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Room-temperature solution-processed and metal oxide-free nano-composite for the flexible transparent bottom electrode of perovskite solar cells†

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The exploration of low-temperature and solution-processed charge transporting and collecting layers can promote the development of low-cost and large-scale perovskite solar cells (PVSCs) through an all solution process. Here, we propose a room-temperature solution-processed and metal oxide-free nano-composite composed of a silver nano-network and graphene oxide (GO) flawless film for the transparent bottom electrode of a PVSC. Our experimental results show that the amount of GO flakes play a critical role in forming the flawless anti-corrosive barrier in the silver nano-network through a self-assembly approach under ambient atmosphere, which can effectively prevent the penetration of liquid or gaseous halides and their corrosion against the silver nano-network underneath. Importantly, we simultaneously achieve good work function alignment and surface wetting properties for a practical bottom electrode by controlling the degree of reduction of GO flakes. Finally, flexible PVSC adopting the room-temperature and solution-processed nano-composite as the flexible transparent bottom electrode has been demonstrated on a polyethylene terephthalate (PET) substrate. As a consequence, the demonstration of our room-temperature solution-processed and metal oxide-free flexible transparent bottom electrode will contribute to the emerging large-area flexible PVSC technologies.

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Introduction

The efficiency of perovskite solar cells (PVSCs) have greatly increased in the last three years,^{1–10} which makes them one of the most promising candidates for next generation solar cells. Since the cost and scalable capability are among the critical issues for their practical application, low temperature and solution-processed methods for each layer of PVSC have been extensively investigated. For example, various low temperature approaches for forming perovskite films have been demonstrated for high performance PVSCs.^{11–22} Low temperature and solution-processed interfacial layers, including electron and hole transporting materials, have also been intensively studied to improve the efficiency and stability of PVSCs.^{23–33} Charge collecting layers, such as silver nanowire and carbon based electrodes, have been adopted to replace conventional top electrodes formed from thermally evaporated metals,^{34–40} which will further reduce the cost of device fabrication.

However, limited studies have been devoted to alternatives for the conventional transparent bottom electrodes of perovskite solar cells, *i.e.* indium tin oxide (ITO) and fluorine-doped tin oxide (FTO), which are difficult to fabricate through low temperature solution-processes and exhibit poor mechanical flexibility. The alternative bottom electrodes reported recently involve the use of physical evaporation and high temperature thermal annealing for their applications in PVSCs.^{41–43} The critical issue of using metal nanowires as the bottom transparent flexible electrode for PVSCs is due to the grand challenge of the strong reaction of the halides and metals (*e.g.* Ag, Cu ... *etc.*). During the fabrication of perovskite films, the halides in liquid or vapor phase will easily penetrate through the conventional interfacial layer and be absorbed on the silver nanowire surface. Moreover, the migration of the halide ion has been demonstrated in MAPbX₃ under electric fields.^{44,45} As a result, silver nanowire based transparent electrodes will be gradually degraded from the corrosion of halides. Besides the corrosion issue, a number of important issues, such as work function alignment and surface wetting properties, have to be addressed before adopting silver nanowires as a potential candidate for transparent bottom electrodes for practical PVSCs.

Here, we demonstrate the formation of a flawless film composed of self-assembled graphene oxide (GO) flakes on a

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silver nano-network under ambient conditions, which can act as the anti-corrosive barrier for preventing halide corrosion against the silver nanowires. It was found that the amount of GO flakes plays an important role in forming flawless films on the silver nano-network to meet the anti-corrosion requirements. Significantly, through controlling the amount of reduction agents added to the pristine GO solution, a nano-composite composed of a silver nano-network and partially reduced GO flawless film with suitable work function and surface wetting properties has been adopted as the bottom electrode for a PVSC with a power conversion efficiency (PCE) of 9.23%. Finally, a flexible PVSC on a nano-composite electrode has been demonstrated on a PET flexible substrate. The demonstration of a room-temperature solution-processed and metal oxide-free nano-composite electrode for PVSCs will contribute to the large-scale and low temperature processing of high performance flexible PVSCs.

Experimental

Preparation of nano-composite electrodes and their stability characterization

Highly conductive silver nano-network transparent electrodes on glass and PET substrates with dimension of 1.5×1.5 cm were prepared under ambient conditions according to previous reports.⁴⁶ The pristine GO aqueous solution was obtained from Sigma-Aldrich without any purification and was diluted to 0.25 mg mL^{-1} . Four different volumes of GO solution (0.25 mg mL^{-1}), *i.e.* 10 μL , 20 μL , 30 μL and 40 μL , were dropped on the four identical silver nano-network electrodes respectively and allowed to uniformly disperse on the entire substrates. The substrates were then dried through natural evaporation under ambient conditions. After that, a layer of film composed of multiple stacked GO flakes formed on the silver nano-network electrode. A bare silver nano-network electrode without any GO protection having the same sheet resistance with the previous four electrodes was adopted as the reference sample. Their initial resistances between the two opposite ends were measured by forming two electrical contacts from silver paste. To characterize the anti-corrosive effect of the nano-composite electrodes against halides, the perovskite film was fabricated on the electrodes by a previously reported method.⁴⁷ Firstly, the as-received PEDOT:PSS (Baytron AI 4083) was spin-coated on the transparent electrodes at a speed of 2000 rpm and allowed to dry on a hotplate at 120°C for 15 minutes. The samples were then transferred to a glove-box after cooling to room temperature. The precursor of MAI (1.2 M) and PbI_2 (1.2 M) in the mixed solvent of dimethyl sulphoxide (DMSO) and gamma-butyrolactone (GBL) with a ratio of 3:7 was spin-coated on the PEDOT:PSS layer at a speed of 1000 rpm for 10 seconds and 4000 rpm for 40 seconds. During the second step of spin-coating, 120 μL toluene was quickly dropped on the substrate, which was then transferred to a hotplate with a temperature of 100°C . Perovskite film with a thickness of 250 nm gradually formed on the

substrate after 10 minutes of heating. A PCBM layer with a thickness of 80 nm was spin-coated on the as-formed perovskite film using the PCBM solution in chlorobenzene (20 mg mL^{-1}) at a speed of 1500 rpm. The five devices were taken out of the glove-box, and the resistance variations upon the duration of their exposure in the room atmosphere were recorded.

Preparation of partially reduced GO flakes and perovskite solar cells on the nano-composite transparent electrodes

The GO was reduced by adding an appropriate amount of NaBH_4 into the pristine GO solution. Five batches of newly prepared aqueous solution containing different amount of NaBH_4 , *i.e.* 16, 32, 48, 64 and 80 μmol , were added into the five pristine solutions containing the same quantity of 0.4 mg GO flakes, keeping GO with a constant concentration of 0.25 mg mL^{-1} . After 8 hours incubation at room atmosphere, 40 μL of the five reduced GO solutions and the diluted pristine GO solution (0.25 mg mL^{-1}) were dropped onto the six identical silver nano-network electrodes respectively for the formation of composite transparent electrodes. Similar to the protocols described above, PEDOT:PSS, perovskite film and PCBM layers were sequentially spin-coated on the composite electrodes. The perovskite solar cells were finally finished by spin-coating a dipolar layer of PFN-P1 and thermally evaporating 150 nm of silver film. A similar process had been adopted for the preparation of flexible perovskite solar cells on a PET substrate using the composite transparent electrode of silver nano-network and anti-corrosive film.

Material and device characterizations

Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 FEG scanning electron microscope. Current density–voltage (J – V) characteristics for all the devices were measured using a ABET AM1.5G solar simulator and Keithley 2635 sourcemeter at a scan rate of 0.1 V s^{-1} . The diffused transmission spectra of the transparent electrodes were obtained from a home-built optics system with an integrating sphere. The work functions of the pristine GO and reduced GO on silver nano-network electrodes were measured by a SKP5050 Scanning Kelvin Probe System (KP Technology Ltd) with a resolution of 1–3 meV. The IPCE measurement was performed using a home-built system combining a xenon lamp, monochromator, chopper, and a lock-in amplifier together with a calibrated silicon photo-detector.

Results and discussion

As the SEM image in Fig. S1† shows, the silver nanowires have been broken into small pieces after spin-coating methylammonium iodide (MAI) solution on the electrode, which indicates serious corrosion of MAI to the silver material. To investigate the protection of graphene oxide composed anti-corrosive film, different volumes of pristine GO aqueous solution with a constant concentration of 0.25 mg mL^{-1} were

dropped on four identical silver nano-network electrodes and allowed to dry naturally under ambient conditions. Two electrical contacts using silver paste were formed on the two sides of the electrode in order to measure its resistance before and after device fabrication. Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3$) film, and phenyl- C_{61} -butyric acid methyl ester (PCBM) were sequentially coated on these four composite electrodes. One control sample on the silver nano-network electrode without GO protection was prepared. Details for the preparation of each layer can be found in the Experimental section.

As shown in Fig. 1, resistance variations of the nano-composite electrodes have been measured under ambient conditions after device fabrication. As denoted by the black square line in the inset figure, the resistance of the silver nano-network without GO protection is already 7 times larger than its initial resistance measured before device fabrication, once the perovskite film on the electrode had formed (*i.e.* at time zero). Despite the presence of the PEDOT:PSS layer on the silver nano-network, the solution of MAI may percolate through the interfacial layer during the dropping of the precursor. In addition, excess MAI molecules in the vapor phase will also penetrate through the PEDOT:PSS layer during the drying process of the perovskite film. All these MAI molecules would be absorbed on the silver surface and corrode the silver nanowires, inducing an increase in resistance of the silver nano-network electrode. In addition, due to the presence of moisture in air, the corrosion of MAI against silver nanowires will be further aggravated because of the protonation of the molecules. That can be directly evidenced by the rapid resistance increase in the silver nano-network electrode in the first several minutes. We also tried coating a TiO_2 nanocrystal layer on the silver nano-network electrode before spin-coating the PEDOT:PSS interfacial layer. However, similar to the bare silver

nano-network, the resistance of the electrode with the protection of TiO_2 nanocrystals and PEDOT:PSS still experienced a rapid increase after the formation of the perovskite film. Therefore, preventing the diffusion of liquid as well as gaseous MAI is the critical issue for silver nanowire electrodes in perovskite solar cell applications.

In contrast, the resistance increase of the silver nano-network electrode with GO protection has been significantly suppressed, even after 60 minutes exposure of the devices at the same ambient atmosphere as shown in Fig. 1. Meanwhile, as indicated by the enlarged figure in Fig. 1, the more GO solution dropped on the silver nano-network, the greater the stability of the electrode. GO flakes have been adopted as the solder for the silver nanowire electrode and oxidation barrier against the oxygen and moisture only under ambient atmospheric conditions.^{48,49} No previous report has investigated the integration of GO and silver nanowire electrode for PVSC applications due to the presence of highly corrosive species of liquid and gaseous halides during the formation of perovskite films. Our results show that the complete coverage of GO flakes and the formation of flawless films on the silver nano-network surface are critical to block the diffusion of halide to the bottom electrode. Consequently, the anti-corrosive effect of GO film on the silver nano-network would greatly depend on the perfection of the film formed from multiple stacked GO flakes. As evidenced by the SEM images from the silver nano-network coated with 10 μL GO solution (0.25 mg mL^{-1}) in Fig. S2,[†] the existence of a contrast difference in the image implies the different conductivity on the sample surface. The bright areas can be attributed to incomplete coverage by GO flakes on the silver nano-network, and the protection against corrosive molecules at these spots would be weakened. Fewer flaws exist in the film, and fewer MAI molecules would penetrate and absorb on the silver nanowire surface during the formation of the perovskite film, which is consistent with the result shown in Fig. 1. In contrast, as shown in Fig. 2(a), the silver nano-network has been fully covered by the GO flakes after being coated by 40 μL GO solution (0.25 mg mL^{-1}). The GO film with crinkled surface can be clearly observed in Fig. 2(b).

It should be noted that multiple layers of pristine GO flakes would be necessary for stacking the flawless film, which will

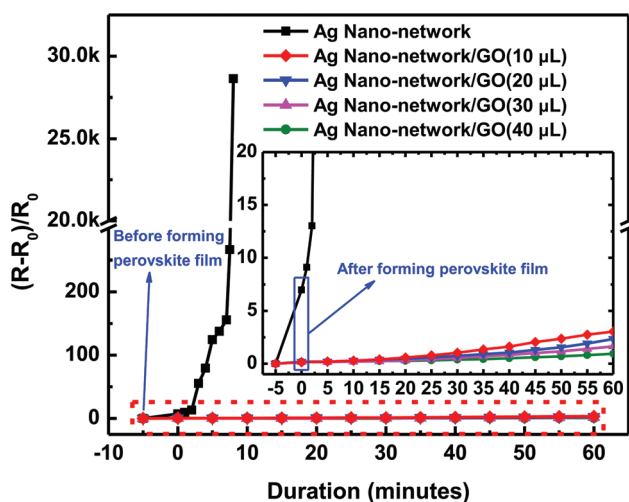


Fig. 1 The resistance variation of the silver nano-network electrodes protected by different volumes of GO solution (0.25 mg mL^{-1}) before and after the fabrication of perovskite devices. The inset clearly shows the change of resistance.

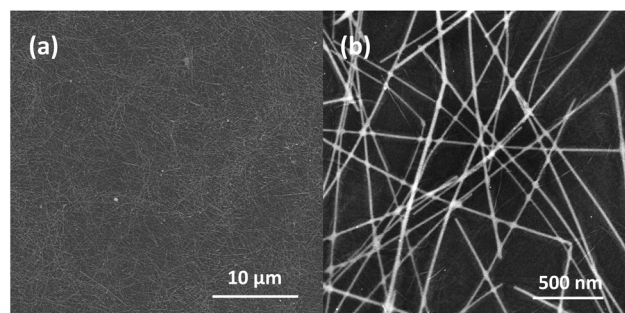


Fig. 2 (a) Large-scale and (b) enlarged SEM images of silver nano-network under the protection of flawless anti-corrosive GO film.

however greatly increase the resistance of the anti-corrosive barrier. To apply the nano-composite electrode for solar cell applications, the poor conductivity of the anti-corrosive film will prevent the collection of charges from the active layer and significantly reduce the solar cell performance. To address the issue, an appropriate amount of sodium borohydride (NaBH_4) aqueous solution was added to the pristine GO solution for reduction, which helped to improve the conductivity of the graphene oxide flakes.⁵⁰ Different amounts of sodium borohydride were added into five batches of solutions containing the same quantity of pristine GO, while keeping final GO concentration constant (0.25 mg mL^{-1}). The reaction between NaBH_4 and the functional groups on pristine GO (*i.e.* hydroxyl, epoxy, carbonyl and carboxyl groups) as well as the removal of these groups with boron oxide complexes from the surface benefit the increase of the C : O ratio of the flakes. The color of the GO solution gradually turned black over 8 hours incubation. It was also noticed that the more NaBH_4 was added, the darker the color of the solution appeared.

The transmission spectra of the silver nano-network electrodes coated with $40 \mu\text{L}$ of GO solution reduced by six different amounts of NaBH_4 are shown in Fig. 3(a). It was noticed that the lowest optical transparency of the composite electrode using the GO reduced by $80 \mu\text{mol NaBH}_4$ was observed, which can be largely attributed to the large optical absorption of the

reduced GO flakes themselves. Therefore, the completely reduced GO flakes are not advised for producing nano-composite transparent electrode with high optical transparency.

To further evaluate the transparent electrodes for perovskite solar cell applications, devices such as those shown in the schematic diagram in Fig. 4(a) have been fabricated on the silver nano-network transparent electrode with the protection of anti-corrosive film formed from six different GO flakes. The control devices of perovskite solar cells on silver nano-network without GO protection and commercial ITO electrode have been also fabricated for reference. The fabrication procedure is adopted from a previous report⁴⁷ and the details can be found in the Experimental section. Fig. 4(b) is the SEM image of the cross-section from one typical perovskite solar cell fabricated on the nano-composite transparent electrode. The SEM images of the as-prepared perovskite film are shown in Fig. S3.† The evenly and uniformly distributed crystals imply that a high quality perovskite film was achieved on the flawless GO film protected silver nano-network electrode.

The J - V characteristic curves from the eight devices are shown in Fig. 3(b), and their photovoltaic parameters are listed in Table 1. Due to the intensive corrosion by the halides, nearly no PCE performance has been obtained from the device fabricated on silver nano-network without GO protection. For the device fabricated on the silver nano-network electrode

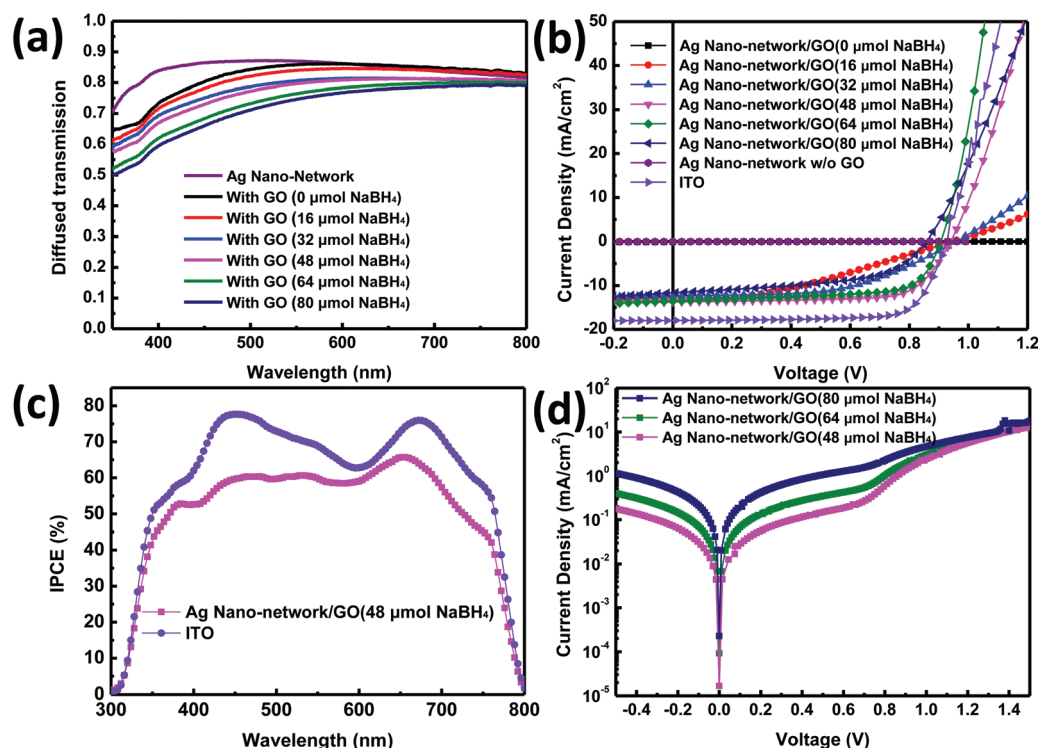


Fig. 3 (a) Diffuse transmission spectra of silver nano-network electrodes without and with anti-corrosive film from different reduced GO flakes. (b) J - V curves of the PVSCs fabricated on the nano-composite electrodes of silver nano-network and self-assembled GO film with different reduction degrees. Data from the control devices fabricated on the silver nano-network without GO protection and commercial ITO substrate are also presented. (c) IPCE performances of the devices fabricated on the nano-composite electrode and ITO substrate. (d) J - V curves of the devices fabricated on the three different nano-composite electrodes characterized under a dark environment.

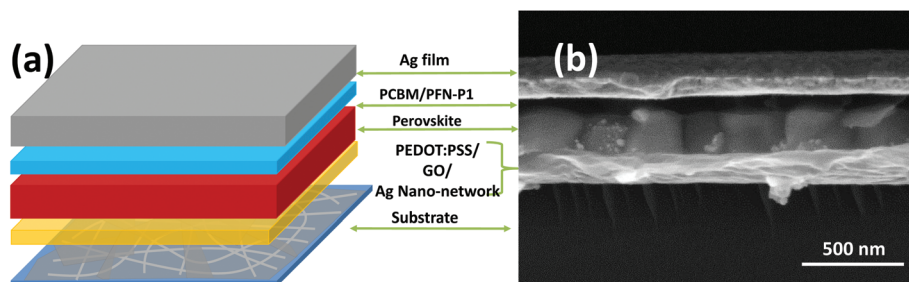


Fig. 4 (a) Schematic diagram of a perovskite solar cell on the flawless anti-corrosive GO film protected silver nano-network electrode and (b) SEM image of the cross section of a typical device.

Table 1 Summary of work function and photovoltaic parameters of the nano-composite electrodes and their corresponding perovskite solar cells

Ag nano-network/GO	Work function (eV)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
0 μ mol NaBH ₄	5.12	0.76	0.061	17.3	0.008
16 μ mol NaBH ₄	4.89	0.95	13.327	35.5	4.495
32 μ mol NaBH ₄	4.85	0.96	12.365	51.8	6.149
48 μ mol NaBH ₄	4.81	0.94	13.776	71.3	9.233
64 μ mol NaBH ₄	4.73	0.91	13.569	67.8	8.372
80 μ mol NaBH ₄	4.65	0.86	11.659	53.6	5.371
Ag nano-network w/o GO	5.06	0.0099	0.0007	38.4	2.54×10^{-9}
ITO	4.70	0.93	17.959	74.7	12.488

coated with pristine GO without reduction by NaBH₄, J_{sc} is very small, which can be explained by the large resistance of the anti-corrosive film from multiple stacked pristine GO flakes. The charges generated in the active layer are difficult to be transported to the silver nano-network electrode. Interestingly, the device performances on the GO protected silver nano-network electrodes increase gradually with an increase of NaBH₄ into pristine GO solution, largely resulting from the enhancement of the FF value. The conductivity improvement of the anti-corrosive film can be attributed to the removal of functional groups on GO flakes along with boron oxide complexes during reduction, which help to reduce the interlayer distance between the reduced GO flakes. A PCE of 9.23% was achieved from the device prepared on the silver nano-network protected with anti-corrosive film from GO flakes reduced by 48 μ mol NaBH₄. As compared to the device on the ITO substrate, similar V_{oc} and FF values have been achieved from the device on the composite electrode, which indicated that suitable conductivity and good work function alignment were obtained from the anti-corrosive film. The large loss of the PCE of the solution-processed device can be attributed to its relatively low photocurrent, which is further evidenced by the incident photon-to-current conversion efficiency (IPCE) of the devices on ITO and the silver nano-network in Fig. 3(c). As shown by the transmission spectra in Fig. 3(a), the coating of the partially reduced GO on the silver nano-network has increased the optical loss of the composite electrode. Importantly, as shown in Fig. S4,[†] the hysteresis phenomenon is negligible for the PVSC fabricated on our nano-composite transparent electrode due to the coating of the PCBM layer.⁵¹

Surprisingly, the GO flakes reduced by a larger amount of NaBH₄ (*i.e.* 64 and 80 μ mol), which should result in higher conductivity, do not contribute to the further improvement of the device performance, as demonstrated by the decrease of J_{sc} , V_{oc} and FF values in Table 1. As shown in Fig. 3(a), lower transparency of the nano-composite electrodes will decrease the charge generation in the active layer, which is the major cause of the slight reduction of J_{sc} value. Their reduced V_{oc} values can be explained by the variation of work function from the nano-composite electrode, which are listed in Table 1. The lowest work function (−4.65 eV) of the nano-composite electrode has been obtained from the GO flakes reduced by adding 80 μ mol NaBH₄ to the pristine GO solution, due to the removal of most of the functional groups from the surface. On the one hand, the elimination of these hydrophilic groups will induce the aggregation of the reduced GO flakes during their self-assembly process on the silver nano-network electrode. On the other hand, the weakened surface wettability of the anti-corrosive film, as shown in Fig. 5, will make the nano-composite electrode difficult to be fully covered by the following coated PEDOT:PSS layer. The aggregation of reduced GO flakes and the weakened blocking effect of PEDOT:PSS film will easily induce direct contact between perovskite film and the composite bottom electrode, which is evidenced by the increased dark current as shown by the J - V curves characterized under dark environment in Fig. 3(d). The leakage of current will result in the decrease of the FF for the devices using the GO reduced by 64 and 80 μ mol NaBH₄. Based on the discussion above, the partially reduced GO is a good candidate for forming anti-corrosive film with good optical transparency,

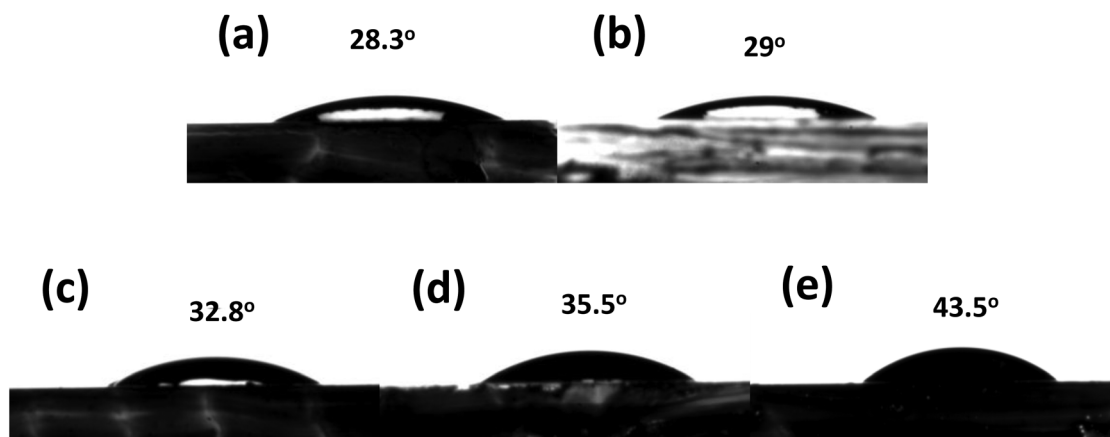


Fig. 5 Contact angle measurements of the flawless anti-corrosive films self-assembled from (a) pristine GO and GO reduced by (b) 16 μmol , (c) 48 μmol , (d) 64 μmol , (e) 80 μmol NaBH_4 .

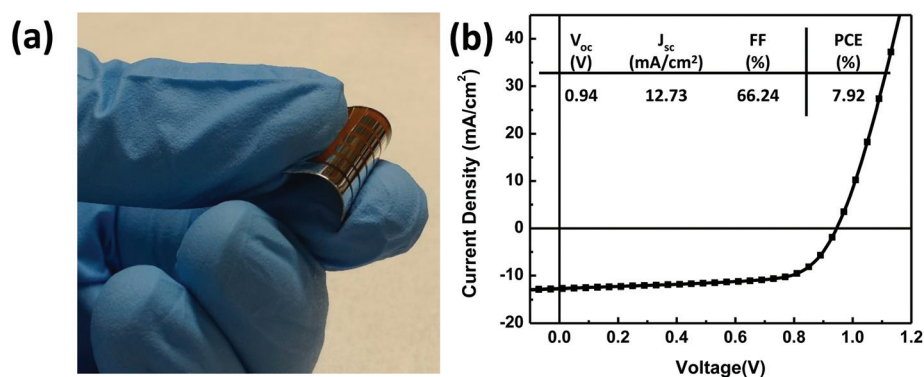


Fig. 6 (a) Digital image of a typical flexible perovskite solar cell fabricated on a PET substrate using the room-temperature and solution-processed nano-composite electrode and (b) its photovoltaic performance.

work function alignment, and surface wetting in the application of perovskite solar cells.

Since our nano-composite electrode is prepared through an all solution-processed method at room-temperature, the demonstration of a silver nano-network transparent electrode for flexible perovskite solar cell can be readily realized on PET flexible substrate. As the digital photography shown in Fig. 6(a), a flexible perovskite device has been prepared. Its performance has been also shown in Fig. 6(b) with a PCE of 7.92%. To the best of our knowledge, this is the first demonstration of a flexible perovskite solar cell on silver nanowire based transparent electrode through a solution-processed method. Together with a previously reported solution-processed top electrode, large-scale and low-cost fabrication of an all solution-processed perovskite solar cell can be feasibly realized through roll-to-roll and similar technologies.

Conclusions

In conclusion, the flawless film composed from the self-assembly of GO flakes has been proposed to act as the anti-corrosive

barrier and address the issue of halide corrosion against the underneath silver nano-network transparent electrode. The amount of GO flakes plays an important role in forming the flawless anti-corrosive film, which helps to prevent the diffusion of liquid or gaseous halides to silver nanowires during the formation of the perovskite film. In order to apply the nano-composite as the bottom electrode of the PVSC, different amounts of NaBH_4 have been added to the pristine GO solution to improve the conductivity of the flawless anti-corrosive film. Experimental results show that partially reduced GO flakes benefit the formation of the flawless film with good work function alignment and surface wetting properties for practical PVSCs. A PCE of 9.23% has been achieved from the PVSC on the metal oxide-free and room-temperature solution-processed nano-composite transparent electrode. Furthermore, flexible a perovskite solar cell has been demonstrated by the solution-processed silver nanowire based transparent electrode on a PET flexible substrate for the first time. Together with a previously reported solution-processed top electrode, our proposed room-temperature and solution-processed strategy for forming a metal oxide-free nano-compo-

site electrode will contribute to the commercial application of perovskite solar cells through low-cost and large-scale fabrication technologies.

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References

- 1 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *J. Am. Chem. Soc.*, 2009, **131**, 6050–6051.
- 2 H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Graetzel and N.-G. Park, *Sci. Rep.*, 2012, **2**, 591.
- 3 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643–647.
- 4 M. Z. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, **501**, 395–398.
- 5 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.
- 6 G. Hodes, *Science*, 2013, **342**, 317–318.
- 7 N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Nature*, 2015, **517**, 476–480.
- 8 J. Burschka, N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Nature*, 2013, **499**, 316–319.
- 9 W. E. I. Sha, X. Ren, L. Chen and W. C. H. Choy, *Appl. Phys. Lett.*, 2015, **106**, 221104.
- 10 W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, *Science*, 2015, **348**, 1234–1237.
- 11 S. Ryu, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Yang, J. W. Seo and S. I. Seok, *Energy Environ. Sci.*, 2014, **7**, 2614–2618.
- 12 C. Bi, Y. B. Yuan, Y. J. Fang and J. S. Huang, *Adv. Energy Mater.*, 2015, **5**, 1401616.
- 13 Z. G. Xiao, C. Bi, Y. C. Shao, Q. F. Dong, Q. Wang, Y. B. Yuan, C. G. Wang, Y. L. Gao and J. S. Huang, *Energy Environ. Sci.*, 2014, **7**, 2619–2623.
- 14 Q. Wang, Y. C. Shao, Q. F. Dong, Z. G. Xiao, Y. B. Yuan and J. S. Huang, *Energy Environ. Sci.*, 2014, **7**, 2359–2365.
- 15 Y. X. Zhao and K. Zhu, *J. Am. Chem. Soc.*, 2014, **136**, 12241–12244.
- 16 K. Y. Yan, M. Z. Long, T. K. Zhang, Z. H. Wei, H. N. Chen, S. H. Yang and J. B. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 4460–4468.
- 17 J. B. You, Z. R. Hong, Y. Yang, Q. Chen, M. Cai, T. B. Song, C. C. Chen, S. R. Lu, Y. S. Liu, H. P. Zhou and Y. Yang, *ACS Nano*, 2014, **8**, 1674–1680.
- 18 J. H. Heo, D. H. Song, H. J. Han, S. Y. Kim, J. H. Kim, D. Kim, H. W. Shin, T. K. Ahn, C. Wolf, T. W. Lee and S. H. Im, *Adv. Mater.*, 2015, **27**, 3424–3430.
- 19 F. X. Xie, D. Zhang, H. M. Su, X. G. Ren, K. S. Wong, M. Gratzel and W. C. H. Choy, *ACS Nano*, 2015, **9**, 639–646.
- 20 D. Liu and T. L. Kelly, *Nat. Photonics*, 2014, **8**, 133–138.
- 21 N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu and S. I. Seol, *Nat. Mater.*, 2014, **13**, 897–903.
- 22 H. Zhang, J. Mao, H. He, D. Zhang, H. L. Zhu, F. X. Xie, K. S. Wong, M. Grätzel and W. C. H. Choy, *Adv. Energy Mater.*, 2015, **5**, 1501354.
- 23 S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith, *Nano Lett.*, 2014, **14**, 5561–5568.
- 24 J. H. Kim, P. W. Liang, S. T. Williams, N. Cho, C. C. Chueh, M. S. Glaz, D. S. Ginger and A. K. Y. Jen, *Adv. Mater.*, 2015, **27**, 695–701.
- 25 J. H. Park, J. Seo, S. Park, S. S. Shin, Y. C. Kim, N. J. Jeon, H. W. Shin, T. K. Ahn, J. H. Noh, S. C. Yoon, C. S. Hwang and S. I. Seok, *Adv. Mater.*, 2015, **27**, 4013–4019.
- 26 D. W. Zhao, M. Sexton, H. Y. Park, G. Baure, J. C. Nino and F. So, *Adv. Energy Mater.*, 2015, **5**, 1401855.
- 27 O. Malinkiewicz, A. Yella, Y. H. Lee, G. M. Espallargas, M. Gratzel, M. K. Nazeeruddin and H. J. Bolink, *Nat. Photonics*, 2014, **8**, 128–132.
- 28 B. Xu, E. Sheibani, P. Liu, J. B. Zhang, H. N. Tian, N. Vlachopoulos, G. Boschloo, L. Kloo, A. Hagfeldt and L. C. Sun, *Adv. Mater.*, 2014, **26**, 6629–6634.
- 29 J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C. S. Lim, J. A. Chang, Y. H. Lee, H. J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Gratzel and S. I. Seok, *Nat. Photonics*, 2013, **7**, 487–492.
- 30 J. Y. Jeng, Y. F. Chiang, M. H. Lee, S. R. Peng, T. F. Guo, P. Chen and T. C. Wen, *Adv. Mater.*, 2013, **25**, 3727–3732.
- 31 K. G. Lim, H. B. Kim, J. Jeong, H. Kim, J. Y. Kim and T. W. Lee, *Adv. Mater.*, 2014, **26**, 6461–6466.
- 32 J. M. Ball, M. M. Lee, A. Hey and H. J. Snaith, *Energy Environ. Sci.*, 2013, **6**, 1739–1743.
- 33 Z. W. Wu, S. Bai, J. Xiang, Z. C. Yuan, Y. G. Yang, W. Cui, X. Y. Gao, Z. Liu, Y. Z. Jin and B. Q. Sun, *Nanoscale*, 2014, **6**, 10505–10510.
- 34 F. Guo, H. Azimi, Y. Hou, T. Przybilla, M. Y. Hu, C. Bronnbauer, S. Langner, E. Spiecker, K. Forberich and C. J. Brabec, *Nanoscale*, 2015, **7**, 1642–1649.
- 35 C. D. Bailie, M. G. Christoforo, J. P. Mailoa, A. R. Bowring, E. L. Unger, W. H. Nguyen, J. Burschka, N. Pellet, J. Z. Lee, M. Gratzel, R. Noufi, T. Buonassisi, A. Salleo and M. D. McGehee, *Energy Environ. Sci.*, 2015, **8**, 956–963.
- 36 Z. Li, S. A. Kulkarni, P. P. Boix, E. Z. Shi, A. Y. Cao, K. W. Fu, S. K. Batabyal, J. Zhang, Q. H. Xiong, L. H. Wong,

- N. Mathews and S.G. Mhaisalkar, *ACS Nano*, 2014, **8**, 6797–6804.
- 37 P. You, Z. K. Liu, Q. D. Tai, S. H. Liu and F. Yan, *Adv. Mater.*, 2015, **27**, 3632–3638.
- 38 L. F. Liu, A. Y. Mei, T. F. Liu, P. Jiang, Y. S. Sheng, L. J. Zhang and H. W. Han, *J. Am. Chem. Soc.*, 2015, **137**, 1790–1793.
- 39 A. Y. Mei, X. Li, L. F. Liu, Z. L. Ku, T. F. Liu, Y. G. Rong, M. Xu, M. Hu, J. Z. Chen, Y. Yang, M. Gratzel and H. W. Han, *Science*, 2014, **345**, 295–298.
- 40 H. Zhou, Y. Shi, Q. Dong, H. Zhang, Y. Xing, K. Wang, Y. Du and T. Ma, *J. Phys. Chem. Lett.*, 2014, **5**, 3241–3246.
- 41 A. Kim, H. Lee, H.-C. Kwon, H. S. Jung, N.-G. Park, S. Jeong and J. Moon, *Nanoscale*, 2015, DOI: 10.1039/C5NR04585A.
- 42 H. Sung, N. Ahn, M. S. Jang, J.-K. Lee, H. Yoon, N.-G. Park and M. Choi, *Adv. Energy Mater.*, 2015, **6**, 1501873.
- 43 J. Han, S. Yuan, L. N. Liu, X. F. Qiu, H. B. Gong, X. P. Yang, C. C. Li, Y. F. Hao and B. Q. Cao, *J. Mater. Chem. A*, 2015, **3**, 5375–5384.
- 44 T. Y. Yang, G. Gregori, N. Pellet, M. Gratzel and J. Maier, *Angew. Chem., Int. Ed.*, 2015, **54**, 7905–7910.
- 45 Z. G. Xiao, Y. B. Yuan, Y. C. Shao, Q. Wang, Q. F. Dong, C. Bi, P. Sharma, A. Gruverman and J. S. Huang, *Nat. Mater.*, 2015, **14**, 193–198.
- 46 H. F. Lu, D. Zhang, J. Q. Cheng, J. Liu, J. Mao and W. C. H. Choy, *Adv. Funct. Mater.*, 2015, **25**, 4211–4218.
- 47 J. Seo, S. Park, Y. C. Kim, N. J. Jeon, J. H. Noh, S. C. Yoon and S. I. Seok, *Energy Environ. Sci.*, 2014, **7**, 2642–2646.
- 48 J. J. Liang, L. Li, K. Tong, Z. Ren, W. Hu, X. F. Niu, Y. S. Chen and Q. B. Pei, *ACS Nano*, 2014, **8**, 1590–1600.
- 49 Y. Ahn, Y. Jeong and Y. Lee, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6410–6414.
- 50 H. J. Shin, K. K. Kim, A. Benayad, S. M. Yoon, H. K. Park, I. S. Jung, M. H. Jin, H. K. Jeong, J. M. Kim, J. Y. Choi and Y. H. Lee, *Adv. Funct. Mater.*, 2009, **19**, 1987–1992.
- 51 Y. H. Shao, Z. G. Xiao, C. Bi, Y. B. Yuan and J. S. Huang, *Nat. Commun.*, 2014, **5**, 5784.