Fiber-Spinning-Chemistry Method toward In Situ Generation of Highly Stable Halide Perovskite Nanocrystals

Xuan Lu, Yang Hu, Jiazhuang Guo, Cai-Feng Wang,* and Su Chen*

All-inorganic halide perovskite nanocrystals (PNCs) have drawn increasing attention owing to their splendid optical properties. However, such nanomaterials suffer from intrinsic instability, greatly limiting their practical application. Meanwhile, environmental regulation has restricted the emissions of volatile organic compounds (VOCs), initiating a search for alternative approaches to PNC synthesis and film forming. Herein, fiber-spinning chemistry (FSC) is proposed for easy-to-perform synthesis of highly stable PNC fibrous films. The FSC process utilizes spinning fibers as reactors, reducing the generation of VOCs. This method enables the fabrication of CsPbX$_3$ (X = Cl, Br, I) PNCs/poly(methyl methacrylate)/thermoplastic polyurethanes fibrous films at room temperature in one step, exhibiting tunable emission between 450 and 660 nm. Significantly, the in situ generation of PNCs in hydrophobic core–shell nanofibers results in highly improved fluorescence stability. PNCs/polymer fibrous films keep constant in photoluminescence (PL) after storage at atmosphere for 90 d and retain 82% PL after water immersion for 120 h (vs fluorescence quenching in 10 d in air or 5 h in water for pristine PNCs). The PNCs/polymer fibrous films endowed with superior optical stability and great flexibility show promising potentials in flexible optoelectronic applications. This work paves a facile way toward high-performance nanoparticles/polymer fibrous films.

1. Introduction

Colloid perovskite nanocrystals (PNCs) have been developed as well-known optical materials with high photoluminescence (PL) quantum yield (QY), adjustable fluorescence wavelength, and narrow full width at half maximum (FWHM).[1] Such nanomaterials have aroused widespread attention in a variety of applications, such as light emitting diodes (LEDs),[2] light-emitting transistors,[3] solar concentrators,[4] solar cells,[5] photodetectors,[6] and next-generation display devices.[7] In particular, many approaches have been achieved to the handy preparation of all-inorganic halide PNCs including CsPbX$_3$ (X = Cl, Br, I) behaving full-visible-spectrum emission.[8]

Nevertheless, an unavoidable challenge remains to improve the stability of PNCs under atmosphere, humidity environment, and UV radiation.[9] To this end, considerable endeavors have been devoted to the introduction of mixed cations allowing ionic radii satisfying the Goldschmidt's tolerance factor $t$ closer to 1.[10,11] For instance, Ho-Baillie and co-workers utilized bulk organic ammonium iodide (iso-butylammonium iodide) and formamidinium iodide to passivate perovskite, to preserve 87% initial performance after storage at ambient condition for 38 d.[12] Besides, PNCs have been encapsulated in inorganic salts, nanosilica, and polymers, which can tighten the connection between the ligand and PNC surfaces, resulting in the enhanced stability of PNCs.[13–17] Lin's group employed CaF$_2$ as hierarchical matrices, preserving 60% of PL after 1 d storage in water.[15] Yang's group encapsulated PNCs with polystyrene (PS) via electrospinning technique, to withhold 70% of initial PL QY after immersed in water for 192 h.[17] Although these efforts have made a great progress on this issue, alternative methods are still highly needed to prepare PNCs with enhanced stability, especially those overcoming complicated procedures. Meanwhile, environmental regulation has restricted the emissions of volatile organic compounds (VOCs).[18] However, large quantities of organic solvents have still been used in the synthesis of PNCs and their film-forming process in most cases, which does not conform to the current environmentally friendly and sustainable concept. As a consequence, there is a growing demand for the preparation of stable PNCs film in an easy-to-perform and green way. Herein, we demonstrate a facile method, named fiber-spinning chemistry (FSC), enabling one-step preparation of highly stable halide perovskite fibrous films with excellent air/water resistance. FSC we propose here means utilizing spinning fibers as reactors to carry out chemical reactions. Depending on spinning conditions, millimeter-scale, microscale, and nanoscale reactors could be provided.[19] This process not only circumvents the use of quantities of organic solvents, greatly

X. Lu, Y. Hu, J. Guo, Prof. C.-F. Wang, Prof. S. Chen
State Key Laboratory of Materials-Oriented Chemical Engineering
College of Chemical Engineering, and Jiangsu Key Laboratory of Fine Chemicals and Functional Polymer Materials
Nanjing Tech University
Nanjing 210009, China
E-mail: caifengwang@njtech.edu.cn; chensu@njtech.edu.cn

© 2019 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/ads.201901694
reducing VOC generation, but also allows fiber substrates to serve as stabilizing ligands to tether nanoparticles in situ, improving the stability of nanoparticles. In this case, we develop FSC in nanoscale reactors established by core–shell polymeric nanofibers, to realize one-step fabrication of highly stable, water-resistant, and greatly flexible PNCs/polymer fibrous films at room temperature. This easy-to-perform and one-step FSC process for preparation of PNCs/polymer films takes advantage over the common procedures usually involving synthesis of PNCs, incorporation into polymeric hosts, and film forming, and also reduces about 40% of waste output compared with spin-coating method. The as-prepared PNCs/polymer fibrous films show tunable PL emission ranging from 450 to 660 nm with narrow FWHM of 18–35 nm. More importantly, compared to the pristine PNCs showing complete PL quenching after storage under ambient condition for 10 d or immersed in water for 5 h, PNCs/polymer nanofiber films show almost no change in PL after storage at atmosphere for 90 d and maintain 75% PL after storage in air for 3 d. Here, core–shell nanofiber reactors were constructed via electro-microfluidic spinning technique to carry out FSC in ambient air at room temperature, yielding PNCs/polymer fibrous films which keep constant in PL after storage at atmosphere for 90 d and retain 82% PL after immersed in water for 120 h. PMMA was chosen as core material owing to its high transparency up to 92%, excellent mechanical property, and good compatibility with precursor solutions of CsPbBr3. Similarly, thermoplastic polyurethane (TPU) was utilized as shell material owing to its good antioxidation and water resistance especially moisture stability.

2. Results and Discussion

In this paper, we employed an electro-microfluidic spinning technique to implement FSC allowing one-step rapid preparation of highly stable PNCs/polymer fibrous films at room temperature. In our previous work, PNC/poly(methyl methacrylate) (PMMA) nanocomposites were fabricated at junctions formed between microfluidic-spinning microfibers and a spin-coating layer, to maintain 75% PL after storage in air for 3 d. Here, core–shell nanofiber reactors were constructed via electro-microfluidic spinning technique to carry out FSC in ambient air at room temperature, yielding PNCs/polymer fibrous films which keep constant in PL after storage at atmosphere for 90 d and retain 82% PL after immersed in water for 120 h. PMMA was chosen as core material owing to its high transparency up to 92%, excellent mechanical property, and good compatibility with precursor solutions of CsPbBr3. Similarly, thermoplastic polyurethane (TPU) was utilized as shell material owing to its good antioxidation and water resistance especially moisture stability. Figure 1a,b shows

![Figure 1](image_url)

Figure 1. Schematic illustrations for fabrication of CsPbBr3–PMMA/TPU fibrous film toward flexible optoelectronic application. a) One-step preparation of CsPbBr3/PMMA/TPU core–shell nanofiber films via electro-microfluidic spinning technique. b) In situ formation mechanism of CsPbBr3/PMMA/TPU fibrous film via FSC strategy. c) Flexible and wearable optoelectronic device constructed from CsPbBr3/PMMA/TPU fibrous film with good water resistance.
Table 1. Characteristics of PNCs/PMMA/TPU fibrous films with different compositions.

| Sample | PL emission peak [nm] | PL QY [%] | PL FWHM [nm] | Diameter [nm] |
|--------|-----------------------|-----------|--------------|---------------|
| CsPb(Br0.3Cl0.7)3/PMMA/TPU | 524 | 39 | 23 | 253 ± 60 |
| Pure CsPbBr3 PNCs | 520 | 42.3 | 21 | – |
| CsPbBr3/PMMA/TPU | 524 | 39 | 23 | 253 ± 60 |
| CsPbBr3/PMMA/TPU | 524 | 39 | 23 | 253 ± 60 |

The high resolution transmission electron microscopy (HRTEM) image testifies high crystallinity of PNCs with lattice fringes measured to be 0.33 nm (Figure 2g). These features reveal the feasibility of in situ generation of PNCs in polymer nanofiber via the one-step electro-microfluidic FSC process.

To further investigate the structure and chemical identity of PNCs/PMMA/TPU fibrous films, we performed energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. EDX spectroscopy reveals the elemental composition of CsPbBr3/PMMA/TPU fibrous film. As shown in Figure 2h, the elemental ratio of Cs:Pb:Br is ≈1:1:3, and the detection of a large amount of C elements is ascribed to the presence of the polymer matrices. Figure 2i shows XRD patterns of CsPbBr3/PMMA/TPU fibrous film and pure CsPbBr3 PNCs. In the XRD pattern of the film, the broadening of diffraction peaks is due to the presence of amorphous polymer matrices, while a series of relatively obvious crystallization peaks (100), (110), (200), (220) of CsPbBr3 could be observed, indicating successful synthesis of PNCs/polymer. Figure 2j shows FT-IR spectra of TPU, PMMA, and CsPbBr3/PMMA/TPU fibrous film. The FT-IR spectrum of TPU demonstrates a symmetric stretching peak of NH at 3438 and 1535 cm⁻¹, a distinct C=O related stretching vibration peak at 1733 cm⁻¹, and a deformation vibration peak of C–O–C at 1078 cm⁻¹. FT-IR spectrum of PMMA manifests strong absorption peaks of methyl group and methylene group at 2950 and 2996 cm⁻¹, and an ester carboxyl absorption peak at 1726 cm⁻¹. Also at 1614 cm⁻¹ is the absorption peak of the unreacted double bond in the polymer while at 1148 cm⁻¹ an ester-based characteristic peak belongs to PMMA. Most of the relevant characteristic peaks are present in the CsPbBr3/PMMA/TPU fibrous film.

We utilized FSC method to prepare perovskite fibrous films with good optical properties and the large tunability in wavelength of fluorescence emission was realized (Figure 3). The CsPbBr3/PMMA/TPU fibrous film has a strong absorption peak at 483 nm and the emission peak is sharp at 525 nm (Figure 3b and Figure S3, Supporting Information). To adjust the PL emission wavelength, mixed halogen PNC fibrous films, CsPb(Br0.3Cl0.7)3/PMMA/TPU and CsPb(Br1.0Cl0.0)3/PMMA/TPU, were synthesized through anion exchange in the electro-microfluidic FSC process. Specifically, the CsPb(Br0.3Cl0.7)3/PMMA/TPU fibrous film shows a PL emission peak centered at 485 nm and UV–vis absorption at 438 nm (Figure 3a). Similarly, the CsPb(Br0.3I0.7)3/PMMA/TPU fibrous film possesses absorption peaks at 509 nm and emission peaks at 616 nm, respectively (Figure 3c). Correspondingly, the CsPb(Br0.3Cl0.7)3/PMMA/TPU, CsPbBr3/PMMA/TPU and CsPb(Br1.0Cl0.0)3/PMMA/TPU fibrous films exhibit blue, green, and red light under irradiation with ultraviolet light, respectively, and have narrow FWHM of 19, 23, and 54 nm, separately. The results indicate that the PNCs are uniform in size and well dispersed in the polymer. To prepare PNCs/PMMA/TPU nanofiber films with different fluorescence emission wavelengths, we changed the concentrations of dopant ions in the precursor solutions. The fluorescence wavelength can be adjusted from 460 to 660 nm (Table 1).

To better understand the effect of polymer coating on the luminescence of PNCs, time-resolved fluorescence decay was
performed (Figure 3e,f). The PL decay curve was fitted by biexponential decay function

$$\text{Fit} = A + B_1 \exp\left( -\frac{t}{\tau_1} \right) + B_2 \exp\left( -\frac{t}{\tau_2} \right)$$  (1) 

As comparison, CsPbBr$_3$ PNC solution was spin coated on PMMA substrate to make a film, termed pure CsPbBr$_3$ film. The corresponding amplitude $B_1$ (10.8%) of fast decay $\tau_1$ (0.54 ns) for CsPbBr$_3$/PMMA/TPU fibrous film is much smaller than that (45.22%) of the fast decay $\tau_1$ (5.15 ns) for pure CsPbBr$_3$ film (Table S1, Supporting Information). Thus, the trap-assisted recombination from PNCs/polymer is much less compared with CsPbBr$_3$.\textsuperscript{[24]} In addition, the slow decay $\tau_2$ of the CsPbBr$_3$/PMMA/TPU fibrous film related to radiative recombination is 21.74 ns, larger than the value 20.02 ns for pure CsPbBr$_3$ film. The increase in fluorescence lifetime could be due to the fact that the polymer matrices have a role in limiting the ion migration of the generated CsPbBr$_3$, whilst well separating PNCs to decrease energy transfer among neighboring dots. In general, the value $\tau$ of CsPbBr$_3$/PMMA/TPU fibrous film is 19.4 ns while that of pure CsPbBr$_3$ film is 13.3 ns.

It is well known that PNCs and their films are very sensitive to moisture and are susceptible to fluorescence quenching. Interestingly, PNCs/PMMA/TPU fibrous films synthesized via electro-microfluidic FSC method herein have significantly improved air stability and water resistance (Figure 4). In order to verify this, we performed long-term stability tests on CsPbBr$_3$ film and CsPbBr$_3$/PMMA/TPU fibrous film under storage at 25 °C and 80% humidity. As shown in Figure 4a, the CsPbBr$_3$/PMMA/TPU fibrous film has almost no change in fluorescence intensity after stored for 90 d, while the CsPbBr$_3$ film shows complete fluorescence quenching in 10 d. Then we tested the stability of the fibrous film immersed in water. Figure 4b shows temporal evolution of PL intensity for CsPbBr$_3$/PMMA/TPU fibrous film fully immersed in water, along with that of pure CsPbBr$_3$ film for comparison. For the CsPbBr$_3$/PMMA/TPU fibrous film, the PL intensity decreases slowly upon immersing.
time, and 82% of initial PL intensity remains after 120 h immersion. As a striking contrast, the PL intensity of CsPbBr₃ film only remains less than 10% after 5 h and quenches completely in less than 10 h. Figure 4d shows photographs of the CsPbBr₃/PMMA/TPU fibrous film immersed in water for different periods, which were taken under irradiation with a 365 nm UV light. We can see that even after soaking for 120 h, the film still emits bright green fluorescence. Recently, many efforts have been devoted to the incorporation of PNCs into the polymer matrices to improve the stability of PNCs in water. As shown in Figure 4c, CsPbBr₃/polyacrylic acid-grafted-graphene oxide preserves 70% of initial PL intensity after immersed in water for 12 h,[9a] while 50% at 24 h for CsPbBr₃/poly(styrene-butadiene-styrene),[25] over 50% at 48 h for CsPbBr₃/polyacrylonitrile (PAN),[26] and 81% at 48 h for CsPbBr₃/PS[17] were realized. The CsPbBr₃/PMMA/TPU fibrous film developed in this case, remaining 82% of initial PL intensity after storage in water for 120 h, shows superior water resistance. In addition, no obvious change in water stability of CsPbBr₃/PMMA/TPU film was observed by varying CsPbBr₃ content (Figure S4, Supporting Information). The effect of fiber diameter on PL performance of the CsPbBr₃/PMMA/TPU film was also investigated. As shown in Figure S5 in the Supporting Information, as the fiber diameter increases, the measured PL intensity and PL QY decrease without obvious change in FWHM, and the water resistance gets further improved.

The origin of improved PL stability for PNCs/PMMA/TPU fibrous films is discussed. PNCs suffer from intrinsic instability and accelerated degradation occurs upon contact with water or moisture, resulting in the fluorescence quenching (Figure 4e).[27] In this case, PNCs were in situ generated in PMMA/TPU polymeric nanofibers via FSC (Figure 2), and hydrogen bonding between TPU and the PMMA makes the core–shell architecture of PNCs/PMMA/TPU nanofibers more stable, and hence the inner PNCs are effectively stabilized by the outer polymers (Figure 4f). On one hand, the peripheral polymers well prevent the direct contact of PNCs with ambient oxygen and water, to effectively circumvent fluorescence quenching caused by the interaction with external stimuli. Specifically, CsPbBr₃/PMMA/TPU fibrous film shows water contact angle of 101.82° while that of pure CsPbBr₃ film is 77.95° (Figure S2, Supporting Information). The enhanced hydrophobicity of the fibrous film could efficiently block water outside. On the other hand, PNCs are well immobilized in the polymeric matrix, and hence the migration of ions could be sufficiently suppressed. Therefore, FSC-developed PNCs/PMMA/TPU fibrous films show greatly improved air stability and water stability.

Thanks to their good optical properties and high stability, PNCs/PMMA/TPU fibrous films show potential as color conversion materials to construct various LED devices. The fibrous films prepared by electro-microfluidic FSC process appear outstanding flexibility (Figure 5) and a certain mechanical strength (Figure S6, Supporting Information). As shown in Figure 5a, the as-prepared CsPb(Br₀.₃I₀.₇)₃/PMMA/TPU fibrous film can be easily bended at different angles of 0°, 90°, 150°, and 180° (Figure 5a). As such, flexible optoelectronic devices with desirable shapes could be achieved. For instance, we constructed different shapes of LED devices by covering PNCs/PMMA/TPU fibrous film on UV LED chips. As shown in Figure 5b, a heart-shape LED and a star-shape LED, constructed with use of CsPb(Br₀.₃Cl₀.₇)₃/PMMA/TPU film and CsPb(Br₀.₃I₀.₇)₃/PMMA/TPU film as color conversion material respectively, emit bright light at ON state. In view of the robust water resistance and bending performance, we also made use of this fibrous film to develop a wearable bracelet, which was constructed by using yellow-emitting CsPb(Br₀.₅I₀.₅)₃/PMMA/TPU fibrous

![Image](https://www.advancedsciencenews.com/content/1901694/fig/3/a)

**Figure 3.** UV–vis absorption and emission spectra of a) CsPb(Br₀.₃Cl₀.₇)₃/PMMA/TPU fibrous film, b) CsPbBr₃/PMMA/TPU fibrous film, and c) CsPb(Br₀.₃I₀.₇)₃/PMMA/TPU fibrous film. Inset: Photographs of the corresponding fibrous film under irradiation with a 365 nm UV light. d) PL emission spectra of nanofiber films with different fluorescence wavelengths. Time-resolved fluorescence decay curves of e) CsPbBr₃/PMMA/TPU fibrous film and instrument response function (IRF) (red) and f) CsPbBr₃ PNC film. The data were fitted by the biexponential decay function (solid lines).
film as color conversion materials covered on a GaN chip (Figure 5c). As shown in Figure 5d, the wearable bracelet emits bright white light and it works even when immersed in water. The results suggest the great potential of PNCs/PMMA/TPU fibrous films for flexible optoelectronic applications.

3. Conclusion

In summary, this work demonstrates an easy-to-perform route to prepare PNCs/polymer fibrous films useful for flexible optoelectronic applications. We developed FSC in nanoscale reactors.
established by electro-microfluidic-spun core-shell polymeric nanofibers, to realize one-step fabrication of PNCs/PMMA/TPU fibrous films at room temperature. The as-prepared PNCs/polymer fibrous films have tunable emission over nearly full visible spectrum, excellent air/water stability, and great flexibility. Specifically, PNCs/polymer fibrous films surpass previously reported PNC composites in stability; they keep unchanged in fluorescence properties after stored under ambient condition for 90 d and preserve 82% of initial PL after immersed in water for 120 h. Furthermore, we employed PNCs/PMMA/TPU fibrous films as color conversion materials to construct various flexible LED devices. We anticipate FSC strategy can be used universally as alternative green synthesis route for fabrication of various nanoparticles/polymer nanofiber films with high performance.

4. Experimental Section

Materials: All chemicals used in this work were commercially available and used without further purification. Lead oxide (PbO, 99.9%), barium acetate (C$_2$H$_3$CsO$_2$, 99%), oleic acid (OA, 85%), oleylamine (OLA, 85%), tetraoctylammonium bromide (C$_{32}$H$_{68}$BrN, 98%), tetraoctylammonium chloride (C$_{32}$H$_{68}$ClN, 98%), tetraoctylammonium iodide (C$_2$H$_3$H$_4$N, 98%), dichloromethane (CH$_2$Cl$_2$, 99.5%), toluene (C$_7$H$_8$, AR), dimethylformamide (DMF, AR), and TPU extrusion grade (SU) were purchased from Tokyo Chemical Industry.

Preparation of Precursor Solutions: To prepare the Cs$^+$/Pb$^{2+}$/PMMA precursor solution, PbO (4 mmol), C$_2$H$_3$CsO$_2$ (4 mmol), oleic acid (16 mL), and oleylamine (4 mL) were added into a 50 mL glass vessel. The mixture was stirred until clarified, followed by the addition of 4 g of PMMA. The resultant mixture was stirred for 48 h to yield the Br'/PMMA precursor solution.

To prepare the Br'/PMMA precursor solution, tetraoctylammonium bromide (1.2 mmol), OA (3 mL), and OLA (1 mL) were added into 40 mL of solvent mixture of CH$_2$Cl$_2$ and toluene (1:1 in volume ratio) in a 50 mL glass vessel. The mixture was stirred until clarified, followed by the addition of 4 g of PMMA. The resultant mixture was stirred for 48 h to yield the Br'/PMMA precursor solution.

2.5 g of TPU was dissolved in 50 mL of DMF by mechanical stirring at 60 °C for 48 h. The shell precursor solution was placed overnight to eliminate bubbles for further use.

Synthesis of CsPbBr$_3$/PMMA/TPU Fluorescent Fibrous Films via FSC: The fabrication of CsPbBr$_3$/PMMA/TPU fluorescent fibrous films was performed on an electro-microfluidic spinning device (Nanjing Janus New-Materials Co. Ltd). A three-fluid coaxial electro-microfluidic spinning mode was designed to fabricate the core-shell fibrous film. Three syringes were used and each one was connected to a separate needle. Two needles having a diameter of 0.41 mm flowing through the core solution were attached to the Y-shaped inlet of the chip, and a needle having a needle diameter of 0.84 mm flowing on the shell solution was on the side thereof. As such, a three-fluid coaxial electro-microfluidic system was obtained to fabricate CsPbBr$_3$/TPU fibrous film. The three precursor solutions were separately injected in 20 mL syringes which were placed in the syringe pump that fed continuously into the coaxial system (Figure 1a). The flow speed of the core and shell precursor solutions were 0.2 and 0.6 mL h$^{-1}$, respectively. The tip of the liquid channel was connected to a power supply. The resulting solution was spun for 2 h at 500 rpm at a voltage of 20 kV and a spinning distance of 15 cm for collecting the nonwoven fibrous film. The electro-microfluidic spinning process was manipulated at 24 °C and 80% relative humidity. Then, the collected fibrous film was dried at 70 °C for 3 h in vacuum oven to remove the residual DMF and toluene.

Synthesis of Other Halide Perovskite/Polymer Fibrous Films via FSC: Anion exchange was carried out to prepare PNCs/PMMA/TPU fibrous films with a widely tunable emission, which provide Cl anion and I anion. From C$_2$H$_3$H$_4$ClN and C$_2$H$_3$I$_4$N, respectively. To obtain CsPb(BrCl$_x$I$_{1-x}$)$_3$ and
A yellow-emitting CsPb(Br0.5I0.5)3/PMMA/TPU fibrous film was placed on to provide the solution of CsPbBr3 PNCs. The PNC solution was spin coated onto a glass substrate at room temperature. Fluorescence images were measured on a laser scanning confocal microscope (Leica Company).

Characterization

- X-ray diffraction (XRD) patterns were obtained from a D8000 X-ray diffractometer (Siemens AG, Munich, Germany) from 5° to 80° at a scanning speed of 5° min⁻¹. The morphology of the fibrous film was observed by SEM with a QUANTA 200 (Philips-FEI, Holland) instrument at 20.0 keV. TEM images were taken with JEOL JEM-2100 operated at 200 keV. The steady-state PL spectra were collected by using a Varian Cary Eclipse spectrophotometer at room temperature. PL QY and time-resolved PL were measured by Edinburgh FLS980. UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 900 UV–vis spectrometer. Fluorescence images were measured on a laser scanning confocal microscope (Leica Company).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21736006), National Key Research and Development Program of China (2016YFB0401700 and 2018YFC1602800), Fund of State Key Laboratory of Materials-Oriented Chemical Engineering (ZK201704 and ZK201716), and Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Conflict of Interest

The authors declare no conflict of interest.
X. Y. Du, Y. W. Zhang, S. Chen, J. Mater. Chem. C 2017, 5, 9398; d) P. Anzenbacher, M. A. Palacios, Nat. Chem. 2009, 1, 165.

[20] a) Q. Zhou, Z. Bai, W. G. Lu, Y. Wang, B. Zou, H. Zhong, Adv. Mater. 2016, 28, 9163; b) J. Song, J. Li, X. Li, L. Xu, Y. Dong, H. Zeng, Adv. Mater. 2015, 27, 7162.

[21] a) G. Yang, X. Li, Y. He, J. Ma, G. Ni, S. Zhou, Prog. Polym. Sci. 2018, 81, 80; b) X. Zhang, X. Gao, L. Jiang, J. Qin, Langmuir 2012, 28, 10026.

[22] a) J. Xue, T. Wu, Y. Dai, Y. Xia, Chem. Rev. 2019, 119, 5298; b) J. Xue, J. Xie, W. Liu, Y. Xia, Acc. Chem. Res. 2017, 50, 1976.

[23] a) P. Zhang, X. Zhao, Y. Ji, Z. Ouyang, X. Wen, J. Li, Z. Su, G. Wei, J. Mater. Chem. B 2015, 3, 2487; b) Z. L. Chen, X. L. Zheng, F. Yao, J. J. Ma, C. Tao, G. J. Fang, J. Mater. Chem. A 2018, 6, 17625.

[24] a) H. C. Cho, S. H. Jeong, M. H. Park, Y. H. Kim, C. Wolf, C. L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T. W. Lee, Science 2015, 350, 1222; b) Z. Ning, X. Geng, R. Comin, G. Walters, F. Fan, O. Voznyy, E. Yassitepe, A. Buin, S. Hoogland, E. H. Sargent, Nature 2015, 523, 324.

[25] C. C. Lin, D. H. Jiang, C. C. Kuo, C. J. Cho, Y. H. Tsai, T. Satoh, C. Su, ACS Appl. Mater. Interfaces 2018, 10, 2210.

[26] P. C. Tsai, J. Y. Chen, E. Ercan, C. C. Chueh, S. H. Tung, W. C. Chen, Small 2018, 14, 1704379.

[27] a) H. S. Kim, J. Y. Seo, N. G. Park, ChemSusChem 2016, 9, 2528; b) T. A. Berhe, W.-N. Su, C.-H. Chen, C.-J. Pan, J.-H. Cheng, H.-M. Chen, M.-C. Tsai, L.-Y. Chen, A. A. Dubale, B.-J. Hwang, Energy Environ. Sci. 2016, 9, 323; c) N. H. Tiep, Z. Ku, H. J. Fan, Adv. Energy Mater. 2016, 6, 1501420.