

## RESEARCH ARTICLE

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10, 1338Cesium manganese halide perovskite-analogue  
nanocrystals with highly efficient energy  
conversion for flexible multifunctional fibers†Xiuqiang Duan,<sup>a</sup> Kun Nie,<sup>b</sup> Xuyi Wang,<sup>c</sup> Chi-An Cheng,<sup>d</sup> Ranran Zhou,<sup>a</sup>  
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In recent years, all-inorganic perovskite materials have been considered and applied in various fields. In this work, we used an improved method to synthesize novel zero-dimensional (0D) lead-free Cs<sub>2</sub>Mn(Cl/Br)<sub>4</sub>·2H<sub>2</sub>O perovskite-analogue nanocrystals (PA NCs) under aerobic conditions. At the same time, lead (Pb) was introduced into manganese (Mn) halide perovskite-analogue nanocrystals of Cs<sub>2</sub>Mn(Cl/Br)<sub>4</sub>·2H<sub>2</sub>O via a hot-injection method. The PA NCs shows an intense orange light under a UV lamp. The fluorescence spectrum peak center of the PA NCs is located at around 598 nm, and the photoluminescence quantum yield (PLQY) is 41.12%. The PLQY of the original PA NCs was almost nonexistent at around 598 nm. The increase in PLQY was due to the replacement of Mn<sup>2+</sup> with Pb<sup>2+</sup>, which effectively promotes the transfer of excitation energy to Mn<sup>2+</sup>. The Pb<sup>2+</sup>-doped Cs<sub>2</sub>Mn(Cl/Br)<sub>4</sub>·2H<sub>2</sub>O PA NCs also exhibit excellent stability and strong PL. We also applied the PA NCs to composite paper. The properties described in this study provide new design ideas and directions for potential optoelectronic devices.

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## Introduction

Since the hot-injection method was used to develop halide perovskites, there has been much interest in this area from researchers and scholars.<sup>1–3</sup> The photoelectric applications and research on various lead halide perovskites have advanced rapidly in recent years.<sup>4–9</sup> Lead halide perovskites are favored in the color changing field due to their unique color adjustability. However, the development of lead halide perovskites has been limited due to their harsh synthetic conditions and toxicity.<sup>10</sup> In terms of the development in this area, researchers

have investigated using different metal elements to replace Pb<sup>2+</sup> in order to obtain a perovskite structure similar to Pb<sup>2+</sup>.<sup>11</sup> Some researchers have used Sn<sup>2+</sup> and Ge<sup>2+</sup> to replace Pb<sup>2+</sup>.<sup>12–14</sup> However, Sn<sup>2+</sup> and Ge<sup>2+</sup> can be rapidly oxidized in air, so more stringent conditions are required to produce lead-free perovskites, but the perovskites obtained under such tough conditions show lower PL and stability compared to lead halide perovskites.

Manganese (Mn), as a transition metal element, is commonly used as a dopant to alter the optical properties and electrical properties of perovskite crystals.<sup>15–18</sup> Studies have shown that the introduction of Mn<sup>2+</sup> into lead halide perovskites can improve the stability and optical properties of perovskites. Double peak emission occurs when Mn<sup>2+</sup> is incorporated into CsPbX<sub>3</sub> (X = Cl, Br) crystals.<sup>19–21</sup> Mn<sup>2+</sup> has the advantages of low toxicity and emits Mn<sup>2+</sup> d–d transitions with a long energized state lifetime. Mn<sup>2+</sup> has been thought to be an effective light emanation center in metal halide perovskites.<sup>22</sup> Moreover, extraordinary advances have been made in terms of the arrangement of manganese-based perovskites using Mn<sup>2+</sup> instead of Pb<sup>2+</sup>.<sup>23–26</sup> Mn<sup>2+</sup> shows different properties in different coordination modes. It ordinarily exhibits green emission in tetrahedral coordination, but orange or red emission in six-coordinate octahedral mode.<sup>27–29</sup> The d–d transitions of Mn<sup>2+</sup> decided by spin and parity selection rules are related to the content of Mn, and Mn–Mn coupling results in

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low photoluminescence quantum yield (PLQY) at high content.<sup>30,31</sup> Dopants should thus be selected to lower the content of  $\text{Mn}^{2+}$ , and as the radius of  $\text{Mn}^{2+}$  is similar to that of  $\text{Pb}^{2+}$ , doping with  $\text{Pb}^{2+}$  is an excellent choice for ideally improving the optical properties of manganese-based perovskites.<sup>17–21,32</sup>

In this study, we successfully synthesized  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  PA NCs and incorporated Pb into these PA NCs *via* hot injection. The replacement of lead improves the optical properties and stability of the PA NCs. We combined the PA NCs with composite paper to create a composite paper with color changing function. Also, the excellent optical properties mean that the resulting PA NCs can be used as a new photoelectric material. Finally, the PA NCs can be produced in an atmospheric environment, which opens up new possibilities for future optoelectronic applications.

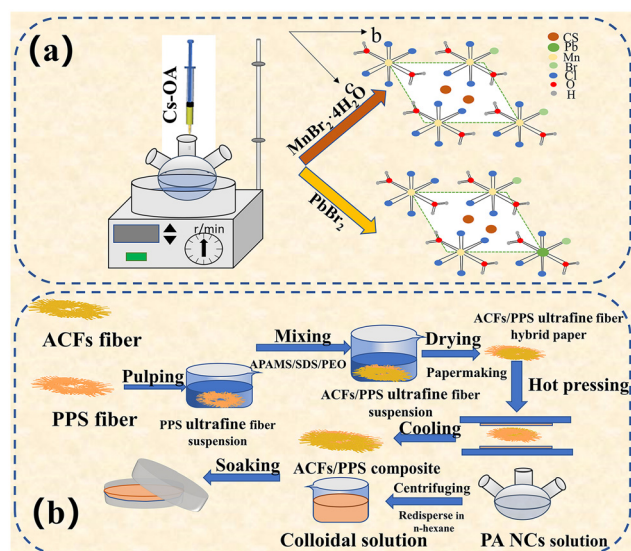
## Results and discussion

In this work, we synthesized  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  perovskite-analogue nanocrystals (PA NCs) with a 0-dimensional (0D) octahedral structure, and  $\text{Pb}^{2+}$ -incorporated  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  PA NCs *via* a hot-injection method. The spatial crystal structure of  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  is projected along the *a*-axis, as illustrated in Fig. 1a.<sup>34</sup>  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  and  $\text{CsMn}(\text{Cl}/\text{Br})_3\cdot 2\text{H}_2\text{O}$  have similar spatial structures, and  $\text{Mn}^{2+}$  in  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  and  $\text{CsMn}(\text{Cl}/\text{Br})_3\cdot 2\text{H}_2\text{O}$  adopts the same six-coordinate structure.<sup>35</sup> The distinction is that the two water molecules in  $\text{CsMn}(\text{Cl}/\text{Br})_3\cdot 2\text{H}_2\text{O}$  move from adjacent positions to inverse positions, forming the 0D structure  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$ . The crystal structures of the original PA NCs

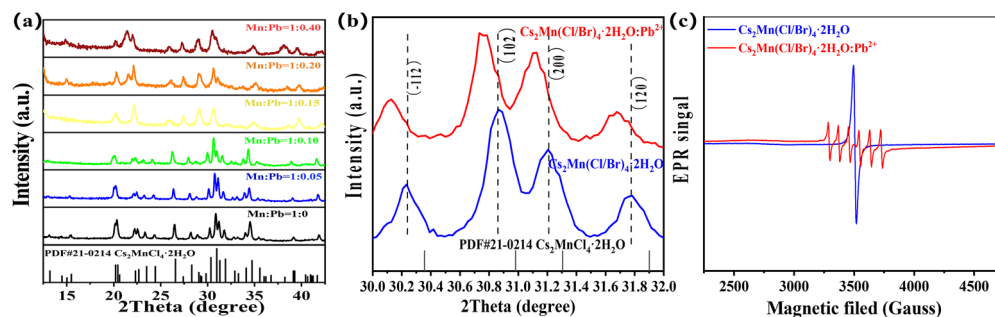
and  $\text{Pb}^{2+}$ -doped PA NCs both contain octahedral  $[\text{Mn}(\text{Cl}/\text{Br})_4(\text{OH})_2]^{4-}$ .<sup>30,35–37</sup> After the introduction of  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$  was replaced with  $\text{Pb}^{2+}$  to form a  $[\text{Pb}(\text{Cl}/\text{Br})_4(\text{OH})_2]^{4-}$  octahedral structure. The preparation of the aramid chopped fibers/polyphenylene sulfide (ACFs/PPS) composite is detailed in the Experimental section. The specific steps for impregnating the composite paper with colloidal solution are shown in Fig. 1b. To determine the specific situation of  $\text{Pb}^{2+}$  incorporation, we recorded X-ray diffraction (XRD) measurements. Most of the peaks in the XRD patterns of the original PA NCs and  $\text{Pb}^{2+}$ -doped PA NCs, as shown in Fig. 2a, can be assigned to the parameters of  $\text{Cs}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$  (PDF#21-0214) with a triclinic crystal structure. With an increase in  $\text{Pb}^{2+}$  content, the XRD pattern shows an extra diffraction peak in the PA NC sample. By comparison with standard cards, we discovered that the reaction generates a relatively small fraction of  $\text{Cs}_2\text{MnBr}_4\cdot 2\text{H}_2\text{O}$  (PDF#50-0630). We improved crystal purity by washing the crystals with hexane many times, it did not affect the final experimental results. If we continued to increase the lead content, there was more inclination towards the formation of a three-dimensional stable structured  $\text{CsPb}(\text{Cl}/\text{Br})_3\cdot \text{Mn}^{2+}$  perovskite (Fig. S1†) due to the lower bond energy of  $\text{Pb}-\text{Cl}/\text{Br}$  than that of  $\text{Mn}-\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{OH}$ ). We selected XRD data with a lower doping content ( $\text{Mn}:\text{Pb} = 1:0.05$ ) for comparison, and the characteristic peaks in the  $2\theta$  region of  $30^\circ$ – $32^\circ$  can be designated to the  $(-112)$ ,  $(102)$ ,  $(200)$  and  $(120)$  crystal planes, as shown in Fig. 2b. As the ionic radius of Br is larger than that of Cl, resulting in lattice expansion, the diffraction peaks of  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  shift to smaller angles than those of  $\text{Cs}_2\text{MnCl}_4\cdot 2\text{H}_2\text{O}$ . Similarly, when a small amount of  $\text{Pb}^{2+}$  content ( $\text{Mn}:\text{Pb} = 1:0.05$ ) was added to the  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  PA NCs, as the ionic radius of Pb is larger than that of Mn the XRD peak moves monotonously to a smaller angle.

X-band electronic parameter resonance (EPR) spectra were used to investigate the surrounding of  $\text{Mn}^{2+}$  ions in the samples. As shown in Fig. 2c, all EPR spectra reveal background signals originating from the  $\text{Mn}^{2+}$  center, while samples lacking  $\text{Pb}^{2+}$ -incorporation show no evident 6-fold hyperfine splitting, indicating severe spin relaxation due to high Mn concentrations. Furthermore, the linewidth of  $\text{Pb}^{2+}$ -doped samples is larger than that of the original samples and the EPR signal intensity is weaker. In general, weak spin-spin coupling results in a wider and weaker EPR signal.<sup>30,36</sup> Thus, the magnetic exchange interaction between  $\text{Mn}^{2+}$  ions appears to be decreased by  $\text{Pb}^{2+}$  incorporation, indicating that  $\text{Pb}^{2+}$  ions were successfully incorporated.

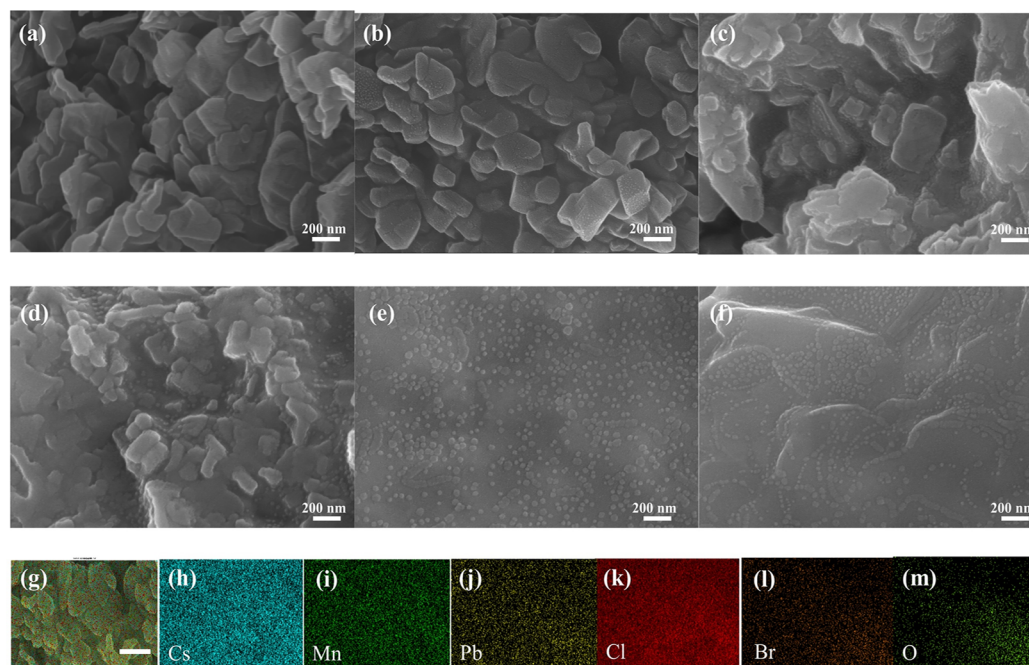
Fig. 3a–f show SEM images of the pristine and  $\text{Pb}^{2+}$ -doped PA NCs. These PA NCs are block-like in appearance with an average diameter of approximately 100 nm. At the same time, we also found that with an increase in  $\text{Pb}^{2+}$  content, some blocks with relatively small diameters began to appear, until the proportion of the addition was  $\text{Mn}:\text{Pb} = 1:0.20$ , the average diameter of PA NCs generated in the same reaction time became much smaller (Fig. 3e). These PA NCs were nucleated quickly at high temperature, and their morphology was very poor due to them containing two water molecules.



**Fig. 1** (a) The spatial crystal structures of  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}$  and  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4\cdot 2\text{H}_2\text{O}:\text{Pb}^{2+}$  projected along the *a*-axis prepared *via* a hot-injection method. (b) Preparation process of an ACFs/PPS composite using a colloidal solution.



**Fig. 2** (a) XRD patterns of the PA NCs. (b) Local broadened view of the crystal planes in the XRD patterns. (c) X-band EPR spectra of pristine and  $\text{Pb}^{2+}$ -doped PA NCs.



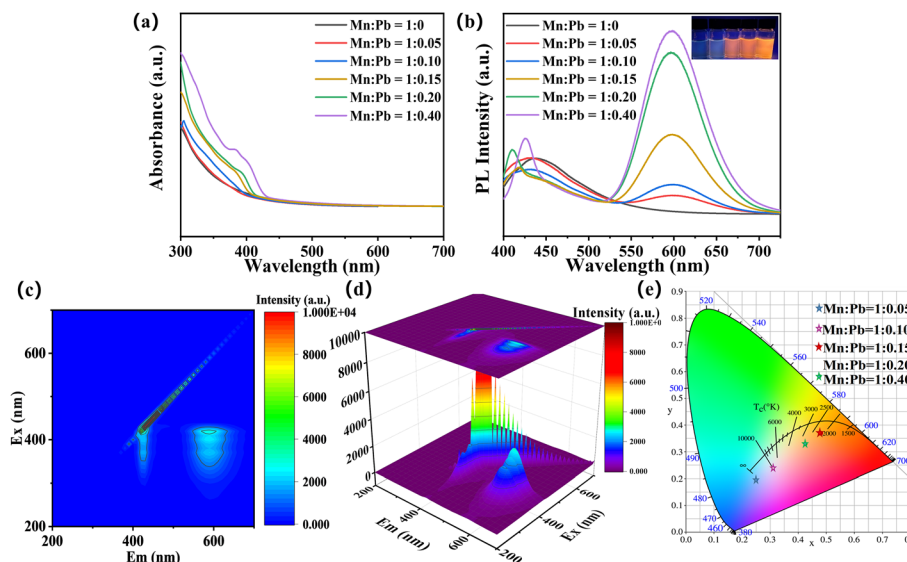
**Fig. 3** SEM images of (a) pristine and  $\text{Pb}^{2+}$ -incorporated  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs. (b)  $\text{Mn}:\text{Pb} = 1:0.05$ . (c)  $\text{Mn}:\text{Pb} = 1:0.10$ . (d)  $\text{Mn}:\text{Pb} = 1:0.15$ . (e)  $\text{Mn}:\text{Pb} = 1:0.20$ . (f)  $\text{Mn}:\text{Pb} = 1:0.40$ . (g)–(m) EDS elemental mapping of  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}:\text{Pb}^{2+}$  PA NCs ( $\text{Mn}:\text{Pb} = 1:0.05$ ). Scale bar: 500 nm.

The incorporation of  $\text{Pb}^{2+}$  reduced the crystallization rate of the PA NCs.<sup>30,35,38</sup> The PA NCs with  $\text{Pb}^{2+}$  were more mono-disperse than the original PA NCs. The energy-dispersive X-ray spectroscopy (EDS) images and relevant elemental mapping of the  $\text{Pb}^{2+}$ -doped sample ( $\text{Mn}:\text{Pb} = 1:0.05$ ) illustrate uniform distributions of the Cs, Pb, Mn, Br, Cl, and O elements (Fig. 3g–m), which also confirms the successful preparation of the  $\text{Pb}^{2+}$ -doped PA NCs (see the details in the ESI, Fig. S2, S3 and Table S1†).

Afterward, we continued to explore the optical properties of the original  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs and  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs doped with different  $\text{Pb}^{2+}$  contents. We researched the UV-vis absorption and photoluminescence (PL) properties of the original and  $\text{Pb}^{2+}$ -incorporated samples, as shown in Fig. 4. Fig. 4a shows that the visible absorption

spectra of the original sample and  $\text{Pb}^{2+}$ -doped sample are similar. The absorption at 520 nm is comparatively weak owing to the low spin band gap of octahedrally coordinated Mn, corresponding to a transition from  ${}^6\text{A}_{1g}$  to  ${}^4\text{T}_{1g}$ .<sup>29,35,36,39</sup> With the addition of more  $\text{Pb}^{2+}$ , evident exciton absorption peaks were observed at 400 and 365 nm, which may be due to the introduction of octahedral  $[\text{Pb}(\text{Cl}/\text{Br})_4(\text{OH})_2]^{4-}$ .<sup>36</sup> Furthermore, we also characterized these PA NCs by PL spectroscopy (Fig. 4b). The scan speed of the F-4700 spectrometer employed was  $1200 \text{ nm min}^{-1}$ , and the slit was 5 nm. It can be seen that the  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs exhibit no fluorescence peak in the range of 550 nm to 725 nm under the excitation of 365 nm. When doped with  $\text{Pb}^{2+}$ , there was a double peak emission at the excitation of 365 nm. The narrow band (blue band) occurring at 400 nm–450 nm is considered to be the intrinsic



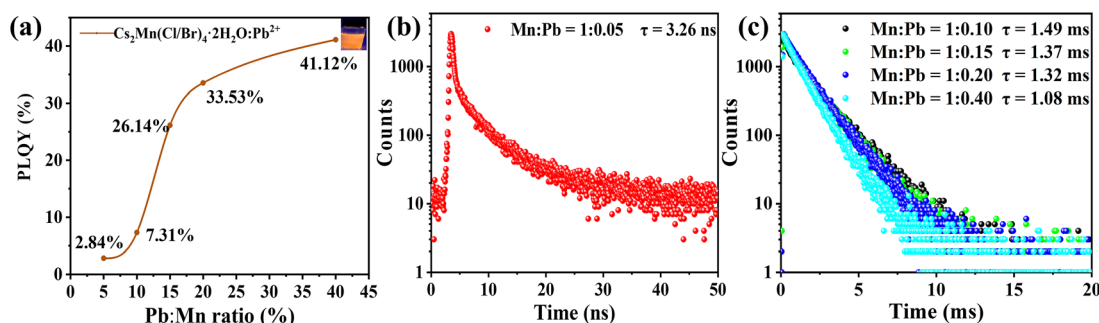


**Fig. 4** (a) UV-vis absorbance of PA NCs. (b) PL spectra of pristine ( $\lambda_{\text{ex}} = 365$  nm) and  $\text{Pb}^{2+}$ -doped  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs ( $\lambda_{\text{ex}} = 365$  nm). (c) and (d) 2D and 3D fluorescence spectra of  $\text{Pb}^{2+}$ -incorporated  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs. (e) Color coordinates of  $\text{Pb}^{2+}$ -incorporated  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs, (inset: a photograph of the several  $\text{Pb}^{2+}$  doped samples under a 365 nm UV lamp).

exciton emission of  $[\text{MnX}_6]^{4-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{OH}$ ) when a low ratio of  $\text{Pb}^{2+}$  is incorporated,<sup>37</sup> which corresponds to the emission spectra. When the ratio of  $\text{Pb}^{2+}$  incorporated increases by a certain ratio ( $\text{Mn}:\text{Pb} = 1:0.15$ ), the blue emission is designated to the intrinsic exciton emission of the lead halide unit  $[\text{PbX}_6]^{4-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{OH}$ ),<sup>15–19</sup> and the full width at half maximum (FWHM) of the blue emission peak also becomes smaller, which is consistent with the intrinsic emission of octahedral  $[\text{Pb}(\text{Cl}/\text{Br})_4(\text{OH})_2]^{4-}$ . This corresponds to the characteristic peak of the absorption of octahedral  $[\text{Pb}(\text{Cl}/\text{Br})_4(\text{OH})_2]^{4-}$  at  $\text{Mn}:\text{Pb} = 1:0.15$ , and also corresponds to the different colors of light emitted under a 365 nm UV light. The blue peak was not fixed at 400–450 nm; its position was dependent on the ratio of doped Cl to Br.<sup>16</sup> The obvious red shifts for both the absorption edge and PL band (blue band) contributed to a reduction in the bandgap of  $\text{Cl}^-$  by  $\text{Br}^-$ . As the content of  $\text{Pb}^{2+}$  increased, the orange became brighter, indicating that octahedral  $[\text{Pb}(\text{Cl}/\text{Br})_4(\text{OH})_2]^{4-}$  transfers most of its

energy to octahedral  $[\text{Mn}(\text{Cl}/\text{Br})_4(\text{OH})_2]^{4-}$  through intersystem crossing (ISC) from the light absorption of the blue-violet band. 3D scanning spectra of  $\text{Pb}^{2+}$  doped PA NCs are shown in Fig. 4c and d, which are consistent with our previous results. Fig. 4e shows the color coordinates of the  $\text{Pb}^{2+}$ -incorporated  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs under UV irradiation.

In addition, as a result of the original PA NCs exhibiting no fluorescence peak from 550 nm to 725 nm, we did not measure related PLQY and time-resolved photoluminescence (TRPL) spectra. We measured the PLQYs of the  $\text{Pb}^{2+}$ -incorporated  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs ( $\text{Mn}:\text{Pb} = 1:0.05, 1:0.10, 1:0.15, 1:0.20, 1:0.40$ ). The absolute PLQYs of the  $\text{Pb}^{2+}$ -incorporated PA NCs at 598 nm were 2.84%, 7.31%, 26.14%, 33.53% and 41.12%, respectively (Fig. 5a). The PLQYs of the  $\text{Pb}^{2+}$ -doped PA NCs are shown in Fig. S4.† These data show that the PLQY was always significantly enhanced with an increase in  $\text{Pb}^{2+}$  content. If the quantum efficiency of the blue part was included, the PLQY reached more than 50%.<sup>15–19,36</sup> TRPL



**Fig. 5** (a) PLQY of  $\text{Pb}^{2+}$ -doped PA NCs at 598 nm, TRPL decay curves of  $\text{Pb}^{2+}$ -doped PA NCs revealed on logarithmic intensity scales at (b)  $\text{Mn}:\text{Pb} = 1:0.05$  and (c)  $\text{Mn}:\text{Pb} = 1:0.10, 1:0.15, 1:0.20, 1:0.40$ .

measurements help to clarify the impact of the incorporation of the  $\text{Pb}^{2+}$  on the optical properties. The TRPL decay curves of  $\text{Mn}^{2+}$  emission were fitted using a double exponential (1):<sup>36,40</sup>

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2). \quad (1)$$

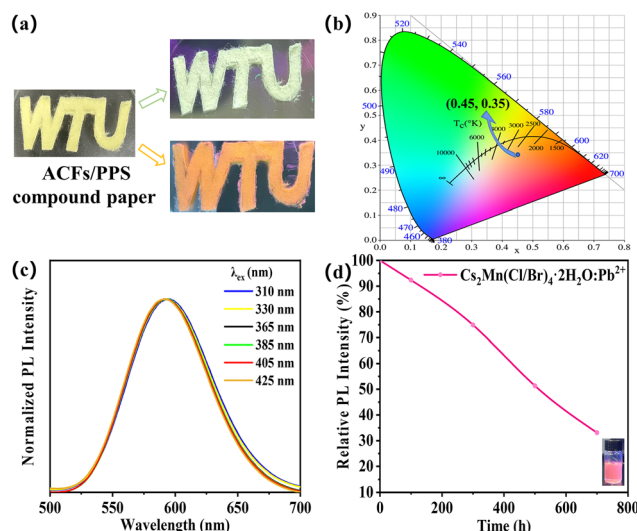
The following eqn (2) was used to calculate the average lifetime:<sup>33</sup>

$$\tau_{\text{avg}} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2). \quad (2)$$

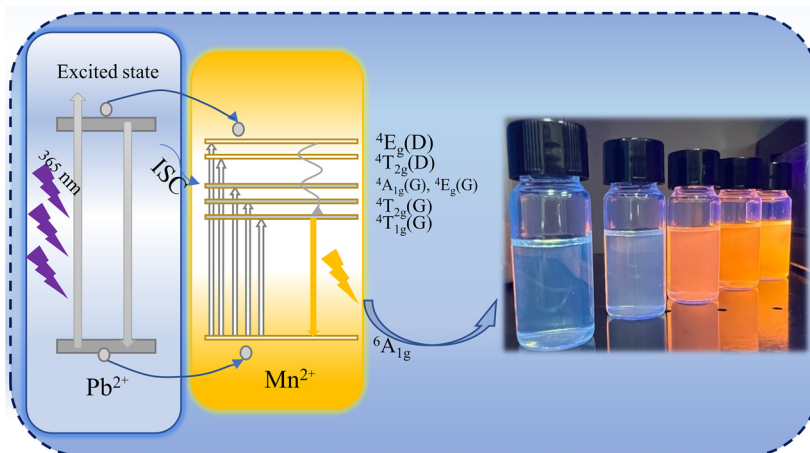
Where  $A_1$  and  $A_2$  are the amplitudes and  $\tau_1$  and  $\tau_2$  represent the fast and slow decay lifetimes, respectively.  $I$  and  $t$  are fluorescence intensity and time, respectively. The fitting parameters are listed in Table S2.† As shown in Fig. 5b, the average lifetime of  $\text{Pb}^{2+}$  at 598 nm was 3.26 ns when it was doped with a low  $\text{Pb}^{2+}$  content. For  $\text{Mn}^{2+}$  transitioning from  ${}^4\text{T}_1$  to  ${}^6\text{A}_1$ , the typical lifetime is ordinarily between 1 and 10 ms, but the fluorescence lifetime of  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}:\text{Pb}^{2+}$  ( $\text{Mn}:\text{Pb} = 1:0.05$ ) is two orders of magnitude less, which is unusual. This ought to be attributed to the multiphonon decay resulting from the affiliation of phonons with the O–H stretching vibration mode of  $\text{H}_2\text{O}$ , resulting in a shortened lifetime.<sup>35,38</sup> While  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  is a 0D structure, the  $\text{H}_2\text{O}$  separated from the octahedron leads to more severe quenching.<sup>35,39</sup> However, upon an increase in  $\text{Pb}^{2+}$  content (Fig. 5c), the average lifetime of the  $\text{Pb}^{2+}$ -doped PA NCs rises to more than 1 ms, which may be caused by a reduction in the coupling between Mn–Mn pairs. After the replacement of  $\text{Mn}^{2+}$  by  $\text{Pb}^{2+}$ , and its average lifetime was 1.08 ms in the PA NCs with the highest  $\text{Pb}^{2+}$  doping content, the lifetime showed a decreasing trend, which may be due to the quenching caused by the increased  $\text{Pb}^{2+}$  content.<sup>35,36</sup> Based on previous analysis, Fig. 6 shows the photophysical process in the  $\text{Pb}^{2+}$ -doped PA NCs. The  $\text{Pb}^{2+}$  in the  $[\text{PbX}_6]^{4-}$  octahedral unit can break the magnetic coupling or symmetry between  $\text{Mn}^{2+}$  pairs, relax the rules of spin and parity selection,<sup>29,30,38</sup> and act as an effective UV absorber for exciton production. The  $\text{Mn}^{2+}$  in the  $[\text{MnX}_6]^{4-}$  octahedral unit works as an effective energy acceptor *via* inter-

system crossing (ISC), and thus improves the  ${}^4\text{T}_{1g}$ – ${}^6\text{A}_{1g}$  transition process caused by an increase in exciton density in  ${}^4\text{T}_{1g}$ , thereby improving the PLQY. By introducing  $[\text{PbX}_6]^{4-}$  as the basic sensitizer, the low PLQY caused by the prohibited transition in the  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs was overcome.<sup>29,38,39</sup>

Meanwhile, we applied the PA NCs with fluorescence properties to ACF/PPS composite paper, as shown in Fig. 7a. We found that ACFs/PPS composite paper soaked in  $\text{Pb}^{2+}$ -doped PA NC solution showed strong orange light under a 365 nm UV lamp, making it of potential use in the anti-counterfeiting field. Fig. 7b shows the CIE chromaticity diagram illustrating



**Fig. 7** (a) Patterned words images of  $\text{Pb}^{2+}$ -doped PA NCs ( $\text{Mn}:\text{Pb} = 1:0.40$ ) under visible and UV light. (b) CIE chromaticity diagram for the composite paper. (c) Excitation-wavelength-dependent (310–425 nm) PL spectra of  $\text{Pb}^{2+}$ -doped PA NCs ( $\text{Mn}:\text{Pb} = 1:0.40$ ). (d) Stability of  $\text{Pb}^{2+}$ -doped PA NCs ( $\text{Mn}:\text{Pb} = 1:0.40$ ) determined to monitor the PL intensity of the solution as a function of hexane at 598 nm. Insets: sample under a 365 nm UV lamp after being dissolved in colloidal solution for one month.



**Fig. 6** Diagram of the light absorption, ISC (intersystem crossing) and PL processes of the  $\text{Pb}^{2+}$ -doped  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs.

the orange emission at (0.45, 0.35) of the composite paper. When the excitation wavelength changed from 310 nm to 425 nm, no changes were observed in the PL emission spectra, as shown in Fig. 7c. The autonomy of the PL emission spectra at excitation wavelength verifies that orange emission was caused by the relaxation of the same excited state.

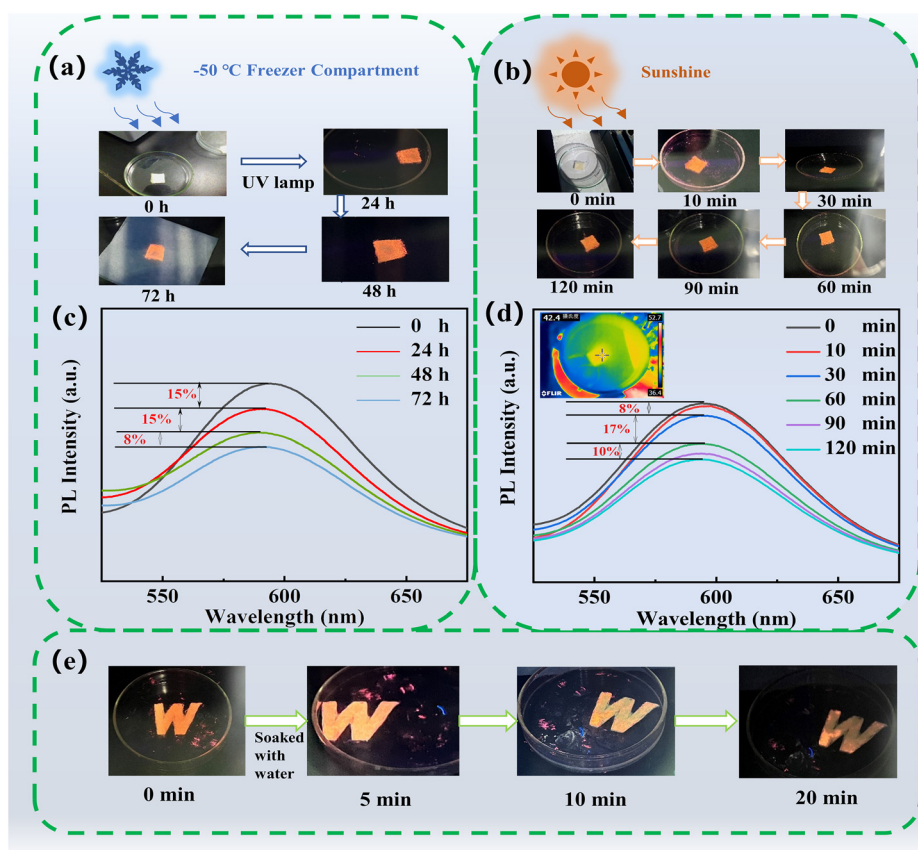
To demonstrate the outstanding stability of the  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}:\text{Pb}^{2+}$  PA NCs, we re-dispersed the centrifugally-precipitated material into 10 mL of *n*-hexane, 1 mL of OA, and 1 mL of OLA to form a colloidal solution, the fluorescence intensity of which was investigated at different time periods under aerobic conditions. Even after one month, the orange light emission at 598 nm still maintained a certain intensity, as shown in Fig. 7d. In order to apply composite paper in real-world scenarios, we tested the stability of the composite paper in different environments. As shown in Fig. 8a, the composite paper was placed in a freezer at  $-50^\circ\text{C}$  for 72 h, and we found that the composite paper still maintained 62% fluorescence performance, as shown in Fig. 8c. As can be seen in Fig. 8b, we exposed the composite paper to the sun to test the fluorescence performance of the composite paper at different time points. After being exposed to an outdoor temperature of  $36^\circ\text{C}$  for 2 h, the composite paper still exhibited bright fluorescence performance under a UV lamp. During its exposure to the sun,

we applied an infrared thermal imager to monitor the surface temperature of the composite paper, as shown in Fig. 8d. Then, we soaked the composite paper with water, and we observed that after soaking in water for 20 min, the composite paper still showed strong orange light under the UV lamp, as indicated in Fig. 8e. These stability experiments show that the composite paper can be well used in color-changing fibers. Due to its excellent luminescence characteristics and stability, this material can be used as a color conversion material for LEDs. As shown in Fig. 9a, the device shows bright orange light with color coordinates of (0.57, 0.37) (Fig. 9c), and the corresponding emission spectrum is shown in Fig. 9b. This LED device has the ability to remain unaltered for extended continuous operation time. In future work, we can also try to react it with APTES as a ligand to ensure that the PA NCs are preserved for a longer period of time.

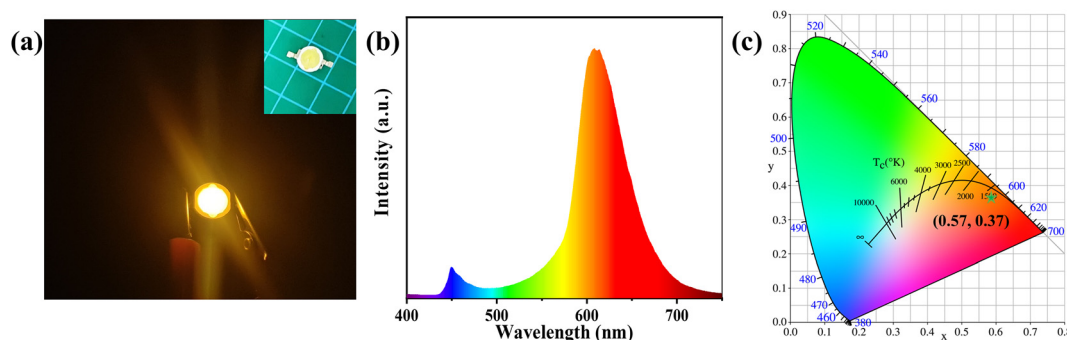
## Experimental section

### Materials

Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99.99%), *n*-hexane (>99%, GC), oleylamine (OAm, 80–90%), 1-octadecene (ODE, >90%, GC), manganese(II) chloride ( $\text{MnCl}_2$ , 99%), lead(II) bromide ( $\text{PbBr}_2$ ,



**Fig. 8** (a) Stability testing of compound paper placed in a  $-50^\circ\text{C}$  refrigerator. (b) Compound paper placed in sunshine. (c) Fluorescence spectra of compound paper placed in a  $-50^\circ\text{C}$  refrigerator. (d) Fluorescence spectra of compound paper placed in sunshine. (e) Stability testing of compound paper soaked in water.



**Fig. 9** (a) Fluorescence image. Inset: optical image of the LED. (b) PL emission spectrum. (c) CIE chromaticity coordinates of the LED from  $\text{Pb}^{2+}$ -doped PA NCs.

99.9%), oleic acid (OA, AR), and manganese(II) bromide tetrahydrate ( $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ , 99%) were used in this work. All reagents were purchased from Aladdin Chemical Co., Ltd (Shanghai, China) and used directly without further purification. Ethyl acetate (EAC, AR) was purchased from Sinopharm. Aramid chopped fibers (ACFs) were supplied by China Bluestar Chengrand Chemical Research and Design Institute Co., Ltd, (China). Polyethylene oxide (PEO,  $M_w = 2 \times 10^6$ ) was purchased from Sumitomo Keiretsu Co., Ltd, Japan. Anionic polyacrylamide (APAM,  $M_w = 3 \times 10^6$ ), acetone and sodium dodecylbenzene sulfonate (SDS) were purchased from China Pharmaceutical Group Chemical Reagent Co., Ltd. Silicone defoamer was provided by China's Lusén Chemical Co., Ltd.

**Preparation of cesium oleate precursors.** Cesium oleate solution was prepared according to the approach detailed by Protesescu *et al.*<sup>33</sup> Briefly, 0.203 g of  $\text{Cs}_2\text{CO}_3$ , 0.6 mL of OA, and 7.5 mL of ODE were added to a three-neck flask and heated to 120 °C for 30 min, and then heated to 150 °C until all the  $\text{Cs}_2\text{CO}_3$  had reacted with OA. The solution turned to a pale yellow. The resulting Cs–OA solution was stored and pre-heated to 150 °C before use.

**Preparation of the  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs.** 0.1183 g of  $\text{MnCl}_2$ , 0.027 g of  $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ , 25 mL of ODE, 2.5 mL of OAm and 2.5 mL of OA were reacted in a three-necked flask for 1 h at 120 °C to completely dissolve  $\text{MnCl}_2$  and  $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ . The color of the solution changed from black to pale yellow and finally brown. After the temperature was raised to 145–150 °C, the temperature was left to stabilize for a while, before 2 mL of hot 150 °C Cs–oleate solution was rapidly added into the reaction solution, and the reaction blend was cooled using a water bath.

**Preparation of  $\text{Pb}^{2+}$ -doped  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs.**  $\text{MnCl}_2$  and  $\text{PbBr}_2$  in a specific molar ratio (1:0.05, 1:0.10, 1:0.15, 1:0.20 and 1:0.40) were mixed with 25 mL of ODE, 2.5 mL of OAm and 2.5 mL of OA in a three-neck flask for 1 h at 120 °C. After  $\text{MnCl}_2$  and  $\text{PbBr}_2$  were used up, the temperature was increased to 145–150 °C, and in the same way as above, 2 mL of hot 150 °C Cs–oleate solution was quickly infused, and the reaction blend was cooled using a water bath.

**Purification.** The  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs and  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}:\text{Pb}^{2+}$  PA NCs were extricated from the unrefined

solution by centrifuging at 10 000 rpm for 5 min to the supernatant containing unreacted precursor and by products was disposed. After that, 5 mL of *n*-hexane was added to the precipitation for dispersion, and then 5 mL of ethyl acetate was also added to induce aggregation. The solution was centrifuged at 10 000 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitates were redispersed in *n*-hexane to form a steady colloidal solution, with some of the precipitate taken and placed in an oven for drying before its subsequent characterization.

**Preparation of the ACF/PPS compound paper.** To remove impurities, the ACF and PPS microfiber non-woven fabrics were first cleaned with acetone. PPS ultrafine fiber pulp was created by beating PPS non-woven fabric in a valley-type beating machine. Then, in a mass ratio of 1:3:6, APAM, SDS, and PEO were added to deionized water and stirred at room temperature for 4 h to obtain a uniformly dispersed solution (APAM/SDS/PEO). Following that, a fiber dissociator was used to disperse the dispersion of a PPS ultrafine fiber pulp and ACFs in a mass ratio of 3:7. A mixed fiber suspension was formed after the fibers were evenly distributed and completely dispersed in the dispersion. Finally, to obtain ACF/PPS hybrid papers, the hybrid fiber suspension was used in wet paper-making directly on a paper sheet forming machine.

**Fabrication of LED from  $\text{Pb}^{2+}$ -doped  $\text{Cs}_2\text{Mn}(\text{Cl}/\text{Br})_4 \cdot 2\text{H}_2\text{O}$  PA NCs.** Commercially available GaN light emitting diode (LED) chips without a phosphor coating were purchased from U King Optoelectronic Technology Inc. The GaN LED chip emission center was 380–385 nm, the operating voltage was 3.4 V. The  $\text{Pb}^{2+}$ -doped PA NCs powder was ground and mixed with *n*-hexane and repeatedly applied to the fluorescent coating, which was then dried in a vacuum oven and finally assembled into an LED.

**Characterization.** The photoluminescence spectra of the PA NCs were measured using a Hitachi fluorescence spectrophotometer F-4700 employing a xenon lamp as the excitation source at room temperature. The UV–vis absorption spectra of PA NCs were recorded using a A590 double beam scanning UV/vis spectrophotometer. An Edinburgh steady/transient fluorescence spectrometer FLS1000 was used for testing the decay of the photoluminescence and photoluminescence quantum



yield (PLQY). Scanning electron microscope (SEM) observations with energy-dispersive X-ray spectroscopy (EDS) analyses of the samples were carried out using a TESCAN MIRA LMS/TESCAN MIRA4 (Czech Republic) microscope. X-ray diffraction (XRD) patterns were measured on a PANalytical Empyrean powder X-ray diffractometer with monochromatic Cu K $\alpha$  radiation, operated at 40 kV and 40 mA. Paramagnetic resonance spectra (ESR/EPR) were recorded using a Bruker EMX PLUS spectrometer at room temperature under a 365 nm lamp. A camera-obscura ultraviolet analyzer (ZF-7N) was used to observe fluorescence effects. A Yossen hand-held professional-grade thermal imager was used for thermal imaging.

## Conclusion

In this study, 0D Cs<sub>2</sub>Mn(Cl/Br)<sub>4</sub>·2H<sub>2</sub>O:Pb<sup>2+</sup> PA NCs were synthesized *via* a simple hot-injection strategy. These PA NCs exhibit strong fluorescence performance, and their emission center is about 598 nm, with a PLQY of 41.12%. With the incorporation of Pb<sup>2+</sup>, Pb exists as octahedral [Pb(Cl/Br)<sub>4</sub>(OH)<sub>2</sub>]<sup>4-</sup>, playing an important role in transferring energy to Mn<sup>2+</sup> and increasing light absorption in the blue-violet band, and decreasing magnetic coupling between Mn<sup>2+</sup> pairs. These excellent properties significantly enhance the PLQY and stability of the Cs<sub>2</sub>Mn(Cl/Br)<sub>4</sub>·2H<sub>2</sub>O:Pb<sup>2+</sup> PA NCs. We applied a ACFs/PPS composite paper soaked in Pb<sup>2+</sup>-doped PA NCs solution, which showed great stability in different environments, meaning that the composite paper can be used in color-changing fibers. Moreover, the Pb<sup>2+</sup>-doped PA NCs also exhibit excellent properties in the field of luminescence. Finally, these PA NCs synthesized in air are expected to be a good choice for the mass production of optoelectronic devices in the future.

## Author contributions

Kun Nie, Xiuqiang Duan, and Hua Wang conceived the concept and idea of the present paper, worked on the study design strategy, and selected the topics to be discussed. Xiuqiang Duan completed the main experiment and paper writing. Kun Nie, Xiaoxue Ma, and Hua Wang were responsible for guidance and supervision work, and at the same time, guided and revised the final paper writing. Xuyi Wang and Chi-An Cheng provided writing assistance and article revisions. Ziyao Hu and Ranran Zhou conducted literature searches, and abstracted the data from the eligible full text articles. Junbao Yan and Songjun Yao provided experimental guidance and experimental tests. Luoxin Wang and Lefu Mei supervised the study. All of the authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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