Towards the fluorescence retention and colloidal stability of InP quantum dots through surface treatment with zirconium propoxide

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ABSTRACT
Through the synthetic development of sophisticated core/shell heterostructures, the fluorescent properties of quantum dots (QDs) have been steadily improved to a level that can ultimately meet the industrial demands, but their reliability is still insufficient, particularly showing low fluorescence stability against degradable conditions. As one solution to this issue, an additional physical barrier typically with an oxide phase has been introduced to protect the QD surface from the environment. In this work, a strategy for improving the stability of QDs involving the passivation of their surfaces with zirconium propoxide (Zr(PrO)₄) is suggested. Multi-shelled green QDs of InP/ZnSeS/ZnS were first synthesized, and then their surfaces were in-situ-treated with Zr(PrO)₄. To confirm the presence of Zr(PrO)₄-derived species on the QD surfaces, chemical analyses of the Zr(PrO)₄-treated QDs were performed through Fourier transform infrared, X-ray photoelectron, and inductively coupled plasma optical emission spectroscopic measurements. A photostability test of two comparative InP/ZnSeS/ZnS QDs – one treated without and one with Zr(PrO)₄ – was performed by exposing their dispersions to ultraviolet (UV) irradiation for prolonged periods of time, up to 120 h. It was revealed that Zr(PrO)₄ treatment is highly effective in improving fluorescence retention and colloidal stability.

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1. Introduction
Cd-based II-VI quantum dots (QDs) exhibit excellent photoluminescent (PL) properties such as high quantum yield (QY), narrow bandwidth, and facile visible color tunability through size/composition control. The inclusion of the harmful element Cd in such QDs, however, is a major obstacle to their application to commercial products. Therefore, various Cd-free compositions, such as III-V InP [1–16], I-III-VI CuInS₂ [17–21], and Pb-based halide perovskite [22–24], have been intensively explored for the synthesis of visible QD emitters. Among them, InP QDs are the leading visible emitters particularly with respect to PL QY, bandwidth, and nontoxicity. With the structural modification of InP QDs by inserting in them a GaP [3,9], ZnSe [4,6,12], or composition-gradient ZnSeS intermediate shell [8,10] to moderate the lattice mismatch at the interface of the InP/ZnS structure, multi- and thick shells have been generated on the InP core. These advanced heterostructures have considerably enhanced > 80% QYs compared to the QYs of the conventional single-shelled InP/ZnS QDs. In addition, the continuous synthetic advancement of InP QDs has led to a narrower emission bandwidth, which is directly associated with the size distribution of the cores. Through a slow growth process associated with the formation of a low-reactivity Zn-P complex in the synthesis of the In(Zn)P core, In(Zn)P QDs can possess a more uniform size distribution and consequently high color purity [11]. Moreover, the homogenous size distribution of small-sized InP cores can be maximally retained by adopting the successive ion layer adsorption and reaction method, resulting in green and red InP QDs with PL bandwidths of 36 and < 45 nm, respectively [12].

When applying QDs to manufactured products like display and lighting devices, the most critical requirements are their reliability and PL performance. Their reliability is related to their fluorescence stability against degradable conditions such as exposure to oxygen, water, photons, and heat. In the case of Cd-based QDs, it has been reported that the formation of a thick shell structure is desirable as it can enhance their stability under degradable environments [25,26]. This can be explained by the beneficial role of a thick shell not only as a physical barrier protecting the cores from the surroundings but also as an energetic barrier confining the electron and hole wave functions into the core region,
away from the surface defect sites (generated from the detaching ligands or from photo-oxidation). Such positive effects have also been observed in the earlier work on thick-shelled, Cd-free QDs [2–4]. Even though a thick-shelled heterostructure has contributed to the improvement of the QD stability, this strategy provides an incomplete solution, thus necessitating supplementary passivation to realize more robust core/shell QD systems. For this, QDs have been physically encapsulated with chemically stable oxides, including SiO2[13,14,24,27,28], In2O3[15], ZnGa2O4[19], and Al2O3[20,21], resulting in improved PL retention after exposure to various degradable conditions. These authors very recently reported the surface passivation of red InP QDs by complexing them with titanium isopropoxide, leading to a strikingly enhanced photo- and thermal stability [16]. In the present work, the surface treatment of multi-shelled InP QDs with another metal propoxide of zirconium propoxide (Zr(PrO)4) was explored. Highly bright green InP/ZnSeS/ZnS QDs with a high QY of 78% were in-situ surface-treated with Zr(PrO)4. By carrying out Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements, the presence of Zr species on the InP/ZnSeS/ZnS QDs was verified. Subsequently, a photostability test was performed on two comparative InP/ZnSeS/ZnS QDs, one without and one with surface treatment, and it was clearly revealed that Zr(PrO)4-based passivation can dramatically improve the PL retention and colloidal stability of QDs against long-term UV irradiation.

2. Experiment

2.1. Synthesis of bare and Zr(PrO)4-treated InP/ZnSeS/ZnS QDs

In a typical synthesis of green-emitting InP core QDs, a mixture of 0.9 mmol InI3, 2.2 mmol ZnCl2, and 6 ml oleylamine (OLA) in a three-necked flask was degassed at 120°C for 30 min and then heated to 180°C under N2 flow. Then 0.35 ml tris(dimethylamino)phosphine (P(N(CH3)2)3, P(DMA)3) was swiftly injected into the mixture, and the mixture was maintained at 180°C for 10 min for InP core growth. For the stepwise formation of a composition-gradient ZnSeS intermediate shell, a Se stock solution (consisting of 0.2 mmol Se in 1 ml tri-octylphosphine (TOP)), a S stock solution (consisting of 6 mmol S in 3 ml TOP), and a Zn stock solution (consisting of 3.5 g zinc stearate in 3 ml oleic acid (OA) and 9 ml 1-octadecene (ODE)) were prepared beforehand, and the resulting anionic and cationic shell stock solutions were alternately added as follows. As the first step of ZnSeS shelling, 0.25 ml of the Se stock solution and 0.3 ml of the S stock solution were introduced, followed by reaction at 195°C for 30 min. Then 3 ml of the Zn stock solution was injected into the mixture, after which the mixture was reacted at 210°C for 30 min. Next, 0.25 ml of the Se stock solution and 0.6 ml of the S stock solution were added to the mixture, followed by reaction at 225°C for 30 min. The same amount of Zn stock solution as above was again injected and reacted at 240°C for 30 min. Subsequently, the Se–S stock solution (0.25 ml of the Se stock solution and 0.9 ml of the S stock solution) was added and reacted at 255°C for 30 min. Then 0.3 ml of the Zn stock solution was introduced, followed by reaction at 270°C for 30 min. In the final step, 0.25 ml of the Se stock solution and 1.2 ml of the S stock solution were injected and reacted at 285°C for 30 min. Next, the same amount of Zn stock solution as above was injected and reacted at 300°C for 1 h. For successive ZnS outer shelling, 3 ml 1-dodecanethiol (DDT) was added in a dropwise fashion to the reactor, followed by reaction at 220°C for 1 h. Afterwards, 6 mmol zinc acetate dihydrate dissolved in 6 ml OA was injected and reacted at 190°C for 2 h, completing the synthesis of multi-shelled green InP/ZnSeS/ZnS QDs. The in-situ reaction of Zr(PrO)4 with the resulting InP/ZnSeS/ZnS QDs then proceeded through the successive injection of 3 ml of the Zr(PrO)4 solution into the above hot growth solution, and through reaction at 190°C for 30 min. The as-synthesized bare and Zr(PrO)4-treated QDs were then precipitated by adding excess ethanol to them, were repeatedly (4 times) purified with a solvent/nonsolvent combination of hexane/ethanol, and were finally redispersed in hexane.

2.2. Characterization

The absorption and PL spectra of the QD dispersions were recorded with a UV–visible absorption spectroscope (Shimadzu, UV-2450) and a 500W Xe-lamp-equipped spectrophotometer (PSI Inc., Darsa Pro-5200). The PL QYs of the QDs were measured with an absolute PL QY measurement system (C9920-02, Hamamatsu). The PL decay dynamics of the QDs were collected by employing the time-correlated single-photon counting method on a spectrofluorometer (FS5, Edinburgh Instruments) equipped with a picosecond pulsed laser diode (EPL-375). The chemical species on the QD surface was analyzed with an FTIR spectrometer (Bruker, Vertex 70). An XPS (Thermo VG) with Al Kα X-ray (E = 1486.6 eV) was employed to identify the chemical compositions/shifts of the QDs in the form of a film on the Si substrate. An inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, Optima 8300) was used to evaluate the chemical compositions of the QDs. Transmission electron microscopic (TEM)
images of the QDs were collected using an electron microscope (JEOL Ltd., JEM-2100F) operated at a 200 kV accelerating voltage. The hydrodynamic size of the QDs was estimated using a particle size analyzer (Otsuka Electronics, ELSZ-2000) operated through the dynamic light scattering (DLS) method.

3. Results and discussion

The as-purified green InP/ZnSeS/ZnS QDs with a 528 nm PL peak wavelength and a 52 nm bandwidth exhibited a high QY of 78%, which is higher than the QY of the conventional single-shelled InP/ZnS QDs that was reported earlier by these authors [7]. Such a remarkable QY improvement was derived from the insertion of a precisely controlled composition-gradient ZnSeS intermediate shell, which can effectively alleviate the interfacial compressive strain between the InP core and the ZnS outer shell. For in-situ surface treatment, Zr(PrO)₄ solution was simply injected into a hot growth solution of InP/ZnSeS/ZnS QDs at the end of the reaction. As can be seen in Figure 1(a), the resulting Zr(PrO)₄-treated InP/ZnSeS/ZnS QDs showed absorption and PL spectra identical to those of the bare QDs, without noticeable variations in PL wavelength and bandwidth. The PL QY slightly increased to 80% after Zr(PrO)₄ treatment. In addition, the PL decay dynamics of the bare and Zr(PrO)₄-treated QD samples nearly matched each other, with 48 and 48.3 ns average lifetimes (τ_avg), respectively (Figure 1(b)). These results strongly indicate that undesired surface defects possibly induced by organic ligand loss and surface oxidation were not formed during the Zr(PrO)₄ treatment reaction.

To ensure the presence of Zr species on the QD surface, FTIR measurement on the bare and Zr(PrO)₄-treated QDs was performed, and the obtained values are compared in Figure 2(a). The peaks in the range of 2850–2920 cm⁻¹ and at 1463 cm⁻¹ monitored from both QD samples are attributed to the stretching and bending modes of the methylene (–CH₂) and methyl (–CH₃) chains of the aliphatic surface ligands [29], while the peak at 1540 cm⁻¹ is attributed to the stretching vibrations of the carboxylate groups of fatty acids [30]. Noticeable differences in the FTIR peaks were observed at 650 and 430 cm⁻¹, which can be attributed to the vibration of the Zr–OH and Zr–O–Zr linkages, respectively [31]. The detection of these bond signals may imply the partial presence of the ZrOₓ phase on the surfaces of the Zr(PrO)₄-treated QDs. The appearance of an additional peak at 1091 cm⁻¹ from the surface-treated QDs likely corresponds to the Zr–O–C stretching vibration associated with the Zr(PrO)₄ molecule [32,33], signifying that Zr(PrO)₄ may sit on the QD surface presumably through the chemical affinity between the hydrophobic species (the propyl groups of Zr(PrO)₄) and the hydrocarbon chains (oleate, stearate, and dodecyl) of organic ligands. XPS analysis of the identical QD samples was carried out to further investigate their chemical compositions. As predicted, distinct photoelectron peaks from Zr 3d₅/₂ and Zr 3d₃/₂ at 182.48 and 184.88 eV, respectively [34], were detected from the Zr(PrO)₄-treated QDs (Figure 2(b)). Moreover, as shown in Figure 2(c), the O 1s signal of the Zr(PrO)₄-treated QDs can be resolved to two sub-spectra peaking at 531.6 and 530 eV, respectively. The latter peak, which was not detected from the bare QD sample, is ascribable to the Zr–O bonds likely from ZrO₂ and Zr(PrO)₄ [34]. As can be seen in Figure 2(d), the Zn 2p₁/₂ and Zn 2p₃/₂ signals were the same in the peak positions for both samples, but their intensities were substantially attenuated for the Zr(PrO)₄-treated QDs because the Zr species overlayer in the forms of ZrOₓ and Zr(PrO)₄ served as a barrier, blocking the
Figure 2. Comparison of (a) the FTIR spectra and high-resolution XPS scans of the (b) Zr 3d, (c) O 1s, and (d) Zn 2p photoelectron peaks of bare and Zr(PrO)₄-treated QDs.

photoelectrons that had been ejected from the QDs, thus lowering their detectivity. Additionally, the actual Zr/In molar ratio of the Zr(PrO)₄-treated QDs was assessed via ICP-AES analysis to be 4, which is lower than a solution value (6.7).

Figure 3(a,b) presents the TEM images of the bare and Zr(PrO)₄-treated InP/ZnSeS/ZnS QD samples. The average size of the bare InP/ZnSeS/ZnS QDs was estimated to be ∼6.6 nm, making them significantly larger than the single-shelled InP/ZnS QDs (average size: < 3 nm) [7]. The growth of such large-sized InP QDs was possible through the appropriate insertion of an elaborately controlled composition-gradient ZnSeS intermediate shell that effectively relieves the interfacial lattice mismatch between InP and ZnS. Although the presence of Zr species on the QD surface was verified by the earlier FTIR and XPS analyses, the TEM size of the Zr(PrO)₄-treated QDs (Figure 3(b)) was not different from that of the bare ones. Figure 3(c,d) shows histograms of the DLS-based hydrodynamic size distributions for the bare and Zr(PrO)₄-treated QDs, respectively. Considering the lengths of the organic ligands like OA (∼1.5 nm) [35], OLA (∼2 nm) [36], and DDT (∼1.5 nm) [37] on the QD surface, the much larger size (10.1 nm) of the bare QDs from the DLS-based analysis compared to the TEM result is acceptable. Meanwhile, the hydrodynamic average size of the Zr(PrO)₄-treated QDs slightly increased to 11 nm due to the presence of the ultra-thin Zr species above, which was not detectable through TEM measurement.
A photostability test was performed on two comparative InP/ZnSeS/ZnS QD dispersions – one without and one with Zr(PrO)₄ treatment – under continuous UV irradiation using a 365 nm multi-band UV lamp, for a prolonged period of time (up to 120 h). In the case of the bare QDs, their PL intensity was progressively reduced with the UV irradiation time, accompanied by a slight PL shift (528 → 526 nm) and PL broadening (52 → 60 nm) after 3 h exposure (Figure 4(a)). Meanwhile, the Zr(PrO)₄-treated QDs exhibited a relatively mild PL reduction, with the PL peak and bandwidth unchanged after 120 h UV irradiation (Figure 4(b)). Figure 4(c) presents the variations in the relative QD PL emission area of the two compared QDs with the UV irradiation time, evidently indicating that the Zr(PrO)₄ treatment of the QD surface worked well in terms of improving the QD stability against long-term exposure to photons. The PL of the bare QDs severely decreased by 62% relative to their original value only after 12 h UV irradiation. The substantial PL deterioration from the bare QDs can be ascribed to the devastation of the QD surface by the UV-photon-induced photochemical oxidation and the detachment of the labile organic ligands [15,16,38,39]. Besides, O₂ molecules can diffuse into the core surface through the defective pathways associated with the imperfect shell passivation and the grain boundaries of the shell [40], and can further oxidize a peripheral part of the core, giving rise to the reduction of the effective core size and consequently to the PL blue shift that was observed (Figure 4(a)) [15,39]. The PL broadening concurrent with PL shift may also be understood by presuming that the individual QDs in dispersion may experience such core oxidation in different degrees [15]. Moreover, at UV exposure for longer than 12 h, the bare QDs began to lose their colloidal stability and thus precipitate (Figure 4(d)) as a result of the removal of the aforementioned organic ligands therefrom. In sharp contrast, the Zr(PrO)₄-treated QDs not only showed a moderate PL drop of 22% (Figure 4(c)) but also showed excellent colloidal stability even after a much longer exposure time of 120 h (Figure 4(e)). These promising results firmly suggest that the present Zr(PrO)₄ treatment strategy is highly helpful in improving the photostability of QDs by effectively preventing the photo-oxidation of the QD surface and preserving the surface ligands.

4. Conclusion
Provided herein is a simple method of surface-passivating highly efficient green InP/ZnSeS/ZnS QDs with zirconium propoxide (Zr(PrO)₄) to render them photostable
with respect to photoluminescence (PL) and dispersion. The comparative PL QY and PL decay dynamics results obtained from the bare and Zr(PrO)₄-treated QDs indicated that the present surface treatment process would not deteriorate the surfaces of the original QDs. The linkage of Zr(PrO)₄ to the QD surface was presumed to occur based on the chemical affinity between the propyl groups of the Zr(PrO)₄ molecule and the hydrophobic surface ligands of the QDs. The FTIR and XPS measurements alluded to the possibility that the Zr species associated with ZrOₓ and Zr(PrO)₄ likely coexist on the QD surface. The 12 h UV irradiation of the bare QDs led not only to considerable QY reduction (62%) but also to severe QD precipitation. On the other hand, the Zr(PrO)₄-treated QDs exhibited a moderate QY drop of 22%, with their colloidal stability well maintained even after a much longer UV exposure of 120 h. These results unambiguously show that the present Zr(PrO)₄-based surface treatment is a promising strategy for effectively suppressing the photo-induced degradation of QDs, and thus retaining their PL and colloidal stability.

Disclosure statement
No potential conflict of interest was reported by the authors.

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