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Ultrathin and compact electron transport layer made from novel water-dispersed Fe$_3$O$_4$ nanoparticles to accomplish UV-stable perovskite solar cells

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Abstract

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

Keywords

Perovskite Solar Cells; UV-Stable; Fe$_2$O$_3$ Film; Water-dispersed Fe$_3$O$_4$ Nanoparticles; Passivation Layer
Introduction

Solar cell is a widely studied clean energy source[1-6]. Perovskite solar cell is one of the most important solar cells for sustainable clean energy in recent years,[7-10] which normally consists of five parts: conductive glass such as F-doped tin oxide (FTO) and In-doped tin oxide (ITO), electron transport layer (ETL), light absorbs layer that is also called perovskite layer, hole transport layer like Spiro-OMeTAD and black electrode like gold and silver.[11-13] The photoelectric conversion efficiency (PCE) of this type of solar cells have increased from 3.8% to more than 25% within about one decade.[14-17] Although the PCE of perovskite solar cells is high, the stability is still not good enough for practical applications. The first comes from corrosion of the solar cells by water and oxygen in the air, which could be solved by well packaging the solar cells or treat the outer surface of the solar cells against water in the air to directly contact with the perovskite layer.[18, 19] The second reason is the decomposition of 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 the low-thermally stable perovskite materials to achieve stable operation of devices.[20-22] Thirdly, the ultraviolet part of sunlight reacts with the ETLs such as TiO₂ to decompose the perovskite layer, for which it is highly demanded to study the use of ultraviolet protection layer for improving the stability.[23,24]

Iron oxide (Fe₂O₃) is a n-type semiconductor with visible light absorption, which has a suitable energy band position, very good chemical stability and low price.[25-27] Also, considering 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, Fe₂O₃ has been widely used as a UV-stable ETL in perovskite solar cells. Wang et al. reported the spin-coated way to prepare Fe₂O₃ thin film as a ETL in perovskite solar cell for 10.7% PCE[28] and stability over 30 days under exposure to ambient air. Fe₂O₃ based devices show good stability performance but the PCE is still low. Guo et al. used a Ni doped Fe₂O₃ thin film as a ETL in perovskite solar cell, in which the Ni dopant could effectively improve the conductivity.[29] The PCE of Ni-Fe₂O₃ ETL based device achieves a PCE of 14.2% with 154% increase than that without the doped Fe₂O₃ devices. High PCE and stable perovskite solar cell can be obtained by preparing high-quality Fe₂O₃ thin films, but it is difficult due to the low electronic conductivity and crystallinity of Fe₂O₃. It has been reported an effective approach to prepare SnO₂ and NiO₃ thin film by firstly preparing nanoparticles and then assembling them for a thin film.[30-33] At the same time, nanocomposites also have unique properties and wide applications.[34, 35]

Here, we made UV-stable perovskite solar cells with Fe₂O₃ film by spin-coating adjustable Fe₃O₄ water-dispersed nanoparticles. Water-dispersed Fe₃O₄ nanoparticles with different sizes can be prepared by magnetic field control, and Fe₂O₃ films can be obtained by post annealing process. The thickness of Fe₂O₃ film can be controlled by spin coating speed, different sizes of Fe₃O₄ nanoparticles and concentration of solution. The best device of nanoparticles as-prepared solar cells has an PCE of 14.3 % which is 185 % higher than the device using Fe₂O₃ ETL by FeCl₃ solution with 7.7 % PCE.
Perovskite solar cells with Fe$_2$O$_3$ film could keep less than 5% decreased under 300W Xe lamp continuous exposure for 10 hours which the TiO$_2$ used 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 Fe$_3$O$_4$ nanoparticles, thickness and annealing temperature of layer, transmittance and absorbance of light usage, leakage current and charge transfer and recombination processes of solar cells. Our work provides an easy, promising and environmentally friendly way to prepare UV-stable Fe$_2$O$_3$ layer to increase the performance of perovskite solar cells.

**Experiment Section**

*Preparation of Fe$_2$O$_3$ and TiO$_2$ films*

Fe$_2$O$_3$ films with Fe$_3$O$_4$ nanoparticles were prepared by spin-coated water-dispersed Fe$_3$O$_4$ nanoparticles with different spin speed from 3000 to 6000 rpm, different concentration from 4 mg/ml to 18 mg/ml and different size from 5 nm to 20 nm. The as-prepared structures were annealed with different temperature from 450ºC to 600ºC. Fe$_2$O$_3$ film with FeCl$_3$ solution was prepared by dissolve FeCl$_3$ • 6H$_2$O (Alfa Aesar, 97%) in DI water with concentration of 0.075M. The as-prepared solution was dropped onto the ITO with 4000 rpm 30 s followed by annealing at 550 ºC for 120 min in air. TiO$_2$ ETL was prepared by spin-coating 0.15 g/ml titanium isopropoxide (Alfa Aesar, 95%) ethanol solution with 3000 rpm 40 s, then annealed at 500ºC for 120 min.

*Fabrication of perovskite solar cells*
Perovskite solar cells were fabricated by a modified two steps approach. Firstly, a PbI$_2$ solution with 600 mg/ml in DMF was dropped on the Fe$_2$O$_3$ substrate with 3000 rpm for 30 s. After spinning PbI$_2$ for 10 seconds, dropping 30 ml of 60 mg/ml FAI, 6 mg/ml MABr and 6 mg/ml MACl solution on the substrate rapidly, and the color of substrate changed from yellow to brown at the same time. Then placing the substrate to a hot plate with 150ºC for 10 min in air. The HTL was prepared by spin-coating 72.3 mg/ml of Spiro-OMeTAD solution in acetonitrile at 2000 rpm for 40 s. After the spin-coating of 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$^2$ 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 diffractometer (Bruker, D8 Advance), X-ray photoelectron spectroscopy (Thermo, Escalab 250Xi) and Raman (Horiba, Labram Hr Evolution). The Photoluminescence and Time-resolved photoluminescence were tested with 530 nm laser (Edinburgh Instruments, LP320). The absorbance measurement was tested by UV-2600 (Shimadzu). The photovoltaic parameters of solar cells were measured under Newport solar simulator AM 1.5G irradiation (100 mW cm$^{-2}$) with a Keithley 2400 Source Meter, and IPCE curves were characterized by Zolix system. Electrochemical Impedance Spectroscopy (EIS and M-S plots) was measured under an AM 1.5G light condition with an alternative signal
amplitude of 10 mV and in a frequency range of 0.1 Hz - 40 KHz (Autolab PGSTAT 302N) in 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 Fe$_3$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 we will apply the nanoparticles in green energy solar cells, we hope to minimize the use of environmentally unfriendly solution. **Figure 1** shows the transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of Fe$_3$O$_4$ nanoparticles with different sizes. **Figure 1a** shows the TEM image of 5 nm Fe$_3$O$_4$ nanoparticles, in which nanoparticles have a very uniform size. **Figure 1b** and **1c** show the TEM images of 10 nm and 20 nm Fe$_3$O$_4$ nanoparticles, in which nanoparticles have same morphology, uniform size and good dispersion. **Figure S1** shows the images of solution with same 6 mg/ml concentration (measured by Fe). The different size nanoparticles in same concentration have different colors which may due to the size effect in light transfer. **Figure 1d** shows the HRTEM of Fe$_3$O$_4$ nanoparticles, from which we can see the high-quality crystalline with 2.52 Å as (311) plane and the surface of nanoparticles is clean which is good for carrier transport.$^{[37, 38]}$

Scanning electron microscopy (SEM) was used in here to show the morphology
of as-prepared films on In-doped tin oxide (ITO) structure. Figure 2a shows the schematic of different Fe$_2$O$_3$ films which were prepared by nanoparticles and FeCl$_3$ solution. Due to the excellent hydrophilic property of water dispersed nanoparticles, the films can be self-assembled on the ITO surface, and the high-quality iron oxide films can be obtained because of the little change of crystal structure in the annealing process. For the films prepared by FeCl$_3$ solution, the spin coated FeCl$_3$ film has a good density, but in the post annealing process, the crystallization process of iron oxide will cause a large number of holes in the original compact film. Figure 2b shows the morphology of ITO glass without any treatment, which has clear surface and acicular grains. Figure 2c shows the morphology of ITO glass with Fe$_2$O$_3$ film which is prepared by spin-coated 10 nm Fe$_3$O$_4$ nanoparticles with the concentration of 6 mg/ml (measured by Fe). After spin-coated the Fe$_3$O$_4$ nanoparticles and annealing to form the Fe$_2$O$_3$ film, the morphology of substrate surface has no obvious change in comparison to ITO glass, and almost no pin-hole could be found. Morphology of devices with 5 nm and 20 nm Fe$_3$O$_4$ nanoparticles could be found in Figure S2, which have similar morphology of 10 nm devices with quite good compact surface, but a small number of particles accumulated on the surface. Figure 2d shows the morphology of Fe$_2$O$_3$ film which is prepared by spin-coating FeCl$_3$ solution and annealed, from which we can see the film is more like a network structure than a compact film. These holes in the mesh may lead to the direct contact between the perovskite layer and ITO glass, which will damage the carriers’ transport process 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 prepared contact angle test and shown in Figure S3.\cite{39, 40} It could be seen from the test that the compact film prepared by 10 nm particles has the similar contact angle as the network film prepared by FeCl$_3$ solution which means they have similar hydrophilicity. Raman spectra was used in here to show more information of samples before and after annealing. From Figure 2e, we can see all curves have three characteristic peaks of Fe$_2$O$_3$ at 247, 288 and 634 cm$^{-1}$, and the curve of after annealed sample has stronger peak at 634 cm$^{-1}$ which indicates that the sample has better crystallization properties of Fe$_2$O$_3$.\cite{41-43} Figure S4 shows the X-ray diffractometer (XRD) pattern of Fe$_3$O$_4$ nanoparticles prepared sample from which we can see there is Fe$_3$O$_4$ peak at nearly 30° of (220) (JCPDS No. 72-2303) and after annealing there is no obviously peaks of Fe$_3$O$_4$ which means Fe$_3$O$_4$ was transferred to Fe$_2$O$_3$ by annealing process. The bulge in low angle is caused by the plastic sample table. Absorbance spectrum (Figure S5) shows devices prepared by different ways have excellent optical transmittance performance and relatively small amounts of absorption during 400 to 600 nm. Through the above discussion, the films prepared with nanoparticles have very good compactness and light transmittance performance. Figure 3 shows the schematic of charge transport mechanism of different Fe$_2$O$_3$ layers. In compact Fe$_2$O$_3$ layer which was prepared by Fe$_3$O$_4$ nanoparticles, carrier can be very good transmission and separation. But, in FeCl$_3$ prepared Fe$_2$O$_3$ layers, perovskite layer may be directly in contact with ITO layer because of the existence of a large number of holes, carrier in the transmission process is easy to occur a large number of recombination, and finally only a small number of carriers can effectively conduct to ITO.
**Figure 4** shows the typical SEM images of perovskite layer on Fe$_2$O$_3$ films with Fe$_3$O$_4$ nanoparticles. **Figure 4a** shows the top-view SEM image of perovskite layer on 10 nm Fe$_3$O$_4$ nanoparticles prepared Fe$_3$O$_3$ ETL, from which we can see the perovskite has very good compactness, and the perovskite grain size is large. Perovskite layer on different nanoparticles and FeCl$_3$ prepared Fe$_3$O$_3$ ETL can be seen in **Figure S6**. All of them show the same compact surface, but perovskite layer on FeCl$_3$ prepared Fe$_3$O$_3$ ETL has a smaller grain size than others which may due to the network morphology of Fe$_3$O$_3$ film which will increase the recombination of photo-generated carriers in the grain interface. From **Figure 4b**, we can see the details of different layer’s thickness which Fe$_2$O$_3$ layer is about 20 nm with red color and perovskite layer is about 600 nm with green color. Photoluminescence (PL) spectra (**Figure 4c**) is used in here to show the carrier transfer and separation performance of perovskite/Fe$_3$O$_3$ film. Single perovskite layer on glass substrate is presented as black curve with the peak at 791 nm which is matched the absorbance edge and bandgap of perovskite. And with the addition of FeCl$_3$ prepared ETL, the value decreased which means carrier can transport from perovskite to Fe$_2$O$_3$ layer. We found that samples with Fe$_3$O$_4$ prepared films have higher value than that of single perovskite layer which means the Fe$_3$O$_4$ prepared ETLs do play the role of passivation layer. The ETL prepared by 10 nm Fe$_3$O$_4$ particles has the highest value, showing the best 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 process of spin-coating, which may damage the properties of the ETL. However, the films prepared with 20 nm nanoparticles may overlap due to the large size of nanoparticles, and there are some defects.
in the ETL. XRD pattern of perovskite is shown in Figure 4d, from which we can see
the peaks of perovskite is sharp and signed with asterisk.\textsuperscript{[44]}

Current density-voltage ($J$-$V$) curves for perovskite with varieties of Fe$_2$O$_3$ films
which were prepared by different Fe$_3$O$_4$ nanoparticles and FeCl$_3$ are shown in Figure
5, all samples are tested under AM 1.5G (from 1.2 V to 0 V, scan step of 0.04 V and
scan rate of 100 mV s$^{-1}$). The photovoltaic parameters including short-current density
($J_{sc}$), open-voltage ($V_{oc}$), fill fact (FF) and PCE are shown in Table 1 and the
summarized average photovoltaic parameters of 20 devices are shown in Table S1.
From Figure 5a, we can see the sample prepared by FeCl$_3$ has the lowest $V_{oc}$, $J_{sc}$, FF
and PCE of 0.77 V, 23.1 mA cm$^{-2}$, 43.5 and 7.72%. We consider this low performance,
especially in the $V_{oc}$ is due to the Fe$_2$O$_3$ layer is not compact enough to fully play the
role of ETL. The potential difference between the quasi-Fermi level of different ETLs
also may cause different $V_{oc}$.\textsuperscript{[45]} For the samples prepared by different Fe$_3$O$_4$
nanoparticles, 10 nm sample show the best performance which 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 best for the Fe$_2$O$_3$ film, while the films composed of 5 nm and 20 nm
nanoparticles still have some defects, which may be due to the accumulation of small
number of particles (Figure S2) 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 cell shown in Figure S7. The curve shows the absorb
edge at 790 nm, which is similar to the absorbance curve of perovskite. The integrated
$J_{sc}$ calculated by IPCE curve is 22 mA cm$^{-2}$ is close to the tested value of $J$-$V$ curve,
while considering the specular reflection of the sample, the integral current is usually less than the measured value. The devices prepared by 10 nm Fe$_3$O$_4$ nanoparticles with different concentration, spin speed and annealed temperature are shown in Figure S8. It could be seen from the samples annealed at different temperatures that the efficiency of the solar cell is very low when Fe$_3$O$_4$ is not converted to Fe$_2$O$_3$ at low temperature. Considering all these parameters that may affect efficiency, 10 nm Fe$_3$O$_4$ nanoparticles samples with 550°C annealing temperature, 5000 rpm spin speed and 6 mg/ml (Fe) concentration show the best performance.

Electrochemical impedance spectroscopy (EIS) measurement was used under AM 1.5G illumination to show the charge transport and recombination performance of different ETLs. Figure 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 in high frequency as the transfer resistance ($R_{ct}$) at the interface of transport layer/perovskite and the transmission line in low frequency represents the recombination impedance ($R_{rec}$) of solar cells. The fitted curves and value of $R_{ct}$ and $R_{rec}$ are summarized in the supporting information (Figure S9 and Table S2). Due to the effective passivation of the defects on the FTO surface, the $R_{ct}$ of the Fe$_3$O$_4$ 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 the $R_{ct}$ of 131 Ω and the $R_{ct}$ of FeCl$_3$ prepared sample is 270 Ω. The $R_{rec}$ of the samples prepared by Fe$_3$O$_4$ nanoparticles has the comparable value of the samples prepared by FeCl$_3$. The bigger value of $R_{rec}$ means the recombination is more difficult to occur and 10 nm samples
have the highest value in Fe$_3$O$_4$ nanoparticles prepared devices of 676 $\Omega$. FeCl$_3$, 5 nm and 20 nm samples has the value of 573, 465 and 577 $\Omega$. Also, the frequency data to the highest point of semicircle of FeCl$_3$, 5 nm, 10 nm and 20 nm sample is 39811, 100000,125890 and 125890 Hz which shows the nanoparticles based samples have better transport ability than that of FeCl$_3$ sample. \( J-V \) curves in dark model also measured to show the leakage performance of different Fe$_2$O$_3$ layer and show in Figure 5c. The lowest point of leakage curve of nanoparticles samples corresponds to higher voltage, which indicates that these have better leakage performance than that of FeCl$_3$ sample. At the same time, the sample with 10 nm nanoparticles in high potential also shows lower leakage value than others, which indicates that it has better anti leakage ability. The Mott-Schottky (M-S) measurement was used in here to further explore the band position of Fe$_2$O$_3$ layer by different methods and shown in Figure 5d. The slope of the curve is a negative value, which indicates that the material tested is an n-type semiconductor. The potential value of nanoparticles sample is 0.65 V versus reversible hydrogen electrode (RHE) and 0.76 V versus RHE of FeCl$_3$ prepared sample. The lower value of nanoparticles sample means it has higher band position than that of FeCl$_3$ sample which is same with the \( V_{oc} \) tendency by \( J-V \) measurement. The X-ray photoelectron spectroscopy (XPS) was carried out to explore the elemental states of different Fe$_2$O$_3$ samples. Figure 5e shows the Fe 2P$_{3/2}$ XPS peak of FeCl$_3$ prepared sample, and the peak can be fitted with three curves as Fe$^{3+}$, Fe$^{2+}$ and Fe-OOH. In the process of annealing, FeCl$_3$ hydrolyzes to produce FeOOH, and then oxidizes as much as possible to produce Fe$_2$O$_3$. At the same time, some partially oxidized Fe elements may be converted into FeO. For the
XPS of Fe$_3$O$_4$ nanoparticles prepared sample in Figure 5f, the curve could be fitted with Fe$^{3+}$ and Fe$^{2+}$. In annealing process, most part of Fe$_3$O$_4$ was convert to Fe$_2$O$_3$ and little amount still exists in the form of divalent iron. From the XPS results, we can find there still some FeOOH in FeCl$_3$ sample which may be the reason for poor charge transport. Time-resolved photoluminescence (TRPL) curves are shown in Figure S10a and the fitted curves are shown in Figure S10b, from which we can see 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 sample, respectively. This increase of carrier lifetime effectively indicates that the Fe$_2$O$_3$ film indeed acts as a passivation layer and 10 nm sample also shows the best performance in passivation performance. The hysteresis effect of different Fe$_2$O$_3$ layer can be calculated by $(\text{PCE}_{\text{reverse}}-\text{PCE}_{\text{forward}})/\text{PCE}_{\text{reverse}}$ and shown in Figure S11, in which 10 nm sample shows the value of 0.3 and FeCl$_3$ prepared sample shows the 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 Fe$_2$O$_3$ layer, we prepared the cells using TiO$_2$ ETL for comparison. The photovoltaic parameters of TiO$_2$ based solar cell could be found in Figure S12. We exposed devices to 300W Xe lamp for continuous irradiation which can obtain the results under strong ultraviolet light, and tested at maximum power point (MPP). The curve of Fe$_2$O$_3$ based cell in Figure 6a has just a little bit lower which may be due to the decomposition of the perovskite during continuous exposure to atmospheric atmosphere. But, for the samples prepared by TiO$_2$ ETL, 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 Fe$_2$O$_3$ based cell in the left
has almost no obvious change, while the TiO$_2$ based sample in the right side has obvious white spots. As all devices used here are prepared and measured with the same procedure, which suggests that the PCE difference mainly come from the Fe$_2$O$_3$ and TiO$_2$ layer. Figure 6b shows the long-time test of Fe$_2$O$_3$ and TiO$_2$ based cells which have been stored in drying oven with less than 17% humidity and 25°C and tested under AM 1.5 G. PCEs of devices can keep more than 80% after two weeks and the efficiency of Fe$_2$O$_3$ based devise still higher than that of TiO$_2$ based one. The efficiency of devices using Fe$_2$O$_3$ is higher and decrease smoother than that of TiO$_2$ devices, which we think this is due to the ultraviolet protection ability of Fe$_2$O$_3$. After 15 days of 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 Fe$_3$O$_4$ nanoparticles was utilized to prepare compact and thin Fe$_2$O$_3$ film based planar Fe$_2$O$_3$ based solar cells, of which 14.3% efficiency was reached by ITO/Fe$_2$O$_3$/(FAPbI$_3$)$_{0.97}$(MAPbBr$_3$)$_{0.03}$/Spiro-OMeTAD/Au combination and good stability of 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 Fe$_2$O$_3$ layer. This approach holds great promises for inexpensive, UV stable and efficient perovskite solar cells.
Author contributions

Song Fang fabricated the whole perovskite solar cells, Bo Chen prepared all Fe₃O₄ 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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Figure Captions

Figure 1. TEM images of Fe₃O₄ nanoparticles: a) 5 nm, b) 10 nm and c) 20 nm. d) HRTEM of 5 nm Fe₃O₄ nanoparticles.

Figure 2. a) Schematic of Fe₂O₃ films. Top view SEM images of substrates: b) ITO glass, c) Fe₂O₃ prepared by 10 nm Fe₃O₄ nanoparticles and d) Fe₂O₃ prepared by FeCl₃ solution. e) Raman spectra of Fe₂O₃ layer.

Figure 3. Schematic of charge transport model of different Fe₂O₃ layer based devices.

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

Figure 5. a) J-V curves, b) Nyquist plots and c) Leakage current of perovskite solar cells with different Fe₂O₃. d) M-S curves of FeCl₃ and 10 nm Fe₃O₄ nanoparticles samples. e) and f) XPS spectra of FeCl₃ and 10 nm Fe₃O₄ nanoparticles sample.

Figure 6. a) Maximum power point curves under 300 W Xe lamp and b) long time test under AM 1.5 G of Fe₂O₃ and TiO₂ based solar cells.

Table 1. Summary of photovoltaic parameters of solar cells with different ETLs
Figure 1
Figure 2
Figure 3

10 nm Fe₃O₄ Sample  FeCl₃ Sample
Figure 4
Figure 5
Figure 6
| Sample  | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | Fill Factor (%) | Efficiency (%) |
|---------|--------------|--------------------------|-----------------|----------------|
| 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          |

Table 1