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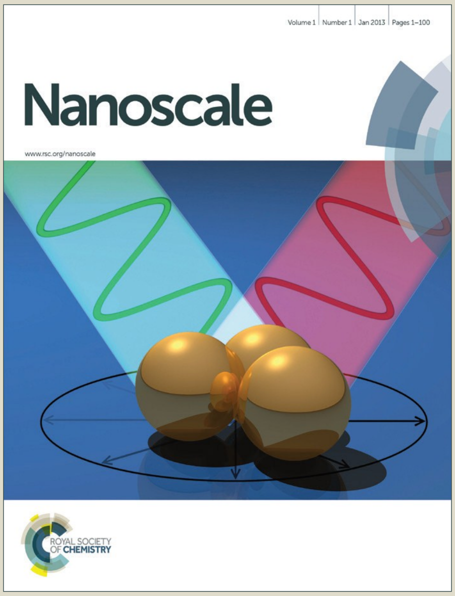

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PAPER

Suppressed blinking behavior of CdSe/CdS QDs by polymer coating†

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Semiconductor quantum dots (QDs) are very important fluorescent nanocrystals with excellent optical properties. However, QDs, at the single–particle level, show severe fluorescence intermittency (or blinking) on a wide time scale from milliseconds to minutes, which limits certain optical and biological applications. Generally, blinking behavior of QDs strongly depends on their surface state and surrounding environment. Therefore, current blinking suppression approaches mostly focused on the introduction of inorganic shell and organic small molecule compounds. In this study, we described a "bottom up" approach for synthesis of CdSe/CdS/polymer core/shell/shell QDs *via* in situ one–pot polymerization approach in order to control the blinking behavior of QDs. Three monomers (dithiothreitol (DTT), phenylenediamine (PDA), and hexamethylenediamine (HDA)) were respectively used to polymerize with hexachlorocyclotriphosphazene (HCCP), and then the polyphosphazene polymers were obtained with cyclotriphosphazene as basic macromolecular backbone. By regulating the molar ratios of the activated comonomers, we can control the blinking behavior of CdSe/CdS/polymer QDs. In the optimal conditions, the percentage of "non–blinking" CdSe/CdS/polymer QDs (the "on time" fraction > 99% of the overall observation time) was up to 78%. The suppression mechanism was attributed to the efficient passivation of QDs surface traps by the sulfydryl or phenyl groups in the polyphosphazene polymers.

Introduction

Due to the superior optical properties and facile preparation, semiconductor quantum dots (QDs) have attracted much attention in recent years.[1-6] However, a major limitation is that the photoluminescence (PL) emission of single–particle QD exhibit severe blinking (also named as fluorescence intermittency) on a wide time scale from milliseconds to minutes.[7-11] The blinking behavior is an obvious intrinsic drawback for certain biological and photoelectric applications that continuous photon emission of single QD is essential.[12, 13] Although the details of blinking mechanism are still under debate,[8, 14-18] it is generally considered to be from the charging–discharging process of individual QDs, in which an electron (or a hole) is temporarily lost to the surrounding matrix through the Auger recombination or captured by surface traps.[8, 17] As a result of such trap state dynamics, one might anticipate that the PL fluctuations could be significantly affected by changing QDs charging state or surrounding environment. Up to now, two general methods were developed towards suppressing QDs blinking. The first method is to prepare the "giant" QDs, and a thick inorganic shell was grown onto the core QDs to fully isolate the excited carriers from QDs surface and local environment.[9, 10, 19] However, these QDs often have large particle size (usually up to 13–20 nm), show poor size distribution with un–uniform particle shape, have broad PL spectra and moderate PL quantum yields (QYs).[20-23] The second method is to change the environment of QDs in solution by adding some compounds containing certain functional groups. Ha's group[24] observed that the blinking behavior of water–soluble, streptavidin–coated CdSe/ZnS QDs was near–completely suppressed in β–mercaptoethanol aqueous solution, which was probably attributed to the modification of QDs surface traps with thiol groups. Barnes's group[25, 26] found that CdSe QDs functionalized with oligo (phenylene vinylene) (OPV) ligands exhibited modified blinking statistics, and this blinking behavior was highly sensitive to the degree of ligand coverage on the QD surface. The suppression effect was interpreted as resulting from charging transport from photoexcited OPV into vacant trap sites on the QD surface. Nesbitt's group[27] reported that the inoculation of streptavidin–conjugated CdSe/ZnS QDs with propyl gallate led to a dramatic suppression of blinking behavior, which was attributed to the chemical modification of the QDs environment and then significantly changed both the radiative and nonradiative rates. Tang's group[28] demonstrated that single CdSe/ZnS QD in agarose gel exhibited suppressed blinking behavior. They speculated that electron transfer from the light state ("on time") to the dark state ("off time") might be blocked due to the negative charge inherent with gel fibers and the electrostatic surrounding around QDs, leading to blinking suppression of QDs in agarose gel. Biju's group[29] introduced fullerene–thiol monolayer into the CdSe/CdS QDs. The fullerene–shell suppressed the blinking of

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single QD by acting as well–defined electron traps, without allowing the transfer of Auger electron to unknown traps, but also a robust protecting layer against the photocorrosion of the core QD. These two general methods highlighted the important roles of inorganic shell and organic small molecule compounds on the blinking behavior of QDs. To the best of our knowledge, there are fewer reports of the polymer effects on the single–particle photophysics behavior of QDs.

Polyphosphazene–containing polymers are a class of organic–inorganic hybrid materials. The presence of P=N structural units in the polymer backbones provides tremendous flexibility to functionalize the materials through chemical modification for various applications.[30, 31] Recently, polyphosphazene polymer has been used to coat carbon nanotubes,[32] silver nanowires,[33] Fe_3O_4 nanoparticles[34] and up–conversion lanthanide–doped nanocrystals.[35] These versatile and highly cross–linked polymers show outstanding thermal stability, solvent resistance, and good interface compatibility with the inorganic phase and water dispersion which also possess plenty of active functional groups.[34, 36, 37]

On the basic of the above idea, in this paper, we designed a "bottom up" approach for fabricating a core/shell/shell structure with CdSe QD as core and CdS as inorganic shell and polyphosphazene as polymer shell. We first synthesized a series of high quality CdSe/CdS QDs and then systematically investigated the effects of different types and concentrations of comonomers on the blinking behavior of CdSe/CdS QDs. We found that the polyphosphazene polymers containing sulfydryl or phenyl groups significantly suppressed the blinking behavior of CdSe/CdS QDs.

Results and Discussion

Preparation and Characterization of CdSe/CdS QDs

CdSe QDs was synthesized using the well–established organometallic–based thermal decomposition method with CdO and Se powder as precursors.[38, 39] Inorganic shell of CdS was grown using the successive ion layer adsorption and reaction approach with a slight modification.[38-40] The shell precursors were typically Cd–oleate and element sulfur, each dissolved in 1–octadecene (ODE), and they were introduced with a syringe pump in an alternating fashion and allowed to react at 240 ºC. Detailed information for the preparation of precursor's solutions, the calculation of precursor's amount for shell growth, and experimental procedures please see the ESI.† TEM measurement results show that, the average particle diameter increased from 3.2 nm, to 6.0 nm and 9.8 nm during shell growth (Fig. 1(a)–1(c)). These QDs demonstrated good monodispersity and excellent size distribution. High–resolution TEM images (HRTEM) revealed that these QDs possessed high crystallinity with lattice fringes through the whole particle (the inserted pictures in Fig. 1(a)–1(c)). This narrow size distribution may be attributed to precisely control of the injection rate of shell precursors (Fig. S1 in the ESI†).

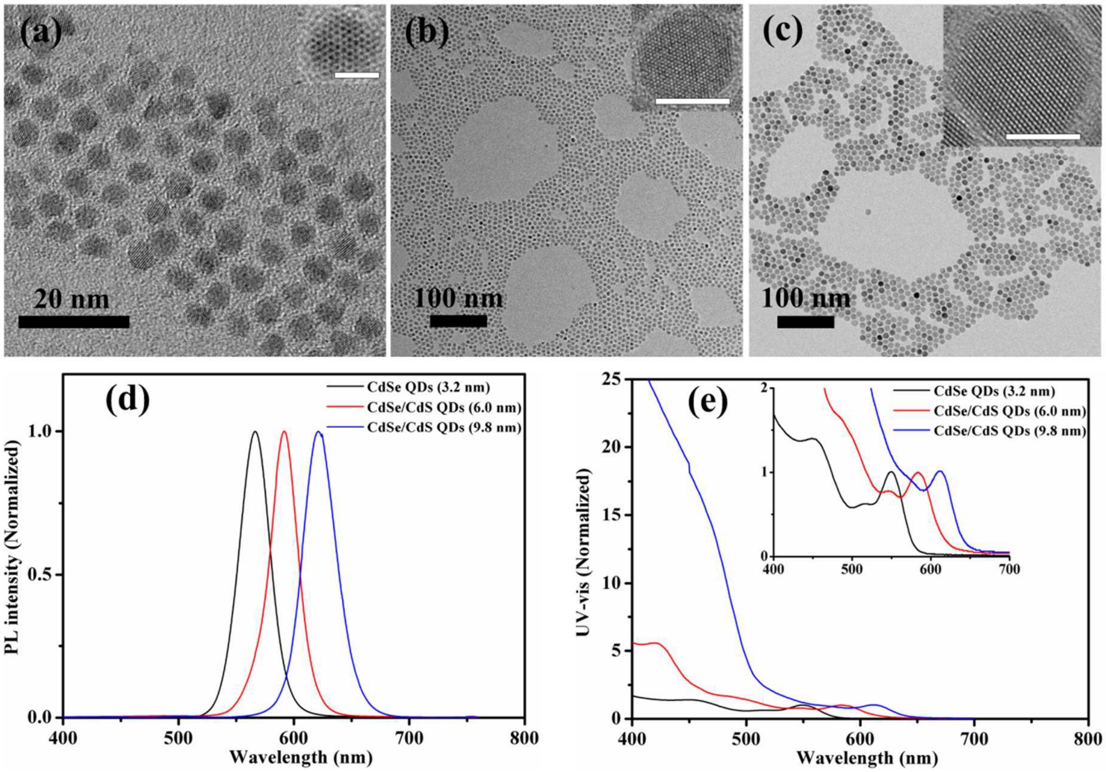

Fig. 1 TEM images of CdSe QDs with average size of 3.2 nm (a), CdSe/CdS QDs with average size of 6.0 nm (b) and 9.8 nm (c). PL spectra (d) and UV–vis spectra (e) of CdSe QDs and CdSe/CdS QDs. The scale bars in the inserted pictures are 2 nm, 5 nm, and 5 nm, respectively.

As shown in Fig. 1(d) and 1(e), both the PL and UV–vis spectra moved towards long wavelength with the introduction of CdS shell. Specifically, CdSe QDs and CdSe/CdS QDs exhibited narrow and symmetric PL spectra with emission maximum at 566 nm, 590 nm, and 621 nm, respectively. The corresponding full widths of half–maxima (FWHM) of PL spectra were *ca*. 32 nm, 27 nm, and 34 nm, respectively. The primary excitonic absorption peaks of the UV–vis spectra moved from 550 nm, to 583 nm and 611 nm, respectively. It should be noted that all the PL and UV–vis spectra (the primary excitonic peaks) always maintained uniform peak shapes during shell growth, suggesting a narrow size distribution. Such uniquely narrow and symmetric ensemble emission peaks are desired in many applications. The PL QYs of CdSe QDs were about 15–20%. After the formation of CdS shell, the QYs were increased to about 40–60%. Figure S2 shows the nanosecond PL decays of CdSe/CdS QDs and CdSe/CdS/PDTT QDs. The PL lifetimes of QDs increased from 24 ns to 39 ns after the introduction of polymer coating. The slight increase in PL lifetime was mainly attributed to the decrease of the nonradiative decay rates.[41]

Preparation and Characterization of CdSe/CdS/polymer QDs

Polyphosphazene polymers were introduced onto the CdSe/CdS QDs using the solvothermal method and the synthesis route is depicted in Fig. 2. Briefly, DTT, PDA, and HDA were respectively used to polymerize with HCCP, and then the polyphosphazene polymers were obtained with cyclotriphosphazene as the basic macromolecular backbone. Herein, for easy writing, we defined the polyphosphazene polymers as follows, poly–(cyclotriphosphazene–*co*–dithiothreitol) (abbreviated as PDTT hereafter), poly–(cyclotriphosphazene–*co*–phenylenediamine) (abbreviated as PPDA hereafter), poly–(cyclotriphosphazene–*co*–hexamethylenediamine) (abbreviated as PHDA hereafter).

FTIR spectra were used to confirm the successful formation of CdSe/CdS/polymer QDs. Fig. 3 shows typical FTIR spectra of the HCCP, DTT, CdSe/CdS QDs, and CdSe/CdS/PDTT QDs. For HCCP [Fig. 3(a)], the peaks at 1191 and 875 cm^{-1} were ascribed to the stretching vibrations of P=N and P–N groups of the cyclotriphosphazene structure, respectively. DTT [Fig. 3(b)] showed an O–H stretching absorption band at 3330 cm^{-1} and S–H stretching vibration band at 2565 cm^{-1}. For CdSe/CdS QDs [Fig. 3(c)], the N–H stretching vibrations emerged as the weak and broad band in the range of 3000–3300 cm^{-1}. The asymmetric and symmetric stretching vibrations of carboxylate group (–COOH^{-}) appeared at 1535 cm^{-1} and 1435 cm^{-1}. The FTIR spectra clearly showed the coexistence of OAm and oleate on the surface of CdSe/CdS QDs. In the FTIR spectra of CdSe/CdS/PDTT QDs [Fig. 3(d)], the strong and broad absorption band between 3450 cm^{-1} and 3200 cm^{-1} represented the –OH group, which was attributed to the association of the hydrogen bond (–OH group). The weak absorption at 1315 cm^{-1} corresponded to the swing vibration peak of CH_2–S group. These characteristic peaks proved the occurrence of the polymerization of the comonomers (HCCP and DTT). Furthermore, the weak peak at 2524 cm^{-1} could be assigned to the S–H stretching vibration band, which indicated that there existed a few of –SH groups in the polyphosphazene polymer (PDTT). A summary of the FTIR analyses of the other polyphosphazene polymers (PPDA and PHDA) are provided in the ESI (Fig. S3 and Fig. S4).†

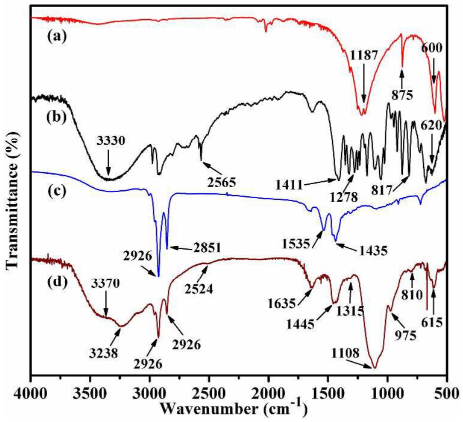

Fig. 3 FTIR spectra of HCCP (a), dithiothreitol (b), CdSe/CdS QDs (c), and CdSe/CdS/PDTT QDs (d).

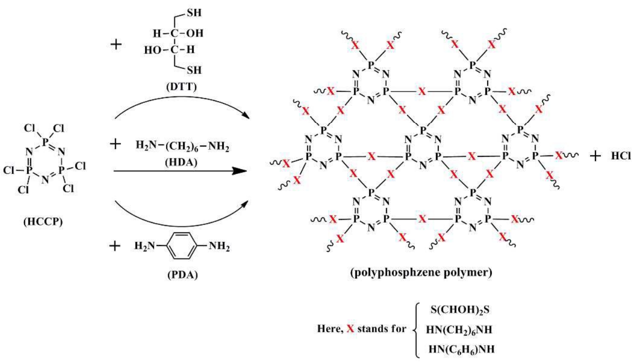

Fig. 2 Synthetic procedure of the polyphosphazene polymers.

Fig. 4(a) demonstrates that the PL spectra of CdSe/CdS/PDTT QDs maintained a uniform peak shape and showed a slight red–shift than CdSe/CdS QDs, from 590 to 601 nm. Usually, ligands exchange or polymer coverage often accompanied by changes in QDs fluorescence properties. The introduction of the polyphosphazene polymers influenced QDs aging and changed the surface states of QDs, which caused the red shift of the PL spectra.[42-44] Meanwhile, the FWHM of CdSe/CdS QDs and CdSe/CdS/PDTT QDs were 27 nm and 31 nm, respectively. It meant that the FWHM of CdSe/CdS/polymer QDs became slightly larger after the introduction of polymer coating, which demonstrated the size distribution became wider. The inserted picture in Fig. 4(a) shows that the CdSe/CdS and CdSe/CdS/PDTT QDs were well dispersed in toluene and tetrahydrofuran. These polymer–coated QDs had QYs of 30–45%. Structural variations resulting from the progressive deposited of polymer shell were studied by HRTEM. Fig. 4(b) is the TEM image of the CdSe/CdS/PDTT QDs. These polymer–coated QDs also possessed desirable monodispersity and uniformity, and no aggregation was observed in the image. Their average particle size was about 6.3 nm. The inserted picture in Fig. 4(b) was the

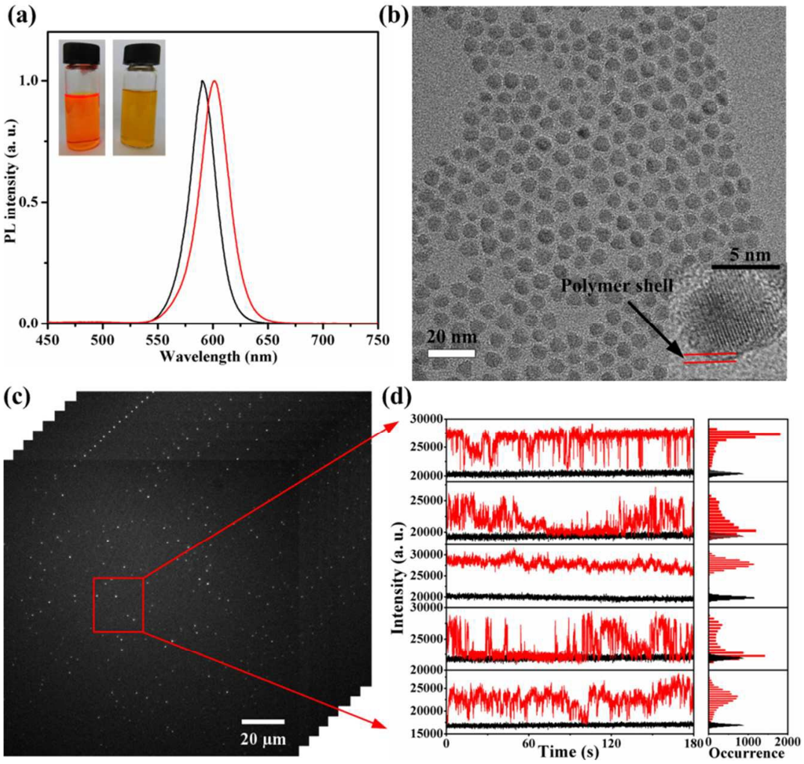

Fig. 4 (a) PL spectra of CdSe/CdS QDs (black line) and CdSe/CdS/PDTT QDs (red line). The inserted picture shows their corresponding QDs solutions under daylight lamp. (b) TEM images of CdSe/CdS/PDTT QDs. The inserted shows a representative HRTEM image of polymer–coated QDs. (c) TIRFM images of CdSe/CdS/PDTT QDs on glass substrate embedded in a PMMA matrix. Exposure time: 30 ms. (d) Temporal evolution of representative fluorescence–intensity trajectories of CdSe/CdS/PDTT QDs (red line). The black line is the intensity of background fluorescence signal. Histograms indicate the corresponding distribution of intensities of the trajectories.

corresponding HRTEM image of the polymer–coated QDs. As indicated by the black arrows, the corrugate structure at the outermost of the QDs was the polymer layer with a thickness of about 0.2–0.5 nm. To evaluate the environment stability of the CdSe/CdS QDs and polymer–coated QDs, thermogravimetric experiment was carried out in a nitrogen atmosphere. Figure S5 demonstrated that the thermal stability of CdSe/CdS/polymer QDs showed a slight decrease compared with CdSe/CdS QDs (ESI†). Overall level, CdSe/CdS/polymer QDs still possessed good thermal stability after the introduction of the polyphosphazene polymer, which was interrelated with the covalently cross–linked structure of polyphosphazene polymer. Similar phenomenon was also observed in the silver nanocables covered with highly cross–linked polyphosphazene structure.[33]

Effects of shell thickness on blinking behavior

A home–built total internal reflection fluorescence microscopy (TIRFM) system was used to investigate the single–particle fluorescent emission behavior of QDs.[39, 45] The distribution of “on time” fraction (the time fraction that the QD stays in the “on” state or fluorescence emission state) of QDs, which is an intuition parameter for assessing the single–particle photophysics behavior, was used to quantify the blinking degree of QDs. In this work, “on time” % represents the fluorescent emission fractions of QDs in the total observation time (180 s). A “non–blinking” QD is defined when the “on time” fraction exceeds 99% of the whole observation time.[20, 39] To clearly distinguish the “on” and “off” events, the threshold level is set to three times of the standard deviation above the average background intensity.[39, 46, 47]

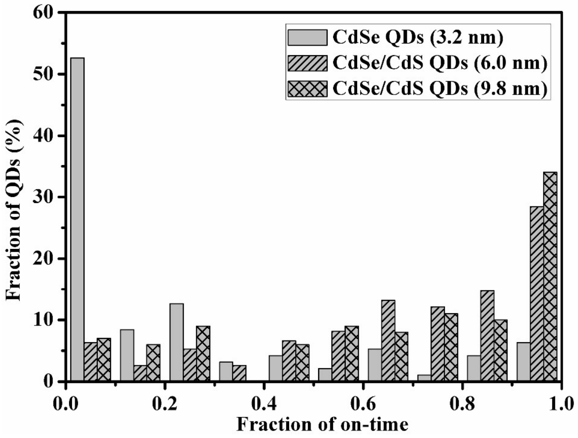

Fig. 5 “on time” distribution histograms for CdSe QDs and CdSe/CdS QDs.

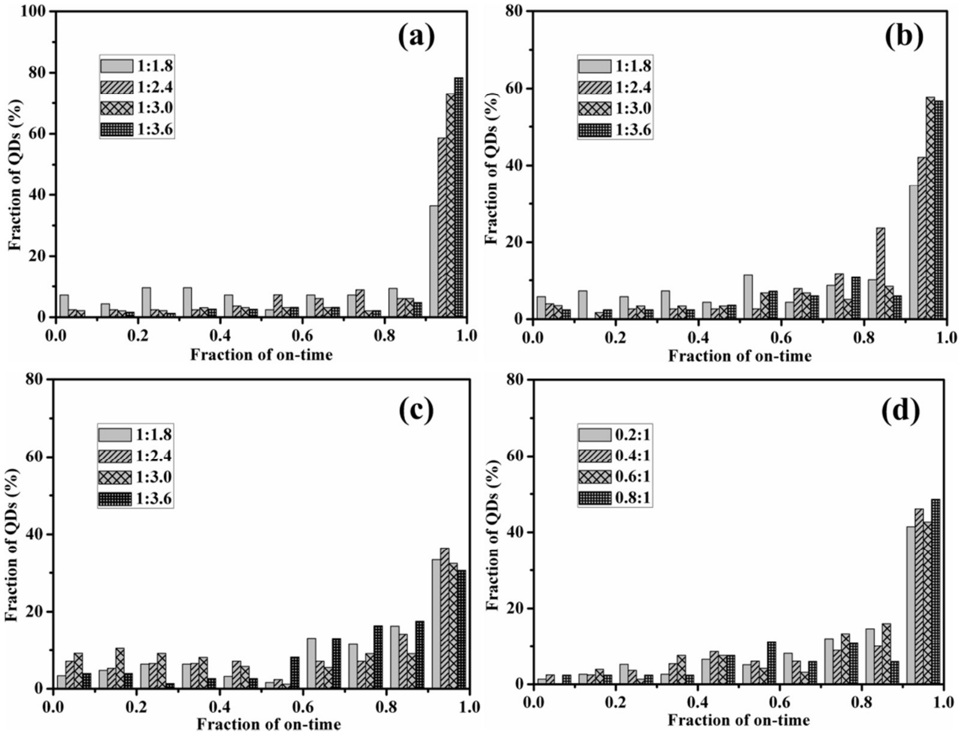

Fig. 6 "On time" distribution histogram for the polymer–coated QDs. (a)–(c) "On time" distribution histograms for CdSe/CdS/PDTT QDs, CdSe/CdS/PPDA QDs and CdSe/CdS/PHDA QDs. (0.2 mL for HCCP, and 0.36, 0.48, 0.60, 0.72 mL for DTT (PDA or HDA)). The molar ratios of HCCP:DTT (HCCP:PDA or HCCP:HDA) were 1:1.8, 1:2.4, 1:3.0 and 1:3.6. (d) "On time" distribution histogram for CdSe/CdS/PDTT QDs (0.48 mL for DTT, and 0.10, 0.19, 0.29, 0.38 mL for HCCP). The molar ratios of HCCP:DTT were 0.2:1, 0.4:1, 0.6:1 and 0.8:1.

Fig. 4(c) shows eight successive frames of TIRFM fluorescent images of CdSe/CdS/polymer QDs with exposure time of 30 ms. Individual QDs were uniformly dispersed, and no aggregation was observed in these cases. Fig. 4(d) displays typical fluorescence intensity trajectories of five randomly selected QDs on glass substrate, and different fluorescence blinking behavior was observed in each of the single CdSe/CdS/polymer QDs in the field of view. In Fig. 5, the percentage of "non–blinking" CdSe QDs ("on time" fraction > 99%) was about 6.3%, and the value of "on time" fraction (< 10%) of QDs was about 52.6%. This result indicated that CdSe QDs showed severe fluorescence intermittency (Video S1 in the ESI†). After introducing CdS shell, the percentages of CdSe/CdS QDs (6.0 nm and 9.8 nm) with "on time" fraction (> 99%) were about 28.5% and 34.1%. Compared with previously synthesized CdSe/CdS QDs,[39] the blinking behavior of these core/shell QDs were further controlled, which may be attributed to the improvement of synthesis process.

We further analysed the log–log plot of the probability densities of the "on time" and "off time" distributions of the CdSe QDs and CdSe/CdS QDs. All the "on time" and "off time" events followed the power–law distributions,

$$P(t_{on/off}) = Bt^{-m_{on/off}} \qquad (1)$$

The statistics from many QDs (over 50 QDs) are plotted on a log–log scale (see Fig. S6 in the ESI†) and the fitting results of the power–law exponents (m_{on} and m_{off}) are shown in Fig. S7. A small m_{on} shows a slow decay of the "on time" probability due to many long "on" events of the QDs. A large m_{off} indicates a fast decay of the "off time" probability because most of the QDs have very short "off" events.[48, 49] With the introduction of CdS shell, there was an obvious decrease in the values of m_{on}, from 1.85 (0.06), to 1.61 (0.08) and 1.48 (0.07) (Fig. S7 in the ESI†), which indicated the CdSe/CdS QDs had a slower decay of the "on time" distribution.

Effects of molar ratios of comonomers on blinking behavior

In subsequent experiments, CdSe/CdS QDs of 6.0 nm were further used for fabricating CdSe/CdS/polymer QDs. Firstly, to investigate the influence of DTT monomer on the blinking behavior of CdSe/CdS QDs, four molar ratios of HCCP/DTT (1:1.8, 1:2.4, 1:3.0, and 1:3.6, respectively) were used to synthesize the PDTT polymer. As shown in Fig. 6(a), the distribution of "on time" fraction was positively correlated with the amount of DTT. The percentages of the "non–blinking" CdSe/CdS/PDTT QDs for different monomer ratios were 36.4%, 58.6%, 73.2% and 78.4%, respectively (Video S2 in the ESI†). This result indicated that the increase of DDT dosage was beneficial for suppressing the blinking behavior of CdSe/CdS QDs. For the power–law distribution of the "on time" and "off time" of CdSe/CdS/PDTT QDs (Fig. S8 in the ESI†), the m_{on} exponents were 1.75 (0.08), 1.53 (0.06), 1.27 (0.10), and 0.72 (0.09), respectively (Fig. S13(a) in the ESI†). These obvious changes in the

m_{on} values predicted an overall increase in the “on time” fractions. As the molar ratios of HCCP/DTT varied from 1:1.8 to 1:3.6, the increase in the amount of DTT led to the reduction in the amount of surface traps, which suppressed the blinking of QDs. The m_{off} exponents were sensitive to the molar ratios of the comonomers, and the values were 1.55 (0.06), 1.53 (0.09), 1.36 (0.07), and 1.41 (0.08), respectively (Fig. S13(a) in the ESI†).

It should be noted that the PDTT polymer also showed blinking suppression for CdSe QDs. For the studied molar ratios of HCCP/DTT, the percentage of “non–blinking” CdSe QDs (“on time” fraction > 99%) were about 5.2%, 5.0%, 5.1%, and 5.6%, respectively (Fig. S9 in the ESI†). Meanwhile, the values of “on time” fraction (< 10%) of CdSe/PDTT QDs were increased to about 18.7%, 16.3%, 13.2%, and 10.5%, respectively. These data demonstrated that the PDTT coated CdSe QDs also showed better control of blinking with the increase of the amounts of comonomers.

Secondly, the blinking behavior of CdSe/CdS/PPDA QDs was investigated. The molar ratios were chosen of 1:1.8, 1:2.4, 1:3.0, and 1:3.6, respectively. The statistical analysis is demonstrated in Fig. 6(b). The distribution of “on time” fraction was sensitive to the amount of PDA. The percentages of “non–blinking” CdSe/CdS/PPDA QDs for the molar ratios of 1:1.8 and 1:2.4 were 34.7% and 42.1%. In the case of 1:3.0 and 1:3.6, the values of QDs with “on time” fraction (> 99%) approximately reached equilibrium of 57.5% and 56.6%. The power–law exponents of the CdSe/CdS/PPDA QDs also showed similar variation compared with the CdSe/CdS/PDTT QDs, and the detailed information was shown in Fig. S10 and Fig. S13(b) in the ESI.†

Thirdly, we investigated the blinking behavior of CdSe/CdS/PHDA QDs with the same molar ratios, and the results are presented in Fig. 6(c). The percentages of QDs for different “on time” fraction was essentially unchanged in the studied molar ratios of HCCP/HDA. In detail, the percentages of “non–blinking” CdSe/CdS/PHDA QDs were 33.3%, 36.4%, 32.4%, and 30.6%, respectively. That meant the blinking behavior of CdSe/CdS QDs was almost unchanged after the introduction of PHDA polymer shell. The power–law exponents of the CdSe/CdS/PHDA QDs were also determined by fitting the “on time” and “off time” statistics to the power law. Detailed results were shown in the Fig. S11 and Fig. S13(c) in the ESI.†

Fourthly, we also designed experiments to verify whether the cyclotriphosphazene structure of the polyphosphazene polymer influenced the blinking behavior of CdSe/CdS QDs. The molar ratios of HCCP/DTT were chosen as 0.2:1, 0.4:1, 0.6:1, and 0.8:1, respectively. As shown in Fig. 6(d), the values of QDs with “on time” fraction (> 99%) were 41.4%, 46.1%, 42.6%, and 48.6%, respectively. These data indicated that the HCCP monomer had less influence on the blinking behavior of QDs. More detailed information about the log–log plot of these CdSe/CdS/PDTT QDs, and their power–law exponents please see the Fig. S12 and Fig. S13(d) in the ESI.†

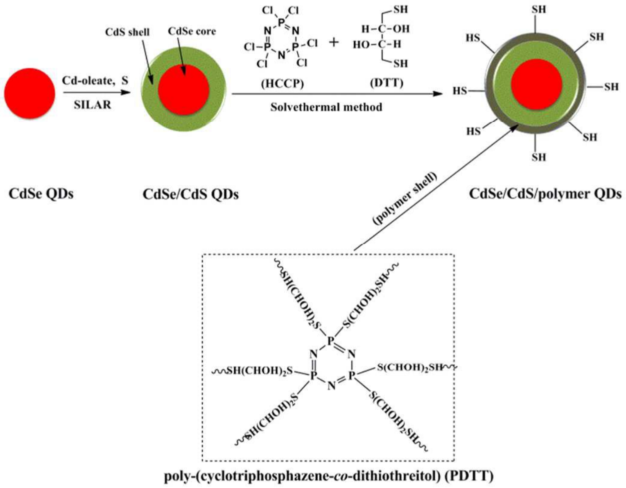

Fig. 7 Preparation procedure of the CdSe/CdS/PDTT core/shell/shell QDs.

Discussion

Currently, the blinking of single QD is generally considered to be from a QD charging process in which a photoexcited electron (or a hole) is temporarily captured by the surface traps sites of the QD or lost to the surrounding matrix through the Auger recombination process.[8, 50-52] Some theoretical simulation and experimental results emphasized that the surface traps sites were the main cause of the blinking behavior.[8, 39, 46] In our work, the synthetic route for the CdSe/CdS/polymer QDs is described in Fig. 7. Briefly, CdSe/CdS core/shell QDs were synthesized by the SILAR approach for the introduction of CdS shell onto the CdSe core QDs, and then CdSe/CdS/polymer QDs were fabricated by coating polyphosphazene polymer onto the CdSe/CdS QDs *via* in situ one–pot polymerization.

A simple model is proposed to explain the aforementioned blinking suppression phenomenon related to the polymer–coated CdSe/CdS QDs. Firstly, the thin CdS inorganic shell can preliminarily passivate the surface trap sites of CdSe QDs by effective isolation of the QD core excitonic wavefunction from the QDs surface.[10, 19, 39] Secondly, the introduction of the polyphosphazene polymer can precisely modify the residual surface trap sites of QDs by its active functional groups (such as sulfhydryl or phenyl groups). Interestingly, experimental results demonstrated that polyphosphazene polymers (PDTT, PPDA, and PHDA) had different influences on the blinking behavior of CdSe/CdS QDs. For the PDTT or PPDA polymer, the sulfhydryl or phenyl groups can act as a potent electron donor and donate electrons to the surface traps, which change the surface states of QDs and further render them incapable of accepting electrons from the QDs.[25-27] As a result, the QDs can maintain charge neutrality and the photoexcited electron and hole will recombine by the radiative recombination pathway.[50-52] Finally, the QD can maintain continuous photon emission. Furthermore, the polymerization degree of the polymer was enhanced with the increase of each of the DTT or PDA monomers. In other words, there would be more functional groups (sulfhydryl or phenyl groups) at the outer surface of the CdSe/CdS QDs. In the end, the CdSe/CdS/PDTT QDs and CdSe/CdS/PPDA QDs possessed more blinking suppression with the increase of the amount of each monomer (DTT or PDA).

For the PHDA polymer, we observed that there was little suppression effect on QDs blinking after different molar ratios of

HCCP/HDA were investigated (Fig. 6(c)). This phenomenon was different from previous research, in which HDA was a very effective ligand and can remove deep trapping sites or hole trapping sites on the surficial Se atoms.[53-55] Probable reason may be that these deep trapping or hole trapping sites had already been removed by the introduction of inorganic CdS shell. For the other two polymers (PDTT and PPDA), they still can eliminate the electron trapping sites located on Cd atoms at the surface of CdS shell, and served as a polymer shell for effective blinking suppression.

Unfortunately, we could not obtain totally non–blinking CdSe/CdS/polymer QDs by regulating the reaction conditions of the activated comonomers, which may be attributed to the following reasons, (1) A certain amount of interior traps and external traps were generated during the fast nucleation and crystal growth process of CdSe QDs, and these interior traps sites could not be modified by the inorganic shell or polymer shell.[45, 56] (2) Hole is another important cause for QDs blinking. Also, thick shell CdSe/CdS QDs was a *quasi*–type–II core/shell QDs, the electron delocalize to the CdS shell, but hole was still confined in CdSe core. And these interior traps from the hole cannot be removed from surface modification.[57] (3) When the CdS shell is thicker, the accumulated lattice strain also increase in the core/shell boundary (the lattice mismatch between CdSe and CdS is about 4%), which possibly triggers the interfacial defects and provide extra traps.[10, 58] (4) A limited number of uncoordinated QD surface traps still exist due to the non–uniform coverage of polymer shell on QD surface.[25, 26] Under this circumstance, these surface traps still can capture the photoexcited carrier, which enable the QDs entered into the Auger recombination process (dark state).

Conclusions

In this paper, we report a "bottom up" approach for preparation of CdSe/CdS/polymer core/shell/shell QDs *via* in situ one–pot polymerization. Three polyphosphazene polymers were synthesized with cyclotriphosphazene as the basic macromolecular backbone. The thickness of the polymer shell was about 0.2–0.5 nm. The blinking behavior of CdSe/CdS/polymer QDs can be controlled by regulating the molar ratios of the activated comonomers. In the optimal conditions, the percentage of "non–blinking" CdSe/CdS/polymer QDs (the "on time" fraction > 99% of the overall observation time) was up to 78%. The suppression mechanism was attributed to the efficient passivation of QDs surface traps by the sulfydryl or phenyl groups of the polyphosphazene polymers. Our work also proved that QDs surface traps can be repaired by polymer containing functional groups. CdSe/CdS/polymer QDs possess high percentage of "non–blinking" QDs, and will be beneficial to the optoelectronics devices and biological tracking fields that rely on single–dot emission.

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