

# Interfacial engineering with amino-functionalized graphene for efficient perovskite solar cells

Xiaoru Wen,<sup>a</sup> Jiamin Wu,<sup>b</sup> Di Gao<sup>b\*</sup> and Changjian Lin<sup>a\*</sup>

<sup>a</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: cjlin@xmu.edu.cn

<sup>b</sup>The Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA. E-mail: gaod@pitt.edu

## Experimental Section

### Material Preparation

2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD), Lead iodide (PbI<sub>2</sub>), N,N-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and chlorobenzene were obtained from the Sigma-Aldrich. Other chemicals were supplied by the Fisher Scientific. All the reagents were used without any purification post-treatment and deionized (DI) water was used throughout the process.

**Synthesis of Meththylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I).** CH<sub>3</sub>NH<sub>3</sub>I was synthesized according to the method described elsewhere.<sup>1</sup> Methylamine (27.86 mL, 40% in methanol, TCI) and hydroiodic acid (30 mL, 57 wt% in water, Aldrich) were mixed at 0 °C and stirred for 2 h. The precipitate was recovered by evaporation at 50 °C for 1 h. The product was washed with diethyl ether three times, and finally dried at 60 °C in a vacuum oven for 24 h.

**Synthesis of amino-functionalized Graphene (NGs).** The amino-functionalized Graphene (NGs) was prepared by a facial solution process with the phenylenediamine (PPDA) covalently bonded onto the surface of GO sheets, followed by the further chemical reduction with the hydrazine.<sup>2</sup> Typically, 100 mg of PPDA was mixed with the GO suspension (100 mL, 0.5 mg/mL), and then being refluxed at 80 °C overnight under the N<sub>2</sub> atmosphere for the surface amino-functionalization. Subsequently, hydrazine monohydrate (1.0 mL) was added to the above reaction solution and re-refluxed for another 24 h at 90 °C. After cooling to the room temperature, NGs can be obtained after being rinsed with DI water to remove the excess PPDA and hydrazine, and dried in a vacuum oven at 50 °C for 24 h.

### Device characterization

The morphology was examined by the field emission scanning electron microscope (FE-SEM, Hitachi S4800). X-ray diffraction patterns were obtained using a Philips X'pert X-ray diffractometer (XRD) with Cu Ka radiation ( $\lambda=1.54 \text{ \AA}$ ) to evaluate the crystal structures of the samples. The surface chemical compositions were analysed by X-ray photoelectron spectroscopy (XPS, PHI Quantum 2000). The light absorption was measured by UV-visible spectroscopy (Varian; UV-Visible spectrophotometer, Cary 5000). Current-voltage (J-V) characteristics were recorded from a solar simulator equipped with a Keithley 2400 source meter and 300 W collimated Xenon lamp (Newport) calibrated with the light intensity to 100 mW/cm<sup>2</sup> at AM 1.5 G solar light condition by the certified silicon solar cell. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 0.1 Hz to 100 KHz in the dark condition, in which the potential bias was applied at 0.9 V. The photoluminescence (PL) measurements were performed by using a fluorescence spectrophotometer (Hitachi F-7000) by using 520 nm excitation wavelength. The Mott-Schottky plots were recorded using the Gamry Instruments (Reference 600) with a frequency of 500 Hz in the dark condition;

## Results and discussion

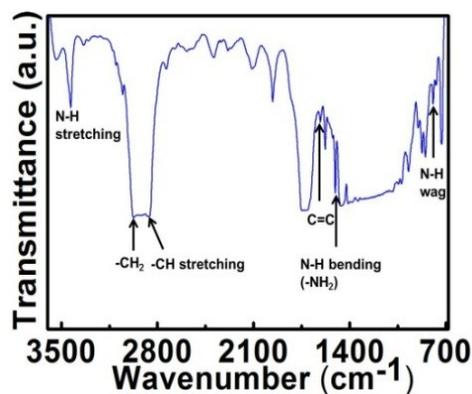


Fig. S1 The FTIR spectroscopy of NGs;

The chemical constituents of NGs were investigated by the FTIR spectroscopy as depicted in Fig. S1. Clearly, the resultant NGs showed the N-H stretching at  $3370\text{ cm}^{-1}$ , N-H bending of primary amine at  $1512\text{ cm}^{-1}$  and N-H wag at  $810\text{ cm}^{-1}$ , which indicated that the PPDA modifier was successfully grafted onto the graphene, and made the graphene with an amino-rich surface,<sup>2</sup> in accordance with XPS result. The amino-rich graphene laid solid foundation for the following surface trap passivation via the coordinate or dative-covalent bond between amines on the graphene and the under-coordinated  $\text{Pb}^{2+}$  on the perovskite surface.<sup>3</sup>

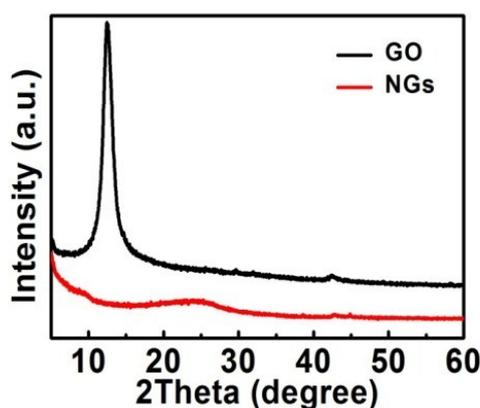


Fig. S2 XRD patterns of GO and NGs;

With the purpose of demonstrating an efficient reduction of NGs, the wide-angle XRD was conducted as shown in Fig. S2. Clearly, a strong diffraction peak centred at about  $10^\circ$  can be found for GO, suggesting the complete oxide of graphite. After the PPDA surface modification and further chemical reduction, only two weak shoulders and broad diffraction peaks centred at ca.  $24^\circ$  and  $44^\circ$  were detected, which were indexed to (002) and (100) diffractions for a typical graphite carbon respectively, indicating the effective reduction of NGs.<sup>4</sup>

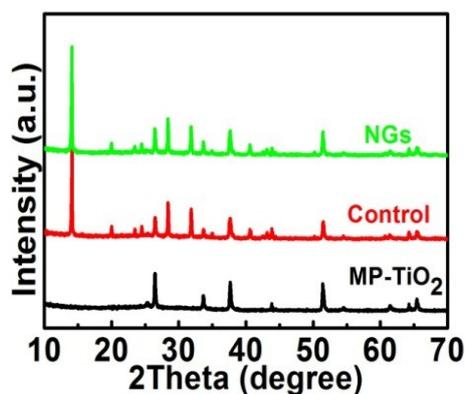


Fig. S3 XRD patterns of different substrates;

The XRD was conducted to investigate the effect of drop-coating NGs interlayer on the crystalline property of perovskite under-layer as shown in Fig. S3. Clearly, the perovskite layer displayed the excellent crystalline, in accordance with the previous work,<sup>5</sup> and the incorporation of NGs interlayer at the perovskite/HTM interface maintained the excellent perovskite crystalline, similar to that of the control film.

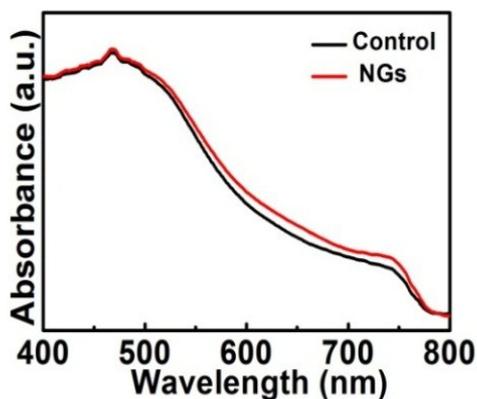


Fig. S4 The UV-Vis spectra of perovskite film before and after NGs modification;

Fig. S4 presents UV-Vis spectra for different substrates to investigate the influence of NGs interlayer on the absorption property of perovskite film. Clearly, NGs-coated perovskite film displayed a similar absorbance behavior to the pristine one with a slightly increased absorption in the long wavelength region.

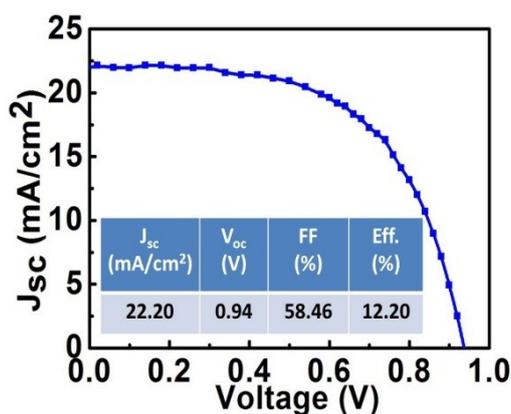


Fig. S5 The J-V characteristic of the best cell based on simple PPDA-modified perovskite layer;

To reveal the dual-functional role of NGs interlayer at the perovskite/HTM junction, the J-V characteristic of PSCs based on PPDA-modified perovskite layer was recorded for comparison as depicted in Fig. S5. Clearly, after the surface modification of perovskite sublayer with the amino-rich PPDA, the best efficiency of 12.20 % was obtained with the  $J_{sc}$ ,  $V_{oc}$  and FF being 22.20 mA/cm<sup>2</sup>, 0.94 V and 58.46 %, respectively, which is higher than that of control device (10.70 %). The improvement of photovoltaic performance can be ascribed to the reduced surface traps of the perovskite, resulting from the passivation of under-coordinated Pb<sup>2+</sup> by electron-rich amino groups, which has been successfully demonstrated in the previous work.<sup>3</sup> However, the efficiency enhancement is still inferior to the PSCs based on NGs interlayer. So the co-existence of amino groups and graphene itself is of much importance for a higher performance of PSCs.

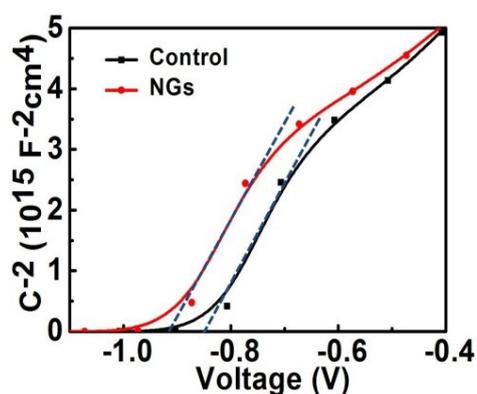


Fig. S6. Mott-Schottky plots of resultant PSCs;

Capacitance–voltage measurements of resultant devices were performed to further understand the effect of the inserted NGs at the perovskite/HTM interface as presented in Fig. S6. Generally, the extracted Mott-Schottky plot of inverse square capacitance ( $C^{-2}$ ) versus applied voltage (V) yields a partial straight line, and the built-in potential can be calculated using the intercept of the linear regime with the x-axis.<sup>6,7</sup> The presence of a built-in-potential has been demonstrated to drive the separation of photo-generated carriers, associated with a reduced charge recombination.<sup>6</sup> As expected, the PSCs with the NGs interlayer exhibited a higher built-in potential than the control one, which indicated an enhanced driving force for the carrier separation. Consequently, more photogenerated holes could transport through the NGs to the spiro-OMeTAD, leading to the reduced carrier recombination at the interface. Therefore, the introduction of the NGs between the perovskite and spiro-OMeTAD layers benefited the better charge extraction, which directly contributed to the improvement of the  $J_{sc}$ .

Table. S1 Summary of surface atomic concentration analysis of prepared GO and NGs from the XPS spectrum;

	C1s Atom (%)	O1s Atom (%)	N1s Atom (%)
GO	60.26	38.38	1.36
NGs	85.24	7.26	7.50

## Notes and references

1. J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C. Lim, J. A. Chang, Y. H. Lee, H. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, *Nature Photon.*, 2013, 7, 486-491.
2. X. Lu, L. Li, B. Song, K.-s. Moon, N. Hu, G. Liao, T. Shi and C. Wong, *Nano Energy*, 2015, 17, 160-170.
3. C. Sun, Z. Wu, H.-L. Yip, H. Zhang, X.-F. Jiang, Q. Xue, Z. Hu, Z. Hu, Y. Shen, M. Wang, F. Huang and Y. Cao, *Adv. Energy Mater.*, 2015, 6, 1501534-1501544.
4. H. F. Yang, Y. Yan, Y. Liu, F. Q. Zhang, R. Y. Zhang, Y. M. Mei Li, S. H. Xie, B. Tu and D. Y. Zhao, *J. Phys. Chem. B*, 2004, 108, 17320-17328.
5. N. Ahn, D.-Y. Son, I.-H. Jang, S. M. Kang, M. Choi and N.-G. Park, *J. Am. Chem. Soc.*, 2015, 137, 8696-8699.
6. L. F. Liu, A. Mei, T. F. Liu, P. Jiang, Y. S. Sheng, L. J. Zhang and H. W. Han, *J. Am. Chem. Soc.*, 2015, 137, 1790-1793.
7. W. A. Laban and L. Etgar, *Energy. Environ. Sci.*, 2013, 6, 3249-3253.