Blue-Emitting InP/GaP/ZnS Quantum Dots with Enhanced Stability by Siloxane Capping: Implication for Electroluminescent Devices

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0.09%, and a much longer lifetime than pristine QDs. As a result, these enable the siloxane capping QDs to achieve a much stronger storage stability and a longer QLED lifetime than pristine QDs.

KEYWORDS: InP quantum dots, blue-emitting, core/shell structure, siloxane capping, stability, QLEDs

INTRODUCTION

Colloidal quantum dots (QDs) have been attracting continuous attention recently as the next-generation efficient, wide color gamut display devices due to their near-unity photoluminescence (PL) quantum yield (QY), high color purity, and convenient band gap tunability.^{1–3} At present, Cd-containing QDs and metal halide perovskite QDs show strong PL properties, which are at the forefront.^{4–6} However, their constituent toxic heavy metals Cd and Pb will cause adverse effects on human health and ecological environment, which restricts their further commercial utilization and promotion.^{7,8} For their environment-friendliness and low toxicity, QDs such as ZnSe, CuInS, and InP have attracted wide attention recently.^{8–10}

InP QDs with low toxicity are regarded as an ideal alternative to Cd-based QDs due to their suitable and similar luminescence range.¹¹ Despite the development of InP QDs being inferior to that of Cd-based QDs, recent significant advances in the synthesis of InP QDs make it possible for them to compete with Cd-based QDs.^{12–16} The corresponding record PL QY for InP QDs with red and green emission has been pushed up to near-unity. Nevertheless, in contrast to red-and green-emitting QDs, synthesis of high-quality and blue-emitting InP QDs still faces challenges.^{17–19} At first, typical blue-emitting InP core sizes are below 2 nm, and thus the precise size control is particularly difficult. Meanwhile, tiny cores tend to generate more surface defects, and the sufficient surface passivation is hard to achieve, resulting in more nonradiative recombination. In an earlier study, wide-band gap

ZnS epitaxy directly on the InP core was implemented,^{20–22} but the lattice mismatch of InP-ZnS resulted in the unexpected interface defects, which prevented the formation of a perfect heteroepitaxial interface without defects and limited the thickness of an epitaxial shell. Most recently, an intermediate buffer layer with a lattice constant close to those of InP and ZnS (e.g., ZnSe,^{12,13,16,23} ZnSeS,^{24–26} and GaP^{15,27,28}) has been used to reduce lattice mismatch between the core and shell. Because the ZnSe shell inevitably causes large red shift of emission, the GaP intermediate shell is widely used in blue-emitting InP QDs. Based on the InP/GaP/ZnS core/shell/ shell structure, the highest PL QY of 81% with emission below 490 nm has been reported by Zhang et al.¹⁵

Besides, QDs with a narrow size distribution are very important for improving color purity of display devices. The separation of nucleation and growth steps of QDs by multiple injection of precursors at different temperatures is an effective method to reduce its size distribution.^{12,13} However, multiple injection of precursors often leads to the growth of QDs, which is unfavorable to the synthesis of small-sized InP cores. Because of the difficulty in controlling the reactivity of the small InP cores, the full width at half-maximum (FWHM) of

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blue-emitting InP QDs is still significantly wider than those of red- and green-emitting InP QDs. To our best knowledge, only Zhang et al. reported InP QDs with an FWHM of 45 nm at the emission peak below 490 nm.¹⁵ In addition, the deterioration of optical properties such as PL QY is another roadblock for QDs' commercially application. Due to the larger specific surface area of the tiny QDs and the higher proportion of dangling bonds, this unstable property is more obvious in blueemitting InP QDs. To enhance the chemical stability of QDs, many efforts have been made. A typical strategy is to further cap SiO₂ on the surface of QDs.²⁹⁻³¹ Zhong et al. successfully coated SiO₂ on CsPbBr₃ QDs through the hydrolysis reaction of tetramethoxysilane, greatly improving the stability of QDs.²⁹ Although this strategy can significantly improve the stability of the QDs, the thickness of SiO₂ is hard to be regulated, resulting in a sharp decrease in the PL QY of the SiO₂-capped QDs. Another strategy is to use hydrophobic alkyl silane oligomers or long alkyl chain polymers to bind to the surface ligands of QDs to form a protective layer.³²⁻³⁵ For instance, Bae et al.^{36,37} have fabricated the QD/siloxane hybrid film. For this approach, QDs were dispersed in the cured oligosiloxane resin, exhibiting outstanding stability. Wu et al.³⁸ coated CsPbBr₃ QDs with a thick poly (maleic anhydride-alt-1octadecene) polymer layer and applied it to white LEDs, achieving reliable UV resistance, oxidation resistance, and water repellency. However, this kind of QD-polymer composites can only be used as a color converter in LED devices rather than as independent electroluminescent devices.

In this work, we have synthesized blue InP/GaP/ZnS core/ shell/shell QDs with high PL QY of 71% with the PL emission of 484 nm, and through a simple prenucleation step, we achieved a narrow FWHM of 45 nm. In order to maintain the optical properties of QDs for a long time and improve the chemical stability, we use siloxane to cap prepared QDs. 3-Trimethoxysilylpropanethiol (TMSPT) was added to QD solution and adsorbed on the surface of QDs as ligands. Because methoxyl groups are easily hydrolyzed in air, the QDs treated by TMSPT are unstable. Therefore, diphenylsilanediol (DPSD) was added to form a siloxane network by condensation reaction with TMSPT. As a result, the siloxane capping QDs (siloxane-QDs) exhibit a much stronger stability against the long-term storage in air, and even its films show excellent stability in water immersion treatment. Furthermore, we successfully applied the resulting QDs in the LED device consisting of a multilayer structure of indium tin oxide (ITO), PEDOT: PSS, poly(9-vinlycarbazole) (PVK), QDs, 1,3,5-tri(mpyrid-3-yl-phenyl)benzene (TmPyPb), and LiF/Al electrode. The siloxane-QD LEDs show a maximum luminance of 690 Cd m⁻², an external quantum efficiency (EQE) of 0.09%, and a half-lifetime (T_{50}) of 20 min. This simple and effective method of preparing siloxane-encapsulated QDs may be extended to other materials with various components. This study not only provides a reliable method for the preparation of siloxaneencapsulated QDs, but also provides some guidance on the stabilization and applications of blue-emitting InP QDs.

EXPERIMENTAL SECTION

Chemicals. Indium acetate $[In(Ac)_3, 99.99\%$ metals basis] was purchased from Sigma Aldrich. Tris(trimethylsily)phosphine $[(TMS)_3P, 10 \text{ wt }\%$ in hexane, 98%] was purchased from Stream Chemicals. Zinc acetate $[Zn(Ac)_2, 99.99\%$ metals basis], myristic acid (HMy, \geq 99%), gallium trichloride (GaCl₃ beads, anhydrous 99.999% trace metal), zinc stearate $[Zn(St)_2, Zn \ 10\% \sim \ 12\%]$, trioctylphos-

phine (TOP, \geq 90%), 1-octadecene (ODE, \geq 90%), and 1dodecanethiol (DDT, \geq 98%) were purchased from Aladdin Chemistry Co., Ltd. TMSPT (>95%), DPSD (>98%), and barium hydroxide (Ba(OH)₂, 94–98%) were purchased from Alfa Aesar. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PE-DOT:PSS, Baytron Al 4083), PVK, and TmPyPb were purchased from Xi'an Polymer Light Technology Corp. Hexane and acetone were purchased from Guangzhou Chemical Reagent Co., Ltd. and stored with 4 Å molecular sieves. All chemical reagents were used without further processing and purification.

Preparation of Precursors. Preparation of 0.2 M (TMS)₃P in ODE. First, 10 wt % (TMS)₃P in hexane was distilled before in the vacuum chamber mounted on a glove box to use. Then, 0.2 mmol of (TMS)₃P was dissolved in 1 mL of ODE in a nitrogen-filled glovebox. Caution: (TMS)₃P should be handled without oxygen and water due to its highly pyrophoric nature.

Preparation of 0.085 M Ga-ODE Solution. $GaCl_3$ (0.034 mmol) was dissolved in 0.8 mL of ODE by mild heating.

Preparation of $ZnSt_2$ Suspension. Two grams of zinc stearate and 10 mL of ODE were mixed by stirring and ultrasonicated in turn.

Synthesis of InP/GaP/ZnS QDs. First, 0.12 mmol of In(Ac)₃, 0.5 mmol of $Zn(Ac)_2$, 1.1 mmol of HMy, and 3.5 mL of ODE were mixed in a 50 mL three-neck flask. The mixture was degassed under vacuum at 120 °C for 20 min and purged with nitrogen three times. After that, 0.5 mL of TOP was injected and 0.4 mL of 0.085 M Ga-ODE and 0.5 mL of 0.2 M (TMS)₃P were quickly added and maintained at 120 °C for 20 min. Then, with 0.7 mmol of DDT injection at 200 °C, the temperature was rapidly increased to 300 °C. It is worth noting that a faster rate of heating tends to result in a narrower size distribution. After maintaining 300 $^\circ C$ for 5 min, 4 mL of $ZnSt_2$ suspension was injected slowly. Then, 2 mmol of DDT was added drop by drop, ensuring that the temperature fluctuation was less than 2 °C. After maintaining 300 °C for 45 min, the reactor was cooled to room temperature by removing the heating mantle. The QDs were precipitated by adding excess acetone and re-dispersed in toluene for further use and characterization.

Preparation of Siloxane-QDs. TMSPT was added to 5 mg/mL of QD-toluene solution and heated to 60 °C under a nitrogen atmosphere and kept for a period of time. Then, an equal molar amount of DPSD (relative to TMSPT) was added to the mixture and 5 mg of Ba(OH)₂ was added as a catalyst for the condensation reaction. The reaction solution temperature was raised to 80 °C and maintained for 5 h. Subsequently, the QDs were centrifuged at 8000 rpm for 5 min to remove residual reactants.

Preparation of the QD Film. QDs (dissolve in toluene, 30 mg/mL) were spin-coated at 3000 rpm for 30 s and then baked at $70 \text{ }^{\circ}\text{C}$ for 5 min.

Device Fabrication. The blue-emitting InP-based QLEDs were fabricated according to the following procedure: The ITO-coated glass substrates were cleaned by ultrasonication sequentially in deionized water, isopropanol, and ethanol for 20 min in turn. The dried substrates were further treated with UV-ozone for 20 min; PEDOT:PSS was spin-coated on the ITO substrate at 4000 rpm for 45 s and then was annealed at 140 °C for 30 min. PVK (dissolved in chlorobenzene, 6 mg mL⁻¹) and QDs (dissolved in toluene, 30 mg mL⁻¹) were deposited layer by layer by spin coating at 3000 rpm for 45 s, PVK layer was baked at 120 °C for 10 min, and QD layers were baked at 80 °C for 5 min. TmPyPb (40 nm) and LiF (1 nm)/Al (100 nm) were deposited by thermal evaporation in a vacuum chamber with a vacuum level of 10^{-6} mbar. Light-emitting areas were 6 mm² defined by the overlapping of the ITO anode and Al cathode.

Characterization. Transmission electron microscopy (TEM) was carried out using a JEM-2100F TEM from JEOL. The size distributions of QDs were estimated with the software of Nanomeasure. The PL spectra and absolute PL QY of QDs dispersed in toluene were recorded at 365 nm excitation using the FLS980 fluorescence spectrometer equipped with an integrating sphere from Edinburgh Instruments Ltd. Transient PL spectra were measured at room temperature using the FLS980 fluorescence spectrometer equipped with a time-correlated single-photon counting spectrofluorScheme 1. (a) Schematic Illustration of the Fabrication Process of Siloxane-QDs. (b) Condensation Reaction Between TMSPT and DPSD



ometer from Edinburgh Instruments Ltd., and the QDs were excited by a 405 nm picosecond laser diode with a 2 MHz repetition rate. Absorption spectra of QDs dispersed in toluene were taken on a Pekin-Elmer Lambda 750 spectrophotometer. Fourier transform infrared (FTIR, Tensor 27, Bruker) spectra were recorded with 2.0 cm⁻¹ resolution. X-ray diffraction (XRD) measurements were performed on a Smartlab X-ray diffractometer from Rigaku Corporation operated at 40 kV and 40 mA with Cu K α radiation $(\lambda = 1.5406 \text{ Å})$. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi instrument with Al K α as the Xray source from Thermo Fisher Scientific. Solution ¹H nuclear magnetic resonance (NMR) spectra were conducted by a Bruker AVANCE III Spectrometer, and all NMR data were collected in a chloroform-d (CDCl₃) solvent. Hydrodynamic particle sizes of the QDs in toluene were determined using a particle size analyzer (nano ZS & Mastersizer 2000E, Malvern).

RESULTS AND DISCUSSION

As shown in Scheme 1a, the preparation of siloxaneencapsulated QDs consists of three main stages: synthesis of InP/GaP/ZnS core/shell/shell QDs, ligand exchange, and condensation reaction. In the first stage, GaP and ZnS were epitaxially grown on the prepared InP core in turn to obtain strong PL properties. Subsequently, TMSPT partially replaced the stearate and adsorbed on the surface of the QDs. Under the catalysis of Ba(OH)₂, DPSD is then condensed with TMSPT to form Si–O–Si frameworks, as shown in Scheme 1b. The geometry and size distribution of the InP core and InP/GaP/ZnS core/shell/shell QDs have been analyzed via TEM. From Figure 1a and its inset, the InP core is approximately triangular and monodispersed, and the size is 1.9 ± 0.3 nm with the relative standard deviation of 15.8%. The high-resolution (HR)-TEM image also shows a lattice distance of 0.22 nm, which corresponds to the (220) lattice spacing of the InP zinc blende structure. After the GaP and ZnS shells were epitaxially grown onto the InP core, the size increased to 5.9 \pm 0.9 nm with the relative standard deviation of 15.3%, as shown in Figure 1b. Meanwhile, the shape obtained became more regular. The close relative standard deviation and more regular shape suggest uniform shell epitaxial and defect passivation. The lattice distance measured from the HR-TEM image (inset at the top right of Figure 1b) is 0.11 nm, which corresponds to the (422) lattice spacing of the ZnS zinc blende structure. The crystal structure was further confirmed by selected area electron diffraction (SAED). As shown in the inset at the bottom of Figure 1b, the three distinct circles with radii of 5.53, 9.29, and 10.64 nm⁻¹ are observed in the reciprocal space, corresponding to the lattice distances of 0.18, 0.11, and 0.09 nm in real space, which match the (311), (511), and (533) planes of the zinc blende crystal.

Because the injection temperature of the P precursor has an impact on the QD emission peak position and FWHM, we optimized the injection temperature of the P precursor and the nucleation time of InP seed. As shown in Figure 2a and Table S1, when the temperature was not maintained, the FWHM of QDs increases gradually with the increase of injection temperature, and PL redshift is associated with the increase of temperature above 110 $^{\circ}$ C. Based on the typical method (30



Figure 1. TEM images (left) and corresponding size distribution diagrams (right) of (a) InP core and (b) InP/GaP/ZnS core/shell/shell QDs. (Insets at the top right of a and b show the corresponding HR-TEM images, and the inset at the bottom right of b shows the corresponding SAED patterns).



Figure 2. (a) PL spectra of InP/GaP/ZnS QDs at different injection temperatures of the P precursor, which were maintained for 0 and 20 min. (b) PL and absorption spectrum of InP/GaP/ZnS QDs (inset: photograph of InP/GaP/ZnS QDs taken under 365 nm illumination). (c) XRD patterns of the InP core and InP/GaP/ZnS core/shell/shell QDs. (d) High-resolution XPS scans of P 2p (bottom), Ga 2p (midium), and S 2p (top) photoelectron peaks for the InP core, InP/GaP core/shell, and InP/GaP/ZnS core/shell/shell QDs.

 $^{\circ}$ C, 0 min),^{15,27} we can obtain the QDs with a PL peak of 484 nm and FWHM of 48 nm. After they were maintained for 20

min at the corresponding temperature, the samples below 110 °C showed no significant difference, while all the samples



Figure 3. (a) ¹H-NMR spectra for InP/GaP/ZnS QDs without and with treatment using different concentrations of TMSPT. (b) Normalized PL QY change as a function of reaction time in QDs treated by different concentrations of TMSPT. (c) Time-resolved PL decay curves of QDs without TMSPT and with TMSPT concentration of 0.010, 0.100, and 0.250 M.

above 110 °C showed different degrees of FWHM narrowing. We believe that when the reaction temperature is near the nucleation temperature of InP, the precursor preferentially forms InP crystal seeds. In the subsequent growth stage, the nucleation process still occurs, resulting in the increase of size distribution. By prolonging the nucleation time, we make the precursor to produce more InP seeds, making the precursor concentration lower than the nucleation concentration, thus separating the growth of nanocrystals from nucleation. As a result, the InP/GaP/ZnS QDs with the narrowest FWHM of 45 nm were obtained at the injection temperature of 120 °C for 20 min. We subsequently analyzed the optical properties and structure of the resulting InP/GaP/ZnS QDs. Figure 2b shows the corresponding absorption and PL spectra. The first exciton peak is at 433 nm with a valley depth (VD, defined as $VD = 1 - (Abs_{min}/Abs_{max}))^{12}$ of 0.26, while the PL peak is at 484 nm with the FWHM of 45 nm. Meanwhile, the measured PL QY of the InP/GaP/ZnS QDs is as high as 71%. The high VD value, narrow FWHM, and high PL QY indicate a strong PL and high color purity, as shown in the inset of Figure 2b. XRD analysis of InP-based QDs before and after shell epitaxial was also carried out, as shown in Figure 2c. As mentioned above, the size of the core is extremely small, and thus, the reflection peaks discerned from the XRD pattern are not clear and the FWHM is wide. The overall diffraction angles are higher than the standard XRD pattern for InP (JCPDF: 032-

0452), which can be attributed to lattice contraction caused by the zinc dopant. After epitaxial growth of GaP and ZnS shells, all peaks shift toward ZnS peaks. Meanwhile, the reflection peaks are much more noticeable due to the increase of the QD volume. Subsequently, XPS analysis was performed to confirm the GaP and ZnS shells. The bottom of Figure 2d shows the XPS scans of P 2p. The high intensity peak recorded at 126-131 eV can be attributed to the P^{3-} for InP, while another weaker peak in the range of 130-135 eV is related to the $P^{3+ to 5+}$ for InPO_x.³⁹ After introducing Ga³⁺, the representative peak of P 2p in InP shifted from 128.5 to 129.2 eV, which is attributed to the slightly higher electronegativity of Ga than In. Meanwhile, due to the presence of both P-Ga and P-In combinations, the P 2p peak in InP of the InP/GaP spectrum is widened significantly. The signal for the InPO_x component disappeared in InP/GaP QDs, and it can be inferred that InP/ GaP QDs have stronger antioxidant activity than the pure InP core, and the coated GaP effectively avoids oxidation of InP. In the XPS scans of Ga 2p (medium of Figure 2d), after introducing Ga³⁺, there are two representative energy states of Ga 2p electrons at 1119.5 and 1146.2 eV, indicating the contributions of Ga $2p_{1/2}$ and $2p_{2/3}$, respectively. In addition, we estimated the surface Ga content of InP/GaP samples via quantitative analysis of XPS elements, and the results showed the In to Ga ratios of 0.43, which indicates that Ga³⁺ ions are more likely to form the GaP shell on the InP core surface

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Figure 4. (a) TEM images (left) and corresponding size distribution diagrams (right) of siloxane-QDs. (b) Comparison of ¹H-NMR spectra for pristine QDs, TMSPT-QDs, and siloxane-QDs in CDCl₃. Illustrations of reference substances are shown at the right with protons for the equivalent protons labeled. (c) FTIR spectra and (d) PL spectra of pristine QDs, TMSPT-QDs, and siloxane-QDs (inset: digital photos of siloxane-QDs and TMSPT-QDs after they were exposed to air).

rather than absorbed on the InP core surface as ions. After coating with the ZnS shell, the signal associated with P and Ga disappeared, while the representative peak of S 2p appeared at 167-161 eV (top of Figure 2d), confirming the successful epitaxial growth of the shell outside the core.

In order to improve the stability of QDs, we encapsulated the QDs with siloxane. First, we discussed the effects of different concentrations of TMSPT on the surface ligands of QDs by ¹H NMR spectroscopy, as shown in Figure 3a. With the introduction of TMSPT, the peaks of $-CH_2S^-$ (top of Figure 3a) and -OCH₃ (bottom of Figure 3a) from TMSPT appeared at 2.20–2.25 ppm and 3.45-3.49 ppm,^{40,41} respectively. The peak of $-CH_2COO^-$ form stearate appeared in all samples at 2.22–2.32 ppm.⁴⁰ With the increase of the TMSPT concentration, the integral ratio of peak intensity of $-CH_2COO^-$ to $-CH_2S^-$ changed (6.32 for 0.01 M, 6.19 for 0.025 M, 6.13 for 0.050 M, 5.72 for 0.100 M, 2.90 for 0.150 M, and 5.89 for 0.250 M). Because zinc stearate is difficult to be removed completely, there must still be residual zinc stearate free in the solution.⁴⁰ Therefore, the abovementioned integral ratio does not follow the stoichiometric ratio. Meanwhile, there was a regular overall chemical shift of -CH2COO- and $-CH_2S^-$ in 0.010-0.150 M samples, which indicated the changes of the coordination between ligands and QDs. However, anomalies occurred in the 0.250 M sample, and we speculated that there were two reasons for this: on the one hand, because the rotation/bending entropy of the C-C σ bond could improve the solubility of the complex in solution,⁴ TMSPT provided much less solubility than stearate, leading to the aggregation of the TMSPT complex with stearate desorption; on the other hand, excessive TMSPT exposure in the air induced the hydrolysis of methoxyl easily, which also led to the aggregation of the TMSPT complex. Then, we have studied the changes of PL QY at various concentrations of

TMSPT and reaction times, as shown in Figure 3b. At the initial stage of the reaction 1h, all samples exhibited a significant decrease in PL QY, which we speculated was related to the desorption of the original stearate ligand. With the progress of the reaction, PL QY gradually rebounded, which can be attributed to TMSPT adsorbed on the QD surface as a ligand. At the lowest TMSPT concentration (0.010 M), PL QY decreased gradually in the first 2 h of the reaction, and although PL QY increased slightly after 3 h, it still maintained a significant downward trend. In other samples with higher TMSPT concentrations, the PL QY rebounded significantly with reaction time and peaked at 3-4 h. In the TMSPT concentration of 0.100 M, the PL QY at 4 h even reached to the initial value, which indicated that TMSPT can also improve the PL performance as a ligand. However, as the reaction time increases, the PL QY of QDs will decrease, which can be attributed to the aggregation of QDs based on the abovementioned presumption, resulting in the fluorescence quenching of QDs. To further confirm our inferences, we did a series of time-resolved PL (TRPL) decays of InP/GaP/ZnS QDs treated without TMSPT and with three typical concentrations of 0.010, 0.100, and 0.250 M; for all, the reaction time was 4 h (Figure 3b). The decay curves were fitted by a triexponential function

$$I(t) = y_0 + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$$
(1)

The parameter τ is the decay time constant, while *B* is the proportion of each component. The fitting parameters are summarized in Table S2. Typically, the faster decay component of <10 ns is assigned to the nonradiative recombination channel caused by defect states, while the



Figure 5. (a) Traces of PL QY for the solution of pristine QDs and siloxane-QDs aged in air for 30 days. (b) PL QY change as a function of time for the films of pristine QDs and siloxane-QDs immersed in water for 36 h (inset: PL QY changes during the first 5 min). (c) Digital photographs of siloxane-QD films and pristine QD films before (top) and after (bottom) immersion in water for 36 h taken under 365 nm illumination.

medium decay component (25-50 ns) is related to the radiative recombination channel. The slowest decay component of >100 ns can be associated to the radiative recombination of deep trap states around the QDs. From the fitting results, the fastest nonradiative recombination component appeared at QDs with TMSPT concentrations of 0.010 M $(\tau_1:1.3 \text{ ns}, A_1: 0.59)$ and 0.250 M $(\tau_1:6.5 \text{ ns}, A_1: 0.21)$. The presence of fast decay components and the reduced population of radiative recombination channels indicate an increase in defective states, which may be caused by the decrease in ligands on the surface of the QDs. Conversely, the other samples show a similar biexponential decay behavior, which is consistent with PLQY. These results suggest that too low or too high concentration of TMSPT will increase the surface defects of QDs and thus reduce its PL properties. Therefore, in order to maximize the PL properties of QDs during ligand exchange, it is necessary to control the appropriate concentration of the ligand.

Furthermore, a SiO₂-like passivation layer around QDs (siloxane-QDs) was formed by the condensation of TMSPT and DPSD. The hydrodynamic size, measured by dynamic light scattering, increased from 6.5 to 8.7 nm (Figure S1). The increased size indicates that the siloxane is not in the expected monolayer form on the surface of the QDs, but rather has accumulated thickness, which might impede the carrier injection in QLEDs. Figure 4a shows the TEM image and corresponding size distribution diagrams of siloxane-QDs. No siloxane aggregation was observed in TEM images, and the morphology and statistical size of QDs did not change. This supports the hypothesis that siloxane is adsorbed to the surface of QDs as ligands rather than forming QD-polymer composites, which is conducive to the further fabrication of QLEDs. Subsequently, the surface ligand exchange and condensation reaction of the resulting QDs were analyzed by ¹H NMR spectroscopy, as shown in Figure 4. In the pristine QDs, the peak at 2.13 ppm can be assigned to the compound of alpha methylene in stearate's carboxylate group and methyl in stearic acetone (residual solvent for purification of QDs), so it has the strongest intensity.^{40,41} Other peaks near 0.85 and 1.18 ppm can be matched to the peaks of methyl and the superposition of methylene (gamma to pi) from stearate, respectively.^{43,44} After introducing TMSPT, a small overall chemical shift appeared. Meanwhile, the characteristic peak of alpha methylene $(-CH_2S^-)$ in TMSPT's thiol group appeared between 2.22 and 2.30 ppm,⁴³ and the peak of methoxy group (-OCH₃) in TMSPT appeared at 3.64 ppm.⁴¹ All of these indicate that the original ligands on the QDs were replaced by TMSPT. Then, as a result of sol-gel condensation reaction

between TMSPT and DPSD, the characteristic peaks of the benzene ring appear at 7.33-7.58 ppm.⁴¹ In addition, as a result of condensation reaction, the proportion of $-OCH_3$ groups decreased, so that the corresponding peak disappeared.

To further understand the ligand exchange and siloxane encapsulating processes, we compared the FTIR spectra of pristine QDs, TMSPT-QDs, and siloxane-QDs, as shown in Figure 4c. For pristine QDs, the peaks at 1463 and 1538 cm⁻¹ are assigned to the symmetric stretching vibration and antisymmetric stretching vibration of $-COO^-$ from stearate, respectively.45 The peaks at 2852 and 2922 cm⁻¹ can be attributed to the stretching vibration of $-CH_3$ and $-CH_2$ -from stearate, respectively.⁴⁵ For TMSPT-modified QDs, the peaks -CH₃ and -CH₂- shifted to a higher wavenumber, and the peaks appeared at 1085 and 1028 cm⁻¹ for the Si-O bond,⁴⁶ which indicates that TMSPT is adsorbed as a ligand. The disappearance of the carboxylate characteristic peaks also indicated the shedding of the stearate ligand. After the condensation reaction of TMSPT and DPSD, a wide absorption band completely different from the Si-O bond appears at 1000-1100 cm⁻¹, which corresponds to the stretching vibration of the Si–O–Si structure.^{36,37} Meanwhile, bands corresponding to stretching vibration of the benzene ring at 1415-1630 cm⁻¹ are also present in siloxane-QDs.⁴⁶ The two abovementioned characteristics show that TMSPT on the surface of QDs undergoes condensation reaction, that is, the siloxane network is successfully formed on the surface of QDs. The result supports the abovementioned ¹H NMR analysis. Figure 4d shows the PL spectra of pristine QDs, TMSPT-QDs, and siloxane-QDs. We note that the emission peaks of the three spectra are not offset, but there is a slight difference in FWHM. After treated by TMSPT, the FWHM of the resulting QDs increases from 45 to 50 nm, which can be attributed to the agglomeration of QDs resulting from the instability of the surface TMSPT ligand. After siloxane encapsulation by the condensation reaction of DPSD, the FWHM was reduced to 48 nm, indicating a reduction in the aggregation of QDs (inset of Figure 4d).

The storage stability of the resulting QDs has been confirmed by monitoring their PL QY changes stored in air at 30 °C \pm 5 °C and 70% \pm 20% relative humidity for 30 days, as shown in Figure 5a. After capped with siloxane, the PL QY of QDs decreased significantly. However, to our surprise, the PL QY of siloxane-QDs solution rebounded noticeably (38.1 to 61.7%) in the first 4 days and gently dropped to 47.7% thereafter. Conversely, the PL QY of pristine QDs decreased dramatically in the first 9 days (70.1 to 27.4%) and finally dropped to 17.6% after 30 days. We speculate that the



Figure 6. (a) Schematic illustration of the QLED structure. (b) PL and EL spectra of pristine QDs and siloxane-QDs. Device characteristics of QLED with pristine QDs and siloxane-QDs: (c) current efficiency versus current density; (d) luminance versus voltage; (e) current efficiency and EQE versus luminance. (f) Lifetime measurements (at the voltage of 8 V) of the QLEDs with pristine QDs and siloxane-QDs (*L* is real-time brightness, while L_0 is the initial brightness).

enhanced PL performance may be related to the previously reported mechanism of water molecule passivation.⁴⁷ To confirm this, we fabricated corresponding film samples and treated them in harsh conditions, that is, they were immersed in water. As shown in Figure 5b and its inset, the PL QY changes were also monitored and similar trends were observed in thin film samples as in solution. The PL QY of the siloxane-QD film increased (28.3 to 33.8%) in the first 30 s, whereas that of pristine QDs continuously declined. Meanwhile, siloxane-QD films also show a stronger stability than pristine QD films. Figure 5c shows the digital photographs of the corresponding films under 365 nm illumination, and after 36 h of the immersion test, the luminescence of the pristine QD film weakened significantly, whereas that of the siloxane-QD film did not change significantly.

The PL QY changes can be corroborated by PL decay dynamics. Figure S2a and Table S3 show the TRPL spectra and summary parameters for the solution of pristine QD and siloxane-QD aging in air. As we defined earlier, ultrafast life components τ_1 associated with nonradiative recombination are present in initial siloxane-QDs and aged pristine QDs. After aging in air, τ_1 disappeared in aged siloxane-QDs, but appeared in aged pristine QDs. For the pristine QD films (Figure S2b and Table S4), obviously, with the increase of immersion time, the τ_2 associated with radiative recombination decreased and the τ_1 component increased, indicating that the defect recombination increased. Conversely, for siloxane-QD films immersed in water, the τ_1 component decreased significantly, suggesting that the defects have been passivated.

To verify the positive effects of QD optimization methods on devices, we fabricated the QLEDs consisting of a multilayer structure of ITO, PEDOT:PSS, PVK, QDs, TmPyPb, and LiF/ Al electrode (Figure 6a). Figure 6b shows the PL and EL spectra (at the voltage of 8 V) of the pristine and siloxane QLEDs. Compared with the PL peaks, both the EL spectra show a redshift and a broader FWHM due to the occurrence of Förster resonance energy transfer in the QLED film. At the same time, the quantum-confined Stark effect caused by polarization fields can also be the reason for the redshift of EL spectra. As shown in Figure 6c, the current density of siloxane-QD devices is smaller than that of pristine ones below the voltage of 8 V, while it is opposite above the voltage of 8 V. This may be due to the lower carrier injection efficiency of the siloxane-QDs, and therefore, the turn-on voltage of the siloxane-QD devices (5.7 V) is higher than that of the pristine QD devices (6.2 V) (Figure 6c). Nevertheless, we are pleasantly surprised to find that the maximum brightness of the siloxane-QD devices (690 Cd m^{-2} at 9 V) was slightly higher than that of the pristine QD devices (480 Cd m⁻² at 9 V). The inset of Figure 6d shows the EL picture of siloxane QLEDs at 8 V. Figure 6e shows the maximum current efficiency of the siloxane-QD devices is 0.15 Cd A⁻¹ with an EQE of 0.09%, while that of the pristine QD devices is 0.10 Cd A^{-1} with an EQE of 0.06%. Moreover, we compared the lifetimes of the two devices, as shown in Figure 6f. The brightness of the pristine QLED decays to half its initial brightness after 6 min ($T_{50} = 6$ min), which is shorter than that for siloxane QLEDs (T_{50} = 20 min). Although the performance of QDs treated with siloxane is not outstanding in improving the properties of QLED devices, it is of great significance for improving the stability of devices.

CONCLUSIONS

In this work, highly luminescent blue-emitting InP/GaP/ZnS core/shell/shell QDs were successfully synthesized. Because the GaP bridging shell reduced the lattice mismatch and the wide band gap ZnS shell confined exciton recombination of the inner core, the PL QY of the resulting QDs reached to 71% emitting at 484 nm, and through a simple prenucleation step, we achieved a narrow FWHM of 45 nm. The PL properties surpass those presented in most other works on blue-emitting InP-based QDs. Furthermore, through the specific ligand exchange and condensation reaction processes, we successfully grafted organosilicon onto the surface of QDs, forming a stable amorphous SiO₂-like capping structure. Based on the obtained QDs, we also have fabricated blue-emitting QLEDs. As a result, the siloxane-capped QDs exhibited a strong stability, which is against the long-term storage in air, and even its films show

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excellent stability in water immersion treatment. The siloxane QLEDs show a maximum luminance of 690 Cd m⁻² and an EQE of 0.09%. Moreover, as the siloxane capped the QDs, the lifetime of QLEDs was significantly improved. Although these numbers are not "record-breaking," it is reasonable to expect that this work will provide some guidance for the preparation of high-performance, heavy metal-free, and stable blue-emitting QDs for use in light-emitting diodes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.1c04486.

PL peak and FWHM of InP/GaP/ZnS QDs at different injection temperatures, TRPL parameters with different TMSPT concentrations, TRPL spectra and parameters of pristine QDs and siloxane-QDs in solution and film, and dynamic laser scattering spectra of pristine QDs and siloxane-QDs (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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