Electronic Supporting Information

Integration of Functionalized Graphene Nano-Network into Planar Perovskite Absorber for High Efficiency Large Area Solar Cells

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Experimental Section

Materials.

Amino-functionalized graphene (G-NH$_2$) was synthesized using a procedure described elsewhere$^{1-2}$. MAI were synthesized according to our previously reported technique. PbI$_2$ were purchased from Alfa Aesar. Anhydrous dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. The SnO$_2$ colloid precursor was obtained from Alfa Aesar (tin(IV) oxide, 15% in H$_2$O colloidal dispersion).

Solar Cell Fabrication.

The solar cells were fabricated on FTO substrates (TEC 15). The substrates were washed sequentially with detergent (2% Hellmanex in water), deionized water, ethyl alcohol, isopropanol, and finally cleaned under UV-ozone treatment for 10 min. The patterned TEC-15 FTO substrate was coated with a compact TiO$_2$ layer by spray pyrolysis of 0.2M Ti(IV) bis (ethyl acetoacetate)-diisopropoxide in 1-butanol solution at 450 °C, followed by annealing at 450 °C for one hour. The SnO$_2$ colloid precursor (1.5% in H$_2$O colloidal dispersion) was then spin-coated onto c-TiO$_2$/FTO substrates at 3000 rpm for 30 s, followed by baking on a hot plate in ambient air at 180 °C for 30 min.

The precursor solution was prepared by dissolving MAI (1.4 M), PbI$_2$ (1.4 M) in DMF: DMSO with 4:1 (v/v) ratio to make a clear MAPbI$_3$ solution. In order to incorporate different amounts of G-NH$_2$ in the MAPbI$_3$ precursor solution, 0.05, 0.10, and 0.20 mg·mL$^{-1}$ of G-NH$_2$ were dispersed in the solvent (anhydrous DMF: DMSO 4:1 (v/v)) using 2-h sonication prior to making the perovskite solution (i.e., MAPbI$_3$/G-NH$_2$, MAPbI$_3$/0.1G-NH$_2$, MAPbI$_3$/0.2G-NH$_2$), respectively. For comparison, we also incorporated 0.05 mg·mL$^{-1}$ rGO in the MAPbI$_3$ precursor solution. All other steps in device preparation were exactly the same. The perovskite layers were deposited in a
dry glovebox by spin-coating the as-prepared precursor solutions onto the SnO\textsubscript{2}/c-TiO\textsubscript{2}/FTO substrates at 5000 rpm for 20 s, with an accelerating rate of 5000 rpm·s\textsuperscript{-1}. 500 μL chlorobenzene was dripped onto the spinning substrate 15 s before the end of the spin-coating program. The perovskite film acquired was then annealed at 100 °C for 20 min.

A layer of hole transport material (HTM) was spin-coated on top of the annealed films, which consisted of 0.1 M spiro-MeOTAD, 0.035 M bis(trifluoromethane) sulfonamide lithium salt (Li-TFSi), and 0.12 M 4-tert-butylpyridine (tBP) in chlorobenzene/acetonitrile (10:1, v/v) solution at 4000 rpm for 25 s. Finally, a 100-nm thick Ag layer was deposited by thermal evaporation.

**Characterization**

The crystal structures of the formed perovskite films were characterized using XRD (Shimadzu XRD-6100 diffractometer with Cu Kα radiation). The absorption spectra of the thin films were measured on an Cary-60 UV-vis spectrophotometer. FTIR experiments were conducted on a Tensor 27 FTIR spectrometer (Nicolet 6700), using KBr pellets of the solid samples. The perovskite films were characterized using a SEM (JEOL JSM-7800F Prime). High-resolution characterization was performed using a TEM (JEOL 2100F), operated at 200 kV accelerating voltage, equipped with an EDS (Oxford Instruments). Thin films for TEM studies were prepared using the same procedure as above, but were deposited directly onto the TEM grids (SPI). The TRPL was recorded on a PTI QM/TM/IM fluorescence spectrofluorometer. c-AFM tip (Pt/Ir coated Si; Budget Sensor ContE-G; force constant = 0.2 N/m; radius ~20 nm; resonance frequency ~14 kHz) was used to scan the sample surface in the contact mode and the current was measured when the probe encountered conducting locations. The image of local variations of current (typically in pA to nA range) is recorded simultaneously with the sample topography and presented as a current map. The small force constant of the c-AFM cantilever helps to image soft surfaces.
without deformation. The conducting probe contacts the perovskite films and measures the current distribution on the surface under a fixed bias. The c-AFM images were recorded at 1 V DC bias.

The J-V characteristics were measured with a Keithley 2401 source meter with a scan rate of 0.05 V·s⁻¹ under the simulated AM 1.5G illumination (100 mW·cm⁻²) using Enlitech’s 3A light source. The EQE was measured on a QE-3011 system (Enlitech). The TPC/TPV were generated by a microsecond pulse of a white light incident on solar cells under short circuit conditions (by a very low resistor at 20 Ω) and open circuit condition (by a large resistor at 1 MΩ). No background light was applied. IMPS was measured to compare the electron transport dynamic in the PSCs. The electron transit time (τ_d) in PSCs can be obtained by τ_d = 1/2πf_{IMPS}, where f_{IMPS} is the frequency of the minimum imaginary component in IMPS measurements. These measurements were performed under white light.

**Computational Methods**

All first-principles computations are performed based on density-functional theory (DFT) methods as implemented in the Vienna ab initio simulation package (VASP 5.4). An energy cutoff of 520 eV is used, and the atomic positions are optimized using the conjugate gradient scheme without any symmetric restrictions, until the maximum force on each atom is less than 0.02 eV Å⁻¹. The charge densities are computed using the Perdew-Burke-Ernzerhof (PBE) functional, and the ion cores are described by using the projector augmented wave (PAW) method. Grimme’s DFT-D3 correction is adopted to describe the long-range van der Waals interaction. A 2×2×1 k-point grid is used for the MAPbI₃/G-NH₂ and the MAPbI₃/rGO slabs. The difference of charge density (e.g., Δρ = ρ_{MAPbI₃/G-NH₂}–ρ_{MAPbI₃}–ρ_{G-NH₂}, ρ_{MAPbI₃/G-NH₂}, ρ_{MAPbI₃} and ρ_{G-NH₂} are charge densities of MAPbI₃/G-NH₂, MAPbI₃ and G-NH₂, respectively) between the whole supercell and the sum
of PACs of two constituents (individual slabs) are obtained after removal of one or the other part without optimizations.
Figure S1 AFM Height line profiles

Figure S2 G-NH$_2$: (a) bright-field TEM image, (b) C elemental map, and (c) N elemental map.

Scale bar = 100 nm.
Figure S3 (a) Photographs of the MAPbI$_3$ precursor solutions with and without the optimal G-NH$_2$ addition, (b) corresponding UV-vis spectra from the fabricated films.

Figure S4 AFM images of thin films: (a) MAPbI$_3$ and (b) MAPbI$_3$/G-NH$_2$. 
Figure S5 (a) Photographs of the MAPbI$_3$ precursor solutions with increasing G-NH$_2$ contents. Corresponding fabricated thin films: (b) UV-vis spectra and (c) XRD patterns.

Figure S6 Top-surface images of the perovskite films with different G-NH$_2$ contents: (a)-(b) MAPbI$_3$/0.1G-NH$_2$, (c)-(d) MAPbI$_3$/0.2G-NH$_2$. Scale bars = 500 nm.
**Figure S7** (a) UV-vis spectra and (b) XRD patterns of MAPbI$_3$ and MAPbI$_3$/rGO thin films. (c) Top-surface SEM image of the MAPbI$_3$/rGO film, (d) TRPL decay curves of MAPbI$_3$/rGO thin films. The measurements were performed from the perovskite film side.

**Figure S8** (a) Schematic illustration of the PSC device structure. (b) Cross-sectional SEM image of the MAPbI$_3$/G-NH$_2$-based PSC device. The dashed oval indicates a grain boundary.
Figure S9 (a) J-V curves of PSCs based on MAPbI$_3$ (with different G-NH$_2$ contents) in reverse scan. (b) The corresponding EQE spectrum of the champion PSCs.

Figure S10 Detailed statistics of the PV parameters of PSCs based on MAPbI$_3$ without and with G-NH$_2$ (0.1 cm$^2$ effective cell area).
Figure S11 Champion PSCs characterization (0.1 cm² effective cell area). (a) PV performance statistics, (b) J-V characteristics of PSCs based on MAPbI₃ with and without G-NH₂ under simulated AM 1.5G solar illumination of 100 mW·cm⁻².

Table S1 PV parameters of ‘champion’ PSCs based on MAPbI₃ without and with G-NH₂ (0.1 cm² effective cell area).

<table>
<thead>
<tr>
<th>Scan</th>
<th>J_sc/mA·cm⁻²</th>
<th>V_oc/V</th>
<th>FF</th>
<th>PCE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃/G-NH₂</td>
<td>Reverse</td>
<td>23.1</td>
<td>1.09</td>
<td>0.815</td>
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<tr>
<td></td>
<td>Forward</td>
<td>23.1</td>
<td>1.07</td>
<td>0.785</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>Reverse</td>
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<td>1.07</td>
<td>0.787</td>
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<tr>
<td></td>
<td>Forward</td>
<td>22.1</td>
<td>1.04</td>
<td>0.746</td>
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Table S2 Average PV parameters of large-area PSCs based on MAPbI₃ without and with G-NH₂ (1 cm² effective cell area; 22 devices).

<table>
<thead>
<tr>
<th></th>
<th>J_sc/mA·cm⁻²</th>
<th>V_oc/V</th>
<th>FF</th>
<th>PCE/%</th>
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</thead>
<tbody>
<tr>
<td>MAPbI₃/G-NH₂</td>
<td>22.1±0.4</td>
<td>1.09±0.02</td>
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<td>MAPbI₃</td>
<td>20.4±0.1</td>
<td>1.06±0.02</td>
<td>0.609±0.025</td>
<td>13.2±0.5</td>
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Figure S12 J-V curves for PSCs based on MAPbI\textsubscript{3} without and with G-NH\textsubscript{2} (1 cm\textsuperscript{2} effective cell area) under a simulated AM 1.5G solar illumination of 100 mW·cm\textsuperscript{-2}.

Table S3 PV parameters of large-area ‘champion’ PSCs based on MAPbI\textsubscript{3} without and with G-NH\textsubscript{2} (1 cm\textsuperscript{2} effective cell area).

<table>
<thead>
<tr>
<th></th>
<th>Scan</th>
<th>$J_{sc}$/mA·cm\textsuperscript{-2}</th>
<th>$V_{oc}$/V</th>
<th>FF/</th>
<th>PCE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI\textsubscript{3}/G-NH\textsubscript{2}</td>
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<td>18.7</td>
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<td></td>
<td>Forward</td>
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<td>1.07</td>
<td>0.709</td>
<td>17.3</td>
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<tr>
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<td>21.1</td>
<td>1.06</td>
<td>0.540</td>
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Figure S13 PCE and J output at a maximum power point of 0.85 V for the MAPbI₃/G-NH₂-based ‘champion’ PSC.

Figure S14 EIS characteristics of PSCs based on MAPbI₃ with and without G-NH₂ under illumination.

Figure S15 PCE of the ‘champion’ PSC based on MAPbI₃ without and with G-NH₂ as a function of storage time in a dark box at 20–30% RH and 25–30 °C.
**Figure S16** Calculated charge density at interfaces of MAPbI$_3$ with rGO (yellow=positive, cyan=negative).

**Figure S17** J-V curves for PSCs based on MAPbI$_3$, MAPbI$_3$/G-NH$_2$ and MAPbI$_3$/rGO (0.1 cm$^2$ effective cell area). (b) Corresponding EQE spectrum of the ‘champion’ PSC.
Reference
