Synthesis of Highly Luminescent InP/ZnS Quantum Dots with Suppressed Thermal Quenching

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Abstract: InP quantum dots (QDs) are promising down-conversion phosphors for white light LEDs. However, the mainstream InP QDs synthesis uses expensive phosphorus source. Here, economic, in situ-generated PH3 is used to synthesize InP QDs and a two-step coating of ZnS shells is developed to prepare highly luminescent InP/ZnS/ZnS QDs. The QDs show a photoluminescence quantum yield as high as 78.5%. The emission can be tuned by adjusting the halide precursor and yellow emissive InP/ZnS/ZnS QDs are prepared by judiciously controlling the synthetic conditions. The yellow QDs show suppressed thermal quenching and retain >90% room temperature PL intensity at 150 °C for the growth solution. Additionally, the PL spectrum matches with the eye sensitivity function, resulting in efficient InP QD white light LEDs.

Keywords: InP; quantum dots; core/shell; InP/ZnS; thermal quenching

1. Introduction

Colloidal quantum dots (QDs) have become important down-conversion phosphors due to their tunable emission colors, high absorption cross sections, broad excitation spectra, high luminescent efficiencies, high stability, and solution processability [1]. So far, CdSe-based core/shell QDs have been widely applied in backlight for high color gamut display and general lighting for tunable color temperature, owing to their mature synthesis and supreme luminescent properties [2]. Recently, lead halide perovskite QDs have emerged as another promising emitters due to their ease of synthesis, high emission efficiencies, and narrow emission spectra [3]. Additionally, the perovskite QDs also showed negligible thermal quenching up to 100 °C via a lattice matched core/shell structure [4]. Despite the excellent luminescent properties, the Cd- and Pb-containing QDs pose environmental health risks. Therefore, highly luminescent and heavy-metal-free QDs are desirable for practical applications.

InP QDs are the most promising alternative emitters in addition to the CdSe and lead halide perovskite QDs. For example, the emission of InP QDs can cover the whole visible region [5]; the photoluminescence quantum yield (PLQY) of InP QDs has reached near unity [6,7] and the emission full width at half maximum (FWHM) is as narrow as 35 nm. However, most of the synthesis of InP QDs relies on the use of a highly flammable and expensive phosphorus source, tris(trimethylsilyl) phosphine (P(TMS)3) [7–10]. In order to reduce the cost, four other phosphorus sources were adopted. Yellow phosphor was first used to replace the P(TMS)3, which was reduced by LiBH(CH2CH3)3 [11]. By using this phosphorus precursor, the synthesis can be conducted at relatively low temperatures (80–120 °C). However, the as-prepared InP QDs showed broad size distributions and low PLQYs. As an improved route, PCl3 was introduced to replace the yellow phosphor, which was reduced to highly reactive elemental phosphorus by the superhydride [12]. The PCl3-based synthesis has better control on the size and size distribution than the...
synthesis using yellow phosphor, but the size distributions are still much broader than that of CdSe QDs. Furthermore, the PLQY of the as-prepared InP QDs is extremely low (~0.25%), which was improved to ~20% via the treatment of HF. Calcium phosphide (Ca₃P₂) was used as another economic phosphorus source, which was converted to highly reactive PH₃ by reacting with HCl [13,14]. The in situ generated PH₃ reacts with indium myristate, forming InP QDs. The adoption of Ca₃P₂ substantially reduces the synthetic cost, nevertheless, the luminescent properties of the InP QDs are still very poor with PLQYs below 30% after coating a ZnS shell [13,14]. The fourth low-cost phosphorus source is P(amio)₃ (amino = dimethylamino, diethylamino), which still produced relatively broader size distributions [15–17]. The P(amio)₃-based synthesis produced improved luminescent properties compared to the above three economic syntheses, exhibiting a highest PLQY of 60% for InP/ZnS QDs [16]. Overall, the economic syntheses produce InP QDs with broad size distributions and relatively low PLQYs compared to the route based on P(TMS)₃. The large size distribution (wide PL FWHM) is acceptable if the InP QDs are applied in general lighting, while the luminescent property needs to be enhanced for the economic syntheses of InP QDs. For efficient general lighting, optical structure is another factor that could enhance the performance in addition to the QD emitters. Theoretical and experimental investigations have shown that the coupling of the QDs and dielectric antennae can produce high directional radiation [18,19], which would improve the out-coupling of light.

In the present work, we focused on the QD materials for general lighting. Specifically, we improved the InP QDs synthesis using PH₃ as the gaseous phosphorus source, and a two-step ZnS coating procedure was developed, producing highly luminescent InP/ZnS QDs with a highest PLQY of 78.5%. Due to the elaborate ZnS coating strategy (effective InP surface passivation), the core/shell QDs exhibited suppressed thermal quenching, retaining >90% room temperature PL intensity at 150 °C. The emission color was tunable by changing the halide precursors and a synthetic route was designed to produce highly luminescent InP/ZnS QDs with emission spectrum matching with the eye sensitivity function, producing an efficient InP QD white light LED (WLED).

2. Materials and Methods

Chemicals: Calcium phosphide (Ca₃P₂, 97%) was purchased from Alfa Aesar. Oleylamine (OLA, 70%), 1-octadecene (ODE, 90%), indium chloride (InCl₃, 99.999%), zinc chloride (ZnCl₂, 99.999%), zinc bromide (ZnBr₂, 99.999%), zinc iodide (ZnI₂, 99.999%), (3-aminopropyl)triethoxysilane (APTES, 98%), polymethylmethacrylate (PMMA, MW = 120,000) and zinc diethyldithiocarbamate (Zn(DDTC)₂, 98%) were purchased from Aladdin (Shanghai, China). Dodecanethiol (DDT, 98%), P₂O₅, hydrochloric acid (HCl), toluene, hexane, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the chemicals were used without further purification.

Synthesis: The synthetic process is shown in Scheme 1. In a typical synthesis, 0.1 g of InCl₃, 0.495 g of ZnBr₂, and 8 mL of OLA were loaded in a 100-mL flask. The mixture was pumped at 120 °C for 15 min, then the flask was filled with N₂ and the temperature was raised to 220 °C. In another container, 0.046 g of Ca₃P₂ reacted with 2 mL 4 M HCl, generating PH₃. The PH₃ was bubbled into the hot indium precursor under N₂ flow through a drying tube containing P₂O₅, initiating the nucleation and growth of InP QDs. The growth was conducted for 30 min. For the growth of ZnS coating (InP/ZnS QDs), the growth solution was cooled to 160 °C, and 3.6 mL of DDT was injected. Then the temperature was raised to 220 °C again and maintained for 15 min. For the growth of a second ZnS shell (InP/ZnS/ZnS QDs), the growth solution was cooled to 120 °C and 0.217 g of Zn(DDTC)₂ (dissolved in 2 mL OLA) was injected. Then the solution was heated to 200 °C and maintained for 10 min. The QDs were purified using hexane and ethanol for 2–3 times. Please note, PH₃ is very toxic, and it should be handled carefully.
Scheme 1. The synthetic process of InP/ZnS/ZnS QDs.

Preparation of InP/ZnS/ZnS@SiO\textsubscript{2} composite and WLEDs: APTES (2 mL), 20 mg of InP/ZnS/ZnS QDs and 10 mL ODE were loaded in a beaker and the mixture was stirred in air for 5 h at room temperature (~60% humidity). InP/ZnS/ZnS@SiO\textsubscript{2} composite was collected by centrifugation and washed with hexane for several times. For the fabrication of WLEDs, the InP/ZnS/ZnS QDs were dispersed in PMMA/toluene solution and the mixture was dropped onto blue LED chips. The amount of InP/ZnS/ZnS QDs was adjusted to tune the emission spectra.

Characterization: Absorption spectra were measured using a Shimadzu UV-3600 plus spectrophotometer (Shimadzu, Kyoto, Japan). PL spectra were collected utilizing a Zolix OmniFluo fluorescence spectrometer (Zolix, Beijing, China). PLQYs and PL decay were measured using an Edinburgh FL980 fluorescence spectrometer (Edinburgh Instruments, Livingston, UK). Powder X-ray diffraction (XRD, PANalytical, Almelo, The Netherlands) patterns were collected on a PANalytical X'Pert PRO. Transmission electron microscopy images were obtained on a FEI Tecnai G2 20 transmission electron microscope (TEM, FEI, Hillsboro, OR, USA) operating at an accelerating voltage of 200 kV.

3. Results and Discussion

PH\textsubscript{3} is a highly reactive phosphorus source and it was used to react with indium myristate in the presence of zinc stearate [14]. Herein, indium and zinc halides dissolved in OLA are used as the In precursor, which was shown to produce highly luminescent InP-based core/shell QDs [16]. The PH\textsubscript{3} was introduced into the In precursor by bubbling, therefore it is impossible to distinguish between nucleation and growth, i.e., the nucleation might last for a period of time. Consequently, a broad size distribution was obtained, demonstrated by a shoulder, rather than a distinguished exciton peak, in the absorption spectrum of InP core QDs, as shown in Figure 1a. To show the strong effect of the introduction of precursors on the size distribution, a control experiment was performed using liquid P(dimethylamino)\textsubscript{3} as the phosphorus precursor. In this case, the phosphorus precursor was quickly injected into the In precursor, and a burst nucleation is expected, leading to a significantly narrower PL FWHM of 49 nm for the InP/ZnS QDs, as shown in Figure S1 (Supplementary Materials). Despite the narrow PL FWHM, the PLQY of the QDs was relatively low (71%), which might be due to the byproduct or impurity originated from the P(dimethylamino)\textsubscript{3}. The InP core QDs showed no emission due to a large number of surface defects. After coating a layer of ZnS shell using DDT, the luminescent property was significantly improved (Figure 1b), exhibiting an emission peak at 533 nm, a FWHM of 66 nm, and a PLQY of 49.1%. The ZnS shell has a wider bandgap compared to InP and forms the type I core/shell structure, which confines both electrons and holes in the InP core, resulting in the enhancement of the PLQY. In order to further enhance the emission, we adopted a single source precursor Zn(DDTC)\textsubscript{2} to grow a second layer of ZnS shell. The Zn(DDTC)\textsubscript{2} was shown to decompose at relatively low temperatures and form ZnS shells [20,21]. Here, the use of Zn(DDTC)\textsubscript{2} was shown to be critical for highly luminescent InP QDs. As shown in Figure 1b, the second ZnS shell improves the PL intensity substantially, reaching a PLQY of 78.5% for the InP/ZnS/ZnS QDs. Additionally, the second ZnS shell redshifts the emission peak to 547 nm with a FWHM of 77 nm. The redshift confirms the epitaxial growth of the second ZnS shell that extends the carrier wavefunctions to
the shell. The PL decay results confirm the effective surface passivation by the second ZnS shell. As shown in Figure 1c, the PL average lifetime ($\tau_{\text{avg}}$) is prolonged to 43.06 ns from 31.92 ns after the growth of ZnS shell using Zn(DDTC)$_2$. TEM images (Figure 1d) show the InP/ZnS/ZnS QDs have near spherical shapes with a diameter of ~3.2 nm and a size distribution of 14.3% as shown in Figure S2 (Supplementary Materials). The high resolution TEM image (inset of Figure 1d) demonstrates the nanoparticle is a single crystal. The XRD pattern (Figure S3 in Supplementary Materials) shows the QDs adopt the zinc blend crystalline structure, and the three main peaks locate between the standard peaks of InP and ZnS, confirming the core/shell structure [22].

**Figure 1.** Absorption (a) and PL (b) spectra of InP and their core/shell QDs, (c) PL decay of InP/ZnS and InP/ZnS/ZnS QDs, (d) a typical TEM image of InP/ZnS/ZnS QDs, and the inset is a high resolution TEM image.

The emission of the InP/ZnS/ZnS QDs can be tuned by simply changing the zinc halide precursors. As shown in Figure 1b, green emission was obtained when ZnBr$_2$ was used. When the ZnBr$_2$ was replaced by equal molars of ZnI$_2$ and ZnCl$_2$, cyan and red emissive InP/ZnS/ZnS QDs were produced, as shown in Figure 2. The emission properties are summarized in Table 1. The change of emission according to the zinc halide can be attributed to the fact that the halide controls the reactivity of the In precursor. Generally, a higher precursor reactivity results in smaller QDs. Therefore, zinc iodide gives rise to the highest In reactivity and produces the smallest InP/ZnS/ZnS QDs, which is consistent with previous work [16]. Despite the tunability of emission by the halides, the use of ZnI$_2$ and ZnCl$_2$ result in much lower PLQYs, as listed in Table 1. For the application of general lighting based on blue LED, yellowish emission is preferred. Therefore, we tried to increase the synthetic temperature to produce relatively larger QDs based on the supreme ZnBr$_2$ synthesis. Consequently, yellow emissive InP/ZnS/ZnS QDs were obtained when the synthesis was performed at 240 °C (Figure 2). These yellow emitters show a PLQY of 72.2%, a peak of 558 nm and a FWHM of 91 nm, which are suitable for WLED as down-conversion phosphors.
In addition to a high PLQY, the yellow InP/ZnS/ZnS QDs also show suppressed thermal quenching. The growth solution of the QDs still exhibited bright emission even at 200 °C, as shown in the inset of Figure 3a. In order to investigate the temperature-dependent luminescent property, we used a fiber optic spectrometer to record the PL spectra of the growth solution at different temperatures under 365 nm excitation, as shown in Figure S4 (Supplementary Materials). The temperature-dependent PL spectra are shown in Figure 3a, and the evolution of the integrated PL intensity with respect to temperature is shown in Figure 3b. The growth solution exhibited excellent luminescent property at relatively high temperatures and retained 91.7% room temperature PL intensity even at 150 °C. It should be mentioned that the green emissive InP/ZnS/ZnS QDs also showed similar temperature-dependent PL property. There are two factors that might account for the suppressed thermal quenching. First, surface passivation was shown to be critical for the emissive property at high temperatures. For example, a fluorine-rich perovskite shell effectively passivates CsPbBr$_3$ nanocrystals, leading to temperature-independent emission efficiency of up to 100 °C [4]. Here, the two-step coating of ZnS shells should effectively passivate the surface, suppressing carrier trapping and thermal quenching. Second, there are a large number of ligands and reactive precursors in the growth solution, which can repair the surface defects at high temperatures.
In order to enhance the stability of purified InP/ZnS/ZnS QDs, SiO$_2$ matrix was used to protect the QDs. APTES was used as the SiO$_2$ precursor, which was proposed to prepare stable and highly luminescent perovskite QDs [23]. The TEM image shown in Figure 3c demonstrates that the InP/ZnS/ZnS QDs were successfully embedded in the SiO$_2$ matrix (more TEM images can be found in Figure S5 (Supplementary Materials)). InP/ZnS/ZnS QDs@SiO$_2$ composite shows bright yellow emission as shown in the inset of Figure 3d. However, the hydrolysis of APTES reduces the PLQY of the QDs, resulting in a PLQY of 58.5%. The InP/ZnS/ZnS QDs@SiO$_2$ composite also shows suppressed thermal quenching, investigated by a fiber optic spectrometer under 365 nm excitation (Figure S6 in Supplementary Materials). The composite retained 78.6% room temperature PL intensity at 100 °C as shown in Figure 3d.

The yellow emissive InP/ZnS/ZnS QDs have a broad PL spectrum and a PL peak of 558 nm which is matched with the peak of the eye sensitivity function. Therefore, they were used as down-conversion phosphors to fabricate WLED in combination with a blue LED chip. The PL spectrum is shown in Figure 4 and the white light emission is shown in the inset. The PL of the QD composite redshifts was slightly comparable to that of the diluted QD solution (Figure 2), which is attributed to reabsorption. However, the PL spectrum still matches with the eye sensitivity function (dashed line in Figure 4). Consequently, the WLED showed a high efficiency of 106 lm/W at a current of 20 mA.
In situ-generated PH$_3$ was used to economically synthesize InP QDs and a two-step coating procedure was applied to synthesize highly luminescent InP-based core/shell QDs. The ZnS shells effectively passivated the InP QDs, leading to a PLQY as high as 78.5%. Additionally, the InP/ZnS/ZnS QDs showed suppressed thermal quenching, demonstrated by the 91.7% room temperature PL intensity at 150 °C for the QD growth solution. The emission of the InP/ZnS/ZnS QDs was tuned by the halide precursor, and yellow emissive QDs were obtained by judiciously controlling the synthetic condition, whose emission matches the eye sensitivity function. After coating the InP/ZnS/ZnS QDs with SiO$_2$ matrix, they also showed suppressed thermal quenching. The highly luminescent yellow InP/ZnS/ZnS QDs were used as down-conversion phosphors to fabricate WLED which showed a high efficiency of 106 lm/W. The present work demonstrates that InP QDs are promising environment-friendly phosphors for general lighting.

### Supplementary Materials

The following are available online at https://www.mdpi.com/article/10.3390/coatings11050581/s1. Figure S1: The absorption and PL spectra of InP/ZnS/ZnS QDs using P(dimethylamino)$_2$ as the phosphorus precursor, Figure S2: The size histogram of the InP/ZnS/ZnS QDs shown in Figure 1d, Figure S3: A XRD pattern of the InP/ZnS/ZnS QDs, Figure S4: The setup for monitoring temperature-dependent PL spectrum of the growth solution, Figure S5: TEM images of the InP/ZnS/ZnS QDs@SiO$_2$ composite, Figure S6: The setup for monitoring temperature-dependent PL spectrum of the InP/ZnS/ZnS@SiO$_2$ composite and the PL spectra.

### Author Contributions

L.L. and Y.L. contributed equally to this work. L.L. and Y.L. performed the experiments and wrote the manuscript. D.Z. and J.Z. supervised the project. All authors have read and agreed to the published version of the manuscript.

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### Informed Consent Statement

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### Data Availability Statement

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### Conflicts of Interest

The authors declare no conflict of interest.
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