Hydrophilic perovskite microdisks with excellent stability and strong fluorescence for recyclable temperature sensing

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In recent years, metal halide perovskites have emerged as a promising new class of semiconductors for solar cells [1–3], light-emitting diodes (LED) [4–6], temperature sensors [7], lasers [8] and photodetectors [9], owing to their excellent optical and electronic properties [10,11], such as, long charge carrier diffusion length [12], high extinction coefficients and tunable band gaps [13]. However, the materials suffer from fast degradation due to their inherent instability [14–17], especially high sensitivity to oxygen [18], UV light [19,20], heat [21,22], moisture [23,24] and even some hydrophilic solvents such as alcohol, which significantly impedes their further applications [25,26]. Compared with organic-inorganic hybrid perovskites [27], all-inorganic cesium lead halide perovskites CsPbX_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) are much stable [28–33], but the stability still needs substantial improvement to satisfy the needs of practical implications.

Up to now, the synthesis of perovskite materials is mainly based on the hot injection in hydrophobic solvents, such as oleylamine and toluene under inert atmospheres [34–37]. The mixture solvents usually could not be recycled and the as-obtained nanocrystals are highly sensitive to hydrophilic solvents such as ethanol and *N,N*-dimethylformamide (DMF) [34]. Therefore, the large-scale green production of these perovskite materials with excellent optical merits and good stability faces great challenges.

Herein, we report a solvothermal method for the large-scale (1.5 g of product per 40 mL of solvents) synthesis of Cs_4PbBr_6 MDs in DMF. Interestingly, the hydrophilic solvent DMF can be reutilized for tens of times and have no degradation on the products. The as-obtained Cs_4PbBr_6 MDs presented excellent fluorescence and

outstanding stability. In addition, unlike the previously reported CsPbX_3 ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) perovskites, the crystal structure of these Cs_4PbBr_6 MDs was well maintained under various temperatures. The temperature shows a great influence on the luminescent properties of luminescent materials. When the temperature increases, the non-radiation transition will be enhanced, resulting in the decrease of the intensity of the luminescence, which is known as thermal quenching [38,39]. The fluorescence of the Cs_4PbBr_6 MDs was quenched with the increased temperature. However, their fluorescence could be well recovered. In view of the excellent fluorescence and stability of Cs_4PbBr_6 MDs, a sensitive fluorescence sensor of temperature with good recyclability was developed, which was utilized for the temperature sensor in the range of 30–200°C.

In the study, we developed a one-pot green wet-chemistry strategy for large-scale synthesis of Cs_4PbBr_6 MDs. Briefly, the CsBr and PbBr_2 were dissolved in DMF with polyvinylpyrrolidone (PVP) as the surfactant, and then the mixture was transferred into a Teflon-lined autoclave and treated at 150°C for 3 h. Finally, the phase-pure Cs_4PbBr_6 MDs with strong green fluorescence and hydrophilic surface were obtained (Fig. 1a). The X-ray powder diffraction (XRD) measurement was carried out to determine the accurate phases of the as-obtained products. As shown in Fig. 1b, from MD-1 to MD-4, the molar ratio of CsBr to PbBr_2 in the precursors for the synthesis of samples was 7, 6, 5 and 4, respectively. The peaks at 29.4°, 42.1° and 52.1° can be indexed to CsBr , which became weak by decreasing the molar ratio of CsBr -to- PbBr_2 . The diffraction peaks of the perovskites became sharper and much more intense from MD-1 to MD-4, suggesting the good crystallinity of as-prepared

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Figure 1 Scheme for the synthesis process (a), XRD patterns (b) and fluorescence spectrum and photograph (c) of Cs_4PbBr_6 MDs. (b) From MD-1 to MD-4, the molar ratio of CsBr-to- PbBr_2 in the precursor was 7, 6, 5 and 4, respectively.

samples. All the diffraction peaks of the perovskites were well assigned to those of Cs_4PbBr_6 (JCPDS number: 54-0750). And no impurity peaks were observed in the XRD patterns of MD-4, which confirms the high purity of the products when the molar ratio of CsBr-to- PbBr_2 was 4:1. The typical photoluminescence (PL) spectrum (Fig. 1c) and ultraviolet-visible (UV-vis) absorption spectrum (Fig. S1) were also obtained. A sharp and symmetric of PL spectrum located at 521.4 nm with a full width at half maximum (FWHM) of 20 nm was observed. The insets in Fig. 1c showed the photographs of Cs_4PbBr_6 powders under UV light (left, $\lambda_{\text{ex}}=365$ nm) and the products prepared on a large scale (right, 1.5 g) in one autoclave (40 mL of DMF). Obviously, the Cs_4PbBr_6 powders showed very bright green fluorescence, with a photoluminescence quantum yield (PLQY) of 42% (Fig. S2). It is noteworthy that the solvent (DMF) could be reutilized for tens of times. There is no difference on the shape and size of the as-obtained Cs_4PbBr_6 MDs (Fig. S3). Meanwhile, their fluorescence is also as strong as that of the Cs_4PbBr_6 MDs synthesized using fresh DMF, although the wavelength of fluorescence had a slight fluctuation (526.8 ± 1.6 nm) (Figs S4–S6).

The typical transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of the as-synthesized Cs_4PbBr_6 were shown in Fig. 2. As

presented in Fig. 2a and b, the Cs_4PbBr_6 MDs presented a disk shape with an average diameter of $\sim 1 \mu\text{m}$ and thickness of ~ 100 nm. Moreover, the energy-dispersive X-ray (EDX) elemental mapping of Cs, Pb and Br (Fig. 2c–f) confirmed the existence and uniform distribution of the elements within the disk. Elemental ratio of Cs:Pb:Br in an individual disk as obtained from EDX spectroscopy (Fig. S7) is calculated to be 4.03:1:6.07, which is in good consistence with the Cs_4PbBr_6 composition observed from XRD. Consequently, the Cs_4PbBr_6 MDs with uniform morphology and high phase purity were synthesized *via* this one-pot green strategy.

It is well known the long-term stability of perovskites is the key issue in perovskite-based devices, considering the intrinsic degradation under real working conditions, where the device is operated continuously with light and heat. Therefore, the thermal stability of these perovskite MDs was carefully investigated. As shown in Fig. 3a, the fluorescence of Cs_4PbBr_6 powders showed a negligible decrease after heating at 200°C for 2 h and then naturally cooling to room temperature (30°C), which was further confirmed by the PL spectra with a PLQY of 38% (Fig. S8). Meanwhile, no obvious changes were observed in the color of the perovskite powder under natural light. On the contrary, the fluorescence of CsPbBr_3 QDs, synthesized using hot injection in hydrophobic solvents,

Figure 2 TEM (a) and SEM (b) images and elemental mapping images (c) of as-prepared Cs_4PbBr_6 MDs.

was completely quenched after heating treatment with the same process (Fig. 3a and Fig. S9), and their color was evolved into yellow under natural light. To reveal the reason that Cs_4PbBr_6 crystals remained the luminescence property after heating treatment, we investigated the crystal structure of Cs_4PbBr_6 powder by means of temperature-dependent XRD measurement. As shown in Fig. 3b, the XRD peaks matched well with the Cs_4PbBr_6

reflections at the temperatures ranging from 30 to 200°C. A slight shift of peak could be attributed to the lattice expansion with temperature increment. However, the crystal structure of CsPbBr_3 QDs was completely destroyed after the heating treatment (Fig. S10). Fig. 3c shows the temperature-dependent fluorescence spectra at room temperature and 200°C. More importantly, the fluorescence intensity of Cs_4PbBr_6 sample was well maintained after 20 heating-cooling cycles (Fig. 3d), implying the excellent thermal stability of as-prepared Cs_4PbBr_6 MDs. The results demonstrate that the thermal responsive fluorescence performance of Cs_4PbBr_6 powder could be attributed to thermal quenching instead of the changes in structure at high temperature [38].

Encouraged by the above-mentioned results, Cs_4PbBr_6 /polydimethylsiloxane (PDMS) composites were further fabricated *via* thermal polymerization and then applied for temperature sensing. As shown in Fig. 4a, the composite disk showed uniform bright green luminescence with excellent recovery ability after heating-cooling cycle between 30 and 200°C. To deeply investigate the feasibility of this luminescent disk for temperature sensing, the temperature-dependent PL was carefully checked. As depicted in Fig. 4b, no obvious red or blue shift was observed in the fluorescence spectra of the

Figure 3 (a) Photographs of Cs_4PbBr_6 MDs and CsPbBr_3 nanocrystals under natural light and UV light before and after heating treatment at 200°C for 2 h; (b) XRD patterns of the Cs_4PbBr_6 MDs at various temperatures; (c) Fluorescence spectra and (d) fluorescence intensity evolution of the Cs_4PbBr_6 MDs during tens of heating-cooling cycles between 30 and 200°C.

Figure 4 Photographs of $\text{Cs}_4\text{PbBr}_6/\text{PDMS}$ composite under natural light and UV light (a); fluorescence spectra (b) and peak intensity (c) of $\text{Cs}_4\text{PbBr}_6/\text{PDMS}$ composite under different temperatures; (d) Linear relationship plot between natural logarithm of luminescence intensity and temperature.

$\text{Cs}_4\text{PbBr}_6/\text{PDMS}$ composite at various temperatures. However, the fluorescence intensity (I) exponentially decreased with the temperature increment (Fig. 4c). Interestingly, the natural logarithm of luminescence intensity ($\log(I)$) and the temperature (T) fell into the linear plot ($R^2=0.998$), as indicated in Fig. 4d, demonstrating that the luminescent $\text{Cs}_4\text{PbBr}_6/\text{PDMS}$ composite can be utilized for temperature sensing [39].

In summary, we developed a one-step green strategy for the large-scale production of pure phase Cs_4PbBr_6 MDs in hydrophilic solvent (DMF) with excellent fluorescent merits and thermal stability. The solvent can be reutilized for tens of times without degrading the final perovskite products. These Cs_4PbBr_6 MDs demonstrated an outstanding thermal stability, which is in favour of the heat processing of the perovskite-based devices. Meanwhile, the samples showed excellent fluorescence recovery after cooling to room temperature from 200°C. Owing to these merits, a luminescent sensor using $\text{Cs}_4\text{PbBr}_6/\text{PDMS}$ composite was fabricated for the fluorescence sensing of temperature. Furthermore, the temperature-dependent XRD results confirmed that the thermal responsive fluorescence of Cs_4PbBr_6 MDs stemmed from thermal quenching instead of structure change at high temperature. We believe this work will promote tremendous

advances for further developing the large-scale green synthesis of perovskites and push all-inorganic halide perovskites to a new stage as a research paradigm in the field of optoelectronic devices, especially in perovskite-based temperature sensing, healthy lighting and wide-colour-gamut displays.

Received 12 November 2018; accepted 14 January 2019;
published online 29 January 2019

- Hou Y, Du X, Scheiner S, *et al.* A generic interface to reduce the efficiency-stability-cost gap of perovskite solar cells. *Science*, 2017, 358: 1192–1197
- Chen H, Ye F, Tang W, *et al.* A solvent- and vacuum-free route to large-area perovskite films for efficient solar modules. *Nature*, 2017, 551: 92–95
- Xu Z, Yin X, Guo Y, *et al.* Ru-Doping in TiO_2 electron transport layers of planar heterojunction perovskite solar cells for enhanced performance. *J Mater Chem C*, 2018, 6: 4746–4752
- Abdi-Jalebi M, Andaji-Garmaroudi Z, Cacovich S, *et al.* Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. *Nature*, 2018, 555: 497–501
- Chin XY, Perumal A, Bruno A, *et al.* Self-assembled hierarchical nanostructured perovskites enable highly efficient LEDs via an energy cascade. *Energy Environ Sci*, 2018, 11: 1770–1778
- Ng YF, Kulkarni SA, Parida S, *et al.* Highly efficient Cs-based perovskite light-emitting diodes enabled by energy funneling. *Chem Commun*, 2017, 53: 12004–12007
- Saidaminov MI, Almutlaq J, Sarmah S, *et al.* Pure Cs_4PbBr_6 : highly

- luminescent zero-dimensional perovskite solids. *ACS Energy Lett*, 2016, 1: 840–845
- 8 Karl M, Glackin JME, Schubert M, *et al.* Flexible and ultra-light-weight polymer membrane lasers. *Nat Commun*, 2018, 9: 1525
- 9 Chen Q, Wu J, Ou X, *et al.* All-inorganic perovskite nanocrystal scintillators. *Nature*, 2018, 561: 88–93
- 10 Zhao Y, Zhu K. Organic–inorganic hybrid lead halide perovskites for optoelectronic and electronic applications. *Chem Soc Rev*, 2016, 45: 655–689
- 11 Su X, Ma H, Wang H, *et al.* Surface-enhanced Raman scattering on organic–inorganic hybrid perovskites. *Chem Commun*, 2018, 54: 2134–2137
- 12 Chen Y, Yi HT, Wu X, *et al.* Extended carrier lifetimes and diffusion in hybrid perovskites revealed by hall effect and photoconductivity measurements. *Nat Commun*, 2016, 7: 12253
- 13 Lou Y, Fang M, Chen J, *et al.* Formation of highly luminescent cesium bismuth halide perovskite quantum dots tuned by anion exchange. *Chem Commun*, 2018, 54: 3779–3782
- 14 Cho H, Kim YH, Wolf C, *et al.* Improving the stability of metal halide perovskite materials and light-emitting diodes. *Adv Mater*, 2018, 30: 1704587
- 15 Wu Y, Wei Y, Huang Y, *et al.* Capping CsPbBr₃ with ZnO to improve performance and stability of perovskite memristors. *Nano Res*, 2016, 10: 1584–1594
- 16 Xue M, Zhou H, Xu Y, *et al.* High-performance ultraviolet-visible tunable perovskite photodetector based on solar cell structure. *Sci China Mater*, 2017, 60: 407–414
- 17 Li X, Xue Z, Luo D, *et al.* A stable lead halide perovskite nanocrystals protected by PMMA. *Sci China Mater*, 2018, 61: 363–370
- 18 Stoeckel MA, Gobbi M, Bonacchi S, *et al.* Reversible, fast, and wide-range oxygen sensor based on nanostructured organometal halide perovskite. *Adv Mater*, 2017, 29: 1702469
- 19 Ummadisingu A, Steier L, Seo JY, *et al.* The effect of illumination on the formation of metal halide perovskite films. *Nature*, 2017, 545: 208–212
- 20 Wang B, Zhang C, Huang S, *et al.* Postsynthesis phase transformation for CsPbBr₃/Rb₄PbBr₆ core/shell nanocrystals with exceptional photostability. *ACS Appl Mater Interfaces*, 2018, 10: 23303–23310
- 21 Tan W, Bowring AR, Meng AC, *et al.* Thermal stability of mixed cation metal halide perovskites in air. *ACS Appl Mater Interfaces*, 2018, 10: 5485–5491
- 22 Li X, Wang Y, Sun H, *et al.* Amino-mediated anchoring perovskite quantum dots for stable and low-threshold random lasing. *Adv Mater*, 2017, 29: 1701185
- 23 Wang H, Yin X, Wang L. Highly stable perovskite nanogels as inks for multicolor luminescent authentication applications. *J Mater Chem C*, 2018, 6: 11569–11574
- 24 Li Y, Wang Y, Zhang T, *et al.* Li dopant induces moisture sensitive phase degradation of an all-inorganic CsPbI₂Br perovskite. *Chem Commun*, 2018, 54: 9809–9812
- 25 Correa-Baena JP, Saliba M, Buonassisi T, *et al.* Promises and challenges of perovskite solar cells. *Science*, 2017, 358: 739–744
- 26 Rong Y, Hu Y, Mei A, *et al.* Challenges for commercializing perovskite solar cells. *Science*, 2018, 361: eaat8235
- 27 Nishikubo R, Tohnai N, Hisaki I, *et al.* Thermoresponsive emission switching *via* lower critical solution temperature behavior of organic-inorganic perovskite nanoparticles. *Adv Mater*, 2017, 29: 1700047
- 28 Smock SR, Williams TJ, Brutchey RL. Quantifying the thermodynamics of ligand binding to CsPbBr₃ quantum dots. *Angew Chem Int Ed*, 2018, 57: 11711–11715
- 29 Song J, Li J, Li X, *et al.* Quantum dot light-emitting diodes based on inorganic perovskite cesium lead halides (CsPbX₃). *Adv Mater*, 2016, 27: 7162–7167
- 30 Chen X, Peng L, Huang K, *et al.* Non-injection gram-scale synthesis of cesium lead halide perovskite quantum dots with controllable size and composition. *Nano Res*, 2016, 9: 1994–2006
- 31 Yang P, Liu G, Liu B, *et al.* All-inorganic Cs₂CuX₄ (X=Cl, Br, and Br/I) perovskite quantum dots with blue-green luminescence. *Chem Commun*, 2018, 54: 11638–11641
- 32 Zhou L, Liao JF, Huang ZG, *et al.* All-inorganic lead-free Cs₂PdX₆ (X=Br, I) perovskite nanocrystals with single unit cell thickness and high stability. *ACS Energy Lett*, 2018, 3: 2613–2619
- 33 Zhou L, Xu YF, Chen BX, *et al.* Synthesis and photocatalytic application of stable lead-free Cs₂AgBiBr₆ perovskite nanocrystals. *Small*, 2018, 14: 1703762
- 34 Protesescu L, Yakunin S, Bodnarchuk MI, *et al.* Nanocrystals of cesium lead halide perovskites (CsPbX₃, X=Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. *Nano Lett*, 2016, 15: 3692–3696
- 35 Zhang D, Eaton SW, Yu Y, *et al.* Solution-phase synthesis of cesium lead halide perovskite nanowires. *J Am Chem Soc*, 2015, 137: 9230–9233
- 36 Nedelcu G, Protesescu L, Yakunin S, *et al.* Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites (CsPbX₃, X=Cl, Br, I). *Nano Lett*, 2015, 15: 5635–5640
- 37 Xu W, Cai Z, Li F, *et al.* Embedding lead halide perovskite quantum dots in carboxybenzene microcrystals improves stability. *Nano Res*, 2017, 10: 2692–2698
- 38 McLaurin EJ, Bradshaw LR, Gamelin DR. Dual-emitting nanoscale temperature sensors. *Chem Mater*, 2013, 25: 1283–1292
- 39 Wang X, Wolfbeis OS, Meier RJ. Luminescent probes and sensors for temperature. *Chem Soc Rev*, 2013, 42: 7834–7869

Acknowledgements This research was supported by the National Natural Science Foundation of China (21725501, 21675009, 21771019 and 21521005) and the Fundamental Research Funds for the Central Universities (buctrc201706, buctrc201812 and buctrc201815). We also thank the support from the Public Hatching Platform for Recruited Talents of Beijing University of Chemical Technology.

Author contributions Luo Q and Wang H performed the main experiments; Wang L and Yin X conceived and supervised the project; Luo Q and Wang H wrote the manuscript with support from Yin X and Wang L. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper. Experimental section; UV-vis absorption spectra, PLQY, TEM images, photographs, fluorescence spectra, fluorescence peak wavelength and EDX spectroscopy of Cs₄PbBr₆ sample; fluorescence spectra and XRD patterns of CsPbBr₃ nanocrystals.

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超稳定强荧光亲水钙钛矿薄片的制备及热传感性能研究

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摘要 铯铅卤化物钙钛矿材料因具有优异的光学特性, 近年来受到广泛关注, 但其固有的不稳定性及现有的制备技术阻碍了它们的实际应用. 本文报道了一种大规模绿色合成亲水钙钛矿 Cs_4PbBr_6 薄片的方法. 本方法用 N,N -二甲基甲酰胺作为可循环使用的溶剂, 所得到的铯铅卤化物钙钛矿 Cs_4PbBr_6 薄片对光、热及亲水溶剂表现出超高稳定性. 此外, Cs_4PbBr_6 /PDMS复合薄膜在热传感应用方面具有优异的稳定性和再现性. 本研究为制备高稳定性钙钛矿材料提供了有效的参考途径.