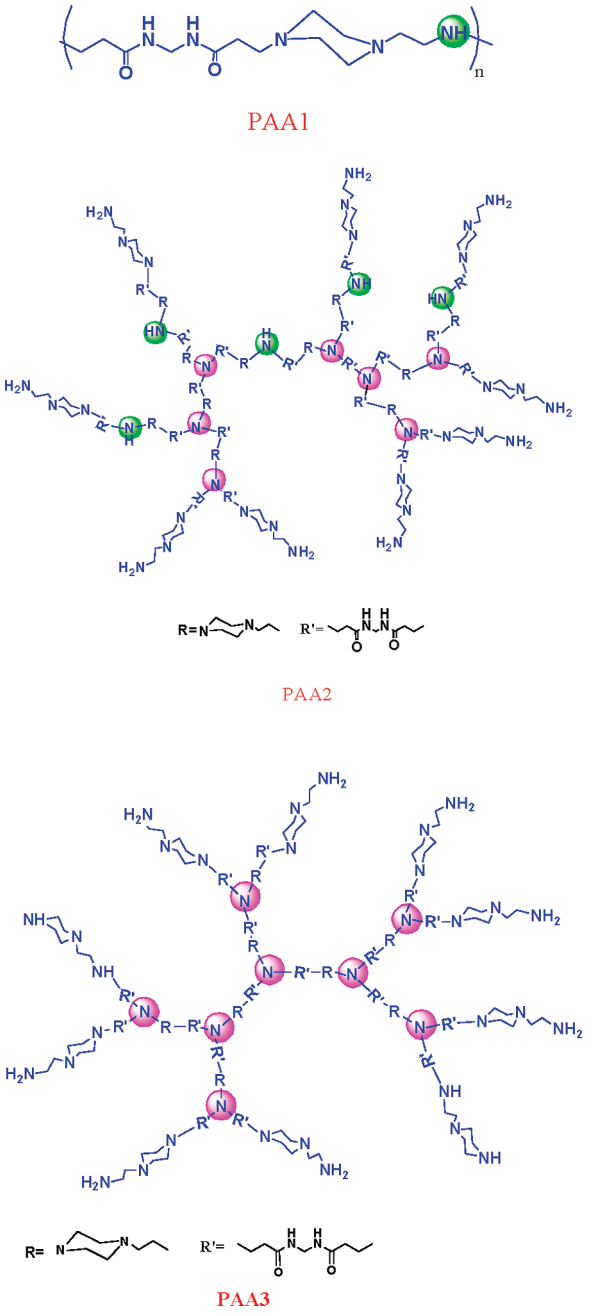

Figure 1. Structures of linear poly(amido amine) (PAA1) and hyperbranched poly(amido amine) (PAA2 with primary, secondary, and tertiary amine units in the backbone and PAA3 with tertiary amines in the inner core and the primary amines only at the periphery).

via tuning the polymerization conditions (such as temperature, solvent, and feed molar ratio).[24−29] PAA1 with linear structure has secondary amines and tertiary amines in the backbone while PAA3 with hyperbranched structure has tertiary amine units only in the inner core and primary amine units only at the periphery as shown in Figure 1. The amine units in the backbone of PAA1 and PAA3 can participate in multiple binding interactions with QD surface based on previous findings.[30] OA-capped CdSe@ZnS and TOPO-capped CdSe quantum dots were prepared based on previous references.[30,31] In the ligand exchange experiment, OA-capped CdSe@ZnS (or TOPO-capped CdSe) in chloroform and PAA1 in methanol were mixed and vortexed at room temperature, the solution turned turbid soon, and subsequently precipitates appeared. After filtration through a 0.2 μm microsyringe filter, the solution appeared almost colorless (as shown in Figure 2); the isolated CdSe@ZnS and CdSe quantum dots were found to be very difficult to redisperse in polar solvents such as DMF and DMSO, which may result from that those secondary and tertiary amine units in PAA1 have weak coordination with CdSe@ZnS and CdSe quantum dots, and hence PAA1 is not a good stabilizer for CdSe@ZnS and CdSe quantum dots. Subsequently, hyperbranched poly(amido amine) (PAA3) with vinyl terminals was prepared at 1/2 monomer feed molar ratio of 1-(2-aminoethyl)piperazine to *N*,*N*′-methylenebis(acrylamide), all the amine units are tertiary amine as shown in Figure 1 and S-Figure 2, and subsequently, the vinyl terminals reacted with 1-(2-aminoethyl)piperazine to form PAA3 with tertiary amine units only in the inner core and the primary amine units only at the periphery. When OA-capped CdSe@ZnS (or TOPO-capped CdSe) in chloroform and PAA3 in methanol were mixed and vortexed at room temperature, the solutions were clear, and no precipitant was observed. PAA3-capped CdSe@ZnS and CdSe quantum dots obtained could be readily redispersed in DMSO and DMF. PAA3-capped CdSe@ZnS and CdSe quantum dot solutions exhibit strong emission under UV lamp, which should result from that the tertiary amine groups of PAA3 could passivate the surface of CdSe@ZnS and CdSe through ligand exchange. Therefore, PAA3 is good cap ligand for QD, and the branched structure and tertiary amine groups are helpful to stabilize CdSe@ZnS and CdSe quantum dots. Although PAA3-capped CdSe@ZnS and CdSe quantum dots are stable in DMF and DMSO, PAA3-capped CdSe@ZnS and CdSe solution cannot be gelled; PAA3 cannot act as a gelator for quantum dots solution under sonication as shown in Figure 2, which may result from that the compact structure of PAA3 makes the intermolecular hydrogen bonding of the amine units at the periphery of PAA3 and the amide units in the inner core very difficult. Different from PAA3, PAA1 can act as a good gelator because the amine and amide units can interact with each other under sonication, but it is not a good ligand for stabilizing QD.

On the basis of above experiments, it is clear that branched structure and tertiary amine units are helpful for stabilizing QD, but primary and secondary amines are essential for gelling QD solutions via hydrogen bonding. Therefore, poly(amido amine) with hyperbranched structure and primary, secondary, and tertiary amine groups in the backbone (as shown in Figure 1) should not only act as good ligand to stabilize QD but also act as a gelator that can gel QD solutions. Consequently, poly(amido amine) (PAA2, MW = 27 000, PDI = 1.6, DB = 0.45) with branched structure and different kinds of amines (primary, secondary, and tertiary amine) was prepared based on previous findings.[24−29] After the ligand exchange, the size of CdSe@ZnS quantum dot increase from 18.2 to ∼30 nm as shown in Figure 3E, indicating successful lingand exchange. Furthermore, the size distribution of PAA2-capped CdSe@ZnS quantum dots is very narrow after the ligand exchange; the size and size distribution are not subject to standing time. All these experiment data indicate that PAA2 is good ligand for CdSe@ZnS quantum dot. Also, PAA2 is good ligand for CdSe quantum dot. PAA2-capped CdSe and CdSe@ZnS quantum dots are very stable in DMF, methanol, and DMSO, demonstrating that PAA2 provided enough binding sites to encapsulate CdSe and CdSe@ZnS quantum dots. Moreover, the emission of CdSe quantum dots increases by 20% after

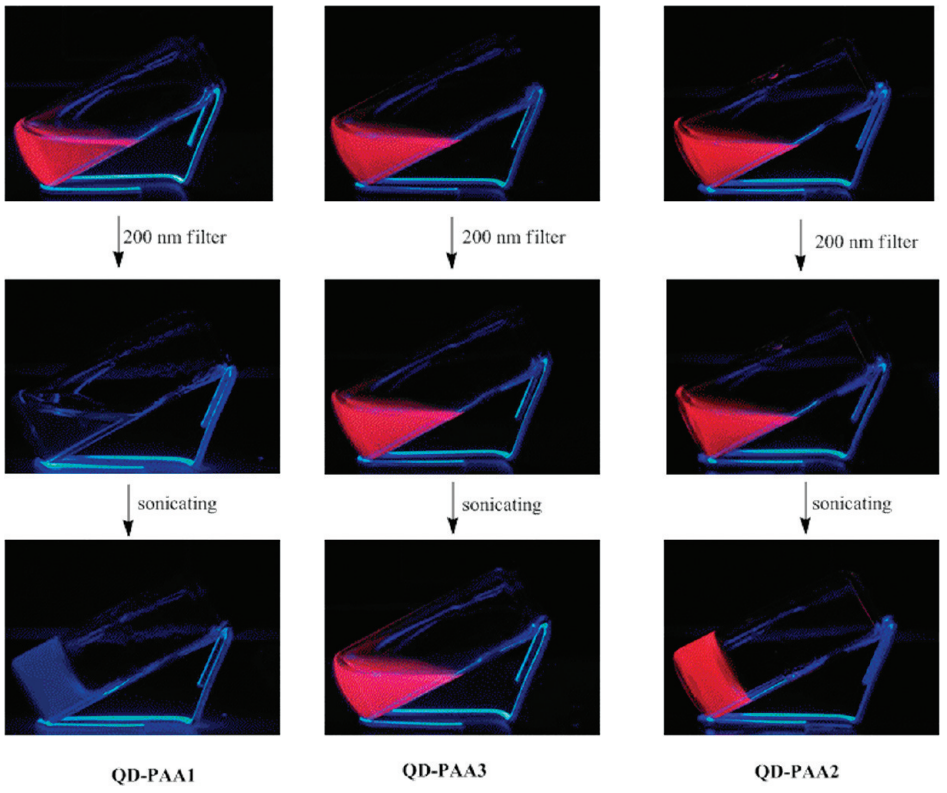

Figure 2. Photographs of CdSe@ZnS-PAA solutions and gels under UV illumination.

ligand exchange, but the emission of CdSe@ZnS quantum dots decreases by 8% after ligand exchange with PAA as shown in Figure 3, which is similar to previous findings of Winnik.[30]

Ultrasound generally was seen as stimuli to destruct self-assemblies previously, but now it gradually is recognized as stimuli that can induce gelation in certain cases.[32] PAA2 has amide and amino functional groups in the backbone, which can facilitate the assembly of PAA2 on the surface of CdSe or CdSe@ZnS quantum dots via hydrogen bonding to form a gel under sonicating.[25,29] DMF solution of CdSe@ZnS-PAA2 quickly gelled under sonicating, and the gel shows strong red emission under UV light. The complete gelation of CdSe@ZnS-PAA2 arrived within 10 min at the sonication power of 160 W and the complete gelation of CdSe@ZnS-PAA2 arrived within 6 min at the sonication power of 400 W, and so the gelation can be controlled by sonicating strength. When nonsonicated samples were left to stand at room temperature, they gelled very slowly. It is interesting that the gelling intensified the emission of CdSe@ZnS-PAA2; the longer the sonicating time is, the stronger emission is. The emission can be enhanced by ~30% after being sonicated for 10 min as shown in Figure 5, which is different from previous finding that the emission decreased after gelation.[22] The intensity correlation function (ICF) can be used to trace the sol-to-gel transition. Figure 4A shows the ICF of CdSe@ZnS-PAA2 before and after gelation. There is big difference of $g^{(2)}{}_{T}(\tau) - 1$ before and after gelation, which should correspond to the macroscopic change in the flow behavior from a solution to a gel; moreover, the observed ICFs were fitted with a stretched-exponential function for solutions or a power-law function for gels.[33] FT-IR spectra before and after gelation are shown in Figure 4B; it is clear that a new absorption band of 3307 cm^{-1} appeared after gelation, which is due to the formation of hydrogen bonding (C═O···H−N) between the amide and amino groups in the gel state. Sonicating accelerates the dispersion of of CdSe@ZnS-PAA2, uncoils PAA2 chain on the surface of CdSe@ZnS quantum dots, extends chains, exposes amide and amine units, enhances the translational motions, and thereby increases association of the amide and amine units via hydrogen bonding. The multivalent hydrogen bondings of amide with amine units among PAA2 are likely to play a significant role in the overall supramolecular stabilization in the gel form in an H bonding competing solvent like DMF. The assembly of functionalized CdSe@ZnS-PAA2 via hydrogen bonding leads to the formation of a physically cross-linked network. In the rheological experiment, G' was virtually independent of ω over 2 orders of magnitude at 1% strain, which was consistent with the dynamic mechanical behavior of physical gels as shown in Figure 4C. G' and G'' of the CdSe@ZnS based gels are higher than those of PAA2 gel without CdSe@ZnS, which result from that the binding of -PAA2-QDs, having more multiple recognition sites, may occur with the "cluster effect" (a phenomenon of an affinity greater than the sum of the corresponding monovalent interactions).[34]

Similar to CdSe@ZnS-PAA2, DMF solution of CdSe-PAA2 can also be quickly gelled via intermolecular hydrogen bonding of amide and amino groups in the backbone of PAA2 on the surface of CdSe quantum dots. The CdSe quantum dot based gel exhibits strong emission after gelation. The gelling intensified emission of CdSe-PAA2; the more the sonicating time is, the stronger the emission of CdSe-PAA2 is. The emission of CdSe quantum dots can be enhanced by ~45% after being completely gelled as shown in Figure 5C.

All the CdSe@ZnS-PAA2 and CdSe-PAA2 gel samples were quite stable at room temperature, but they are thermo-switchable.

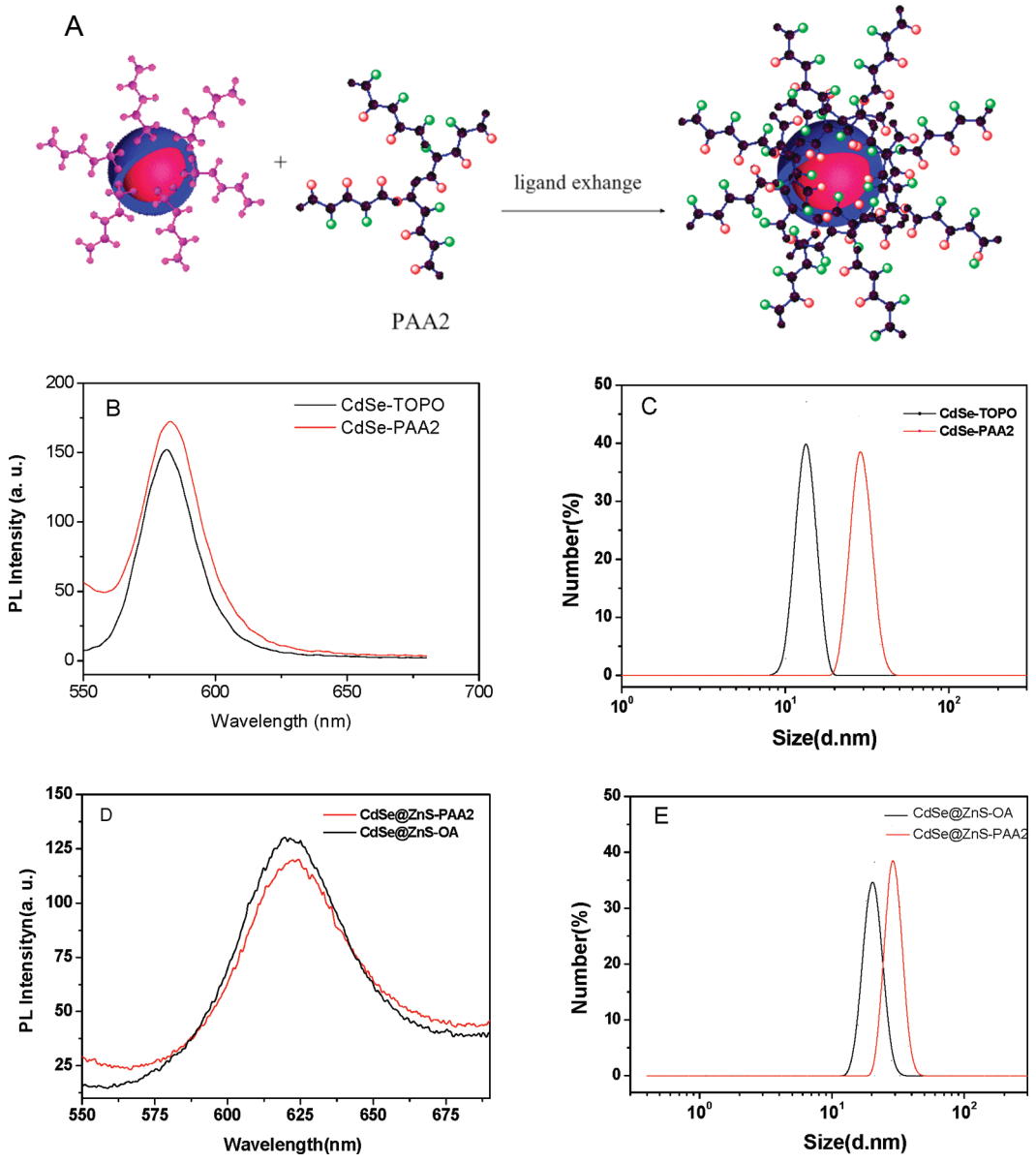

Figure 3. Illustration of QD ligand exchange with PAA2 (A); the photoluminescence spectra of CdSe (300 mg/L) before and after ligand exchange in DMF (B); the size of CdSe before and after ligand exchange in DMF from DSL (C); the photoluminescence spectra of CdSe@ZnS (300 mg/L) before and after ligand exchange in DMF (D); and the size of CdSe@ZnS before and after ligand exchange in DMF obtained from DSL (E).

These gels were easily converted to solution by heating to ~70 °C, and the solution could regel upon subsequent cooling and sonicating at room temperature. Both of the solution and gel phase showed strong fluorescence under UV light, but the solution shows much lower photoluminescence intensity than that of the corresponding gel as shown in Figure 5A,B. The longer the sonicating time is, the stronger the photoluminescence is, but the photoluminescence reaches it maximum after 10 min's sonicating (the gelation is completed after 10 min sonicating) (as shown in Figure 5A). Furthermore, it is clear that the photoluminescence intensity changes due to sol−gel transition are reversible as shown in Figure 5B. The increase of photoluminescence intensity should result from the physically cross-linked gel net work. The sol−gel phase transitions could be repeated numerous times without the loss of gelation capability and change of QD emissions due to that the compatibility of QD with PAA is very good. Furthermore, the formed gels are responsive to mechanical stimulus, for example, the vigorous agitating can break the gel, and the solution could regel upon subsequent sonicating at room temperature; this process is reversible.

The QD gels formed in this way were found to be responsive to temperature but also responsive to pH and some chemicals. For example, CdSe@ZnS-based gel can easily dissociate into a stable solution under sonicating in the presence of small amounts of H_2O as shown in Figure 6. CdSe@ZnS fluorescent gels breaking down in the presence of H_2O is mainly due to that the competing hydrogen bonding between H_2O and amide groups or H_2O and amino units are much stronger that those of the intermolecular hydrogen bonding (C═O···H−N)

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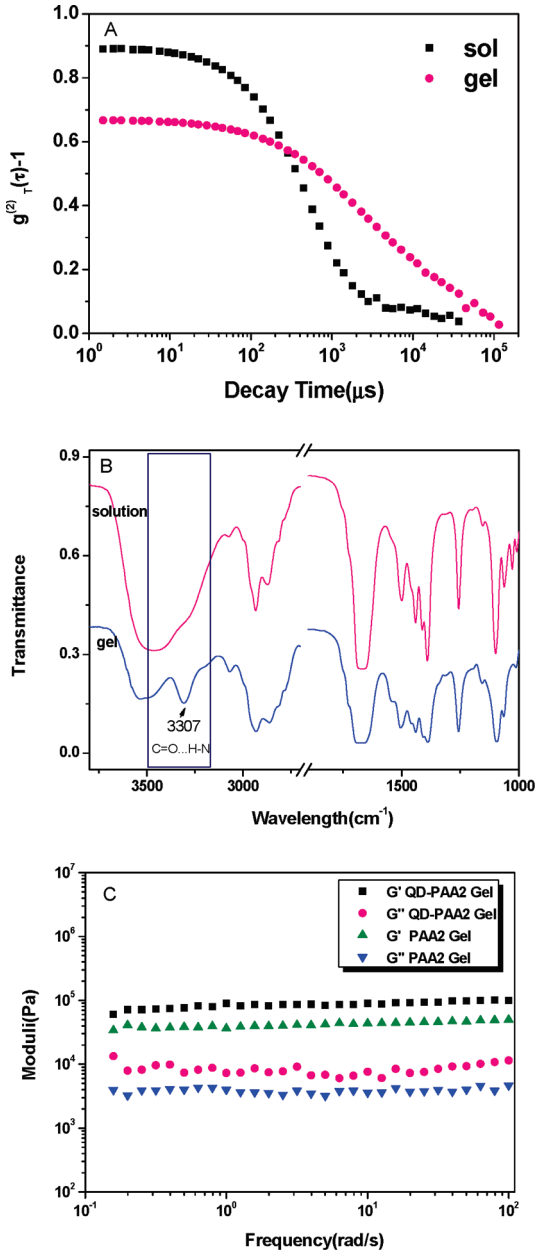

Figure 4. (A) Time−intensity correlation function, $g^{(2)}{}_T(\tau) - 1$, for CdSe@ZnS-PAA2 solution and gel. (B) FT-IR spectra of CdSe@ZnS-PAA2 in DMF before and after gelation. (C) G' and G'' on frequency for QD-PAA2 gel and PAA gel in DMF using $\gamma_0 = 0.01$ and $T = 25$ °C.

among the amide and amine groups in the PAA. Also, CdSe@ZnS fluorescent gel is sensitive to acids; the gel can easily dissociate under sonicating in the presence of acids (such as hydrochloride acid and sulfuric acid) as shown in Figure 6. We guess that the acids not only break the intermolecular hydrogen bonding but also interact with the amino groups in the polymer chains to form salts, and there is small amount precipitations (salts) appeared after adding hydrochloride acid. However, the ultrasound induced CdSe@ZnS gel is stable under sonicating in the presence of some organic solvents such as ethanol, methanol, and DMSO as shown in Figure 6. The multivalent hydrogen bonding of amido with amine units of PAA2 is much stronger than the interaction between poly(amido amine) and ethanol,

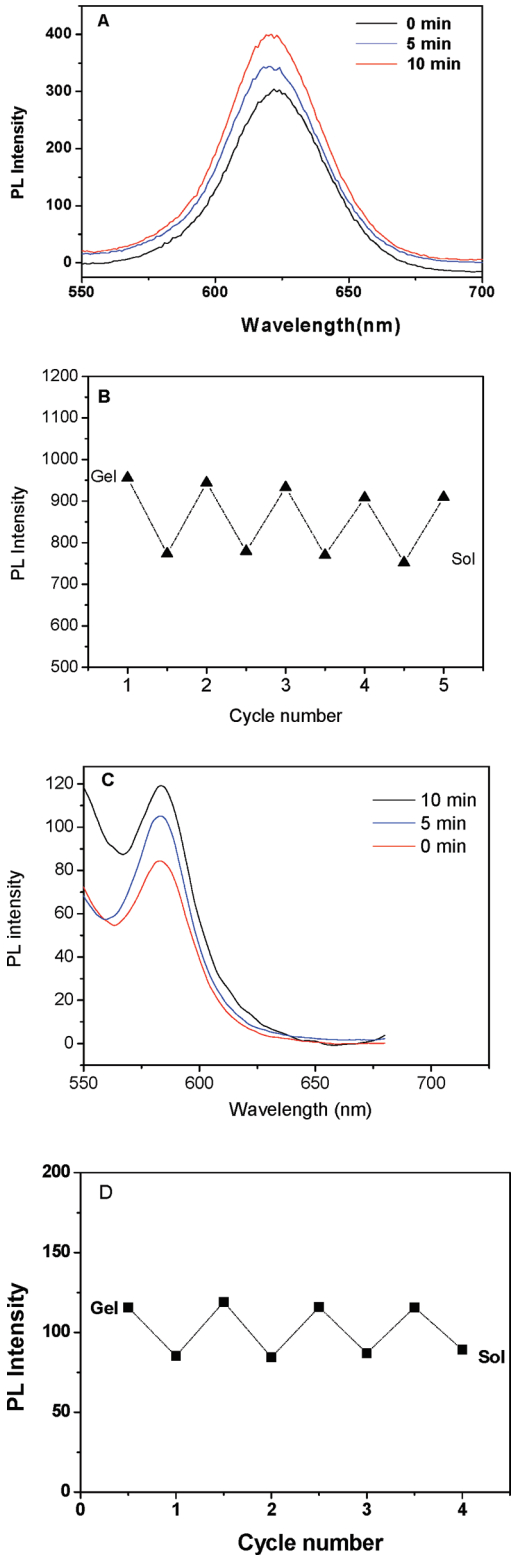

Figure 5. Photoluminescence spectra of CdSe@ZnS-PAA2 under different sonicating time (A) and the maximum emission as a function of sol−gel switching cycles of CdSe@ZnS-PAA2 (B). Photoluminescence spectra of CdSe-PAA2 under different ultrasonication time (C) and the maximum emission as a function of sol−gel switching cycles of CdSe-PAA2 (D).

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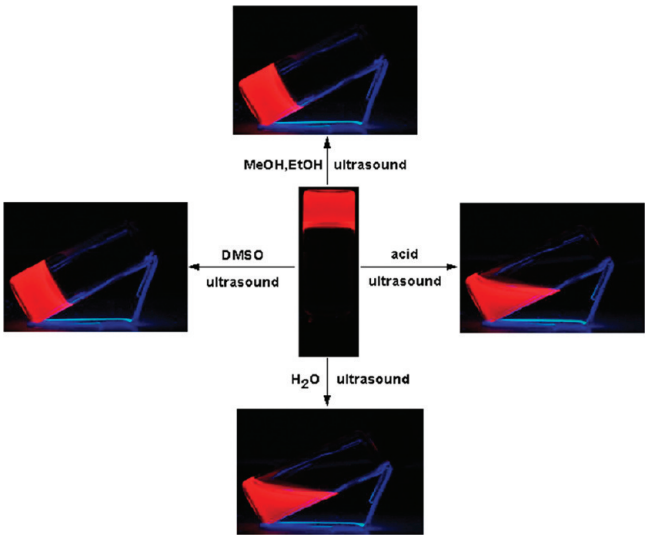

Figure 6. Outline of multiresponse of CdSe@ZnS quantum dot DMF gels under UV light (λ_{EX} = 365 nm).

methanol, and DMSO, resulting in resistance of CdSe@ZnS gels to organic solvents.

CONCLUSIONS

Quantum dots functionalized by hyperbranched poly(amido amine) were prepared via ligand exchange method. External stimuli of ultrasound can trigger the assembly of hyperbranched poly(amido amine) on the surface of QD into reversible QD gels via hydrogen bonding. The sol−gel switching can be easily realized via heating and ultrasonicating, and it is completely reversible. The formed QD gels not only show much stronger fluorescence but also are multiresponsive. This novel QD-PAA fluorescent inorganic/organic hybrid networks show promise in fields such as imaging, sensors, drug release, and nanoscience.

ASSOCIATED CONTENT

Supporting Information. Information about the experimental materials and methods, ^{1}H NMR and ^{13}C NMR spectra of PAA1, PAA3, and PAA2, FT-IR spectra of CdSe@ZnS and CdSe quantum dot before and after ligand exchange, ^{1}H NMR spectra of CdSe@ZnS and CdSe quantum dot before and after ligand exchange. This material is available free of charge via the Internet at http://pubs.acs.org.

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