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# Core-shell CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals dispersed in thermoplastic polyurethane as writeable heat-resistant fluorescent inks



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#### ABSTRACT

The cesium lead halide perovskites CsPbX<sub>3</sub> (X = Cl, Br, I) have received extensive attention in the solar cell and light-emitting devices owing to their excellent optical and electronic properties. However, in practical applications, CsPbX<sub>3</sub> often suffers from many disturbances caused by changes in the external environment, which will weaken its performance. In order to better solve this issue, a series of encapsulation strategies have been proposed to protect the stability of CsPbX<sub>3</sub>. In particular, the derivative Cs<sub>4</sub>PbX<sub>6</sub> of CsPbX<sub>3</sub> was well received as a shell protective material because it does not introduce new elements. Here, we prepared large-yield stable CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell nanocrystals (NCs) by adjusting the initial ratio of Cs/Pb using one-pot route. At the same time, the growth process of CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> NCs were analyzed, and their stability was evaluated under atmospheric conditions. The results show that CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> NCs exhibit excellent stability compared to the pure phase CsPbBr<sub>3</sub> NCs, and thus the passivation of Cs<sub>4</sub>PbBr<sub>6</sub> NCs and thermoplastic polyurethane (TPU) was developed, which held excellent heat-resistance stability under multiple heating-cooling cycles. Our research will greatly simplify the preparation process of stabilized CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs and provide alternative options for the commercial development of perovskite materials.

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# 1. Introduction

In recent years, all-inorganic lead halide perovskites are of technical importance due to its excellent photophysical properties [1–3] and its facile synthesis [4–6]. Construction of optoelectrical devices has been systematically researched in solar cells with updating high-efficiency record [4,7–10] and light-emitting diodes (LEDs) with higher brightness [11–13]. In particular, the colloidal CsPbX<sub>3</sub> (X<sup>=</sup>Br, I, Cl) perovskite nanocrystals (NCs) was firstly reported by Kovalenco et al. in 2015 [14]. It is regarded as a potential luminescent for next generation of materials due to its bright photoluminescence (PL) [15,16], high photoluminescence quantum yields (PLQYs) [17,18], narrow emission bandwidth [17,19], and tunable emission features [20,21]. Unfortunately, CsPbX<sub>3</sub> NCs exhibit instability under atmospheric conditions due to its special ionic structure and large surface energy [22,23]. Therefore, a large number

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https://doi.org/10.1016/j.jallcom.2021.158768 0925-8388/© 2021 Elsevier B.V. All rights reserved. of strategies for improving the stability of CsPbX<sub>3</sub> NCs have been proposed [24–27]. Among them, the introduction of external materials for encapsulating to form a stable core-shell structure has been advocated a key step [28,29].

The immaculate encapsulation grants CsPbX<sub>3</sub> NCs excellent optical and electronic stability under atmospheric conditions, which will broaden its application prospects in the field of photo-voltaic devices and solar cells [24,30,31]. Typically, 0-dimensional perovskite Cs<sub>4</sub>PbX<sub>6</sub> (a derivative of 3-dimensional perovskite CsPbX<sub>3</sub>) was favored as an encapsulation material [32,33]. There were no other new elements introduced into the production process, which will greatly save production costs compared to other encapsulation materials. The newly formed CsPbX<sub>3</sub>@Cs<sub>4</sub>PbX<sub>6</sub> core-shell material shows excellent stability in many applications [34]. Such a reliable stability behavior is because CsPbBr3 was encapsulated by Cs4PbBr6 to form stable CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs, which effectively improves optical operation stability of CsPbBr<sub>3</sub> in a higher thermal environment [35]. Beyond that, the Cs<sub>4</sub>PbBr<sub>6</sub> shell can reduce the agglomeration of the CsPbBr<sub>3</sub> core forming a protecting layer, thereby increasing the PLQY of CsPbBr<sub>3</sub> [36]. The previous reports





Fig. 1. TEM images of Cs-Pb-Br series compounds with Cs/Pb molar ratios of (a) 0.2, (b) 0.6, (c) 0.8, (d) 0.9, and (e) 1.0. (f) is an enlargement of (e), insets in (b) and (c) show the corresponding HRTEM images.

indicate that the highly stable CsPbX<sub>3</sub>@Cs<sub>4</sub>PbX<sub>6</sub> core-shell NCs will accelerate the process of commercial application of perovskite.

Emphatically, the currently reported preparation method of CsPbX<sub>3</sub>@Cs<sub>4</sub>PbX<sub>6</sub> core-shell NCs has an intricate process, which will severely limit its large-scale commercial production [37,38]. In this work, we proposed a method for preparing pure phases of CsPbBr<sub>3</sub> NCs and CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs by adjusting the ratio of initial Cs/Pb using one-pot method. The results of a series of characterization tests show that both CsPbBr<sub>3</sub> NCs and CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs were successfully prepared, and the presence of  $Cs_4PbBr_6$  can effectively prevent the agglomeration effect of CsPbBr<sub>3</sub>, thereby improving its PLOYs. Stability test shows that Cs<sub>4</sub>PbBr<sub>6</sub> with a stable structure can passivate CsPbBr<sub>3</sub>, making CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> NCs have long-term stability under atmospheric conditions. Moreover, a highly transparent thermoplastic polyurethane (TPU) was incorporated with CsPbBr<sub>3</sub> and CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> respectively to form two types of writable fluorescent ink. Through the thermal stability test of the two inks, the CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> ink showed more excellent heat-resistance stability. This work not only greatly simplifies the process of perovskite materials in actual production, but also provides a new path for the application of perovskite materials in the commercial field.

# 2. Experimental

#### 2.1. Chemicals

Lead bromide (PbBr<sub>2</sub>, 99%), cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>, 99%), 1-Octadecene (ODE, 95%), Oleylamine (OAm, 99%), Oleic acid (OAc, 99%), cyclohexane (C<sub>6</sub>H<sub>12</sub>, 99.5%). Tetrahydrofuran (THF, 99%) and Thermoplastic polyurethane (TPU).

# 2.2. Prepare Cs-Pb-Br series compounds with different Cs/Pb molar ratios

2 mL of OAc, 2 mL of OAm, and 8 mL of ODE were mixed into a 50 mL two-neck flask, stirred and heated to 120 °C. The solution was degassed for 30 min to obtain a suitable environment without oxygen and moisture. PbBr<sub>2</sub> and various amount Cs<sub>2</sub>CO<sub>3</sub> were added to the above solution (the molar ratio of Cs/Pb was 0.2, 0.6, 0.8, 0.9 and 1.0). The solution was heated to 120 °C under nitrogen

atmosphere for 30 min. After the reaction was completed, the solution was cooled to room temperature. The crude solution was washed with a pure cyclohexane. The final sample was extracted from the crude solution by centrifuging at 10,000 rpm for 3-5 min, and dried at 40 °C.

#### 2.3. Prepare fluorescent ink

5 mL of THF and 6 g of TPU were placed in an empty beaker, and stirred on a magnetic stirrer at 600 rpm for 2 h at room temperature to dissolve. After that, the perovskite products with the initial Cs/Pb molar ratio of 0.2 and 1.0 were added to the dissolved TPU, and stirring was continued for 3 h until completely mixed. At this time, a perovskite fluorescent ink was obtained.

### 3. Characterization

### 3.1. Phase and structural characterization

XRD patterns were performed on DX-2700BH diffractometer (CuK<sub> $\alpha$ </sub>, K $\alpha$  = 1.5406 Å). TEM images were obtained by a Tecnai G2 microscope with an operating voltage of 200 kV. The elemental analysis was studied by the XPS spectra utilizing a Perkin-Elmer model PHI 5600. The contact angle value was determined with a DSA30 CA analyzer.

### 3.2. Optical spectroscopy

The absorbance of the samples as well as the PL spectra were collected by a high-resolution spectrometer (Ocean Optics, USA). The 365 nm UV light was used as excitation sources. Time-resolved fluorescence intensity decay was measured by using a fluorescence lifetime spectrophotometer (Fluotime 100, PicoQuant, Germany).

#### 4. Results and discussion

Morphology and structural characteristics of perovskite nanocrystals with different Cs/Pb molar ratios were examined by TEM. According to the TEM images, pure cubic CsPbBr<sub>3</sub> NCs, hexagonal phase Cs<sub>4</sub>PbBr<sub>6</sub> NCs and mixtures were demonstrated in Fig. 1a–e. The cubic CsPbBr<sub>3</sub> quantum dots (QDs) were obtained, when the



Fig. 2. XRD patterns (a) of NCs with different molar ratios of Cs/Pb. Photographs (b) of powder yields with Cs/Pb molar ratios of 0.2 and 1.0 under daylight (top) and 365 nm UV light (bottom).

molar ratio of Cs/Pb was 0.2:1. The average size of CsPbBr<sub>3</sub> QDs is about 10 nm, showing the approximate size similar with its exciton Bohr radius (7 nm). The morphology of the product evolved from cube to hexagonal structure. The volume of the cube gradually reduces, and the number as well as volume of the hexagonal crystals gradually increase as the molar ratio of Cs/Pb increases. Uniform Cs<sub>4</sub>PbBr<sub>6</sub> hexagonal crystals are neatly arranged, when the molar ratio of Cs/Pb increased to 1.0:1. The average size of the hexagonal Cs<sub>4</sub>PbBr<sub>6</sub> is about 30 nm, and there are no obvious other crystals attached to the surface, revealing the high-purity hexagonal phase of Cs<sub>4</sub>PbBr<sub>6</sub> NCs.

As shown in the inset of Fig. 1a and e, the high-resolution transmission electron microscopy (HRTEM) was used to precisely study the microstructure of CsPbBr<sub>3</sub> and Cs<sub>4</sub>PbBr<sub>6</sub>. The typical CsPbBr<sub>3</sub> ODs show clear lattice diffraction fringes, indicating that the quality of crystal is high. The diffraction lattice spacing is 0.34 nm, in consistent with the (202) plane of the cubic CsPbBr<sub>3</sub>. Similarly, the crystallinity of the Cs<sub>4</sub>PbBr<sub>6</sub> NCs is also high, and the lattice spacing is 0.27 nm, identified with the (125) plane of the hexagonal  $Cs_4PbBr_6$ . Usually, lattice matching and surface morphology observation are combined to analyze the structure of nanomaterials [36,39]. It can be seen from the enlarged Fig. 1e that extraneous phase exists in the hexagonal crystal of Cs<sub>4</sub>PbBr<sub>6</sub>, and the lattice spacing corresponds to the cubic crystal of CsPbBr<sub>3</sub> (Fig. 1f). Taking the fact that no obvious other crystals attached to the surface of Cs<sub>4</sub>PbBr<sub>6</sub> NCs (Fig. 1e) in to account, it can be concluded that the tiny CsPbBr<sub>3</sub> QDs incorporated the hexagonal Cs<sub>4</sub>PbBr<sub>6</sub> to form a more stable CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs. To further confirm the elemental uniformity of CsPbBr3 and CsPbBr3@Cs4PbBr6, Energy Dispersive Spectrometer (EDS) spectroscopy was performed on the samples (Fig. S1). The results show that the elements Cs, Pb and Br are uniformly distributed in the perovskite NCs.

The XRD patterns of the NCs with different molar ratios of Cs/Pb are shown in Fig. 2a. A pure phase CsPbBr<sub>3</sub> could be obtained when the molar ratio of Cs/Pb was 0.2:1. Additionally, the content of Pb ions is higher than that of Cs ions to form Pb-rich environment, which can be explained by the growth mechanism of CsPbBr<sub>3</sub> NCs as shown below [40].

# 2Cs-oleate + 3PbBr<sub>2</sub> $\rightarrow$ 2CsPbBr<sub>3</sub> NCs + Pb(oleate)<sub>2</sub>

All the diffraction peaks can be retrieved without any noticeable secondary phase, according to the reference CsPbBr<sub>3</sub> (PDF: 97–009–7851). The CsPbBr<sub>3</sub> possesses a cubic structure (space group: *Pbnm*, 68), which is consistent with the results observed in the TEM images, indicating that the pure phase CsPbBr<sub>3</sub> QDs have been prepared. The molar ratio of Cs/Pb was tuned by increasing the

amount of  $Cs_2CO_3$ , and then some new diffraction peak appeared in the XRD patterns, which corresponded with the reference  $Cs_4PbBr_6$ (PDF: 97–016–2158). This is due to the fact that Pb ions are no longer excessive resulting in a part of CsBr was formed, which further react with CsPbBr<sub>3</sub> NCs to obtain hexagonal  $Cs_4PbBr_6$  crystals. The specific growth mechanism is as follows [41].

2Cs-oleate +  $PbBr_2 \rightarrow 2CsBr$  + Pb-oleate

# $CsPbBr_3 NCs + 3CsBr \rightarrow Cs_4PbBr_6 NCs$

As the molar ratio increases, the intensity of diffraction peak of Cs<sub>4</sub>PbBr<sub>6</sub> gradually increases, while that of CsPbBr<sub>3</sub> gradually decreases. The reference Cs<sub>4</sub>PbBr<sub>6</sub> belongs to the hexagonal crystal phase (space group: R-3c, 167), observed from the TEM images (Fig. 1e). Combining with the XRD and HRTEM, our result suggested that CsPbBr<sub>3</sub> @Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs were obtained when the molar ratio of Cs/Pb increased to 1.0:1. At this time, the diffraction peak of CsPbBr<sub>3</sub> will be covered by Cs<sub>4</sub>PbBr<sub>6</sub> due to its small content. Therefore, the diffraction peak of CsPbBr<sub>3</sub> does not appear in the XRD pattern. To further understand the perovskite composition at different molar ratios, XPS was performed. According to the analysis, the element Cs 3d, Pb 4f, and Br 3d bands are transferred to the low energy region (Fig. S2), when the molar ratio of Cs/Pb increases from 0.2 to 1.0, revealing the distribution of cations increases. The atomic ratios of the samples (Table S1) also showed that Cs<sub>4</sub>PbBr<sub>6</sub> contains impure phase, when the molar ratio of Cs/Pb was 1.0:1. This is consistent with the observation observed in the HRTEM image, and it is true that CsPbBr<sub>3</sub> QDs are dispersed in the Cs<sub>4</sub>PbBr<sub>6</sub> hexagonal crystal. Therefore, these characterization methods manifest that the CsPbBr<sub>3</sub> @Cs<sub>4</sub>PbBr<sub>6</sub> core-shell structure has been successfully prepared by adjusting the initial ratio of Cs/Pb. In addition, the sample yield has always been a major obstacle restricting the commercial application of perovskite, so that the convenient preparation method to obtain large-scale perovskite should be paid attention to. The powders with Cs/Pb molar ratios of 0.2 and 1.0 were weighed into 0.11 g and 0.38 g, respectively (Fig. 2b), and the theoretical productions of the samples at the two ratios were calculated using the conservation of Cs ions. The yields are calculated separately by the following formulas to confirm that this one-pot preparation method has broad application prospects in the industrial field.

# $Yield = \frac{Actual production}{Theoretical production}$

It can be obtained by calculation that the yield of a sample with Cs/Pb molar ratio of 0.2 is 91%, and a sample with Cs/Pb molar ratio of 1.0 is 87%. The results show that this preparation method can



**Fig. 3.** The photograph (a) of NCs dispersed in cyclohexane under daylight (top) and 365 nm UV light (bottom). The PL spectra (b) of the samples at different molar ratios of Cs/Pb excited by 365 nm UV light. Absorption spectra (c) and corresponding (Ahv)<sup>2</sup> vs photon energy (eV) curves d) of different samples. Inset in (d) shows the band gap of the sample varies with the Cs/Pb molar ratio.

obtain high-yield perovskite samples, which may represent an important step toward their practical applications.

In order to better explore the PL behavior of samples, the samples at different molar ratios of Cs/Pb were studied using a high-sensitivity spectrometer under the 365 nm excitation. The result indicate that different molar ratios of Cs/Pb samples have the same PL characteristics, which suggests that the fluorescence characteristics of the CsPbBr<sub>3</sub> core are not affected by the Cs<sub>4</sub>PbBr<sub>6</sub> shell. Fig. 3a shows the sample dispersed in cyclohexane under daylight, and was illuminated under 365 nm UV light. It can be seen that the solution gradually becomes cloudy with the molar ratio of Cs/Pb increasing under the daylight. This phenomenon reveals the presence of more dispersible materials in the solution, which may be attributed to CsPbBr<sub>3</sub> QDs with a small grain size. All solutions showed pure green emission under 365 nm UV and their colors became brighter with increasing molar ratio of Cs/Pb. This is due to the presence of CsPbBr<sub>3</sub> in all samples, and its strong quantum confinement effect can cause differences in fluorescence when the size of CsPbBr<sub>3</sub> changes. The normalized PL spectra (Fig. 3b) of samples with different Cs/Pb molar ratios corresponding to Fig. 3a were detected. It can be seen that during the PL process, the PL peak positions of all samples concentrate at 523-531 nm, which also coincides with their absorption spectra (Fig. 3c). The full-width wavelength at half maximum (FWHM) is narrow and high purity green emissions are obtained. However, new peaks appear in the UV absorption region as the molar ratio increases (Fig. S3). This is due to the existence of Cs<sub>4</sub>PbBr<sub>6</sub>, consistent with the report from Akkerman et al [41]. On the other hand, under the same concentration (0.5 mg/mL), the absorption coefficients of samples obtained with different molar ratios also have obvious differences. The CsPbBr<sub>3</sub> NCs prepared at a lower ratio (0.2:1) of Cs/Pb have a relatively low dispersibility in the solution and some precipitation, while the remaining material dispersed in the solvent will reduce the amount of light absorption in the channel, further reducing its absorption coefficient. However, the CsPbBr<sub>3</sub> @Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs prepared under the higher Cs/Pb ratio (1.0:1) have a large number of smaller-sized CsPbBr<sub>3</sub> NCs with

higher dispersibility in the solution, thereby obtaining a larger absorption coefficient. Therefore, it can be concluded that the CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell material prepared by this one-pot method has excellent PL characteristics. The bandgap of the corresponding sample increases from 2.23 eV to 2.27 eV (Fig. 3d), which verifies the blue shift in the PL spectrum. This is attributed to the quantum confinement effect of CsPbBr<sub>3</sub> QDs, increasing the absorption coefficient of the exciton band as the particle size of CsPbBr<sub>3</sub> QDs decreases. The lowest energy of the exciton moves toward the high energy direction under the influence of the quantum confinement effect. Based on the previous discussions, the one-pot method achieves the feasible encapsulation of Cs<sub>4</sub>PbBr<sub>6</sub> to CsPbBr<sub>3</sub>, and the synthesized CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell material exhibited green PL characteristics under the excitation of a 365 UV light (Fig. 4).

Here, the lifetime curve test was performed on all samples in order to further analyze the decay behaviors of CsPbBr<sub>3</sub> QDs embedded in  $Cs_4PbBr_6$  NCs. The multi-exponential function was used to fit all the decay curves (Fig. 5a).

# $Y(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$

The multi-exponential decay can be attributed to the presence of multiple different sizes of CsPbBr<sub>3</sub> QDs with green emissions [42]. Moreover, the PL decay curves fitting of the samples changed from the initial tri-exponential decay to the bi-exponential decay with the increase of the Cs/Pb molar ratio, which proved that the surface traps of CsPbBr<sub>3</sub> QDs were passivated (Table S2) [43]. At the same time, the decay time of the samples has also been prolonged (Inset in Fig. 5a), which can be attributed to the gradually decreasing size of CsPbBr<sub>3</sub> QDs, thereby expanding the range of radiation recombination. The phenomenon also confirmed the blue shift of the PL spectra of the samples obtained in the previous section, when the molar ratio rises. Interestingly, we have found that the intensity of green emissions also increased (Fig. 5b), as the size of CsPbBr<sub>3</sub> QDs decreased under the excitation of 365 nm UV light. This can be explained by the fact that CsPbBr<sub>3</sub> QDs were dispersed in Cs<sub>4</sub>PbBr<sub>6</sub>



Fig. 4. The process of preparing CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs by one-pot method and its PL characteristics.

crystal matrix, which can effectively prevent the agglomeration effect between the QDs, thereby increasing their PLQYs [36]. The result also agreed with the change in the fluorescence brightness of the sample under the 365 nm UV light. Therefore, preparation of CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs can be used to improve the luminous efficiency of CsPbBr<sub>3</sub> QDs.

It is well known that the stability of perovskites is affected by the moisture in the atmosphere and its own auto-degradation [44,45]. We studied the structural stability and spectral stability of two samples (Cs/Pb = 0.2, 1.0) under atmospheric conditions (Fig. 6a–d). The XRD patterns of the samples aged 15 days and 30 days showed significant changes compared with the as-grown CsPbBr<sub>3</sub> QDs (Fig. 6a). At the same time, the emission spectra PL also undergo a significant red shift (Fig. 6b), which can be attributed to the size change of the perovskite. By contrast, the structure of CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> NCs are stable, as can be seen from the XRD pattern (Fig. 6c). This greatly enhances its ability to resist the effects of moisture and auto-degradation. The CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> perovskite composites also showed good photo-stability, and the peak position of the PL spectrum did not shift (Fig. 6d). It confirmed that Cs<sub>4</sub>PbBr<sub>6</sub> crystal plays an indispensable role in the passivation protection of CsPbBr<sub>3</sub> ODs. More remarkably, the encapsulation strategy overcomes the influence of poor structure and luminescence stability of perovskite.

The availability of bright perovskite materials offers promising opportunities for anticounterfeiting and security applications. Two types of writable inks (Fig. 7a) prepared by incorporating samples of different molar ratios (0.2 and 1.0) with thermoplastic polyurethane (TPU) materials, and the inks showed bright green fluorescence under irradiation of 365 nm UV light. Films of different shapes are coated on paper by using two inks, and their PL properties are preserved, which indicates that this material can be widely used as a fluorescent ink. The optical behavior of two perovskite inks was explored. The normalized PL spectrum (Fig. 7b) shows that the position of the emission peak of the two perovskite materials encapsulated by TPU has not shifted, which is consistent with the original pure phase material. These excellent optical properties benefit from the high transparency of the TPU matrix, which prevents the perovskite material from being affected by the protective shell when absorbing UV light and emitting fluorescence. Surface wettability property tests were performed on the two coated films. The test results showed that the contact angle of the ink film with a molar ratio of 0.2 was 124.43<sup>0</sup> (Fig. 7c), and the contact angle of the other ink film (molar ratio of 1.0) was 120.10<sup>0</sup> (Fig. 7d). This means



Fig. 5. PL decay curves and multi-exponential fitting curves (a) of all samples. PL intensity spectra (b) of samples with different Cs/Pb molar ratios at the same concentration under 365 nm UV light. Inset in (a) highlight the differences in the all samples.



Fig. 6. XRD patterns (a) and PL (b) spectra of the sample with Cs/Pb molar ratio of 0.2 stored for 30 days under atmospheric conditions. XRD patterns (c) and PL (d) spectra of the sample with Cs/Pb molar ratio of 1.0 under the same conditions.

that the encapsulated perovskite ink has obvious hydrophobicity, which will greatly improve the PL stability of the product in a humid environment, making it more attractive in commercial application.

As a proof-of-concept, write different demonstration examples (TPU and SUST) on paper (Fig. 8a) by using two perovskite inks, which can be clearly displayed under ultraviolet irradiation. Subsequently, thermal stability tests were conducted on these two examples, raising the temperature to 80 °C, and then lowering it to

room temperature, operating for several cycles (Fig. 8b). After heating several times for a perovskite ink with a molar ratio of 0.2, the fluorescence was irreversibly quenched, while the perovskite ink with a molar ratio of 1.0 performed outstanding PL stability. By analyzing the relative PL intensity of the perovskite ink with a molar ratio of 0.2 at different cycles (Fig. S4), it can be clearly seen that the PL characteristic of the perovskite ink disappeared during the third heating and cooling cycle (Fig. 8c), and did not recover afterwards.



**Fig. 7.** Writable ink (a) was formed by mixing TPU with two samples with molar ratios of 0.2 (left) and 0.1 (right), and films of different shapes are coated on paper by using two kinds of ink. The PL spectrum (b) of these two writable inks. Water contact angle values of ink coated films with different Cs/Pb molar ratios of 0.2 (c) and 1.0 (d).



**Fig. 8.** Two different examples (a) were written using two inks. Photographs (b) of two different examples under several heating and cooling cycles. The relative PL intensity change (c) of the example written with ink with a molar ratio of 0.2. The relative PL intensity change (d) of the example written with ink with a molar ratio of 1.0.

This is due to the instability of CsPbBr<sub>3</sub>, which will thermally degrade at higher temperatures, resulting in the disappearance of fluorescent properties [46]. The relative PL intensity of the perovskite ink with a molar ratio of 1.0 does not change significantly (Fig. S5). After several heating and cooling cycles, the PL intensity can still return to the original intensity (Fig. 8d). This excellent heat recyclability can be attributed to the passivation of Cs<sub>4</sub>PbBr<sub>6</sub> on the CsPbBr<sub>3</sub> surface. The solid Cs<sub>4</sub>PbBr<sub>6</sub> shell can hinder the degradation of the CsPbBr<sub>3</sub> core caused by the external thermal environment. Through the above comparison, the perovskite ink synthesized using the sample with a molar ratio of 1.0 can exhibit more excellent environmental resistance, which is more suitable for the commercial development of perovskite.

#### 5. Conclusions

We used a one-pot method to prepare high-yield pure phase CsPbBr<sub>3</sub> QDs and obtained the CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs by adjusting the initial Cs/Pb molar ratio. It is confirmed that the Cs<sub>4</sub>PbBr<sub>6</sub> shell does not interfere with the PL characteristics of the CsPbBr<sub>3</sub> core by analyzing the growth process and optical behavior of the CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> core-shell NCs. After that, CsPbBr<sub>3</sub> QDs and CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> NCs were placed under atmospheric conditions, and the results showed that CsPbBr<sub>3</sub>@Cs<sub>4</sub>PbBr<sub>6</sub> NCs exhibited excellent structural and optical stability, which originated from protective effect from the solid Cs<sub>4</sub>PbBr<sub>6</sub> shell to the surface. For further commercial development, CsPbBr<sub>3</sub> passivated by Cs<sub>4</sub>PbBr<sub>6</sub> was used to mix with TPU to form a writeable fluorescent ink. After completing several heating and cooling cycle tests, it still maintains the initial PL intensity and has a stronger heatresistant stability. Our report achieves low-cost and convenient completion of the surface passivation task of CsPbBr<sub>3</sub>, and the development of perovskite heat-resistant fluorescent ink also greatly promotes the application of perovskite materials in the future commercialization.

# **CRediT** authorship contribution statement

**Wanyin Ge:** Conceptualization, Resources, Methodology, Software, Investigation, Writing - original draft, Writing - review &

editing. **Jindou Shi:** Data curation, Investigation, Methodology, Project administration, Writing - original draft, Writing - review & editing. **Ye Tian:** Formal analysis, Methodology, Software, Validation, Visualization. **Meimei Xu:** Formal analysis, Methodology, Software. **Yuanting Wu:** Conceptualization, Writing - review & editing, Supervision. **YongXiang Li:** Conceptualization, Writing - review & editing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.158768.

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