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## An ultrathin and compact electron transport layer made from novel water-dispersed $\text{Fe}_3\text{O}_4$ nanoparticles to accomplish UV-stable perovskite solar cells†

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UV induced decomposition of perovskite material is one of the main factors to severely destroy perovskite solar cells for instability. Here we report a UV stable perovskite solar cell with an  $\text{Fe}_2\text{O}_3$  electron transport layer (ETL) made by spin-coating water dispersed  $\text{Fe}_3\text{O}_4$  nanoparticles. Devices with  $\text{Fe}_2\text{O}_3$  ETLs prepared from 10 nm  $\text{Fe}_3\text{O}_4$  nanoparticles show nearly no decrease of photoelectric conversion efficiency (PCE) upon continuous exposure to very high UV light irradiation (300 W Xe lamp) for 10 hours in contrast to the  $\text{TiO}_2$  ETL based samples with more than 30% reduction of PCE, and their PCE (14.33) is also much superior to those of devices with  $\text{Fe}_2\text{O}_3$  ETLs made conventionally from  $\text{FeCl}_3$  solution (7.7%). Through the study of  $\text{Fe}_2\text{O}_3$  thin film prepared perovskite solar cells, it is found that compact, high transmittance, low leakage and low transmission impedance devices can be obtained by using an appropriate size of  $\text{Fe}_3\text{O}_4$  nanoparticles. Our major findings are expected to provide a guide to design UV-protected compact electron transport layers for UV-stable perovskite solar cells.

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## Introduction

Solar cells are a widely studied clean energy source.<sup>1–6</sup> Perovskite solar cells have been one of the most important solar cells for sustainable clean energy in recent years,<sup>7–10</sup> and normally consist of five parts: conductive glass such as F-doped tin oxide (FTO) and In-doped tin oxide (ITO), an electron transport layer (ETL), a light absorbing layer that is also called the perovskite layer, a hole transport layer like Spiro-OMeTAD and a black electrode like gold and silver.<sup>11–13</sup> The photoelectric conversion efficiency (PCE) of this type of solar cell has increased from 3.8% to more than 25% within about one decade.<sup>14–17</sup> Although the PCE of perovskite solar cells is high, their stability is still not good enough for practical applications. The first reason is the

corrosion of solar cells by water and oxygen in air, which could be solved by well packaging the solar cells or by treating the outer surface of the solar cells against water in air to directly come into contact with the perovskite layer.<sup>18,19</sup> The second reason is the decomposition of the perovskite layer caused by the rise of temperature during the use of the solar cells. In this case, we can use perovskite materials with better thermal stability or two-dimensional perovskite materials instead of low-thermally stable perovskite materials to achieve stable operation of devices.<sup>20–22</sup> Thirdly, the ultraviolet part of sunlight reacts with the ETLs such as  $\text{TiO}_2$  to decompose the perovskite layer, for which it is highly demanded to study the use of the ultraviolet protection layer for improving the stability.<sup>23,24</sup>

Iron oxide ( $\text{Fe}_2\text{O}_3$ ) is an n-type semiconductor with visible light absorption, which has a suitable energy band position, very good chemical stability and low price.<sup>25–27</sup> Also, it can be considered that the ultraviolet instability of perovskite materials is mainly due to the photocatalytic reaction between the electron transport layer materials and the perovskite layer, which destroys the perovskite layer and reduces the stability of the device. Therefore,  $\text{Fe}_2\text{O}_3$  has been widely used as a UV-stable ETL in perovskite solar cells. Wang *et al.* reported the spin-coating method to prepare an  $\text{Fe}_2\text{O}_3$  thin film as an ETL in perovskite solar cells with 10.7% PCE<sup>28</sup> with stability over 30 days upon exposure to ambient air.  $\text{Fe}_2\text{O}_3$  based devices show good stability performance but their PCE is still low. Guo *et al.* used a Ni doped

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$\text{Fe}_2\text{O}_3$  thin film as an ETL in perovskite solar cells, in which the Ni dopant could effectively improve the conductivity.<sup>29</sup> The PCE of Ni- $\text{Fe}_2\text{O}_3$  ETL based devices reaches 14.2% with a 154% increase compared to that without the  $\text{Fe}_2\text{O}_3$  doped devices. High PCE and stable perovskite solar cells can be obtained by preparing high-quality  $\text{Fe}_2\text{O}_3$  thin films, but it is difficult due to the low electronic conductivity and crystallinity of  $\text{Fe}_2\text{O}_3$ . It has been reported to be an effective approach to prepare  $\text{SnO}_2$  and  $\text{NiO}_x$  thin films by firstly preparing nanoparticles and then assembling them for a thin film.<sup>30–33</sup> At the same time, nanocomposites also have unique properties and wide applications.<sup>34,35</sup>

Here, we made UV-stable perovskite solar cells with  $\text{Fe}_2\text{O}_3$  films by spin-coating adjustable  $\text{Fe}_3\text{O}_4$  water-dispersed nanoparticles. Water-dispersed  $\text{Fe}_3\text{O}_4$  nanoparticles with different sizes can be prepared by magnetic field control, and  $\text{Fe}_2\text{O}_3$  films can be obtained by the post annealing process. The thickness of  $\text{Fe}_2\text{O}_3$  films can be controlled by the spin coating speed, different sizes of  $\text{Fe}_3\text{O}_4$  nanoparticles and concentration of solution. The best device with nanoparticle prepared solar cells has a PCE of 14.3% which is 185% higher than the device using  $\text{Fe}_2\text{O}_3$  ETLs by  $\text{FeCl}_3$  solution with 7.7% PCE. Perovskite solar cells with  $\text{Fe}_2\text{O}_3$  films could retain less than 5% decreased PCE upon continuous 300 W Xe lamp exposure for 10 hours while the  $\text{TiO}_2$  prepared samples show 30% reduction in PCE. The mechanism for excellent performance has been studied by investigating the cell parameters including the size and concentration of  $\text{Fe}_3\text{O}_4$  nanoparticles, thickness and annealing temperature of the layer, transmittance and absorbance of the used light, leakage current and charge transfer and recombination processes of solar cells. Our work provides an easy, promising and environmentally friendly method to prepare UV-stable  $\text{Fe}_2\text{O}_3$  layers to increase the performance of perovskite solar cells.

## Experimental section

### Preparation of $\text{Fe}_2\text{O}_3$ and $\text{TiO}_2$ films

$\text{Fe}_2\text{O}_3$  films with  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared by spin-coating water-dispersed  $\text{Fe}_3\text{O}_4$  nanoparticles with different spin speeds from 3000 to 6000 rpm, different concentrations from 4 mg ml<sup>-1</sup> to 18 mg ml<sup>-1</sup> and different sizes from 5 nm to 20 nm. The as-prepared structures were annealed at different temperatures from 450 °C to 600 °C. The  $\text{Fe}_2\text{O}_3$  film with  $\text{FeCl}_3$  solution was prepared by dissolving  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Alfa Aesar, 97%) in DI water with a concentration of 0.075 M. The as-prepared solution was dropped onto the ITO layer with 4000 rpm for 30 s followed by annealing at 550 °C for 120 min in air. The  $\text{TiO}_2$  ETL was prepared by spin-coating 0.15 g ml<sup>-1</sup> titanium isopropoxide (Alfa Aesar, 95%) ethanol solution with 3000 rpm for 40 s, and then annealed at 500 °C for 120 min.

### Fabrication of perovskite solar cells

Perovskite solar cells were fabricated by a modified two step approach.<sup>36</sup> Firstly, a  $\text{PbI}_2$  solution with 600 mg ml<sup>-1</sup> in DMF

was dropped on the  $\text{Fe}_2\text{O}_3$  substrate with 3000 rpm for 30 s. After spinning  $\text{PbI}_2$  for 10 seconds, 30 ml of 60 mg ml<sup>-1</sup> FAI, 6 mg ml<sup>-1</sup> MABr and 6 mg ml<sup>-1</sup> MACl solution was dropped on the substrate rapidly, and the color of the substrate changed from yellow to brown at the same time. Then the substrate was placed on a hot plate at 150 °C for 10 min in air. The HTL was prepared by spin-coating 72.3 mg ml<sup>-1</sup> of Spiro-OMeTAD solution in acetonitrile at 2000 rpm for 40 s. After the spin-coating of the HTL, devices were oxidized in air for 36 h. Finally, a 100 nm thick Au electrode was deposited by thermal evaporation with a shadow mask (0.15 cm<sup>2</sup> active area).

## Characterization and measurement

The morphologies of the samples were characterized using transmission electron microscopy (JEOL, 2100F) and field-emission scanning electron microscopy (Hitachi, SU8010). The films were also investigated by X-ray diffractometry (Bruker, D8 Advance), X-ray photoelectron spectroscopy (Thermo, Escalab 250Xi) and Raman spectroscopy (Horiba, Labram Hr Evolution). The photoluminescence and time-resolved photoluminescence were tested with a 530 nm laser (Edinburgh Instruments, LP320). The absorbance measurement was tested using UV-2600 (Shimadzu). The photovoltaic parameters of solar cells were measured under Newport solar simulator AM 1.5G irradiation (100 mW cm<sup>-2</sup>) with a Keithley 2400 Source Meter, and IPCE curves were characterized using a Zolix system. Electrochemical Impedance Spectroscopy (EIS) and *M-S* plots were measured under AM 1.5G light conditions with an alternative signal amplitude of 10 mV and in the frequency range of 0.1 Hz–40 kHz (Autolab PGSTAT 302N) in a glove box.

## Results and discussion

A high-quality nanoparticle film requires very good size uniformity, and thereby we use a magnetic field control method to prepare  $\text{Fe}_3\text{O}_4$  nanoparticles to effectively avoid agglomerations of crystal nuclei in the growth process by adjusting the magnetic field while tuning the reaction time for differently sized nanoparticles. Besides, growing in aqueous solution is also a very important condition. Considering that we will apply the nanoparticles in green energy solar cells, we hope to minimize the use of environmentally unfriendly solutions. Fig. 1 shows the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of  $\text{Fe}_3\text{O}_4$  nanoparticles with different sizes. Fig. 1a shows the TEM image of 5 nm  $\text{Fe}_3\text{O}_4$  nanoparticles, in which nanoparticles have a very uniform size. Fig. 1b and c show the TEM images of 10 nm and 20 nm  $\text{Fe}_3\text{O}_4$  nanoparticles, in which nanoparticles have the same morphology, uniform size and good dispersion. Fig. S1 (ESI<sup>†</sup>) shows the images of solution with the same 6 mg ml<sup>-1</sup> concentration (measured by Fe). The different size nanoparticles in the same concentration have different colors which may due to the size effect in light transfer. Fig. 1d shows the HRTEM image of  $\text{Fe}_3\text{O}_4$



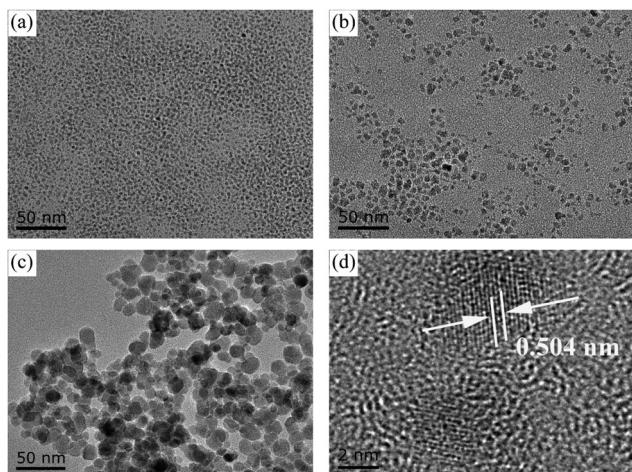


Fig. 1 TEM images of  $\text{Fe}_3\text{O}_4$  nanoparticles: (a) 5 nm, (b) 10 nm and (c) 20 nm. (d) HRTEM of 5 nm  $\text{Fe}_3\text{O}_4$  nanoparticles.

nanoparticles, from which we can see a high-quality crystal with  $2.52\text{ \AA}$  in the (311) plane and that the surface of nanoparticles is clean which is good for carrier transport.<sup>37,38</sup>

Scanning electron microscopy (SEM) was used here to show the morphology of the as-prepared films on the In-doped tin oxide (ITO) structure. Fig. 2a shows the schematic of different  $\text{Fe}_2\text{O}_3$  films which were prepared by nanoparticles and  $\text{FeCl}_3$  solution. Due to the excellent hydrophilic properties of water dispersed nanoparticles, the films can be self-assembled on the ITO surface, and high-quality iron oxide films can be obtained because of the small change in the crystal structure in the annealing process. For the films prepared using  $\text{FeCl}_3$  solution, the spin coated  $\text{FeCl}_3$  film has a good density, but in the post annealing process, the crystallization process of iron oxide will cause the formation of a large number of holes in the original compact film. Fig. 2b shows the morphology of ITO glass without any treatment, which has clear surface and acicular grains. Fig. 2c shows the morphology of ITO glass with the  $\text{Fe}_2\text{O}_3$  film which is prepared by spin-coating 10 nm  $\text{Fe}_3\text{O}_4$  nanoparticles with a concentration of  $6\text{ mg ml}^{-1}$  (measured by Fe). After spin-coating the  $\text{Fe}_3\text{O}_4$  nanoparticles and annealing to form the  $\text{Fe}_2\text{O}_3$  film, the morphology of the substrate surface shows no obvious change in comparison to that of ITO glass, and almost no pin-hole could be found. The morphologies of devices with 5 nm and 20 nm  $\text{Fe}_3\text{O}_4$  nanoparticles are shown in Fig. S2 (ESI†), and are similar to the morphology of 10 nm devices with quite a good compact surface, but a small number of particles accumulated on the surface. Fig. 2d shows the morphology of the  $\text{Fe}_2\text{O}_3$  film which is prepared by spin-coating  $\text{FeCl}_3$  solution and annealing, and we can see that the film is more like a network structure than a compact film. These holes in the mesh may lead to direct contact between the perovskite layer and ITO glass, which will damage the transport process of the carriers of the device. Generally speaking, the local network structure has better hydrophilicity, which is conducive to the diffusion of liquid on the surface, so we performed a contact angle test and is shown in Fig. S3 (ESI†).<sup>39,40</sup> It could be seen

from the test that the compact film prepared by 10 nm particles has a similar contact angle to the network film prepared using  $\text{FeCl}_3$  solution which means that they have similar hydrophilicity. Raman spectra were used here to give more information on samples before and after annealing. From Fig. 2e, we can see that all curves have three characteristic peaks of  $\text{Fe}_2\text{O}_3$  at 247, 288 and  $634\text{ cm}^{-1}$ , and the curve of the sample after annealing has a stronger peak at  $634\text{ cm}^{-1}$  which indicates that the sample has better crystallization properties of  $\text{Fe}_2\text{O}_3$ .<sup>41-43</sup> Fig. S4 (ESI†) shows the X-ray diffraction (XRD) pattern of the prepared sample with  $\text{Fe}_3\text{O}_4$  nanoparticles from which we can see that there is an  $\text{Fe}_3\text{O}_4$  peak nearly at  $30^\circ$  of (220) (JCPDS No. 72-2303) and after annealing there is no obvious peaks of  $\text{Fe}_3\text{O}_4$  which means that  $\text{Fe}_3\text{O}_4$  was converted into  $\text{Fe}_2\text{O}_3$  by the annealing process. The bulge at low angle is caused by the plastic sample table. The absorbance spectrum (Fig. S5, ESI†) shows that devices prepared by different ways have excellent optical transmittance performance and relatively small amounts of absorption at 400 to 600 nm. Through the above discussion, the films prepared with nanoparticles are found to have very good compactness and light transmittance performance. Fig. 3 shows the schematic of the charge transport mechanism of different  $\text{Fe}_2\text{O}_3$  layers. In the compact  $\text{Fe}_2\text{O}_3$  layer which was prepared using  $\text{Fe}_3\text{O}_4$  nanoparticles, carriers can be very well transmitted and separated. But, in  $\text{FeCl}_3$  prepared  $\text{Fe}_2\text{O}_3$  layers, the perovskite layer may be in direct contact with the ITO layer because of the existence of a large number of holes, carriers in the transmission process is easy to recombine.

Fig. 4 shows the typical SEM images of the perovskite layer on  $\text{Fe}_2\text{O}_3$  films with  $\text{Fe}_3\text{O}_4$  nanoparticles. Fig. 4a shows the top-view SEM image of the perovskite layer on the 10 nm  $\text{Fe}_3\text{O}_4$  nanoparticle prepared  $\text{Fe}_3\text{O}_3$  ETL, from which we can see that the perovskite has very good compactness, and the perovskite grain size is large. The perovskite layer on different nanoparticles and the  $\text{FeCl}_3$  prepared  $\text{Fe}_3\text{O}_3$  ETL can be seen in Fig. S6 (ESI†). All of them show the same compact surface, but the perovskite layer on the  $\text{FeCl}_3$  prepared  $\text{Fe}_3\text{O}_3$  ETL has a smaller grain size than others which may be due to the network morphology of the  $\text{Fe}_3\text{O}_3$  film which will increase the recombination of photo-generated carriers in the grain interface. From Fig. 4b, we can see the details of the thickness of different layers where the  $\text{Fe}_2\text{O}_3$  layer is about 20 nm represented with red color and the perovskite layer is about 600 nm represented with green color. Photoluminescence (PL) spectra (Fig. 4c) are used here to show the carrier transfer and separation performance of the perovskite/ $\text{Fe}_2\text{O}_3$  film. A single perovskite layer on the glass substrate is presented as a black curve with a peak at 791 nm which matches the absorbance edge and bandgap of the perovskite. And with the addition of the  $\text{FeCl}_3$  prepared ETL, the value decreased which means that carriers can transport from the perovskite to  $\text{Fe}_2\text{O}_3$  layer. We found that samples with  $\text{Fe}_3\text{O}_4$  prepared films have a higher value than a single perovskite layer which means that the  $\text{Fe}_3\text{O}_4$  prepared ETLs do play the role of passivation layers. The ETL prepared using 10 nm  $\text{Fe}_3\text{O}_4$  particles has the highest value, showing the best



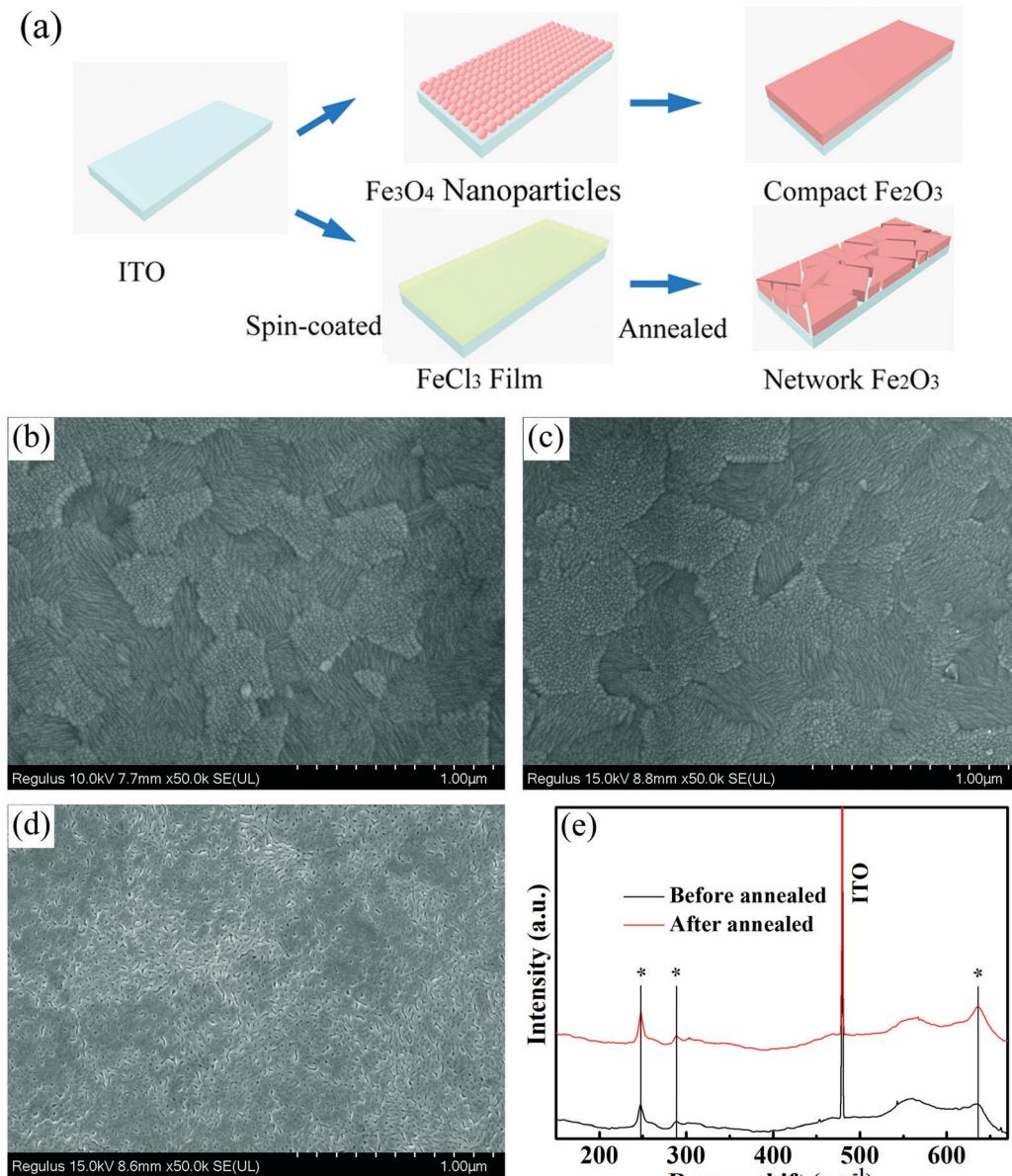


Fig. 2 (a) Schematic of Fe<sub>2</sub>O<sub>3</sub> films. Top view SEM images of substrates: (b) ITO glass, (c) Fe<sub>2</sub>O<sub>3</sub> prepared with 10 nm Fe<sub>3</sub>O<sub>4</sub> nanoparticles and (d) Fe<sub>2</sub>O<sub>3</sub> prepared with FeCl<sub>3</sub> solution. (e) Raman spectra of the Fe<sub>2</sub>O<sub>3</sub> layer.

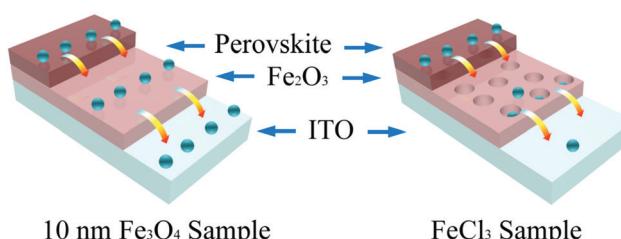


Fig. 3 Schematic of the charge transport model of different Fe<sub>2</sub>O<sub>3</sub> layer based devices.

passivation ability and 5 nm and 20 nm samples have slightly lower values. This may be due to the accumulation of 5 nm nanoparticles in the spin-coating process, which may damage

the properties of the ETL. However, the films prepared with 20 nm nanoparticles may overlap due to the large size of the nanoparticles, and there are some defects in the ETL. The XRD pattern of perovskite is shown in Fig. 4d, from which we can see that the peaks of the perovskite are sharp and represented with an asterisk.<sup>44</sup>

Current density–voltage (*J*–*V*) curves for perovskite with varieties of Fe<sub>2</sub>O<sub>3</sub> films which were prepared with different Fe<sub>3</sub>O<sub>4</sub> nanoparticles and FeCl<sub>3</sub> are shown in Fig. 5, and all samples are tested under AM 1.5G (from 1.2 V to 0 V, a scan step of 0.04 V and a scan rate of 100 mV s<sup>-1</sup>). The photovoltaic parameters including short-current density (*J*<sub>sc</sub>), open-voltage (*V*<sub>oc</sub>), fill factor (FF) and PCE are shown in Table 1 and the summarized average photovoltaic parameters of 20 devices are

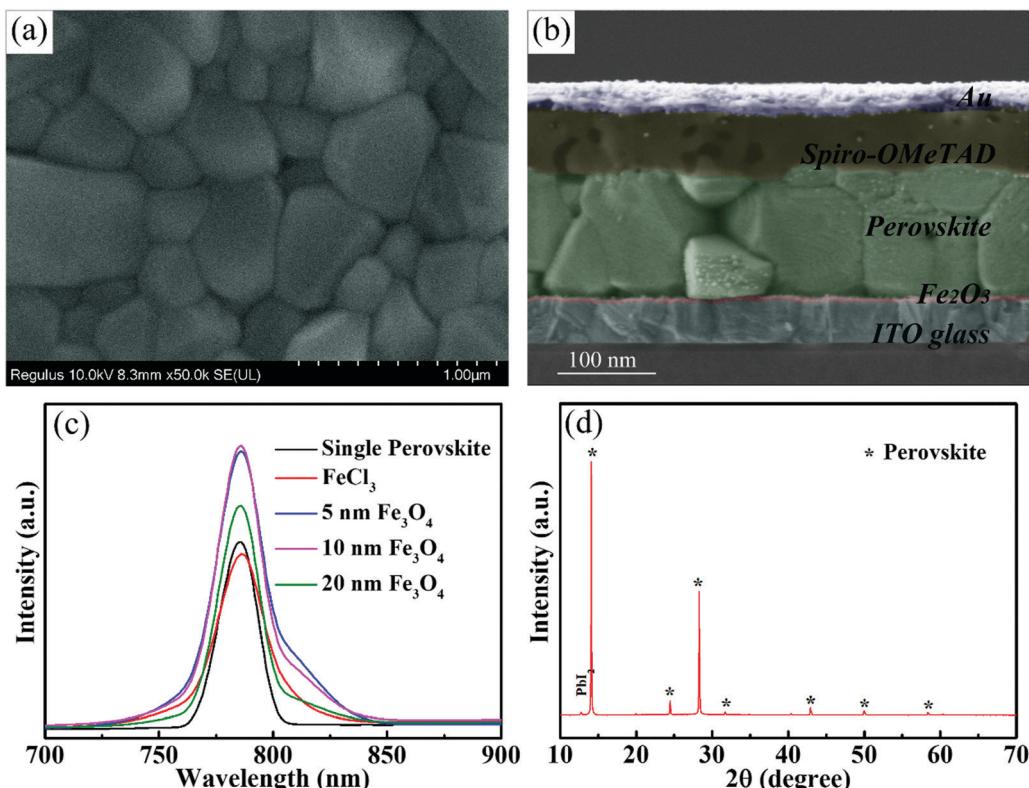


Fig. 4 (a) Top view SEM of the perovskite layer. (b) Cross sectional SEM of the solar cell. (c) PL spectra of perovskite with different substrates. (d) XRD pattern of the perovskite layer.

shown in Table S1 (ESI<sup>†</sup>). From Fig. 5a, we can see that the sample prepared with  $FeCl_3$  has the lowest  $V_{oc}$ ,  $J_{sc}$ , FF and PCE of 0.77 V,  $23.1\text{ mA cm}^{-2}$ , 43.5 and 7.72%. We consider that this low performance, especially in the  $V_{oc}$  is because the  $Fe_2O_3$  layer is not compact enough to fully play the role of an ETL. The potential difference between the quasi-Fermi levels of different ETLs may also cause different  $V_{oc}$ .<sup>45</sup> For the samples prepared with different  $Fe_3O_4$  nanoparticles, the 10 nm sample shows the best performance and has the highest  $V_{oc}$  of 0.99 V, FF of 58.3 and PCE of 14.33%. This highest efficiency also reflects that 10 nm nanoparticles are the best for the  $Fe_2O_3$  film, while the films composed of 5 nm and 20 nm nanoparticles still have some defects, which may be due to the fact that the accumulation of a small number of particles (Fig. S2, ESI<sup>†</sup>) may damage the performance of the ETLs. The incident photon-to-electron conversion efficiency (IPCE) spectrum is also used here to see the light absorption of solar cells shown in Fig. S7 (ESI<sup>†</sup>). The curve shows the absorption edge at 790 nm, which is similar to the absorbance curve of perovskite. The integrated  $J_{sc}$  calculated by the IPCE curve of  $22\text{ mA cm}^{-2}$  is close to the tested value of the  $J-V$  curve; while considering the specular reflection of the sample, the integral current is usually less than the measured value. The devices prepared with 10 nm  $Fe_3O_4$  nanoparticles with different concentrations, spin speeds and annealing temperatures are shown in Fig. S8 (ESI<sup>†</sup>). It could be seen from the samples annealed at different temperatures that the efficiency of solar cells is very low when  $Fe_3O_4$  is not

converted to  $Fe_2O_3$  at low temperatures. Considering all these parameters that may affect efficiency, 10 nm  $Fe_3O_4$  nanoparticle samples with 550 °C annealing temperature, 5000 rpm spin speed and 6 mg ml<sup>-1</sup> (Fe) concentration show the best performance.

Electrochemical impedance spectroscopy (EIS) measurement was performed under AM 1.5G illumination to show the charge transport and recombination performance of different ETLs. Fig. 5b shows the Nyquist plots of different ETLs, in which the tested results are shown with symbol curves and the fitted results are shown with solid line curves. We consider the semicircle at high frequency as the transfer resistance ( $R_{ct}$ ) at the transport layer/perovskite interface and the transmission line at low frequency represents the recombination impedance ( $R_{rec}$ ) of solar cells. The fitted curves and values of  $R_{ct}$  and  $R_{rec}$  are summarized in the ESI<sup>†</sup> (Fig. S9 and Table S2). Due to the effective passivation of the defects on the FTO surface, the  $R_{ct}$  of the  $Fe_3O_4$  nanoparticle film is significantly smaller than that of the sample prepared with  $FeCl_3$  solution. The 10 nm sample with the best passivation effect has a  $R_{ct}$  of 131 Ω and the  $R_{ct}$  of the  $FeCl_3$  prepared sample is 270 Ω. The  $R_{rec}$  of the samples prepared with  $Fe_3O_4$  nanoparticles has a comparable value to the samples prepared with  $FeCl_3$ . The bigger value of  $R_{rec}$  means that it is more difficult for the recombination to occur and 10 nm samples have the highest value of 676 Ω in  $Fe_3O_4$  nanoparticle prepared devices.  $FeCl_3$ , 5 nm and 20 nm samples have values of 573, 465 and 577 Ω. Also, the frequency data to



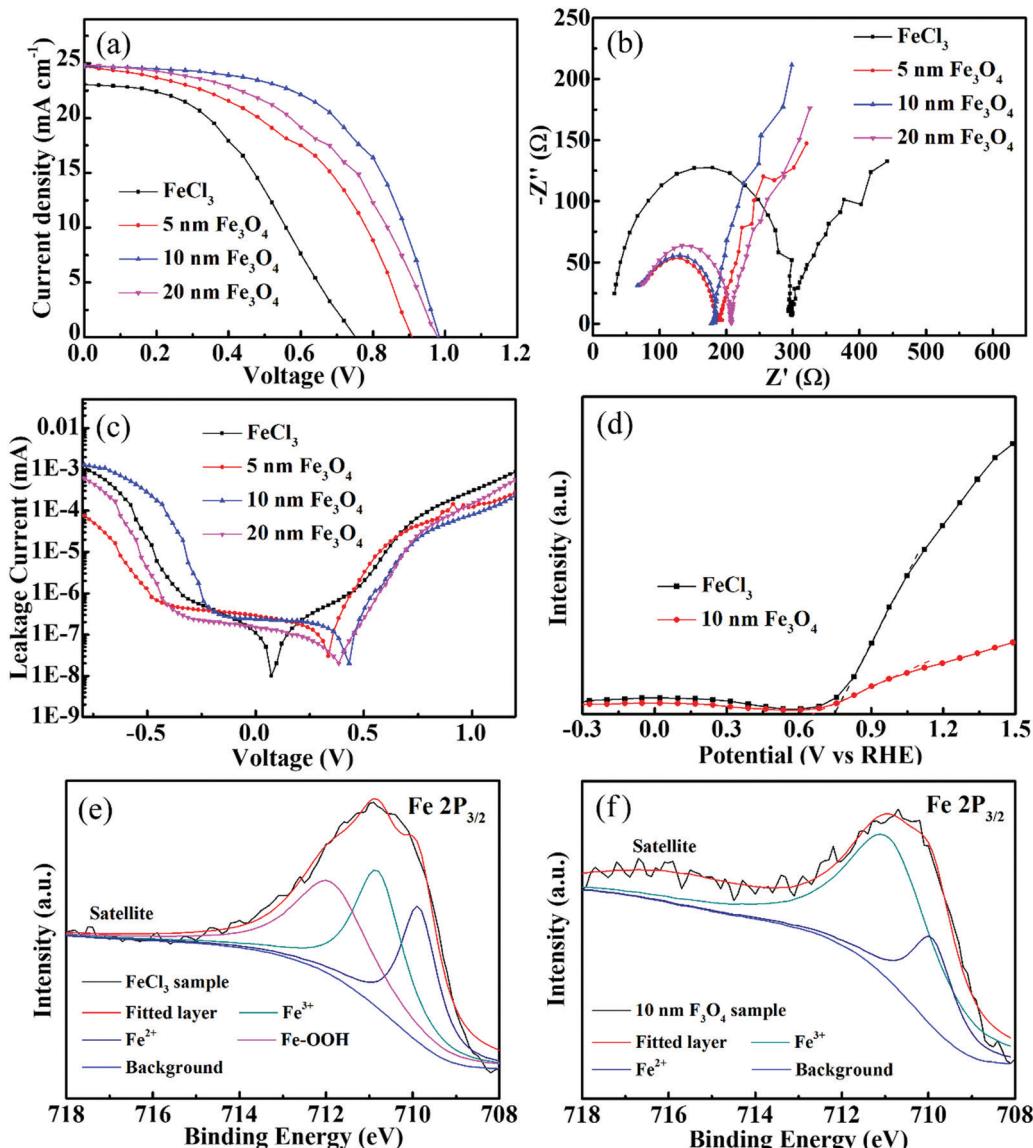


Fig. 5 (a)  $J$ – $V$  curves, (b) Nyquist plots and (c) leakage current of perovskite solar cells with different  $\text{Fe}_2\text{O}_3$ . (d) M–S curves of  $\text{FeCl}_3$  and 10 nm  $\text{Fe}_3\text{O}_4$  nanoparticles samples. (e) and (f) XPS spectra of  $\text{FeCl}_3$  and 10 nm  $\text{Fe}_3\text{O}_4$  nanoparticle samples.

Table 1 Summary of photovoltaic parameters of solar cells with different ETLs

Sample	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	Fill factor (%)	Efficiency (%)
$\text{FeCl}_3$	0.77	23.1	43.5	7.72
5 nm	0.92	24.83	47.83	10.95
10 nm	0.99	24.79	58.31	14.33
20 nm	0.98	24.97	49.62	12.26

the highest point of the semicircle of  $\text{FeCl}_3$ , 5 nm, 10 nm and 20 nm samples are 39 811, 100 000, 125 890 and 125 890 Hz which shows that the nanoparticle based samples have better transport ability than the  $\text{FeCl}_3$  sample.  $J$ – $V$  curves in the dark model are also measured to show the leakage performance of different  $\text{Fe}_2\text{O}_3$  layers and are shown in Fig. 5c. The lowest

point of the leakage curve of nanoparticle samples corresponds to the higher voltage, which indicates that these have better leakage performance than the  $\text{FeCl}_3$  sample. At the same time, the sample with 10 nm nanoparticles at high potential also shows a lower leakage value than others, which indicates that it has better anti leakage ability. The Mott–Schottky (M–S) measurement was used here to further explore the band position of the  $\text{Fe}_2\text{O}_3$  layer by different methods and is shown in Fig. 5d. The slope of the curve has a negative value, which indicates that the material tested is an n-type semiconductor. The potential value of the nanoparticle sample is 0.65 V *versus* reversible hydrogen electrode (RHE) and 0.76 V *versus* RHE of the  $\text{FeCl}_3$  prepared sample. The lower value of the nanoparticle sample means that it has a higher band position than the  $\text{FeCl}_3$  sample which is the same as the  $V_{\text{oc}}$  tendency by  $J$ – $V$  measurement. X-ray photoelectron spectroscopy (XPS) was carried out to



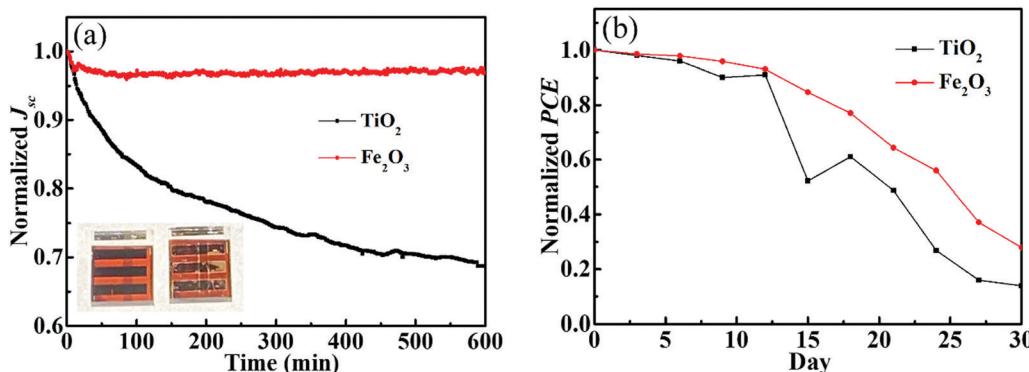


Fig. 6 (a) Maximum power point curves under a 300 W Xe lamp and (b) long time test under AM 1.5G of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  based solar cells.

explore the elemental states of different  $\text{Fe}_2\text{O}_3$  samples. Fig. 5e shows the Fe 2p<sub>3/2</sub> XPS peak of the  $\text{FeCl}_3$  prepared sample, and the peak can be fitted with three curves as  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}-\text{OOH}$ . In the annealing process,  $\text{FeCl}_3$  hydrolyzes to produce  $\text{FeOOH}$  and then oxidizes as much as possible to produce  $\text{Fe}_2\text{O}_3$ . At the same time, some partially oxidized Fe elements may be converted into  $\text{FeO}$ . In the XPS spectrum of the  $\text{Fe}_3\text{O}_4$  nanoparticle prepared sample in Fig. 5f, the curve could be fitted with  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ . In the annealing process, most part of  $\text{Fe}_3\text{O}_4$  was converted to  $\text{Fe}_2\text{O}_3$  and the remaining small amount still exists in the form of divalent iron. From the XPS results, we can find that there is still some  $\text{FeOOH}$  in the  $\text{FeCl}_3$  sample which may be the reason for poor charge transport. Time-resolved photoluminescence (TRPL) curves are shown in Fig. S10a (ESI<sup>†</sup>) and the fitted curves are shown in Fig. S10b (ESI<sup>†</sup>), from which we can see that the carrier lifetime values are 10.71, 22.3, 41.6 and 27.81 ns for single perovskite, 5 nm, 10 nm and 20 nm samples, respectively. This increase of carrier lifetime effectively indicates that the  $\text{Fe}_2\text{O}_3$  film indeed acts as a passivation layer and the 10 nm sample also shows the best passivation performance. The hysteresis effect of different  $\text{Fe}_2\text{O}_3$  layers can be calculated by  $(\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}})/\text{PCE}_{\text{reverse}}$  and is shown in Fig. S11 (ESI<sup>†</sup>), in which the 10 nm sample shows a value of 0.3 and the  $\text{FeCl}_3$  prepared sample shows a value of 0.2.

Stability is one of the most important parameters of perovskite solar cells. In order to show the stability of perovskite cells with the  $\text{Fe}_2\text{O}_3$  layer, we prepared the cells using  $\text{TiO}_2$  ETLs for comparison. The photovoltaic parameters of  $\text{TiO}_2$  based solar cells are shown in Fig. S12 (ESI<sup>†</sup>). We exposed devices to a 300 W Xe lamp for continuous irradiation to obtain the results under strong ultraviolet light, and tested at the maximum power point (MPP). The curve of the  $\text{Fe}_2\text{O}_3$  based cell in Fig. 6a has just a slightly lower which may be due to the decomposition of the perovskite during continuous exposure to the ambient atmosphere. But, for the samples prepared with  $\text{TiO}_2$  ETLs, nearly 30% of the  $J_{sc}$  has been lost after 10 hours of irradiation. It can also be seen from the illustration that after 10 hours of irradiation, the  $\text{Fe}_2\text{O}_3$  based cell in the left shows almost no obvious change, while the  $\text{TiO}_2$  based sample on the right side has obvious white spots. All devices used here are prepared and measured with the same

procedure, which suggests that the PCE difference mainly comes from the  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  layer. Fig. 6b shows the long-time test of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  based cells which have been stored in a drying oven with less than 17% humidity and 25 °C and tested under AM 1.5G. PCEs of devices can be retained at more than 80% after two weeks and the efficiency of the  $\text{Fe}_2\text{O}_3$  based device is still higher than that of the  $\text{TiO}_2$  based one. The efficiency of devices using  $\text{Fe}_2\text{O}_3$  is higher and decreases smoother than that of  $\text{TiO}_2$  devices, which we think is due to the ultraviolet protection ability of  $\text{Fe}_2\text{O}_3$ . After 15 days of the continuous test, there was a significant decrease in the efficiency of both solar cells. We consider this may be due to the instability and etching of the silver electrode.

## Conclusions

In summary, water-dispersed  $\text{Fe}_3\text{O}_4$  nanoparticles were utilized to prepare compact and thin  $\text{Fe}_2\text{O}_3$  film based planar  $\text{Fe}_2\text{O}_3$  based solar cells, in which 14.3% efficiency was reached by ITO/ $\text{Fe}_2\text{O}_3$ /(FAPbI<sub>3</sub>)<sub>0.97</sub>(MAPbBr<sub>3</sub>)<sub>0.03</sub>/Spiro-OMeTAD/Au combination and good stability at more than 95% efficiency after 10 hours of 300 W Xe lamp irradiation was delivered. The superior performance of the as-prepared solar cells is attributed to the excellent passivation of interface defects and high UV stability by the compact nanoparticle-prepared  $\text{Fe}_2\text{O}_3$  layer. This approach holds great promise for inexpensive, UV stable and efficient perovskite solar cells.

## Author contributions

Song Fang fabricated the whole perovskite solar cells and Bo Chen prepared all  $\text{Fe}_3\text{O}_4$  nanoparticles. Bangkai Gu and Linxing Meng commented on the manuscript. All authors wrote the manuscript and analysed the data. Hao Lu designed the whole experimental process. Hao Lu and Changming Li supervised the whole project.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 H. Liang, F. Wang, Z. Cheng, C. Xu, G. Li and Y. Shuai, *ES Energy Environ.*, 2020, **8**, 29–41.
- 2 J. P. Sawant, H. M. Pathan and R. B. Kale, *ES Energy Environ.*, 2020, **10**, 73–79.
- 3 S. Rakhunde, K. Gadave, D. Shinde and P. Bhujbal, *Eng. Sci.*, 2020, **12**, 117–124.
- 4 S. Sayyed, N. Beedri, P. Bhujbal, S. Shaikh and H. Pathan, *ES Mater. Manuf.*, 2020, **10**, 45–51.
- 5 R. Kapadnis, S. Bansode, A. Supekar, P. Bhujbal, S. Kale, S. Jadkar and H. Pathan, *ES Energy Environ.*, 2020, **10**, 3–12.
- 6 S. Satpute, J. Jagtap, P. Bhujbal, S. Sonar, P. Baviskar, S. Jadkar and H. Pathan, *ES Energy Environ.*, 2020, **9**, 89–94.
- 7 J. Burschka, N. Pellet, S. J. Moon, R. Humphrey-Baker, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Nature*, 2013, **499**, 316–319.
- 8 H. P. Zhou, Q. Chen, G. Li, S. Luo, T. B. Song, H. S. Duan, Z. R. Hong, J. B. You, Y. S. Liu and Y. Yang, *Science*, 2014, **345**, 542–546.
- 9 F. Bella, G. Griffini, J.-P. Correa-Baena, G. Saracco, M. Gratzel, A. Hagfeldt, S. Turri and C. Gerbaldi, *Science*, 2016, **354**, 203–206.
- 10 M. Jeong, I. Choi, E. Go, Y. Cho, M. Kim, B. Lee, S. Jeong, Y. Jo, H. Choi, J. Lee, J. Bae, S. Kwak, D. Kim and C. Yang, *Science*, 2020, **369**, 1615–1620.
- 11 M. A. Green, A. Ho-Baillie and H. J. Snaith, *Nat. Photonics*, 2014, **8**, 506–514.
- 12 H. Lu, K. Deng, N. Yan, Y. Ma, B. Gu, Y. Wang and L. Li, *Sci. Bull.*, 2016, **61**, 778–786.
- 13 H. Lu, W. Tian, B. K. Gu, Y. Y. Zhu and L. Li, *Small*, 2017, **13**, 1701535.
- 14 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050–6051.
- 15 H. Lu, J. Zhong, C. Ji, J. Zhao, D. Li, R. Zhao, Y. Jiang, S. Fang, T. Liang, H. Li and C. M. Li, *Nano Energy*, 2020, **68**, 104336.
- 16 J. Yoo, G. Seo, M. Chua, T. Park, Y. Lu, F. Rotermund, Y. Kim, C. Moon, N. Jeon, J. Correa-Baena, V. Bulović, S. Shin, M. Bawendi and J. Seo, *Nature*, 2021, **590**, 587–593.
- 17 NREL, Research Cell Record Efficiency Chart, 2020.
- 18 W. Yang, D. Zhong, M. Shi, S. Qu and H. Chen, *iScience*, 2019, **22**, 534–543.
- 19 L. Ono, Y. Qi and S. Liu, *Joule*, 2018, **2**, 1961–1990.
- 20 J. Yan, W. Qiu, G. Wu, P. Heremans and H. Chen, *J. Mater. Chem. A*, 2018, **6**, 11063–11077.
- 21 B. Wygant, A. Ye, A. Dolocan, Q. Vu, D. Abbot and C. Mullins, *J. Am. Chem. Soc.*, 2019, **141**, 18170–18181.
- 22 J. Seo, H. Nishiyama, T. Yamada and K. Domen, *Angew. Chem., Int. Ed.*, 2018, **57**, 8396–8415.
- 23 B. Roose, J. Baena, K. Godel, M. Graetzel, A. Hagfeldt, U. Steiner and A. Abate, *Nano Energy*, 2016, **30**, 517–522.
- 24 M. Huang, Q. Zhao, Z. Chen, C. Shou, Q. Shen and S. Yang, *Chem. Lett.*, 2019, **48**, 700–703.
- 25 Y. Makimizu, J. Yoo, M. Poornajar, N. Nguyen, H. Ahn, I. Hwang, S. Kment and P. Schmuki, *J. Mater. Chem. A*, 2020, **8**, 1315–1325.
- 26 K. Sivula, F. L. Formal and M. Gratzel, *ChemSusChem*, 2014, **4**, 432–449.
- 27 C. Tang, B. Sun, M. Li, J. Zhang, X. Fan, F. Gao, Y. Tong, L. Dong and Y. Li, *J. Mater. Chem. A*, 2019, **7**, 8050–8054.
- 28 W. Hu, T. Liu, X. Yin, H. Liu, X. Zhao and S. Luo, *J. Mater. Chem. A*, 2017, **5**, 1434–1441.
- 29 J. Guo, Y. Guo, T. Liu, N. Wang, Q. Luo, H. Lin, J. Li, Q. Jiang, L. Wu and Z. Guo, *Nano Energy*, 2017, **38**, 193–200.
- 30 Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin and J. You, *Nat. Photonics*, 2019, **13**, 460–466.
- 31 G. Niu, S. Wang, J. Li, W. Li and L. Wang, *J. Mater. Chem. A*, 2018, **6**, 4721–4728.
- 32 Z. Liu, F. Cao, M. Wang, M. Wang and L. Li, *Angew. Chem., Int. Ed.*, 2020, **132**, 4190–4196.
- 33 J. Kim, P. Liang, S. Williams, N. Cho, C. Chueh, M. Glaz, D. Ginger and A. Jen, *Adv. Mater.*, 2015, **27**, 695–701.
- 34 P. Xie, Y. Liu, M. Feng, M. Niu, C. Liu, N. Wu, K. Sui, R. Patil, D. Pan, Z. Guo and R. Fan, *Adv. Compos. Hybrid Mater.*, 2021, **4**, 173–185.
- 35 H. Wu, Y. Zhang, R. Yin, W. Zhao, X. Li and L. Qian, *Adv. Compos. Hybrid Mater.*, 2018, **1**, 168–176.
- 36 H. Sun, K. Deng, Y. Zhu, M. Liao, J. Xiong, Y. Li and L. Li, *Adv. Mater.*, 2018, **30**, 1801935.
- 37 A. Demortiere, P. Panissod, B. P. Pichon, G. Pourroy, D. Guillou, B. Donnio and S. Begin-Colin, *Nanoscale*, 2011, **3**, 225–232.
- 38 H. Lu, S. Fang, J. Hu, B. Chen, R. Zhao, H. Li, C. Li and J. Ye, *ACS Omega*, 2020, **5**, 19861–19867.
- 39 K. Deng, Z. Liu, Y. Xin and L. Li, *Adv. Mater. Interfaces*, 2018, **5**, 1800499.
- 40 X. Zhang and Y. Qin, *J. Colloid Interface Sci.*, 2019, **545**, 231–241.
- 41 A. Lassoued, B. Dkhil, A. Gadri and S. Ammar, *Results Phys.*, 2017, **7**, 3007–3015.
- 42 J. Lu and C. Tsai, *Nanoscale Res. Lett.*, 2014, **9**, 230–238.
- 43 P. Panta and C. Bergmann, *J. Mater. Sci. Eng.*, 2015, **5**, 100217.
- 44 J. Wang, F. Meng, R. Li, S. Chen, X. Huang, J. Xu, X. Lin, R. Chen, H. Wu and H. Wang, *Sol. RRL*, 2020, **4**, 2000091.
- 45 S. Ryu, J. Noh, N. Jeon, Y. Kim, W. Yang, J. Seo and S. Seok, *Energy Environ. Sci.*, 2014, **7**, 2614–2618.

