Self-selective recovery of photoluminescence in amphiphilic polymer encapsulated PbS quantum dots

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Self-selected recovery of the photoluminescence (PL) of amphiphilic polymer encapsulated PbS quantum dots (QDs) was observed in water for the first time and possible mechanisms were proposed based on investigations by means of transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction and fluorescence spectroscopy. Water-soluble PbS QDs were synthesized by transferring monodispersed QDs capped with hydrophobic ligands of oleylamine from an organic solvent into water *via* amphiphilic polymers poly(maleic anhydride-*alt*-1-octadecene-*co*-poly(ethylene glycol)). The water transfer process leads to a double size distribution (5.6 ± 0.9 nm and 2.7 ± 0.4 nm), attributed to ligand etching together with Ostwald ripening, as well as the fast decay of PL. The automatic recovery of the PL in PbS QDs stored in water in the dark for 3 months was only observed for the subset of smaller QDs and is largely due to the removal of surface defects with aging, as evidenced by the decreased percentage of unpassivated surface atoms from XPS studies. In contrast, the PL of the subset of larger QDs in the same sample does not self-recover in water and can only be slightly recovered by transferring them into environments with less external quenches. The results strongly suggest that it is the surface defect in the larger QDs themselves, introduced during Ostwald ripening, that is primarily responsible for their non-emitting status or rather low PL intensity under different conditions. The increase of unpassivated Pb atoms in larger PbS QDs after the 3 month aging has been confirmed by XPS, which explains their non-recovery behavior in water. The PL-recovered QD sample in water is very stable and shows comparable photostability to the initial QDs dispersed in an organic phase.

1. Introduction

Semiconducting colloidal quantum dots (QDs) have attracted a great deal of interest due to their size tunable optical properties arising from the quantum confinement effect. They are widely used in optoelectronics, biological imaging and sensors.[1–4] It is known that light scattering and autofluorescence are significantly reduced and light penetration through biological tissues tends to be deeper in the near infrared (NIR) range of 1100–1600 nm,[5] which makes NIR emitters promising for *in vivo* deep-tissue imaging.[5–7] Among various NIR-emitting lead chalcogenide QDs, PbS is of particular interest because of its large exciton Bohr radius (18 nm) composed of nearly equal contributions from the electron and hole and small band gap (bulk: 0.41 eV at 300 K). These characteristics allow attainable quantum confinement in relatively large sized PbS QDs and hence enhanced size-tunable NIR emission.[7–10]

For biomedical applications, QDs are required to be soluble and bright in water. Direct synthesis of water-soluble PbS QDs in an aqueous system unfortunately leads to relatively low quantum yields.[11–15] Recently, ligand exchange method has been applied to transfer the high quantum-yield QDs from the

organic phase into water.[16,17] However, the quantum yield is found to decrease by 30–60% after transfer due to the stripping of initial surface ligands during the ligand exchange process. With this finding, the use of amphiphilic polymers in the water transfer process of QDs appears to be more promising in terms of maintaining the quantum yield as it is believed that the encapsulation of QDs into amphiphilic polymers will not disturb the surface ligands and thus the initial high quantum yield can be retained. Although this amphiphilic polymer approach has been successfully applied to ultraviolet (UV)-visible emitting QDs,[18,19] there are very limited relevant reports on NIR-emitting PbS QDs.[20]

The optical properties of QDs are strongly dependent on their surface conditions on account of their high surface area. The low quantum yield has often been attributed to the presence of surface defects (such as unpassivated surface atoms), which serve as charge trapping sites.[21] Therefore much effort has been made to realize better surface passivation in order to make QDs more photoluminescent. Better surface passivation has been achieved by using suitable surface capping ligands, which can coordinate with the dangling bonds at the QD surface to prevent nonradiative recombination at these surface sites.[22] For example, the quantum yield of PbS QDs has been increased to 25%–60% by using oleic acid (OA)/trioctylphosphine (TOP) double-type ligands,[22] as compared to that (~20%) reported for PbS QDs capped only with OA ligands, since in the former case both Pb and

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S surface sites are effectively passivated. An alternative successful approach to obtain better surface passivation and thereby removing the surface defect states from the band gap region is intentionally over-coating the QD core with a thin layer of another material of larger band-gap.[23] The quantum yield of CdSe QDs can reach up to 60–85% after the growth of a ZnSe shell.[23] Similarly, surface oxidation has been demonstrated to enhance the PL of CdSe QDs and this process can be accelerated by high intensity illumination.[24] However, massive oxidation will eventually cause the significant drop in PL intensity due to the newly created defects.[25] The addition of strong binding ligands to as-synthesized QDs dispersed in nonpolar solvents can also cause the variation of PL intensity of QDs.[26,27] Exposure of as-synthesized CdSe QDs to a relatively low amount of *n*-butylamine leads to an enhancement of the PL intensity due to the improvement of surface passivation. However, high concentration of *n*-butylamine causes the etching of the QD surface, leading to the decrease in the size of QDs and the quenching of PL.[26] In another case, Hess *et al.* presented interesting results; they found that the surface transformation of CdSe QDs can take place during heating or the environment change in such a way that the QDs can enter a metastable dark state in which the PL is totally lost. Exposure of these dark QDs to light reverses the transformation, leading to the full recovery of PL or even higher PL efficiency.[28]

Although there has been much work on the correlation of the surface with optical properties of UV-visible QDs, relatively few results have been reported on NIR-emitting QDs.[29,30] An interesting phenomenon of reversible photo-darkening in PbS QDs was discovered and identified to result from carrier trapping under high-intensity laser illumination.[29] It was also reported that light-induced ligand desorption can dominate the photobleaching behavior in PbSe QDs.[30] Despite these recent advances, research on the optical property of polymer encapsulated water-soluble NIR-emitting PbS QDs is still lacking.[20]

Here, we report the interesting observation of PL disappearance and self-selective recovery behavior in PbS QDs in water, which was found to be closely related to the interactions among the QD surface, ligands, amphiphilic polymers and solvent. The water-soluble PbS QDs were achieved by transferring QDs from chloroform into water *via* poly(maleic anhydride-*alt*-1-octadecene)-*co*-poly(ethylene glycol) (PMAO–PEG). The size distribution of PMAO–PEG encapsulated QDs changes from monodisperse to bimodal after transfer from chloroform into water, accompanied by the fast decay of PL. These variations are due to ligand etching together with Ostwald ripening. The automatic PL recovery behavior of QDs stored in water in the dark is found to depend on the size of QDs. With decreasing surface defects in the smaller QDs with time, their PL recovers in water. In contrast, the PL of the subset of larger QDs in the same sample does not recover at all in water. By investigating the PL behavior of QDs under different conditions, it is found that it is the presence of surface defects in the larger QDs, introduced during the low temperature Ostwald-dominated ripening, which is primarily responsible for their non-emitting status in water.

2. Experimental section

2.1 Materials

Lead chloride (98%), oleylamine (OLA) (technical grade, 70%), sulfur (100%) poly(maleic anhydride-*alt*-1-octadecene) (PMAO, number average molecular weight, 30 000–50 000), poly(ethylene glycol) methyl ethers (PEG–OH, molecular weight 2000) and concentrated H_2SO_4 (98%) were obtained from Sigma-Aldrich Inc. Hexane, ethanol, tetrahydrofuran (THF) and chloroform were purchased from Fisher Scientific Company. All chemicals were used as purchased.

2.2 Synthesis of PbS QDs

PbS QDs were synthesized by using OLA as ligands.[9,10] Typically, 1.0 g of $PbCl_2$ (3.6 mmol) and 2.4 mL of OLA were loaded into a 20 mL three-neck flask at room temperature. The mixture was first purged by N_2 for 45 min to remove oxygen and then heated to 160 °C to form the homogeneous $PbCl_2$–OLA suspension under magnetic stirring. Sulfur (0.36 mmol) in OLA (0.24 mL) stabilized at 25 °C and purged with nitrogen for 30 min was quickly injected into the $PbCl_2$–OLA suspension after the temperature was cooled to 100 °C under vigorous stirring and the reaction was allowed to continue at the same temperature for 10 min.

The PbS QDs were isolated by adding alcohol to precipitate them and then re-dispersed in hexane. The un-reacted precursors were completely removed by repeated centrifugation and decantation for at least three times. The PbS QDs were dispersed in chloroform finally.

2.3 Synthesis of amphiphilic polymers

Amphiphilic polymers were synthesized according to published methods.[19,20] A typical reaction is as follows: 1 g of PMAO and 1.5 g of PEG–OH were mixed with 50 μL of concentrated H_2SO_4 and refluxed in chloroform (10 mL) for 12 h. The mixture was neutralized by 1 M NaOH and then centrifuged to remove Na_2SO_4 and water.

2.4 Synthesis of water-soluble PbS QDs

Water-soluble PbS QDs were achieved by performing the following procedures: monodispersed PbS QDs (1 mL, absorbance = 1 at 1460 nm) were mixed with PMAO–PEG (1.6 mL, 30 mM) in chloroform and stirred for 6 h, and after that nitrogen bubbled water (2.6 mL) was added to the QD solution. Chloroform was then gradually removed by evaporation. The water-soluble PbS QDs were further centrifuged at 8000 revolutions per minute (rpm) for 30 min. The supernatant was collected and stored at 4 °C in the dark.

PbS QDs were then stored in the dark for 3 months. For XPS measurements, smaller and larger QDs were separated by high speed centrifugation with the aid of a little amount of THF.

2.5 Characterization

Transmission electron microscopy (TEM) images were obtained using a JEOL 2100F microscope. The powder X-ray diffraction (XRD) study of PbS QDs after extensive purification was carried out with a Philips X'pert diffractometer

using Cu K$_\alpha$ radiation source (λ = 0.15418 nm). X-Ray photoelectron spectrometry (XPS) was performed using a VG Escalab 220i-XL equipped with an Al Kα source. The XPS data were analyzed by using Casa software.

PL spectra were taken with a Fluorolog®-3 system (Horiba Jobin Yvon). Quantum yield was measured by using dye IR-125 as a reference. The photostability of PbS QDs dispersed in water or chloroform was tested using a 4 W UV lamp (115 V, 60 HZ, Model 22-UV, Optical Engineering, UV light Inc.).

3. Results and discussion

3.1 Synthesis of amphiphilic polymer encapsulated PbS QDs

PMAO–PEG was synthesized by reacting PMAO with bio-compatible PEG–OH in chloroform at the PMAO/PEG molar ratio of 1 : 30.[19,20] Then PbS QDs capped by OLA ligands were transferred into water *via* PMAO–PEG. The structure of PbS QDs before and after transfer into water was investigated by TEM characterization. As shown in Fig. 1a and b, the PbS QDs maintain the structural intactness after going through the polymer encapsulation process in chloroform (5.2 ± 0.2 nm *versus* 5.2 ± 0.3 nm). They are, however, dissolved and broken up quickly after being transferred into water and exhibit a double size distribution (5.6 ± 0.9 nm and 2.7 ± 0.4 nm) (Fig. 1c). In contrast, the PMAO–PEG encapsulated PbS QDs (hereafter denoted as PbS/PMAO–PEG QDs) transferred from chloroform into ethanol still show a single size distribution while with a slight size decrease (from 5.2 ± 0.3 nm to 4.9 ± 0.2 nm, Fig. 1d).

The obvious variation in the size distribution of PbS QDs after transfer into water is related to ligand etching, which has been reported for thiol capped PbS QDs[31] and dodecylamine capped gold nanoparticles.[32] The etching of the QD surface by OLA seems to be significantly accelerated by the co-presence of amphiphilic polymers and water since only mild ligand etching was observed for PbS/PMAO–PEG QDs transferred
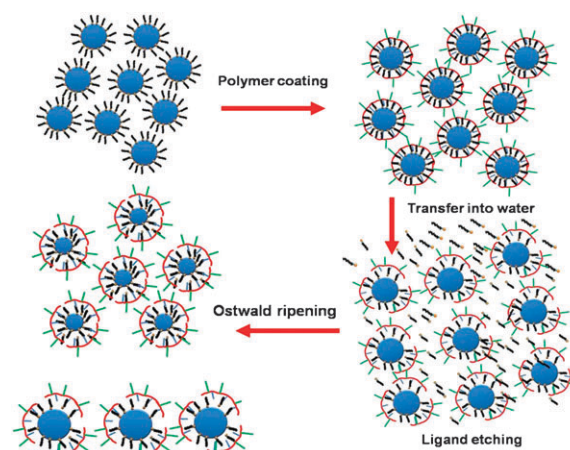
Fig. 2   Schematic representation of the process leading to the double size distribution of PbS QDs after transfer into water.

in ethanol, as evidenced by a slight size reduction in the latter. We postulate that it is this efficient ligand etching process in water that leads to the double size distribution of PbS/PMAO–PEG QDs.[20] Severe ligand etching may immediately cause an important broadening of the size distribution of QDs considering that etching is often faster for smaller QDs in a group (even in a monodispersed sample, there are some QDs a little bit smaller than others).

As a result, efficient Ostwald ripening is initiated and eventually results in the two populations of QDs of distinctly different sizes.[10,20,33] This mechanism is schematically displayed in Fig. 2. It is worth noting that both the ligand etching and Ostwald ripening processes disturb the ligands on the QD surface and modify the surface structure of PbS itself. It is highly likely that these processes simultaneously introduce considerable amounts of surface defects including unpassivated surface sites, which quench the PL of PbS QDs. This will be further discussed in the following sections.

Since the polarity of ethanol is much lower than that of water (ε: 24.3 *versus* 80) and it is the hydrophilic groups of the polymer molecules that stick out from the QD surface, the interaction between the attached polymer molecules and solvent must be weaker in ethanol as compared to that in water. This is believed to be the reason for much less significant etching observed in ethanol than in water; the ligand etching may not only be directly related to the first layer of ligands, but also be indirectly related to the second layer of polymers because of the strong hydrophobic interaction between the ligands and polymers. This mild ligand etching process in alcohol does not cause any obvious broadening to the size distribution of PbS QDs and does not seem to result in any obvious Ostwald ripening. This study in alcohol confirms the important role of water in the ligand etching process.

3.2 Fast PL decay

The PL spectra of as prepared PbS QDs in chloroform, and those after PMAO–PEG encapsulation in chloroform, following transfer into water and further aged at 4 °C for different times are presented in Fig. 3a, respectively. No discernable loss of QDs was observed in any of the above mentioned
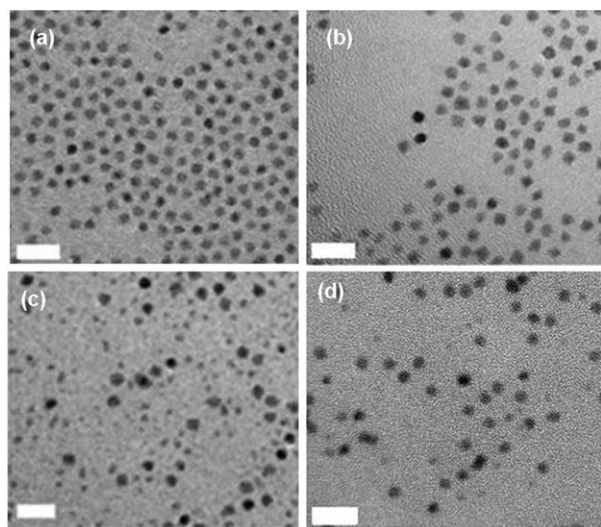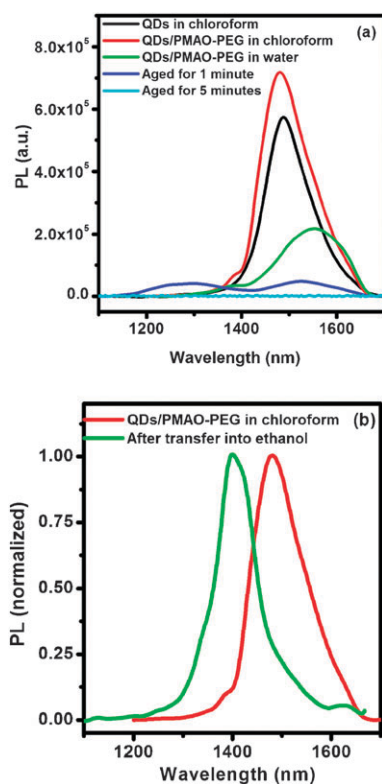

Fig. 1   TEM images of as prepared PbS QDs in chloroform (a) and PbS/PMAO–PEG QDs in chloroform (b), immediately after transfer into water (c) and ethanol (d). Scale bar is 20 nm.

Fig. 3 (a) PL of PbS QDs in chloroform prior to polymer encapsulation, after PMAO–PEG encapsulation in chloroform, following transfer into water and after being stored in water at 4 °C for 1 minute and 5 minutes. (b) PL of PbS/PMAO–PEG QDs in chloroform and following transfer into ethanol.

preparations. In other words, the QD concentration remains constant for all the samples in comparison. The PL intensity of PbS QDs after PMAO–PEG encapsulation reveals a 20% increase as compared to the initial value in chloroform. The quantum yield reaches the value of 30%. This increase of quantum yield is possibly due to the better isolation of PbS QDs from their environments with the introduction of an additional polymer shell. However, a large PL drop of 58% was observed after the QDs were transferred into water from chloroform. The PL peak centered at 1557 nm with a shoulder at 1380 nm rapidly evolves into a double peak structure within 1 minute, and then totally disappears within 5 minutes. The double PL peaks correlate very well with the observed double size distribution of transferred PbS QDs in water.

It is worthwhile to find out the reason for the fast PL decay of PbS/PMAO–PEG QDs after being transferred into water. As mentioned above, the optical properties of QDs are highly sensitive to surface states.[7,16,17,21] As ligand etching and Ostwald ripening cause the change of the surface structure of QDs (including PbS surface structures and ligand capping status), they are most likely to introduce surface defects, which certainly affect the PL. The initial broadening and red shift (72 nm) of the PL band of PbS/PMAO–PEG QDs in water is possibly due to the degradation of size distribution[17,20,34] and surface passivation, and possible aggregation at nanoscale. With the rapid formation of many smaller PbS QDs and more surface defects in larger QDs, the emission at shorter

wavelengths appears and that at longer wavelengths becomes weaker. As a consequence, the double PL peaks emerge shortly. With the fast Ostwald ripening process, more and more surface defects are possibly introduced which lead to the total loss of PL eventually. The darkening of PbS QDs may also be explained from the presence of "external" molecular quenchers in water. It has been reported that water and dissolved oxygen molecules can lead to the PL quenching of QDs.[30,35] This has actually been further confirmed by the PL recovery behavior of QDs in environments containing less external quenchers (to be discussed below).

In contrast, only a single PL peak was observed for PbS/PMAO–PEG QDs transferred into ethanol from chloroform (Fig. 3b); this is consistent with their mono-modal size distribution as presented in Fig. 1d. Furthermore, the blue shift of 100 nm in emission was observed for PbS/PMAO–PEG QDs with ethanol transfer. This spectral shift is believed to be mainly due to slight ligand etching, as supported also by the observed slight size reduction (Fig. 1d). Although it has been reported that the variation of solvent polarity shifts the PL spectra of QDs, it should not be the case here since polar solvents often cause red shifts of PL spectra.[36,37] In addition, the PL spectrum of PbS/PMAO–PEG QDs in ethanol does not show any obvious spectral broadening, indicating the absence of Ostwald ripening in this system. It should be noted that PL spectrum broadening has often been used as a sign of the presence of the Ostwald ripening in QD studies.[10,33] All these results suggest that relatively strong ligand etching is necessary for the start of Ostwald ripening in the samples studied herein and the strength of ligand etching is not only determined by the type of ligands as expected, but also related to the polymer–solvent interactions.

3.3 PL recovery

Although the pronounced loss of PL can be expected considering severe QD structural variation during ligand etching and Ostwald ripening, it is interesting to observe the partial PL recovery of PMAO–PEG encapsulated QDs in water after being aged in the dark at 4 °C for 3 months. As shown in Fig. 4a, the PL intensity of PbS QDs in water recovers to 40% of their initial value in chloroform, with the single PL peak at 1297 nm. The PL-recovered smaller PbS QDs are very stable in water for at least one year and show the minimum quantum yield of ~10%.

The TEM image shows the PbS QDs are still in double size populations (6 ± 0.4 nm and 1.9 ± 0.3 nm) with slight changes of their respective average sizes as compared with those in the freshly water transferred sample (Fig. 5a). The result suggests that Ostwald ripening continues even at a relatively low temperature of 4 °C. The number percentage of larger QDs was found to be ~57% based on TEM image counting, which is close to that estimated from XRD results (49%) (Fig. 5b). In the XRD calculation, a simple equation is applied:

$$D_{XRD} = D_{small}x + D_{large}(1 - x)$$

where D_{XRD} is the QD size calculated from the Scherrer equation,[38] D_{small} is the average size of smaller QDs and D_{large}
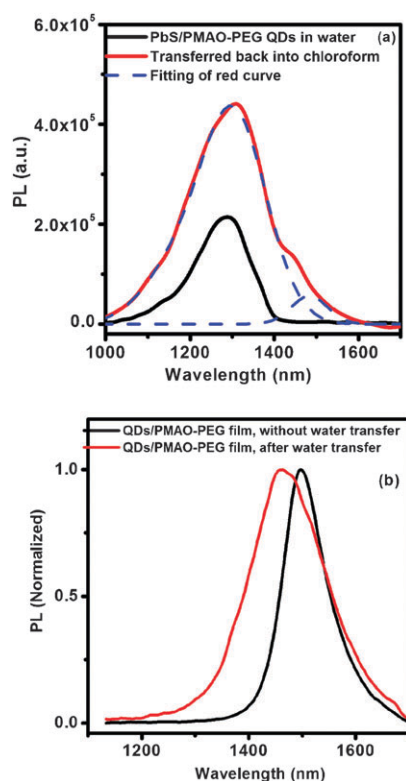
Fig. 4 (a) PL of PbS QDs being stored at 4 °C for 3 months in water and following transfer back into chloroform. Two resolved PL peaks from the Gauss fitting for the PL curve of PbS QDs in chloroform are also shown. (b) PL of PbS solid films dried from PbS/PMAO–PEG QDs dispersed in chloroform or stored in water for 3 months.
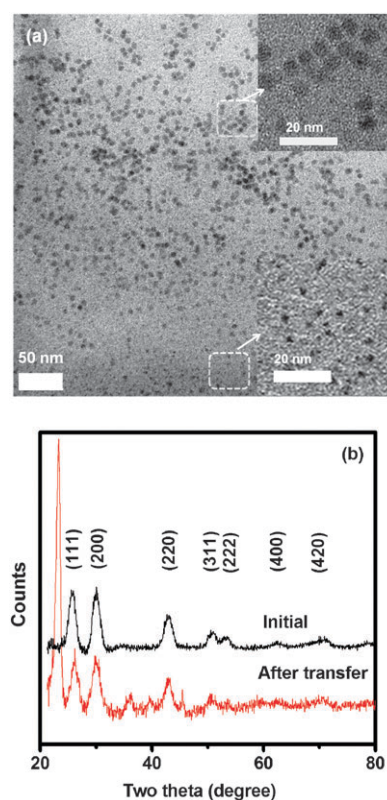

Fig. 5 (a) Representative TEM photographs of PbS QDs stored at 4 °C for 3 months in water. (b) XRD of PbS QDs prior to water transfer and after being stored in water for 3 months. Inset of (a): enlarged TEM images of the larger and smaller QDs.

is the average size of larger ones based on TEM observations and x is the number percentage of smaller QDs.

According to the correlation between emission peak positions and particle sizes,[39] the single emission band centered at 1297 nm was identified to be contributed from smaller QDs. It means that the larger QDs representing about half of the QDs in the sample are still non-emitting even after long time aging. The remarkably different recovery behavior in smaller and larger QDs is quite intriguing and may be explained from two aspects: the difference in the density of surface defects ("internal" quenchers) or in the compactness of the ligand/polymer structure (related to "external" quenching events). The effective surface aging of PbS and thereby the removal of defect states and improved surface passivation due to ligand re-organization may contribute together to the recovery of PL in the smaller QDs. Nonetheless, the annealing of the surface of the larger QDs may turn out to be slower or more difficult in view of their relatively low surface activity with respect to their smaller counterparts. Furthermore, more surface defects or un-passivated surface atoms, resulting in PL quenching, may be created during the formation of less ordered crystalline surfaces in the low-temperature Ostwald growth process of larger QDs.[7] On the other hand, it is also possible that the ligand/polymer structure on larger QDs is less compact than that on smaller ones, rendering their surfaces more accessible to "external" quenchers (such as solvent or oxygen molecules) present in solution.[30,35] Previous studies have shown that polar

solvent molecules can interact with QD surfaces and lead to the decrease in PL intensity.[36,37]

In order to figure out which mechanism is mainly responsible for the non-emitting status of the larger PbS/PMAO–PEG QDs, the QDs stored in water for three months were transferred back into chloroform, which is expected to have much less numbers of "external" PL quenchers.[35–37] If it is molecular quenching that is mainly responsible for the darkening of larger QDs in water, their emission should largely recover in chloroform. Furthermore, chloroform may help improve the compactness of the amphiphilic polymer structure on the surface of QDs as the polymer is less soluble in chloroform, which will also aid in the reduction of quenching effect. As shown in Fig. 4a, the PL intensity of PbS QDs transferred back into chloroform doubles that of the QDs in water. In addition, a shoulder located at a longer wavelength appears clearly in their PL spectrum. Gauss fitting yields two PL bands: the one situated at 1297 nm is again attributed to smaller QDs, while the one at a longer wavelength of 1486 nm is assigned to larger QDs. The integrated PL intensity ratio of larger to smaller QDs is found to be only 6.4% in chloroform, which is much lower than that (131.6%) expected from the QD number ratio (small-to-large: 76/100) extracted from TEM observations. The value of 131.6% is obtained by assuming that each QD exhibits the same quantum efficiency whatever its size. Actually, according to previous studies,[10] larger PbS QDs have even higher quantum efficiency than smaller ones.

If it also holds true here for polymer-encapsulated QDs, it means that larger QDs should contribute more than 57% of the total emission. The apparently contradictory result strongly indicates that either a significant number of larger QDs are still in the dark state or the PL efficiency of each larger QD is extremely low in chloroform. Considering the quencher concentration in chloroform is already much lower than that in water, it is clear that "external" quenching could not be a dominating factor for the total loss of PL of PbS/PMAO–PEG QDs in water although it partially contributes to the darkening of PL. It can be reasonably concluded that it is the presence of considerable numbers of surface defects or un-passivated surface atoms in larger QDs themselves that is mainly responsible for their loss in PL in water.

The above conclusion is further supported by the PL investigation of dried PbS QD films, in which the molecule quenching event is eliminated or at least minimized as the collapse of amphiphilic polymers during the drying process provides QDs with good isolation from their environments. The PbS/PMAO–PEG QDs freshly prepared in chloroform show red shift from 1480 nm to 1497 nm after film preparation, which is understandable as the QD coupling in the film often leads to the red shift of PL peaks.[40] Hence, for PbS/PMAO–PEG QDs (which have gone through the 3 month storage in water) with a bimodal PL band, two emission bands situated at 1297 nm and 1486 nm in chloroform are both expected to shift to red when the QDs are dried into a film. In addition, considering the distinct difference in the size distribution of two QDs/PMAO–PEG samples (5.2 ± 0.3 nm in chloroform *versus* a double size distribution of 6 ± 0.4 nm and 1.9 ± 0.3 nm in water), the spectrum of the film sample of PbS/PMAO–PEG QDs that have been stored in water for three months should appear expanding towards both shorter and longer wavelengths as compared to that of the film sample of PbS/PMAO–PEG QDs from chloroform. However, it can be seen clearly in Fig. 4b that although, as expected, there is obvious red shift of the emission peak when the PbS/PMAO–PEG QDs are dried into a film from water and a significant fraction of bluer emission as compared to that of the PbS/PMAO–PEG QDs dried from chloroform, there is only very slight spectral difference at the side of longer wavelength (above 1500 nm). This observation is a strong indication that larger QDs in the transferred sample do not make any important contribution to the PL even in the solid state. We further did simple calculations to estimate the contribution from larger QDs to PL. If we assume that all the emission above 1486 nm is contributed only by larger QDs, by comparing the integrated PL intensity above this wavelength to the PL intensity integrated over the entire PL band, it is estimated that larger QDs only account for ∼30% of total emission, indicating that most of PL still comes from smaller QDs. In fact, this value may even much overestimate the contribution from larger QDs. It is known that in the solid film, the resonant electronic energy transfer from smaller to larger QDs takes place even in a nominally single-sized QD sample, which results in the quenching of higher-energy PL of smaller QDs.[40] The smaller QDs may also form clusters and show emission at much longer wavelengths, which could be mistaken as the emission from larger QDs. Considering this

complexity, the above results suggest that even by almost excluding the possibility of PL quenching caused by external quenchers, the emission from the larger QDs only constitutes a much smaller fraction of the entire emission band than that expected from the molar ratio of larger-to-smaller QDs. The larger QDs must have more surface defects or unpassivated surface atoms than smaller ones.

In order to better understand the difference in the PL recovery behavior between smaller and larger QDs, we made effort to obtain the XPS spectra on smaller and large QDs, respectively, for the QD samples just after water transfer and after the 3 month aging. Although it is difficult to separate the smaller ones from larger QDs due to the very good solubility of PbS/PMAO–PEG QDs in water, we tried to achieve it by using high-speed centrifugation with the help of tiny amounts of THF. The separation is not very complete; the portion consisting of mostly smaller QDs also contains some larger QDs and *vice versa*. Nonetheless, useful information can still be extracted from the high resolution Pb 4f XPS spectra taken on these two portions. The peaks at 137.7 eV and 142.5 eV for all the samples are assigned to the binding energy of Pb 4f 7/2 and Pb 4f 5/2 of PbS, respectively;[41] while two additional peaks appearing at 136.5 eV for Pb 4f 7/2 and 141.3 eV for Pb 4f 5/2 (Fig. 6) are associated with the presence of unpassivated Pb atoms as we reported in ref. 20. These unpassivated Pb atoms, only observed for the QDs subject to water transfer, are highly likely responsible for the observed PL drop in PbS QDs after water transfer.

As shown in Fig. 6, the percentage of unpassivated Pb atoms (estimated from the deconvoluted Pb 4f peak areas) from freshly transferred to three-month-aged samples varies in an opposite way in the smaller and larger QDs. The percentage of unpassivated Pb atoms of smaller QDs decreases from 21% to 9% after three-month aging; while that of larger ones increases from 7% to 11%. The significant decrease of unpassivated surface sites in the smaller QDs is a strong indication of the effective and beneficial surface re-structuring of these QDs during the aging and must be the main reason for their PL recovery. The improved surface state may arise from the surface transformation of smaller QDs themselves, thanks
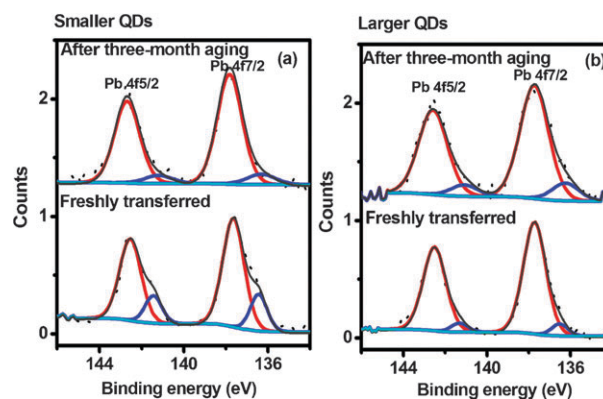

Fig. 6 High resolution Pb 4f XPS spectra of smaller (a) and larger (b) PbS/PMAO–PEG QDs following transfer into water and after being stored in water at 4 °C for 3 months. The dots represent experimental data. The red and blue lines are fitting curves and the gray line is the sum of them. The light blue line is a background curve.
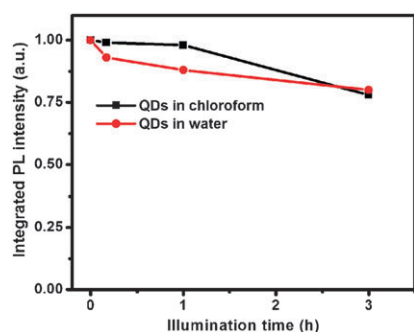
Fig. 7 Normalized integrated PL intensity of PbS QDs in chloroform or in water as a function of illumination time.

to their relatively high surface activity, or better passivation due to the improved organization of the ligands on the QD surface. In contrast, it seems very difficult to remove unpassivated surface states in larger QDs in the process of low-temperature aging. Moreover, more surface defects are introduced during the low-temperature Ostwald growth. The increase of unpassivated surface atoms reasonably explains why the PL recovery behavior is absent in larger QDs stored in water.

3.4 Photostability of recovered QDs

The photostability of the PbS QDs aged in water for three months was investigated by monitoring the PL variation of these QDs subject to continuous UV illumination. After three-hour irradiation, the integrated PL intensity can maintain $\sim 80\%$ (Fig. 7) and such photostability is comparable to that of QDs dispersed in chloroform. Meanwhile, it is worth mentioning that no photo-induced oxidation was observed for these QDs (or more accurately, for smaller QDs) under continuous UV illumination, as evidenced by the lack of any peak shift in their PL spectra with illumination, although photooxidation has been reported for QDs capped only by ligands in organic solvents.[25,30] It indicates that the amphiphilic polymer on smaller QDs is compact enough to retard O_2 diffusion and surface oxidation.

4. Conclusions

The automatic size-dependent recovery of PL was observed for the first time for PbS/PMAO–PEG QDs in water and found to be related to the interactions among the QD surface, ligands, amphiphilic polymers and solvent. The water-soluble PbS QDs were achieved by transferring monodispersed QDs from chloroform into water *via* PMAO–PEG. The water transfer process leads to a double size distribution (5.6 ± 0.9 nm and 2.7 ± 0.4 nm) together with the rapid disappearance of PL, due to severe ligand etching enhanced by the co-presence of water and amphiphilic polymers and thereby initiated Ostwald ripening. The PL of PbS QDs, however, can recover automatically after the storage in the dark for 3 months. Interestingly, the recovery behavior is found to be quite different for the smaller and larger QDs in the same sample and the primary reason consists in the difference in the variation of their surface defect states during the aging process. The effective removal of surface defect

states, as evidenced by the decrease of unpassivated surface atoms from XPS studies, is a dominant factor for the observed PL recovery in the smaller QDs. In contrast, the increase of the surface defects, which are introduced during the Ostwald growth (started immediately after water transfer and continued during the low-temperature aging) and not able to be efficiently annealed out, of larger QDs is mainly responsible for their non-recovery behavior in water. The water-soluble PL-recovered PbS QDs show the minimum quantum yield of 10% with good photostability in water, comparable to that of QDs dispersed in organic solvents.

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