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Colloidal synthesis of lead chalcogenide/lead chalcogenide core/shell nanostructures and structural evolution

Yang Liu^{1,5}, Kunyuan Lu^{1,5}, Yujie Zhu¹, Xudong Hu¹, Yusheng Li³, Guozheng Shi¹, Xingyu Zhou¹, Lin Yuan¹, Xiang Sun¹, Xiaobo Ding¹, Irfan Ullah Muhammad¹, Qing Shen³, Zeke Liu^{1,2} , and Wanli Ma^{1,2}

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Abstract: Lead chalcogenides (PbX₂, X = Cl, Br, I; Y = S, Se) is an extension of the classic Pb chalcogenides (PbY₂). Constructing the heterogeneous integration with PbX₂ and PbY₂ material systems makes it possible to achieve significantly improved optoelectronic performance. In this work, we studied the effect of introducing halogen precursors on the structure of classical PbS nanocrystals (NCs) during the synthesis process and realized the preparation of PbS/Pb₂S₂X₂ core/shell structure for the first time. The core/shell structure can effectively improve their optical properties. Furthermore, our approach enables the synthesis of Pb₂S₂Br₂ that had not yet been reported. Our results not only provide valuable insights into the heterogeneous integration of PbX₂ and PbY₂ materials to elevate material properties but also provide an effective method for further expanding the preparation of PbX₂ material systems.

Key words: lead chalcogenides, lead chalcogenides, PbS nanocrystal, core/shell structure, Pb₂S₂X₂ nanocrystal

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Colloidal synthesis of lead chalcogenide/lead chalcohalide core/shell nanostructures and structural evolution

Yang Liu^{1,†}, Kunyuan Lu^{1,†}, Yujie Zhu¹, Xudong Hu¹, Yusheng Li³, Guozheng Shi¹, Xingyu Zhou¹, Lin Yuan¹, Xiang Sun¹, Xiaobo Ding¹, Irfan Ullah Muhammad¹, Qing Shen³, Zeke Liu^{1,2,†}, and Wanli Ma^{1,2,†}

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Abstract: Lead chalcohalides (PbYX, X = Cl, Br, I; Y = S, Se) is an extension of the classic Pb chalcogenides (PbY). Constructing the heterogeneous integration with PbYX and PbY material systems makes it possible to achieve significantly improved optoelectronic performance. In this work, we studied the effect of introducing halogen precursors on the structure of classical PbS nanocrystals (NCs) during the synthesis process and realized the preparation of PbS/Pb₃S₂X₂ core/shell structure for the first time. The core/shell structure can effectively improve their optical properties. Furthermore, our approach enables the synthesis of Pb₃S₂Br₂ that had not yet been reported. Our results not only provide valuable insights into the heterogeneous integration of PbYX and PbY materials to elevate material properties but also provide an effective method for further expanding the preparation of PbYX material systems.

Key words: lead chalcohalides; lead chalcogenides; PbS nanocrystal; core/shell structure; Pb₃S₂X₂ nanocrystal

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1. Introduction

Chalcohalides consisting of mixed chalcogen and halogen anions and metal cations are an emerging family of semiconductors^[1–3]. The rich composition and crystal structure of chalcohalides has provided significant opportunities for fundamental materials research and energy applications^[4–9]. Among them, the expansion of Pb chalcohalides, as an extension of two classic material systems, namely Pb chalcogenides (such as PbS, PbSe) and lead halide perovskites (such as CH₃NH₃PbI₃, CsPbI₃), has sparked great interests^[10–16]. Pb chalcohalides (PbYX) can be understood as binary phase diagrams composed of two phases, PbY–PbX₂ (Y = S, Se; X = Cl, Br, I), combined in different proportions^[17]. However, early studies found that only a few combinations of phases could exist stably at ambient temperature and pressure, such as Pb₅S₂I₆ and Pb₇S₂Br₁₀^[18]. It was not until recently that the Manna group discovered the synthesis of Pb₃S₂Cl₂, Pb₄S₃Br₂, and Pb₄S₃I₂ nanocrystals (NCs) through chemical methods^[19]. These phases do not conform to stable bulk PbY–PbX₂ diagrams but can exist stably in the form of NCs at ambient temperature and pressure^[17]. Based on the novel material systems, they further find these PbYX exhibits remarkable lattice matching with lead-halide perovskite, making them poten-

tial structures to enhance the optoelectronic properties and stability of perovskite materials^[20–23].

Furthermore, halide ions have been identified as the optimal surface passivating agents for classical PbS and PbSe NCs, playing a crucial role in enhancing the performance of near-infrared and mid-infrared optoelectronic devices based on PbY NCs^[24–28]. The formation of Pb–X bonds on the surface can also act as a bridge, connecting them with novel lead halide perovskite materials, thereby achieving superior material and device performance^[20, 23]. The successful synthesis of PbXY NCs has deepened our understanding of traditional classical material systems. For instance, passivation with Cl ions significantly improves the luminescence efficiency and stability of PbS and PbSe NCs^[29, 30]. In earlier studies, it was speculated that the surface adsorbed only Cl ions or formed a PbCl_x shell^[31–33]. Although not confirmed yet, recent research suggests that the surface layer may be a Pb sulfochloride surface layer based on the similarity of reaction conditions^[32]. Further exploration of the relation of PbXY with classical PbS and PbSe NCs will deepen our understanding of the structure-property relationships in materials, facilitating the design and synthesis of new materials and structures with superior optoelectronic performance.

In this study, we have discovered that within the framework of the classical PbS NC synthesis approach, the straightforward introduction of bis(trimethylsilyl) halide (TMS–X, X = Cl, Br, I) precursors enables the synthesis of a series of materials, starting from PbS NCs and progressing to PbS/Pb₃S₂X₂ core-shell structures, ultimately leading to the formation of Pb₃S₂X₂ NCs. We have conducted a detailed investigation of

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the evolution process and its impact on the optical properties of the NC materials. Notably, we found that the growth of a $\text{Pb}_3\text{S}_2\text{X}_2$ shell on the surface of PbS effectively enhances its photoluminescence quantum yield (PLQY) from 49.3% to 72.0%. Furthermore, this strategy enables the synthesis of $\text{Pb}_3\text{S}_2\text{Br}_2$ NCs, which have not been previously reported.

2. Experimental

2.1. Chemicals and materials

Lead acetate trihydrate ($\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$, 99%), hexamethyldisilathiane (TMS-S , 98%), trimethylsilyl chloride (TMS-Cl , 99%), trimethylsilyl bromide (TMS-Br , 99%), trimethylsilyl iodide (TMS-I , 99%), sulfur powder (S , 99.99%), oleylamine hydrochloride (OLA-Cl , 99.5%), oleic acid (OA , 90%), 1-octadecene (ODE , 90%), hexane (Hex , 95%), isopropanol (IPA , 95%), acetone (95%).

2.2. Synthesis of PbS NCs and $\text{Pb}_3\text{S}_2\text{X}_2$ ($\text{X} = \text{Cl, Br, I}$) NCs

The NC synthesis was performed with a modified recipe previously documented^[34]. All operations were performed under a nitrogen atmosphere using standard air-free Schlenk line techniques. Briefly, 1 mmol of $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ and 0.8 mL of OA were dissolved in 10 mL of ODE in a three-neck flask. The solution was then heated to 100 °C under vacuum for 1 h. The TMS-S (0.25 mmol) and different amounts of TMS-X ($\text{X} = \text{Cl, Br, I}$) precursor were dissolved in 1 mL of ODE. The reaction was initiated by rapid injection of the TMS-S and TMS-X precursors into the lead precursor solution at 100 °C under nitrogen. The NCs were grown at this temperature for 10 min and then cooled to room temperature slowly. The solution was then transferred into a nitrogen-filled glove box and purified by precipitation once in hexane/isopropyl alcohol and once in hexane/acetone. The obtained NC solids were stored in a nitrogen-filled glove box.

For the synthesis of large PbS NCs and $\text{Pb}_3\text{S}_2\text{X}_2$ NCs, 1.2 mmol of $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ and 12 mL of OA were added in a three-neck flask by heating the mixture to 100 °C under vacuum for 1 h. The TMS-S (0.2 mmol) and different amounts of TMS-X ($\text{X} = \text{Cl, Br, I}$) precursor were dissolved in 1 mL of ODE. The reaction was initiated by rapid injection of the TMS-S and TMS-X precursor into the lead precursor solution at 150 °C under nitrogen. The NCs were grown at this temperature for 5 s and then cooled to room temperature quickly. The solution was then transferred into a nitrogen-filled glove box and purified by precipitation once in hexane/isopropyl alcohol and once in hexane/acetone. The obtained NC solids were stored in a nitrogen-filled glove box.

2.3. Direct synthesis of large $\text{Pb}_3\text{S}_2\text{Cl}_2$ NCs

Briefly, 1 mmol of $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ and 0.8 mL of OA were dissolved in 10 mL of ODE in a three-neck flask by heating the mixture to 100 °C under vacuum for 1 h. The anion precursors were prepared by sonicating 0.5 mmol sulfur powder and 0.8 mmol OLA-Cl in 2 mL dried ODE. The reaction was initiated by rapid injection of the anion precursors into the lead precursor solution at 150 °C under nitrogen. The NCs were grown at this temperature for 30 min and then cooled to room temperature slowly. The solution was then transferred into a nitrogen-filled glove box and purified by precipitation twice in hexane/isopropyl alcohol and once in hexane/acetone. The obtained NC solids were stored in a nitrogen-filled

glove box.

2.4. Measurement and characterization

The absorption spectra of NCs in hexane were recorded at room temperature using an ultraviolet–visible–near infrared (UV–VIS–NIR) spectrophotometer (Lambda950, PerkinElmer). Photoluminescence (PL) spectra and PL lifetime were measured by a FluoroMax-4 spectrofluorometer (HORIBA Scientific). The PLQY was measured using an integrating sphere equipped on FLS1000 fluorescence spectrometer. The excitation wavelength was 750 nm. The PbS NC films for the XPS test were made by spin-coating ~100 nm thick film onto a silicon substrate. The X-ray diffraction (XRD) spectra were obtained on an X-ray diffractometer with a Cu K α source (PANalytical B.V. Empyrean). TEM measurements were performed by a Tecnai G2 F20 S-Twin system.

3. Results and discussion

The NCs were synthesized based on the typical hot injection method with lead-oleate as the Pb precursor^[34]. The reaction was initiated by injecting mixtures of TMS-S and TMS-X with different molar ratios (represented by $\text{X} : \text{S}$). Taking TMS-Cl as an example, at low $\text{Cl} : \text{S}$ values, the reaction proceeded similarly to the synthesis of conventional PbS NCs, where the colorless reaction solution turned red and then rapidly black. As the $\text{Cl} : \text{S}$ value increased, the transition from red to black gradually slowed down. The obtained XRD pattern of the NCs is presented in Fig. 1(a). The graph reveals that the crystal structure of the NCs obtained at $\text{Cl} : \text{S}$ values below 0.6 is nearly identical to the cubic phase of PbS, with only a slight shift observed in the (111) plane (Fig. 1(b)). When the $\text{Cl} : \text{S}$ value exceeded 0.6, the intensity of the (220) peak of PbS NCs gradually decreased and eventually disappeared. Simultaneously, the (111) plane at 25.9° shifted to lower angles, and the (200) plane at 29.7° shifted to higher angles. When the $\text{Cl} : \text{S}$ value reached 1.8, the two planes settled at 24.4° and 31.8°, respectively, corresponding to the (112) and (013) planes of $\text{Pb}_3\text{S}_2\text{Cl}_2$. Additionally, when the $\text{Cl} : \text{S}$ value reached 0.8, a broad peak started to appear around ~35°, and with an increasing $\text{Cl} : \text{S}$ value, it continued to shift to higher angles, ultimately reaching ~37°, corresponding to the (123) plane of $\text{Pb}_3\text{S}_2\text{Cl}_2$. This phenomenon is highly reminiscent of the typical evolution from core to core/shell NC structures^[35–37]. Furthermore, the above XRD diffraction behavior differs significantly from that of a simple mixture of PbS and $\text{Pb}_3\text{S}_2\text{Cl}_2$ phases (Fig. S1). Therefore, we hypothesize that a $\text{PbS/Pb}_3\text{S}_2\text{Cl}_2$ core/shell structure is formed under intermediate $\text{Cl} : \text{S}$ ratios of 0.8–1.6 (with further evidence presented in the subsequent text). When the $\text{Cl} : \text{S}$ ratio reaches 1.8, pure-phase $\text{Pb}_3\text{S}_2\text{Cl}_2$ NCs can be obtained. The crystal structure of PbS and $\text{Pb}_3\text{S}_2\text{Cl}_2$ is shown in Figs. 1(c) and 1(d). The cubic PbS exhibits a regular Pb and S octahedral structure, with the Pb atoms coordinated by six S anions. In contrast, for the $\text{Pb}_3\text{S}_2\text{Cl}_2$, the Pb is of different chemical environments compared with the PbS. All the Pb atoms occupy the 12a site, which has a point group symmetry of 4 bar and is coordinated by eight anions.

To ascertain the exact nature of surface chemistry after introducing TMS-Cl , we conducted X-ray photoelectron spectroscopy (XPS) measurement. The well-defined Cl 2p peaks in the XPS spectra clearly demonstrate the incorporation of Cl

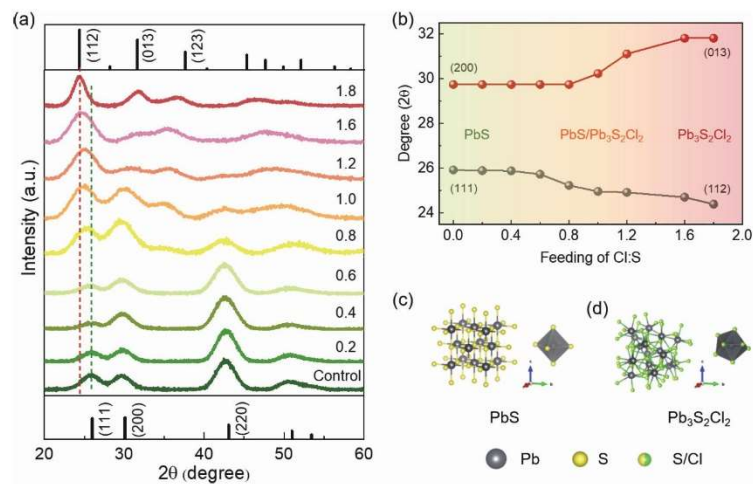


Fig. 1. (Color online) (a) The XRD pattern of the NCs with different feeding ratios of Cl and S. (b) The (111) and (200) peak shift vs. feeding ratio of Cl and S. (c) and (d) The crystal structure of PbS and Pb₃S₂Cl₂.

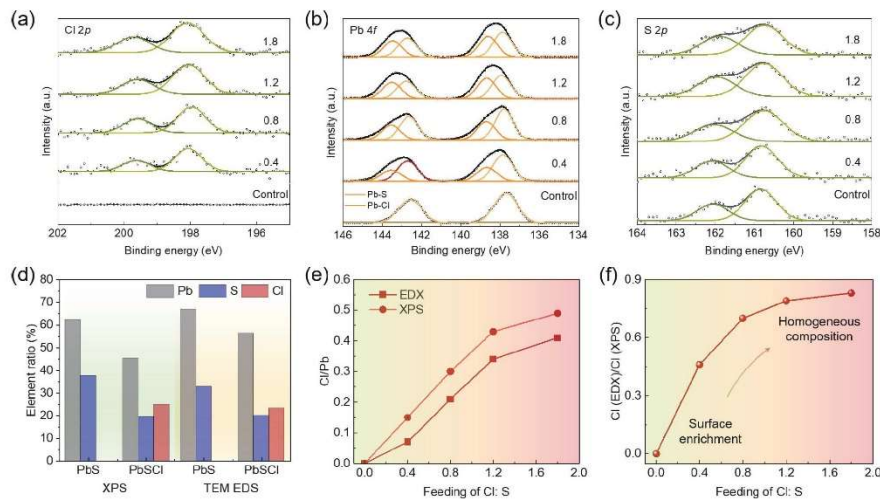


Fig. 2. (Color online) (a)–(c) High-resolution XPS spectrum in the (a) Cl 2p, (b) Pb 4f, (c) S 2p regions of the NCs with different feeding ratios of Cl and S. (d) The element ratios of the PbS and Pb₃S₂Cl₂ NCs obtained by XPS and SEM-EDS. (e) Cl contents measured by SEM-EDS and XPS the NCs with different feeding ratios of Cl and S. (f) Plot of the ratio between Cl concentrations determined by SEM-EDS and XPS measurements in (e).

in the obtained NCs (Fig. 2(a)). The Pb 4f^{7/2} spectra were deconvoluted by fitting the sum of the Lorentz–Gaussian functions. They were found to contain two chemical states, observed at 137.7 and 138.6 eV, respectively (Fig. 2(b)). The main peak at 137.7 eV was assigned to the Pb–S bond, while the peak at 138.6 eV corresponded to Pb–Cl bonds^[29]. The Pb–Cl peak becomes stronger as increasing the Cl : S input during the synthesis, providing further evidence for the incorporation of Cl in the NCs. The S 2p spectra become broader as increasing

Cl : S ratio, due to the more complicated coordination environment in Pb₃S₂Cl₂ compared to that in PbS crystal (Fig. 2(c)). The element ratio of the NCs is extracted by fitting the peak areas in XPS spectra and presented in Fig. 2(d). The molar ratio of Cl in the final NCs increases with the increment of the Cl : S ratio. When the input Cl : S ratio reaches 1.8, the obtained Pb : S : Cl = 50.3 : 23.6 : 26.1, which is close to the ratio in the chemical formula (Pb₃S₂Cl₂). XPS is a surface-sensitive technique because of the shallow escape depth of photo-

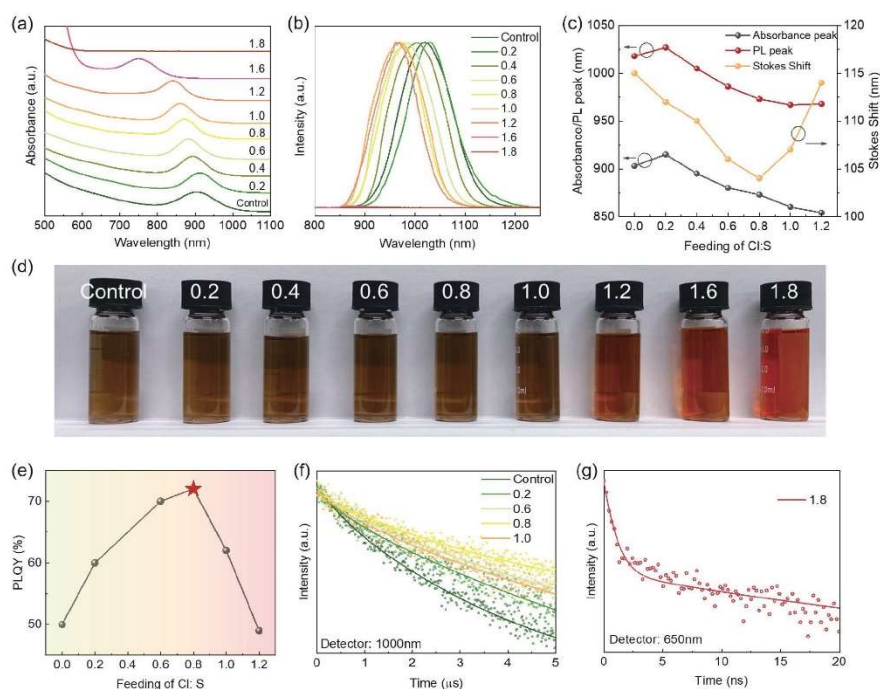


Fig. 3. (Color online) (a) and (b) The absorbance (a) and PL (b) of the NCs with different feeding ratios of Cl and S. (c) The peak position of absorbance and PL, as well as Stokes shift. (d) The images of the NC solutions. (e)–(g) The PLQY (e) and TRPL (f) and (g) of the NCs with different feeding ratios of Cl and S.

electrons, whereas the sampling depth of SEM-EDX measurement is typically above $1\ \mu\text{m}$. The Cl concentrations measured by XPS for different Cl : S were found to be consistently higher than the values obtained from SEM-EDX analysis, indicative of the presence of a Cl-rich near-surface region within NCs (Fig. 2(e)). The extent of Cl surface enrichment can be estimated by taking the ratio between atomic percent values obtained from XPS and EDX measurements. As shown in Fig. 2(f), the Cl(EDX)/Cl(XPS) ratio monotonically increases and approaches 1 with the increment of the input Cl : S ratio, which indicates that the NCs gradually transform into a homogeneous composition (e.g. $\text{Pb}_3\text{S}_2\text{Cl}_2$)^[38]. The above observation aligns with the previous XRD results, confirming the structural evolution from PbS to $\text{PbS}/\text{Pb}_3\text{S}_2\text{Cl}_2$ core/shell and eventually to pure-phase $\text{Pb}_3\text{S}_2\text{Cl}_2$ as increasing the input Cl : S ratio.

We further investigated the influence of the aforementioned structural evolution on the optical properties of the NCs. As depicted in Figs. 3(a) and 3(b), a slight red shift is observed in the absorbance and PL peaks when the input Cl : S ratio is 0.2. Subsequently, as the molar ratio of Cl : S increased, the absorbance and PL peaks blueshifted, PLQY gradually increased and Stokes shift decreased, reaching a maximum at Cl : S = 0.8, with a minimum Stokes shift of 104 nm and a PLQY of 72.0% (Figs. 3(c) and 3(e) and S2). Further increase in the Cl : S ratio leads to a decrease in PLQY and an increase in Stokes shift. Interestingly, as the Cl : S ratio

reaches 1.2, a new peak located at $\sim 680\ \text{nm}$ appears, which can be assigned to the emission from the $\text{Pb}_3\text{S}_2\text{Cl}_2$ phase (Fig. S3). As the Cl : S ratio reaches 1.6, the exciton absorption peak blue shifts to $\sim 710\ \text{nm}$ from the $\sim 906\ \text{nm}$ of initial PbS NCs. The color of the obtained NC solution gradually transitions from brownish to red (Fig. 3(d)). Meanwhile, the NCs lose PL entirely in the near-infrared region. Further increasing the Cl : S ratio to 1.8 results in the vanishing of both PL and exciton absorption peaks. To understand the variation of optical properties, we further tested their size and morphology through transmission electron microscopy (TEM) characterization. As shown in Fig. S4 and Fig. S5, with the increase of input Cl/S ratio, the size of NCs gradually decreases. Under low concentration (Cl : S = 0.2), the size reduction effect of Cl may not be significant, but the excitons in the PbS core can delocalize to the shell, resulting in a slight redshift of absorption and PL^[39]. As Cl content increases, the binding of Cl and Pb precursors limits the growth of NCs and causes a decrease in the size of the PbS core, resulting in a gradual blueshift of the absorption and PL peaks. The simultaneous appearance of PL peaks from both PbS and $\text{Pb}_3\text{S}_2\text{Cl}_2$ confirms the formation of a $\text{PbS}/\text{Pb}_3\text{S}_2\text{Cl}_2$ core/shell structure^[40, 41]. The time-resolved PL (TRPL) data shows that increasing the amount of Cl can enhance the PL lifetime of the NCs when the Cl : S ratio is below 0.8 (2.01 to $3.70\ \mu\text{s}$), (Fig. 3(f) and Table S1), which is consistent with the increase of PLQY, demonstrating

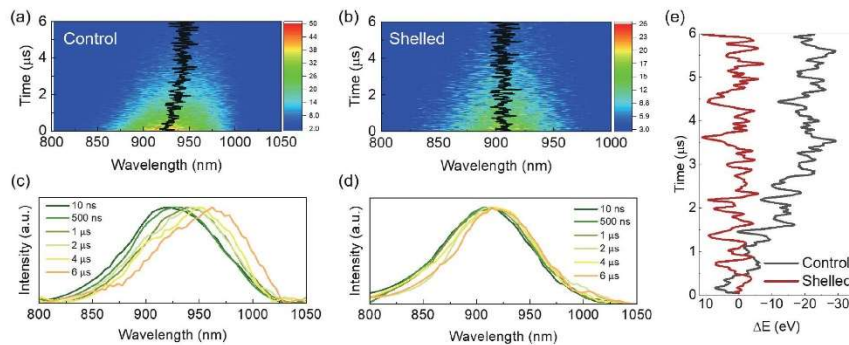


Fig. 4. (Color online) Time-resolved emission spectroscopy (TRES) of PbS NCs. (a) and (b) TRES map of control and shelled. (c) and (d) Time-slices of the emission spectra of control and shelled. (e) Summary of dynamic red-shifts of the NC photoluminescence peak after excitation for control and shelled PbS NCs. All experiments are conducted in dilute (1 mg/mL) hexane solution.

the passivation effect at low input Cl : S ratios. Further increasing the Cl : S ratio can significantly reduce PL lifetime, with the value as low as 8.68 ns for pure-phase $\text{Pb}_3\text{S}_2\text{Cl}_2$ NCs (input Cl : S = 1.8), which is also consistent with PL lifetime reported previously (Fig. 3(g), Table S2). Similar structural and optical evolutions can be observed with large PbS NCs (first exciton peak at 1627 nm) as starting materials (Fig. S6–Fig. S8). The dominant size of the final pure $\text{Pb}_3\text{S}_2\text{Cl}_2$ can reach 3.2 nm, which was larger than the size of pure $\text{Pb}_3\text{S}_2\text{Cl}_2$ NCs (1.5 nm) triggered from small PbS NCs. Additionally, the NCs absorbance band edge of these two methods were all around 600 nm, indicating the size of $\text{Pb}_3\text{S}_2\text{Cl}_2$ NCs has little effect on their optical characterization due to their negligible quantum confinement effects, which is also consistent with the previous report^[19].

Seeking to clarify the impact of the $\text{Pb}_3\text{S}_2\text{Cl}_2$ shell on ensemble photophysics, we further investigate the consequences of $\text{Pb}_3\text{S}_2\text{Cl}_2$ shelling on PbS NCs by using time-resolved emission spectroscopy (TRES). To avoid the Förster resonant energy transfer and self-absorbance phenomenon, we dilute the PbS NCs solution (1 mg/mL) in hexane. The PbS NC solution displays transient emission spectra with a dynamic spectral red-shift without TMSCl introduction. (Figs. 4(a) and 4(c), monitored via the emission peak). Conversely, the shelled NCs with $\text{Pb}_3\text{S}_2\text{Cl}_2$ display much less overall spectral red-shifting after photoexcitation and the early (<2 μs) component is effectively eliminated (Figs. 4(b) and 4(d)), which reveals the $\text{Pb}_3\text{S}_2\text{Cl}_2$ can well passivate PbS NCs^[42].

We also find this phase and structural evolution from PbS NCs to $\text{Pb}_3\text{S}_2\text{Cl}_2$ can be extended to Br and I systems. The XRD pattern and optical evolution Br system show similar behavior as that in the Cl case (Fig. S9). The solution of $\text{Pb}_3\text{S}_2\text{Br}_2$ and $\text{Pb}_3\text{S}_2\text{I}_2$ NCs also exhibits a red color (Fig. 5(a)). The extracted bandgap values are 2.2, 2.1, and 1.9 eV for $\text{Pb}_3\text{S}_2\text{Cl}_2$, $\text{Pb}_3\text{S}_2\text{Br}_2$ and $\text{Pb}_3\text{S}_2\text{I}_2$, respectively. To validate the crystal structure, we compared the XRD patterns of $\text{Pb}_3\text{S}_2\text{Cl}_2$ and $\text{Pb}_3\text{S}_2\text{Br}_2$ NCs with those of the bulk structure published by Ni *et al.* The XRD analysis confirmed a good match between the NCs and the bulk structures (Fig. 5(b))^[43, 44]. It should be noted that we have discovered that $\text{Pb}_3\text{S}_2\text{Br}_2$ NCs

have not yet been reported. However, this method cannot deliver pure-phase $\text{Pb}_3\text{S}_2\text{I}_2$ NCs, the XRD pattern from the PbS phase can also be observed even at input I : S ratio up to 1.0 in large PbS NCs (Fig. S10). The obtained $\text{Pb}_3\text{S}_2\text{X}_2$ all exhibit sphere shapes with sizes around 3 nm (Figs. 5(c)–5(e)). Additionally, we found that by reducing the reactivity of the anion precursors, using ODE–S and oleylamine hydrochloride (OLACl) to replace TMS–S and TMSCl, larger-sized $\text{Pb}_3\text{S}_2\text{Cl}_2$ NCs can be synthesized, with size up to ~10 nm (Fig. S11).

4. Conclusion

In this work, we reported the synthesis of $\text{PbS}/\text{Pb}_3\text{S}_2\text{X}_2$ (X = Cl, Br, I) core-shell structures for the first time. Compared to pure PbS NCs, this core-shell structure effectively enhances the optical properties, increasing the PLQY from 49.8% to 72.0% and the fluorescence lifetime from 2.01 to 3.70 μs. Under conditions of high halogen incorporation, we obtained pure-phase $\text{Pb}_3\text{S}_2\text{Cl}_2$ and $\text{Pb}_3\text{S}_2\text{Br}_2$ NCs. Notably, our approach enables the synthesis of stable $\text{Pb}_3\text{S}_2\text{Br}_2$ that had not yet been reported. This work provides a novel synthetic approach to achieve heterogeneous integration of lead chalcogenides (PbYX , X = Cl, Br, I; Y = S, Se) with lead chalcogenides (PbY) and explores their impact on the structure and properties, potentially encouraging further exploration of other metal chalcogenides and heterostructure synthesis and applications.

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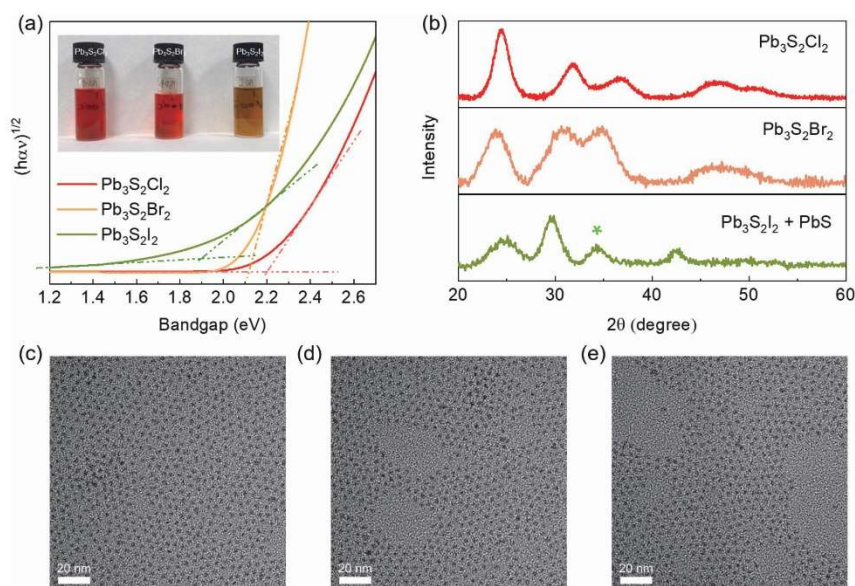


Fig. 5. (Color online) (a) The absorbance of $\text{Pb}_3\text{S}_2\text{Cl}_2$, $\text{Pb}_3\text{S}_2\text{Br}_2$, and $\text{Pb}_3\text{S}_2\text{I}_2$ NCs. (The photo of $\text{Pb}_3\text{S}_2\text{X}_2$ solution is shown in the inset). (b) The XRD pattern of $\text{Pb}_3\text{S}_2\text{Cl}_2$, $\text{Pb}_3\text{S}_2\text{Br}_2$, and $\text{Pb}_3\text{S}_2\text{I}_2$ NCs. The peak marked with an asterisk represents unreacted PbS phase. (c)–(e) The TEM images of $\text{Pb}_3\text{S}_2\text{Cl}_2$, $\text{Pb}_3\text{S}_2\text{Br}_2$, and $\text{Pb}_3\text{S}_2\text{I}_2$ NCs.

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Appendix A. Supplementary material

Supplementary materials to this article can be found online at <https://doi.org/10.1088/1674-4926/24050026>.

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Y Liu et al.: Colloidal synthesis of lead chalcogenide/lead chalcogenide core/shell nanostructures and

3、康振辉教授推荐意见

SCI 论文专家鉴定意见

本人证明纳米科学技术学院学生朱宇杰所发表学术论文 *Colloidal synthesis of lead chalcogenide/lead chalcogenide core/shell nanostructures and structural evolution* 符合创新学分申请要求，特予以认定证明。 (DOI: 10.1088/1674-4926/24050025)

申请人签名: 朱宇杰

证明专家签名:

康振辉

4、刘泽柯副教授推荐意见

SCI 论文专家鉴定意见

本人证明纳米科学技术学院学生朱宇杰所发表学术论文 *Colloidal synthesis of lead chalcogenide/lead chalcogenide core/shell nanostructures and structural evolution* 符合创新学分申请要求，特予以认定证明。DOI: 10.1088/1674-4926/24050025

申请人签名: 朱宇杰

证明专家签名: 刘泽柯

5、论文发表状态说明书

论文发表情况说明书

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2024年12月4日

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2024年04月3日