

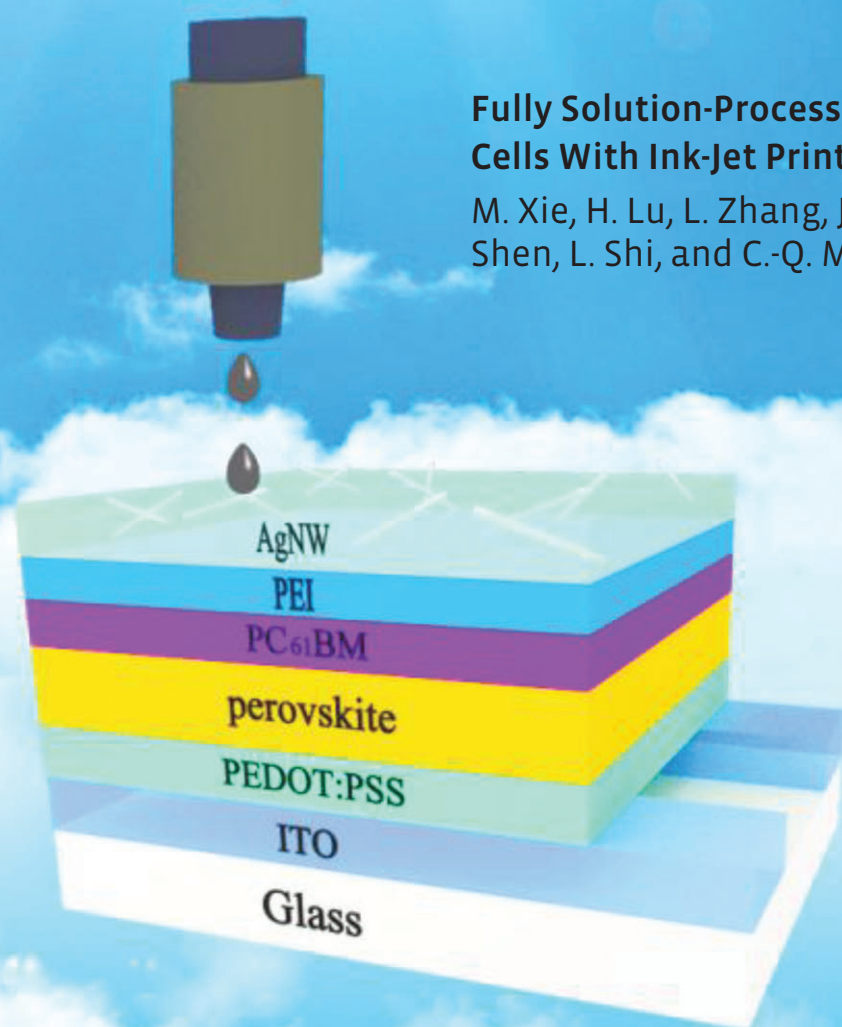
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Fully Solution-Processed Semi-Transparent Perovskite Solar Cells With Ink-Jet Printed Silver Nanowires Top Electrode

Menglan Xie, Hui Lu, Lianping Zhang, Jie Wang, Qun Luo,* Jian Lin,* Lixiang Ba, Hong Liu, Wenzhong Shen, Liyi Shi,* and Chang-Qi Ma*

Owing to the sensitivity of the perovskite thin film to solvent, preparation of metal top electrode by solution process is of great challenging. This is the key technology for the realization of fully solution processed perovskite solar cells. In this paper, we report the preparation of transparent silver nanowires (AgNW) top electrode for perovskite solar cells using inkjet printing process. Experiment results demonstrate that low device performance with low fill factor was obtained when the AgNW is directly printed onto the PC₆₁BM layer. This is ascribed to the mismatched work functions of the AgNW electrode and PC₆₁BM layer, and the solvent assisted chemical corrosion of the AgNW electrode by halogen anions. By inserting a thin layer of polyethylenimine (PEI), the charge injection barrier between PC₆₁BM and AgNW electrode was minimized. More importantly, such a thin PEI layer suppresses the chemical corrosion of AgNW electrode during printing, yielding a condensed and uniform AgNW networks. The introduction of a thin PEI layer greatly improves the device performance and stability. A high power conversion efficiency of 14.17% with an averaged light transmittance of 21.2% was achieved for the PEI/AgNW cells. In addition, improved performance stability was measured for the PEI/AgNW cells.

1. Introduction

Organic-inorganic halide perovskite solar cells are considered as the most promising next generation photovoltaic technology owing to their high power conversion efficiencies (PCE) and potential low processing cost. The highest PCE reported thus far for the perovskite solar cells is 22.1%,^[1] and the cost of perovskite solar cell can be lower than that of the traditional energy sources.^[2] In terms of device fabrication, highly crystalline perovskite thin films can be prepared via solution process, such as printing^[3] or coating procedure,^[4] which are considered as simple and economical mass production procedures. High vacuum-based thermal evaporation is typically used to deposit the metal electrode for the perovskite solar cells,^[5] which tends to be the bottom neck for the mass production of perovskite solar cells. Preparation of top metal electrode using solution processes is therefore the key technology to fully realize low-cost

perovskite solar cells. In this respect, Han et al. reported a pioneering work of using printed carbon black/graphite composite material as top electrode for perovskite solar cells, and a high power conversion efficiency of 12.8% with excellent long-term stability were achieved,^[6] demonstrating the possibility of realizing fully solution-processed perovskite solar cells. Recently, device performance was further increased to 15.8% after optimization on the perovskite composite and interfacial layers.^[7]

The other highly attractive feature of perovskite solar cells is their tunable optical band gap, which makes them excellent candidates for tandem cells.^[8] By using a transparent top electrode, semi-transparent perovskite solar cells can be also used as solar windows in building integrated photovoltaics.^[9] To achieve high performance semi-transparent perovskite solar cells, transparent top electrode plays also a very important role. Till now, different type of transparent top electrodes, including dielectric-metal-dielectric (DMD) electrode,^[10] conductive metal oxides,^[11] conductive polymers,^[12] silver nanowires,^[13] carbon nanotubes,^[14] graphene,^[15] were reported. Among various semi-transparent top electrodes, silver nanowires (AgNWs) electrodes exhibit excellent application

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prospects for their excellent transparency and electronic conductivity, as well as good solution processibility. Till now, semi-transparent perovskite solar cells based on spray^[16] or spin coated AgNW electrode^[17] were reported, and a good balance of visible light transparency (10–40%) and photovoltaic performance (with PCE of 5–10%) were achieved both for the conventional or inverted devices. Inkjet printing, which can precisely deposit functional materials onto the substrate using a non-contact and maskless approach and can serve as an effective tool for the fabrication of metal electrode.^[18] It is therefore highly interesting to develop AgNW electrode for organic or perovskite solar cells using ink-jet printing. Recently, we reported the use of ink-jet printing process to deposit AgNW top electrode for organic polymer solar cells, our results demonstrated that solvent of the AgNW ink has great influence on the polymer solar cell device performance.^[19] However, to best of our knowledge, using ink-jet printing technique to make AgNW top electrode for perovskite solar cells has not been reported yet.

In this paper, we report the fabrication and performance characterization of semi-transparent perovskite solar cells having ink-jet printed AgNW top electrode. Results show that perovskite solar cells having AgNW electrode directly deposited onto the electron transport layer (PC₆₁BM) display poor device performance, which is on one hand due to the mismatched work functions of the PC₆₁BM layer and silver electrode, on the other hand, due to the solvent corrosion on the perovskite layer during printing. By introducing a thin polyethylenimine (PEI) layer, which serves as the work function modifier as well as the perovskite protecting layer, semi-transparent perovskite solar cells with high power conversion efficiency of more than 14% and good device stability were achieved.

2. Experimental Section

2.1. Materials, Instruments, and Method

Patterned ITO glasses with a sheet resistance of $25\ \Omega\text{sq}^{-1}$ were purchased from Shenzhen South China Xiangcheng Technology Co., Ltd. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS Clevios PVP AI 4083) was purchased from Heraeus Precious Metals GmbH & Co. KG. [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) was purchased from Solenne B.V. Poly(sodium p-styrenesulfonate) (PSSNa, $M_n = 70\,000\ \text{g mol}^{-1}$) was purchased from Acros Organic. For one step to fabricate perovskite layer, PbCl₂ (99%), CH₃NH₂, HI (30% in water) were purchased from Sinopharm Group Co. Ltd. Methylammonium iodide (MAI) was synthesized according to the report.^[20] For anti-solvent to fabricate perovskite layer, PbCl₂ (>99.99%), methylammonium iodide (MAI >99.5%) were purchased from Xi'an Polymer Light Technology Corp. PbI₂ (99.9985%) was purchased from Alfa Aesar, Branched polyethylenimine (PEI, average $M_w \sim 25\,000$ by LS, average $M_n \sim 10\,000$ by GPC) was purchased from Sigma-Aldrich. Ag nanowire dispersions for this study were purchased from Blue Nano (SLV-NW 35S, 10 mg mL⁻¹ in isopropanol), with average 35 nm diameter, and 15 μm length. To avoid nozzle clogging and to achieve better printability, the

AgNW ink was diluted to 1 mg mL⁻¹ with isopropanol. We fixed the printing speed as 16 mm s⁻¹, and a printing space of 60 μm . A balanced transparency and conductivity of the AgNW electrode was achieved by changing the printing times. The transmittance and absorption of the semi-transparent devices were measured using a Lambda 750 UV/VIS spectrometer. The thicknesses of each layer were determined with a AlphaStep profilometer (Veeco, Dektak 150). Scanning electron microscope (SEM) images of the electrodes and solar cells were measured using a field scanning electron microscope (Hitachi S-4800). Atomic Force Microscope images of AgNW film were measuring using Dimension 3100. Transparent AgNW electrodes directly printed onto the glass substrates were made as models to check the conductivity and transparency. Sheet resistance of the conductive films was measured by the multifunction digital four-probe tester. (ST-2258A, Suzhou Jingge Electronic Co., Ltd.).

2.2. Preparation of Perovskite Solar Cells via a One-Step Coating Method

Structural inverted planar perovskite solar cells were fabricated according to the method previous report.^[21] The ITO glass was sequentially cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, followed by ultraviolet-ozone (UVO) treatment for 30 min. PEDOT:PSS (CleviosTM PVP AI 4083) aqueous solution filtered through a 0.45 μm filter was spin-coated on the ITO electrode (3500 rpm, 60 s), and then baked at 140 °C in air for 10 min. Then PSSNa solution (2%, wt. % in water) was spin-coated (3500 rpm, 30 s), and the resulting films were annealed at 140 °C for 5 min. After that the ITO/PEDOT:PSS/PSSNa substrates were then transferred to a nitrogen-filled glove-box for the deposition of perovskite layer.

Methylammonium iodide (MAI, 381.7 mg) and lead chloride (PbCl₂, 222.5 mg, 99%) were stirred in anhydrous DMF (1 mL) at 60 °C overnight to form a perovskite precursor solution. Inside the glovebox, the perovskite precursor solution was spin-coated onto the as-prepared ITO/PEDOT:PSS/PSSNa layer at 6000 rpm for 60 s, and the resulting perovskite precursor films were annealed at 95 °C for 70 min subsequently. After that, PC₆₁BM solution (20 mg mL⁻¹ in chlorobenzene) was then spin-cast onto the CH₃NH₃PbI₃-xCl_x layer at 1000 rpm for 60 s. For devices with the PEI interface layer, PEI solution with different concentration was spin-cast onto the PC₆₁BM at a speed of 5000 rpm for 1 min. Reference perovskite solar cells with thermal evaporated thin Ag layer (100 nm) was deposited through a shadow mask under a vacuum of 10⁻⁵ torr. Semi-transparent perovskite solar cells with AgNW electrode were fabricated by printing AgNWs from the isopropanol dispersion onto the PC₆₁BM or PC₆₁BM/PEI directly using a MicroFab jetlab II inkjet printer. Finally, the solar cells with the printed AgNWs electrodes were annealed at 80 °C for 10 min.

2.3. Perovskite Solar Cells Prepared by Anti-Solvent Method

ITO/PEDOT:PSS substrates for perovskite solar cell fabrication were prepared by the same procedure as described before. Deposition of the perovskite layer is following a method reported

in the literature with slight modification.^[22] Methylammonium iodide (MAI, 206.7 mg), lead iodide (PbI₂, 613.1 mg), and lead chloride (PbCl₂, 38.9 mg) were stirred in a mixture of GBL and DMSO (7:3 v/v, 1 mL) at 60 °C for 3 h to form a perovskite precursor solution. The perovskite precursor was spin-cast at 1000 rpm for 10 s and then was spin-cast at 4500 rpm for 30 s. At the second-step spin-coating, 450 μ L anhydrous toluene was added at 20th second. Then the perovskite layer was annealed at 100 °C for 10 min. The thickness of the CH₃NH₃PbI_{3-x}Cl_x layer is approximately 250–270 nm from the SEM images of the device cross section. The electron transporting layer PC₆₁BM, the PEI protecting layer as well as the silver electrode (both for the thermal evaporated or printed silver electrode) were prepared according to the method described above.

2.4. Device Characterization

Current density versus voltage (*J*–*V*) curves were measured with a Keithley 2400 source meter in nitrogen atmosphere under dark and under simulated solar light (100 mW cm⁻²) from a Class AAA Solar Simulator (Oriel[®] VeraSol-2 LED, Newport). The active area of the cells was 0.09 cm² defined by a shadow mask. External quantum efficiencies (EQE) were measured under simulated one sun operation conditions using a bias light of 532 nm from a solid state laser (Changchun New Industries, MGL-III-532). Light from a 150W tungsten halogen lamp (Osram 64642) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Zolix, Omni-l300) to select the wavelength. The response was recorded as the voltage by an IeV converter (QE-IV Convertor, Suzhou D&R Instruments), using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The test device was kept behind a quartz window in a nitrogen filled container.

Long-term stability of the perovskite solar cells with printed AgNW top electrode was measured with a PVL-T-G8001 photo-voltaics performance decay testing system (Suzhou D&R Instruments) according to the ISOS-L1 testing protocol.^[23] The cells were aged inside the glovebox without encapsulation. The cells were illuminated with a simulated white LED light with color temperature of 3000 K (D&R light L-W3000KA-150). External load was attached to the cells during aging to meet the maximum power output point according to the IV measurement results for individual cell.

3. Results and Discussion

3.1. Conductivity and Transparence of the Ink-Jet Printed AgNW Electrodes

Figure 1a shows the transmission spectra of the ink-jet printed AgNW electrode with different printing times on clean glass substrates. The correlation between the sheet resistance (*R*_s) and averaged visible transparency (AVT) of the AgNW electrode with the printing times is shown in Figure 1b. As seen here, the sheet resistance decreased from 60.5 to 25.9, and to 9.8 Ω sq⁻¹, for the electrodes with printed one, two and three times, respectively,

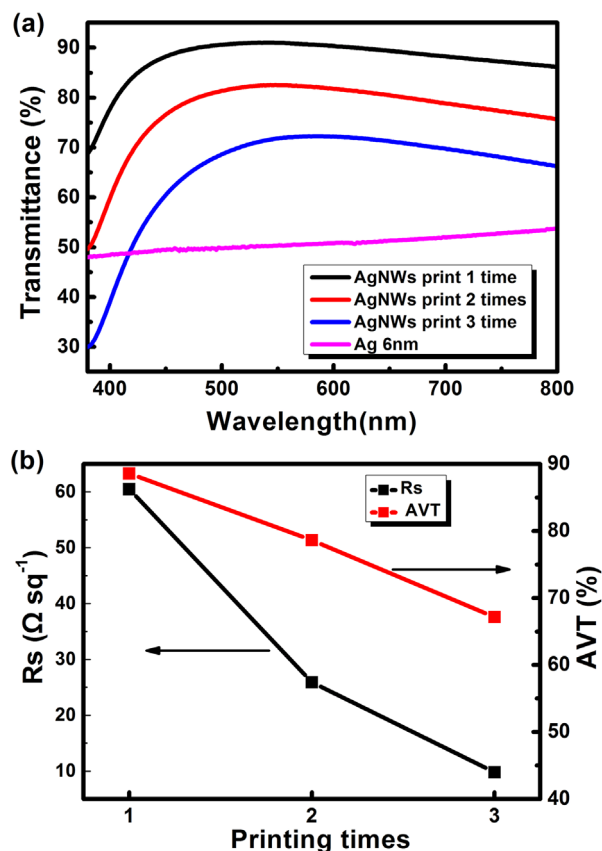


Figure 1. a) Transmission spectra and (b) conductivity of these printed AgNW electrodes.

whereas the average visible transparency (AVT) decreased from 88.6%, 78.6 to 67.2%, respectively. Figure S1a in supporting information shows the SEM of AgNWs printed one to three times, clearly demonstrating the different AgNW density by different printing times, which explains the change of transparency and conductivity of the AgNW electrode. The Haacke Figure of merits for these printed AgNW electrode, as defined as $\Phi_{TC} = T^{10}/R_s$, where *T* is the optical transmission and *R*_s is the electrical sheet resistance,^[24] were calculated to be 1.8×10^{-2} , 5.99×10^{-3} , and $3.82 \times 10^{-3} \Omega^{-1}$ for these films, which are higher than that of the ITO film deposited by sputtering without post thermal annealing ($2.4 \times 10^{-3} \Omega^{-1}$),^[25] demonstrating that excellent characteristics as transparent conductive electrodes for these printed AgNW electrodes. For comparison, transmission spectrum of the thin Ag electrode (7.2 nm) prepared by thermal evaporation is also shown in Figure 1a. As seen here, the thermal evaporated thin Ag electrode with a layer thickness of 7.2 nm showed a low AVT of 47.5%. Surprisingly, this 7.2 nm Ag electrode is not conductive at all, which is speculated to be due to the island formation mechanism.^[26] Figure S1b, in Supporting Information shows the photographic images of the printed AgNW electrode, clearly shows the transparency of the different Ag electrodes. These results clearly demonstrate that AgNWs electrodes fabricated by inkjet-printing are superior to thin metal electrodes prepared by evaporation in terms of conductivity and transparency.

3.2. Perovskite Solar Cells With Different Top Metal Electrodes

Our previous work on printed AgNW electrode for polymer solar cells confirmed that solvent of the AgNW ink have a great influence on the underlying layer, and consequently influence the device performance.^[19] Since perovskite thin film is highly sensitive to the moisture as well as to the organic solvent,^[27] it is still quite challenging to print the AgNW electrode for the perovskite solar cells. Perovskite solar cells with a device structure of ITO/PEDOT:PSS/CH₃NH₃PbCl_xI_{3-x}/PC₆₁BM/metal electrode were fabricated and tested (see Figure S2a, in Supporting Information for the layer sequence of the device), where metal electrode is defined as the top electrode, since it is the last step for finishing device fabrication. The perovskite layer was fabricated via a one-step or anti-solvent procedure to see the influence of the perovskite layer preparation method. For the perovskite cells fabricated via one-step procedure, an additional PSSNa layer was inserted between the PEDOT:PSS and perovskite layer to improve the device performance.^[21,28] Figure 2a and b shows the current density-voltage (*J*-*V*) and external quantum efficiency (EQE) spectra of the two devices. The corresponding photovoltaic performance data are summarized in Table 1.

As seen in Figure 2a and Table 1, perovskite solar cells prepared by a one-step method with thermal evaporated Al top electrode (entry 1) showed a highest power conversion efficiency (PCE) of 11.65% (average PCE of 11.21%) with a *V*_{OC} of 0.86 V, *J*_{SC} of 19.36 mA cm⁻², and an FF of 0.70, which is comparable with the result reported previously.^[21] However, much lower device performance (with averaged PCE of 5.44%) with a typical “S-shaped” *J*-*V* character was found for the “one-step” cells with printed AgNW top electrode (entry 2, Figure 2a). Averaged PCE of 2.13% was also found for the perovskite cells fabricated via an anti-solvent procedure with

printed AgNW electrode (Entry 5), which is much lower than the cells with thermal evaporated Al electrode (entry 4, with averaged PCE of 14.50%). To better understand the reason for the low device performance of the printed AgNW electrode, solar cells with thermal evaporated Ag electrode were also fabricated and tested for both type of perovskite films (Entry 3 and 6). As seen in Figure 2a and c, typical “S-shaped” *J*-*V* curves were also found for both type of cells with e-Ag based cells. Knowing that the work function of Ag (-4.6 eV)^[29] is much higher than the LUMO energy level of PC₆₁BM (-4.01 eV).^[30] The large energy barrier between PC₆₁BM layer and Ag electrode was then ascribed to the main reason for the low device performance of the cells. This was further confirmed by the improved device performance of the cells after inserting a thin interfacial layer, such as PDINO,^[31] PFN,^[32] and PEI^[33] (Figure S3 in supporting information), which have been used in polymer solar cells to minimize the charge injection barrier between PC₆₁BM and silver electrode. Therefore, the mismatched work function between the AgNW electrode and the PC₆₁BM layer is ascribed to be one of the reasons for the low performance of the perovskite solar cells with printed AgNW electrode.

Furthermore, lower *J*_{sc} was measured for these AgNW electrode based cells than corresponding thermal evaporated Ag electrode based cells. Since AgNW is light transparent, and no light reflection is then ascribed to be one of the reason for the lower *J*_{sc}. This can be clearly seen in the EQE spectra in Figure 2b and d, where lower external quantum efficiency over 500–800 nm was measured for the AgNW based cells. However, lower EQE over the entire 350–800 nm was also found for the AgNW based cells than the thermal evaporated Ag electrode based cells. This indicates that there might be other reasons causing the lower performance for the AgNW based cells. Surface morphology of the AgNW electrode was investigated by scanning electronic microscope (SEM). Figure 3a–c depict the top view and cross section SEM images of the AgNW electrode that directly deposited on the PVSK/PC₆₁BM. As seen here, inhomogeneous AgNW electrode with dark spots can be clearly distinguished. Note that the thermal evaporated Ag electrode that deposited on top of PC₆₁BM displays a homogenous surface over a large area (Figure 3d–f), dark spots on the AgNW electrode can be directly related to the printing process. It was reported that in perovskite solar cells halogen anion might migrate through the PC₆₁BM layer and lead to the chemical corrosion of metal electrode.^[34] The dark spots in the printed AgNW electrode can therefore be ascribed the chemical corrosion of the silver electrode during printing. The absence of such a chemical corrosion on the thermal evaporated Ag electrode indicating that solvent in the AgNW inks assist the halogen migration during the printing process. In addition, very rough AgNW surface with lots of nanowires pointing toward the surface was found for the AgNW networks that directly deposited onto the PC₆₁BM layer (Figure 3c). This suggested that the adhesion between the AgNW network and the

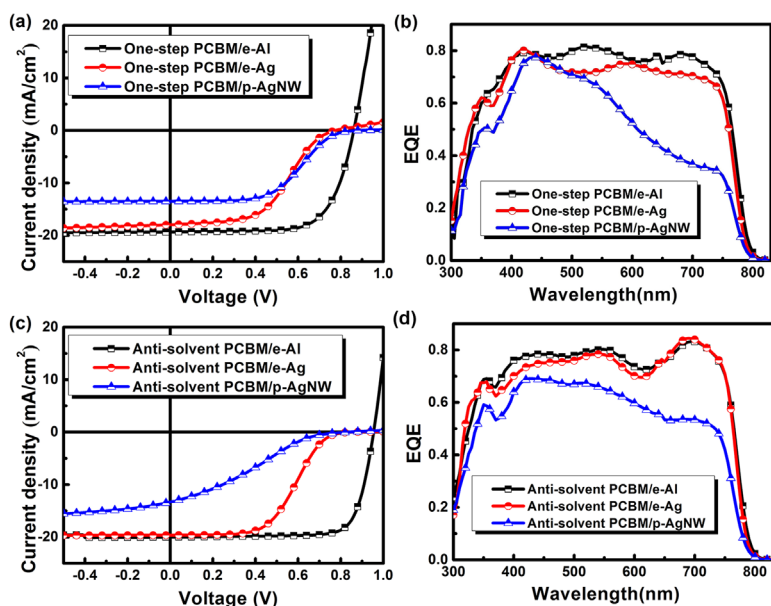


Figure 2. *J*-*V* curves (a, c) and EQE (b, d) of the best perovskite cells without PEI layer prepared by one-step method (a, b) and anti-solvent (c, d) with different top electrode.

Table 1. Photovoltaic performance parameters of the best solar cells with different interface electrodes.

Entry	Electrode	PVSK ^{a)}	J_{sc} (mA cm ⁻²) ^{b)}	V_{oc} (V)	FF	PCE (%)	Averaged PCE (%)
1	e-Al ^{c)}	One-step	19.36	0.86	0.70	11.65	11.21 ± 0.45
2	p-AgNW ^{d)}	One-step	13.51	0.88	0.48	5.71	5.44 ± 0.25
3	e-Ag ^{e)}	One-step	17.97	0.77	0.48	6.64	6.33 ± 0.25
4	e-Al ^{c)}	Anti-solvent	20.00	1.01	0.75	15.15	14.50 ± 0.20
5	p-AgNW ^{d)}	Anti-solvent	12.04	0.87	0.25	2.65	2.13 ± 0.70
6	e-Ag ^{e)}	Anti-solvent	19.64	0.85	0.48	8.01	7.24 ± 0.65

^{a)}Method for preparation of the perovskite films; ^{b)} J_{sc} was calculated by convoluting the EQE spectrum with AM 1.5G sun spectrum; ^{c)}Thermal evaporated silver electrode; ^{d)}Thermal evaporated aluminum electrode; ^{e)}Ink-jet printed silver nanowire electrode.

PC₆₁BM layer is rather poor, which could also lead to poor device performance.

3.3. Improve interface Connection Between PC₆₁BM and AgNW Electrode by PEI Layer

As shown in Table S1 in supporting information, a thin PEI layer can improve the performance of the perovskite solar cells with thermal evaporated Ag electrode, which is ascribed to the decrease of the electron injection barrier between PC₆₁BM and

Ag electrode by lowering the work function of Ag electrode by PEI layer.^[35] Note that “S-shaped” J - V curves were also found for the perovskite cells where AgNW electrode is directly printed on the PVSK/PC₆₁BM surface. A thin PEI layer was then inserted between the PC₆₁BM and printed AgNW electrode. Since the perovskite solar cells prepared by an anti-solvent approach showed higher device performance, interfacial optimization for the printed cells was only performed for the cells prepared by the anti-solvent method. The PEI layer thickness was then optimized by varying the PEI concentration. **Figure 4a** depicts the J - V curves of the fully

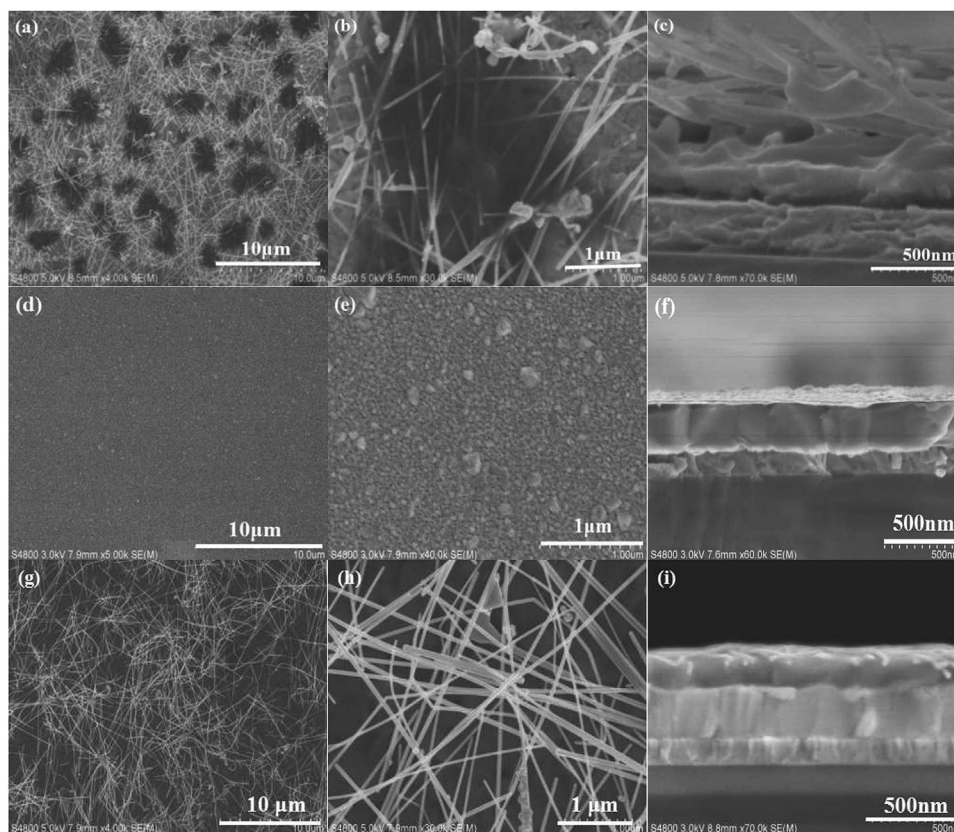


Figure 3. SEM top view images (a, b, d, e, g, h) and cross section view (c, f, i) of the printed AgNW electrode (a–c) and thermal evaporated Ag electrode (d–f) that directly on PVSK/PC₆₁BM surface, and the printed AgNW electrode that deposited on PVSK/PC₆₁BM/PEI surface (g–i).

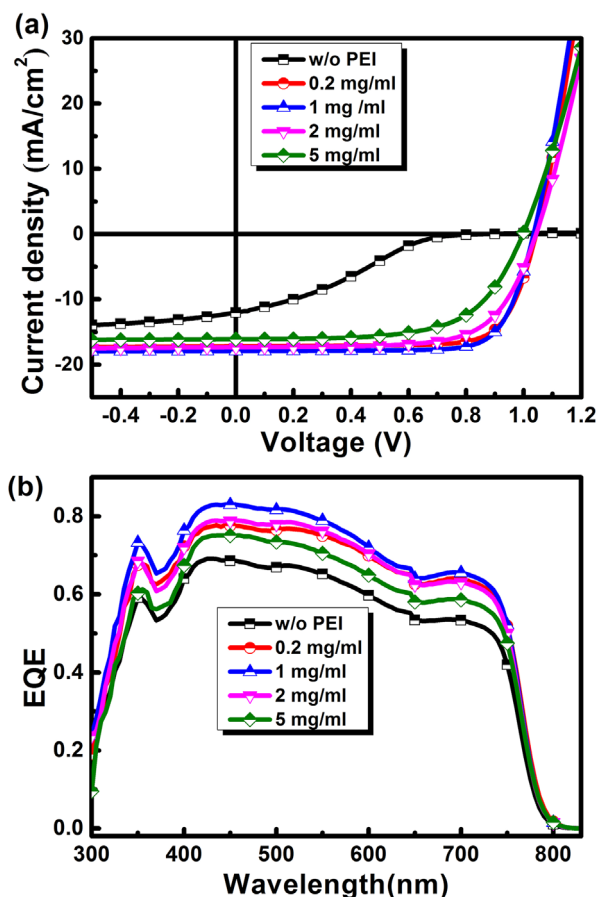


Figure 4. a) J - V curves of devices with PEI between the PC₆₁BM and Ag NW top electrode, where PEI layer was prepared by spin coating PEI solution with different concentration. (b) Corresponding EQE characteristics of the devices.

solution processed perovskite cells with PEI layer prepared from different PEI solutions. For comparison, devices without PEI layer (Entry 5) were also included. As seen here, solar cell with a thin PEI layer prepared from a 0.2 mg mL⁻¹ PEI solution gives a PCE of 13.43% with a high FF of 0.75, where “S-shape” of the J - V curve diminished. The PCE of the PEI included cell is five times higher than that without PEI layer (2.6%, entry 5). In

addition to the FF enhancement, both V_{oc} and J_{sc} were also improved after the insertion of PEI layer (Table 2). With the increase of PEI concentration to 1 mg mL⁻¹, a highest PEC of 13.98% was achieved with a high V_{oc} of 1.04 V, J_{sc} of 17.92 mA cm⁻² and a FF of 0.75 (Table 2, entry 8). Analysis on the light J - V curves reveals that reduced series resistance (R_s) and increased shun resistance (R_{sh}) for the cells after the insertion of PEI layer (Table 2), indicating improved interfacial connection between PC₆₁BM and AgNW electrode after interfacial modification. Further increase of the PEI concentration, however, decreases the device performance, which can be ascribed to the insulating property of PEI film. Nevertheless, the use of PEI layer obviously improves the interfacial connection between the PC₆₁BM and Ag electrode, which consequently improve device performance.

EQE spectra of the corresponding cells are shown in Figure 4b. In comparison with the perovskite cells with opaque silver electrode (see Figure S4, in Supporting Information for a direct EQE spectra comparison between these two devices), quantum efficiency over 600–800 nm decreases for these AgNW based cells, which is ascribed to the less of light reflectance on the AgNW electrode. On the other hand, EQE enhancement over the entire visible light range (300–780 nm) can be seen for the devices with PEI layer, suggesting again that charge injection at the cathode was improved for the PEI involved devices. More interestingly, the PEI/p-AgNW electrode based cells show comparable EQE over 300–600 nm to the device with thermal evaporated Ag electrode based cells. This implies that the PEI layer indeed protect the PC₆₁BM layer, and a good interface connection between PC₆₁BM/PEI/AgNW formed, which are beneficial for device performance achievement.

To further understand the role of PEI layer between the PC₆₁BM and AgNW, SEM images of the ITO/PEDOT:PSS/PSS/PVSK/PC₆₁BM/PEI/AgNW were measured. Figure 3g and h show the top view of the AgNW electrode deposited onto the PC₆₁BM/PEI surface. As seen here, uniform AgNW networks can be detected for the AgNW network on the PC₆₁BM/PEI surface, which is different to the morphology of the AgNW electrode on PC₆₁BM (Figure 3a, b). This indicates that chemical corrosion on the AgNW electrode was totally suppressed after the insertion of PEI layer. In other word, the inserted PEI layer is able to block the halogen anion immigration. This phenomenon was also reported by Tsang et al., where polymeric buffer layer using PEI was found can effectively separate the ZnO-NPs and

Table 2. Photovoltaic performance parameters of the solar cells with different thickness of PEI.

Entry	PEI (mg mL ⁻¹) ^{a)}	J_{sc} (mA cm ⁻²) ^{b)}	V_{oc} (V)	FF	PCE (%) ^{c)}	R_s (Ω cm ²) ^{d)}	R_{sh} (Ω cm ²) ^{d)}
5	0	12.04	0.87	0.25	2.65 (2.13 ± 0.70)	774.13	148.41
7	0.2	17.22	1.04	0.75	13.43 (12.97 ± 0.41)	8.76	6756.76
8	1.0	17.92	1.04	0.75	13.98 (13.21 ± 0.20)	8.24	8602.15
9	2.0	17.33	1.05	0.68	12.37 (11.79 ± 0.59)	11.16	4305.71
10	5.0	16.11	1.00	0.63	10.15 (9.51 ± 0.45)	12.89	5055.61

^{a)} PEI precursor solution for deposition of PEI layer; ^{b)} J_{sc} was calculated by convoluting the EQE spectrum with AM 1.5G sun spectrum; ^{c)} Power conversion efficiency (PCE) of the best cell, the number in the blanket is the averaged PCE over 8 individual devices; ^{d)} R_s and R_{sh} were obtained directly from the slope of the J - V curves of the best cell at the V_{oc} and J_{sc} point.

perovskite.^[36] In addition, in comparison to the AgNW deposited onto the PC₆₁BM directly (Figure 3c), the AgNW electrode on PC₆₁BM/PEI is more compacted and smooth (Figure 3i), suggesting an enhanced adhesion between AgNW and PC₆₁BM. It worth pointing out that, both V_{OC} and FF of the cells with printed AgNW are similar to that with thermal evaporated cell (Entry 3 in Table S1 in Supporting information), indicated the interfacial properties at the PC₆₁BM/PEI/AgNW are similar to that of PC₆₁BM/PEI/e-Ag.

3.4. Fabrication of Semi-Transparent Perovskite Solar Cells

Figure 5a shows the UV–vis absorption and transmittance of the perovskite solar cells with different perovskite layer thickness. The photographic pictures of semitransparent perovskite solar cells are showed in Figure S5, in supporting information. J – V curves and EQE spectra of the corresponding cells are depicted in Figure 5b and c, respectively. The detailed photovoltaic performance data as well as the averaged visible transmittance (AVT) of the cells are summarized in Table 3. As seen here, a PCE of 7.3% with an AVT of 36.5% was achieved for the cell with a thin perovskite layer of 80 nm, which is comparable to that reported in the literature for the semi-transparent perovskite solar cells with Ni micro grid

electrode (PCE of 6.1%, AVT of 38%),^[37] or spray-coated AgNW electrode (3.6%, 44.3% AgNW).^[38] On the other hand, when the perovskite layer thickness is increased to 270 nm, a highest PCE of 14.17% with an AVT of 21.1% was achieved, which are among the highest PCE values reported in the literatures with solution processed top electrode,^[39] or even higher than some of the device with vacuum assisted thermal deposited top electrode.^[40] Although PCE of semitransparent cells with laminated ITO electrode (with a PCE of 15.8%),^[41] or with DC sputtered ITO electrode (with a PCE of 15.3%),^[8a] or with thin Cu/Au film (with a PCE of 16.5%),^[42] the average transmittance of the present AgNW based cell is higher than these cells owing to the high light transmittance of the AgNW electrode.

Figure 5d depicts the histograms of solar cell efficiencies of 30 individual cells with PEI/p-AgNW electrode. Figure S6, in Supporting Information shows the full histograms of V_{OC} , J_{SC} , FF, and PCE. As seen here, most of the cells with PEI/p-AgNW electrode show high V_{OC} of over 1.0 V, J_{SC} of over 17 mA cm^{−2}, FF of more than 0.7, and efficiency of more than 13%, demonstrating an excellent reproducibility for this type of cells. This result confirms again that the protection of the perovskite layer with a thin PEI layer is an effective way to achieve high performance fully solution-processed perovskite solar cells with printed AgNW electrode.

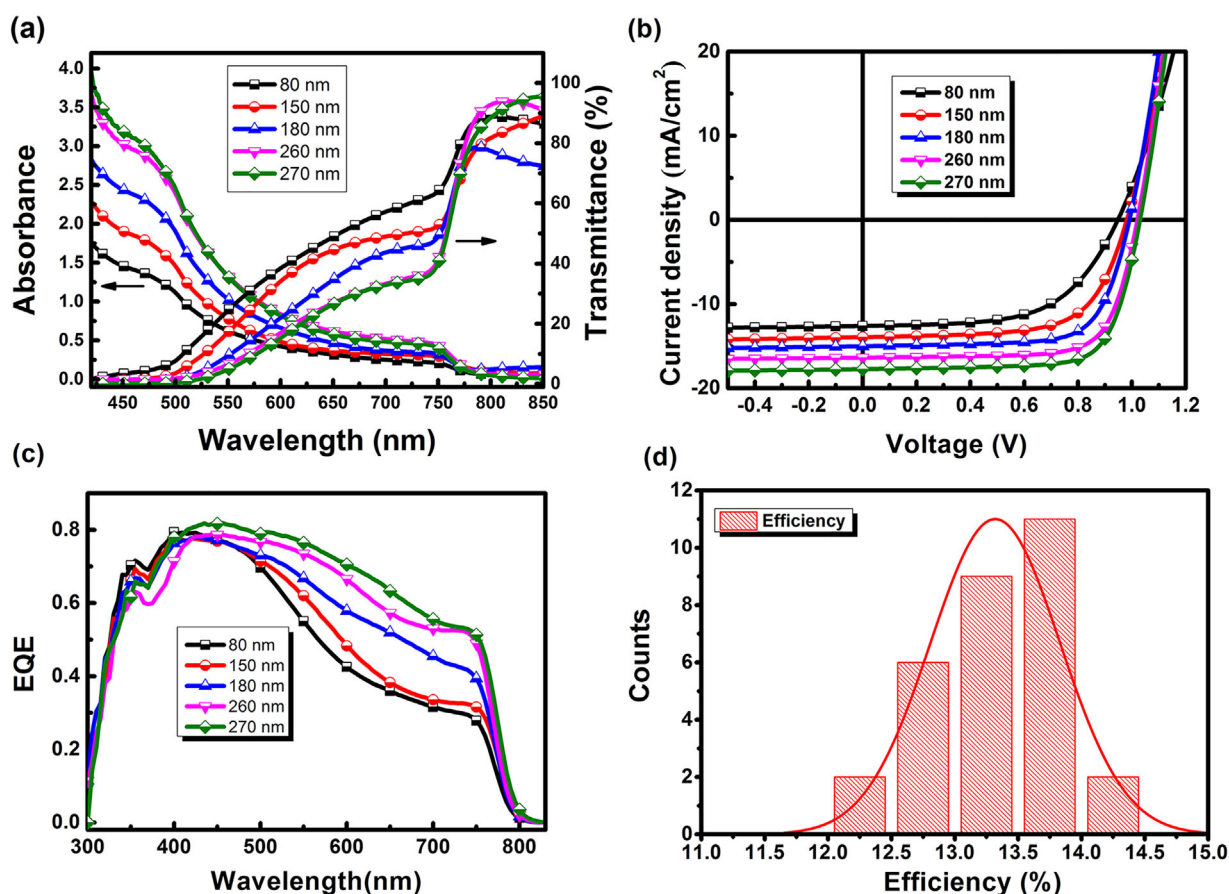


Figure 5. a) UV–vis transmittance and absorption of the perovskite cells with different perovskite layer thickness, the perovskite films were prepared by an anti-solvent method; J – V curves (b) and EQE spectra of the corresponding best cells; (d) Histogram of solar cell efficiencies for 30 individual cells respectively.

Table 3. Summary of the photovoltaic properties of the semi-transparent perovskite solar cells with different perovskite layer prepared by anti-solvent method.

Entry	MAI (mol L ⁻¹) ^{a)}	Thickness (nm) ^{b)}	AVT (%) ^{c)}	J_{sc} (mA cm ⁻²) ^{d)}	V_{oc} (V)	FF (%)	PCE (%) ^{e)}
11	0.7	80	36.5	12.67	0.96	60	7.30 (7.01 ± 0.25)
12	0.9	150	30.6	13.94	1.00	66	9.10 (8.91 ± 0.20)
13	1.1	180	25.6	15.01	1.00	71	10.55 (10.28 ± 0.35)
8	1.3	260	22.6	17.92	1.04	75	13.98 (13.21 ± 0.20)
14	1.35	270	21.1	18.17	1.04	75	14.17 (13.32 ± 0.51) ^{f)}

^{a)}Concentration of the perovskite precursor solution; ^{b)}Layer thickness of the perovskite film, measured by SEM cross section, with uncertainty of 5 nm; ^{c)}Averaged visible transmittance, including glass substrate; ^{d)} J_{sc} was calculated by convoluting the EQE spectrum; ^{e)}Power conversion efficiency (PCE) of the best cell, the number in the blanket is the averaged PCE over 8 individual devices; ^{f)}Averaged PCE over 30 individual devices.

To further confirm that PEI layer can suppress the chemical corrosion of the silver electrode, long-term stability of the perovskite solar cell with solution processed PEI/AgNW top electrode was investigated. Perovskite solar cell with thermal evaporated silver electrode (e-Ag) was investigated for comparison. Figure S7, in Supporting

Information depicts the evolution of the V_{oc} , J_{sc} , FF, and PCE of the prepared cells electrode aged inside glovebox with white light illumination. As seen here, although V_{oc} was reasonably stable both for e-Ag and PEI/AgNW cells, the cell with e-Ag electrode showed losses of 30–40% for J_{sc} and FF, leading to overall 50% decay after aging 30 hours. On the contrary, the PEI/AgNW based cells show much better stability under the same aging condition, and almost no performance decay was measured for this type of cell over 100 hours. It is known that PEI layer is able to reduce moisture intrusion into the CH₃NH₃PbI₃ layer^[43] and to block the ion migration.^[44] These explain the stability improvement of the perovskite solar cells after introducing PEI layer. Nevertheless, this result clearly demonstrates that PEI layer is able to improve device stability under real working condition.

To further characterize the transparency of these semi-transparent perovskite solar cells, photovoltaic performance of the best cell illuminated on both the ITO and AgNWs sides were measured. Figure 6a and b show the J - V curves and EQE spectrum of the best cell illuminated over different side, and the photovoltaic performance data are listed in Table 4. As seen here, slightly lower PCE (12%) was measured for the cell illuminated on the AgNW side than on the ITO side (14%), which is mainly due to the lower J_{sc} . EQE spectrum showed that lower quantum efficiency over 300–500 nm for the cell illuminated on the AgNW side, which is on one hand ascribed to the lower light transmittance of AgNW networks over 380–500 nm (Figure 1a), on the other hand to the light absorption of PC₆₁BM layer

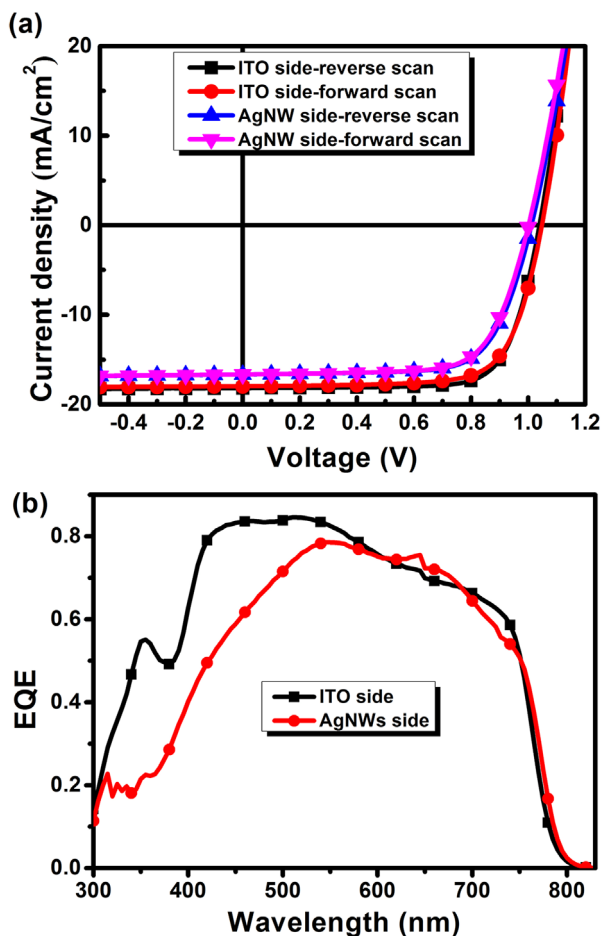


Figure 6. a) J - V curves of the best device fabricated illuminated from ITO side and illuminated from AgNW electrode (b) Corresponding EQE characteristics of the device.

Table 4. Performance metrics of the best perovskite device when illuminated from the ITO side and AgNW side and scanned from reverse and forward respectively.

Illumination direction	V_{oc} (V)	J_{sc} (mA cm ⁻²) ^{a)}	FF	PCE (%) ^{b)}
ITO side-reverse scan	1.04	18.17	0.75	14.17
ITO side-forward scan	1.05	17.97	0.75	14.15
AgNW side-reverse scan	1.02	16.65	0.71	12.05
AgNW side-forward scan	1.00	16.56	0.70	11.59

^{a)} J_{sc} was calculated by convoluting the EQE spectrum with AM 1.5G sun spectrum;

^{b)}PCE = $V_{oc} \times J_{sc} \times FF$.

(60 nm).^[45] However, almost identical quantum efficiency over 500–800 nm for cell illuminated on both side demonstrating excellent transparency for this cell. In addition, negligible hysteresis was measured for this cell, demonstrating a good device performance for these cells.^[7] With these, we have clearly demonstrated that improved interfacial connection between the PC₆₁BM and AgNW electrodes can be achieved by insertion a thin layer of PEI, which leads to the successful preparation of semi-transparent perovskite via full-solution-processing.

4. Conclusion

In summary, we have successfully prepared fully solution-processed semi-transparent perovskite solar cells with ink-jet printed AgNW top electrode. High power conversion efficiency of 14.17% with averaged visible transparency of 21.2% was achieved. A thin layer of PEI between the PC₆₁BM and AgNW electrode plays the key role in achieving the high performance, which, on one hand, decreases the work function of AgNW electrode and consequently decreases the electron injection barrier between these two layers, on the other hand, prevent the chemical corrosion of AgNW during printing. Excellent transparency of these cells was proved by measuring the photovoltaic performance illuminated over different side. The current work provides a simple and feasible inkjet printing technique for the preparation of metal electrode for perovskite solar cells, which will effectively reduce the production cost and promote the commercial application of perovskite solar cells.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

interfacial protecting, perovskite solar cells, printed top electrodes, semi-transparent solar cells, silver nanowires

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