Interface Engineering of Layer-by-Layer Stacked Graphene Anodes for High-Performance Organic Solar Cells

Yu Wang, Shi Wun Tong, Xiang Fan Xu, Barbaros Özyilmaz, and Kian Ping Loh*

The major efforts in solar energy research are currently directed at developing cost-effective systems for energy conversion and storage. The high cost of materials and preparation methods that are required for the fabrication of inorganic solar cells prevent their widespread deployment. Seeking a low-cost alternative in the form of solution-processable or roll-to-roll printable organic solar cells features prominently in the energy research roadmap. The conventional anode of choice for organic solar cells has been indium tin oxide (ITO), which consumes as much as 30% of the fabrication cost in solar cells. High quality ITO is expensive due to the dwindling supplies of indium. ITO also suffers from drawbacks like brittleness, sensitivity to acids and bases during processing, and reactive interface formation with copper indium sulfide during high-temperature sintering.

Graphene films have been proposed as the new generation of multifunctional, transparent, and conducting electrodes. The attractiveness of graphene arises from their low cost, transparency, high electrical conductivity, chemical robustness, and flexibility, as opposed to the rising cost and brittleness of ITO. In particular, the 2D graphene sheet is emerging as a possible substitute for ITO in flexible displays, touch screens, and solar cells. The sheet resistance of graphene is given by $R_\text{s} = (\sigma_D N)^{-1}$ where $\sigma_D$ is the 2D sheet conductivity and $N$ is the number of layers. The intrinsic sheet resistance of single layer graphene is calculated to be $\approx 6 \, \Omega$ and is inferior to that of ITO ($10-20 \, \Omega$ sq$^{-1}$). In principle, increasing the thickness (increasing $N$) of graphene using layer-by-layer stacking and doping the graphene (increasing $\sigma_D$ by increasing the carrier concentration) can allow the extrinsic sheet resistance values to be reduced to as low as $20 \, \Omega$ sq$^{-1}$ although it is not trivial to reach this limit at present. Many are excited about the transparency and conductivity of multilayered graphene films, however the ultimate performance of graphene in solar cells may be limited by other factors. First, the interfacial energy offset between graphene and the photoactive materials has to be tuned in order to optimize charge transfer. Second, the planarity and hydrophilic character of multilayer graphene has to be improved to allow for spin-coating with hole-transporting layers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). Third, the preparation of the graphene films has to be improved in terms of achieving large grain crystal growth, as well as reducing contaminations from organic residues in the transfer process. The organic residues have a deleterious effect on the conductivity, transparency, and roughness of graphene films. To date, there have been no reports that graphene can exhibit a power conversion efficiency (PCE) higher than ITO when replacing the latter in solar cell devices. This underscores the difficulty in optimizing any factors in the fabrication of the solar cell devices. It is timely to investigate the interface engineering of graphene in the context of high-performance solar cells. In this work, we carry out a systematic study of the different modification methods for graphene sheets with the aim of optimizing its role as an anode of solar cell. In this context, we have developed a direct layer-by-layer (LBL) transfer method of graphene sheets that is free from the residual impurity (poly(methyl methacrylate) (PMMA)) between the layers. Most importantly, by engineering the interface between the graphene film and the hole transfer layer, we have attained $\approx 83.3\%$ of the PCE of control devices based on ITO as anode. The interface engineering developed here is highly relevant for realizing photovoltaic (PV) and organic light-emitting diode (OLED) devices using graphene electrodes.

A single layer of graphene does not have sufficiently high sheet conductivity. Stacking multilayers together and doping them is needed to achieve higher extrinsic conductivity. Here, we propose a direct LBL interface coupling route for fabricating multilayer graphene films. A schematic diagram for the route is shown in Figure 1a. The difference between the reported route A and our LBL assembly method (route B) is this: as opposed to method A where the PMMA needs to be spin-coated and removed, N times with the transfer of N layers, in method B, we only need to spin-coat the first layer graphene with PMMA once. In method B, the PMMA-coated graphene (first layer) is directly transferred onto the second layer graphene on copper foil. By annealing in 120 °C for 10 min, the π-π interaction between the two layers of graphene bond them together. After etching the copper foil, the two-layer graphene film can be directly transferred onto a third later graphene on copper foil, forming a three-layer graphene film. Based on these steps, N-layer graphene without any organic impurity between the layers can be obtained. Finally, the multilayer graphene can be transferred to other substrates, followed by the removal of the top PMMA in acetone. Figure 1b shows the LBL stacked graphene from 1 to 8 layers transferred onto quartz. The transmittance of the graphene film decreases with increasing number of layers.

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The crystalline quality of the LBL stacked graphene films was analyzed by Raman spectroscopy (514 nm). It can be observed in Figure 1g that the defect-related D-band around 1350 cm$^{-1}$ is not affected by the assembly on the whole, the intensity ratio of (G)/(2D) from 1 to 4 layer increases from 0.4 to 2.7. The blueshift in the Raman 2D band with increasing layer is associated with the reduction in the Fermi velocity of the stacked graphene sample. Different twist angles between layers will affect the Fermi velocity differently, resulting in different degrees of blueshifting for the 2D band (Figure 1h). The 2D band of the LBL assembly graphene is also increasingly broadened from 1 to 4 layer, which should originate from the local, coupled interaction between the layers.

The as-grown graphene samples show standard bipolar field effect (Figure 2a) with a field-effect mobility of 5520 cm$^2$ V$^{-1}$ s$^{-1}$ and 7780 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature (300 K) and low temperature (1.6 K), respectively. The high mobility allows the observation of the quantum Hall effect (QHE). We can access the quantum Hall state when tuning the electron density by adjusting the gate voltage $V_g$ at high magnetic field and low temperature. Figure 2b shows the longitudinal resistivity ($\rho_{xx}$) and the Hall resistivity ($\rho_{yx}$) of chemical vapor deposition (CVD) graphene as a function of the gate voltage at temperature ($T$) = 2 K and magnetic field ($B$) = 9 T. A series of half-integer plateaus with an integer filling factor $\nu$ = 2, 6, 10, 14, and 18 are clearly observed, which are the hallmark of the monolayer graphene. The unusual sequence of integer QH features is related to the quasirelativistic nature of the charge carriers due to the particular graphene band structure near the Dirac point. In graphene, the conventional integer QH quantization for the resistivity $\rho_{xx}$ is shifted by a half-integer due to the half-filling of the $n = 0$ Landau level compared to the other levels: $\rho_{xx} = (\hbar/4e^2) / (n + 1/2) = \hbar/\nu e^2$, where $e$ is the elementary charge, $n$ is the Landau level index, and $\hbar$ is Planck’s constant. Despite the inhomogeneity of the carrier density when $\nu = 14$ and 18, the Hall resistance plateaus at $\rho_{yx}$ are robust and are accompanied by less prominent longitudinal resistance $\rho_{xx}$. The high mobility and QHE provides sufficient evidence for the high quality of such monolayer graphene samples.

To achieve high-performance organic solar cells, control of the surface free energy and work function of the electrodes is essential. In conventional poly(3-hexylthiophene-2,5-diyl)(6,6)-phenyl C$_{61}$ butyric acid methyl ester (P3HT:PCBM)-based polymer solar cell, PEDOT:PSS is spin-coated on top of the TO anode to prevent electron leakage and to aid in hole extraction. The active layer of P3HT:PCBM is sandwiched between an ITO/PEDOT:PSS anode and a low work function cathode. However, in the case of the graphene anode, PEDOT:PSS does...

Previously, Shrotriya et al. reported that the insertion of MoO3 on ITO could increase \( V_{oc} \) from 0.49 V to 0.6 V.\(^{22}\) Similarly, the work function increment on MoO3-coated graphene can yield an improvement of \( V_{oc} \). Similarly, we found that large \( V_{oc} \) value (0.59 V) can also be achieved in the MoO3-modified graphene devices. The \( V_{oc} \) of polymer bulk heterojunction devices depends mainly on the bandgap (\( E_g \)) of the donor and acceptor. Vandewal et al. proposed with ohmic contacts at both the anode and cathode side.

\[
V_{oc} \approx E_{F/m} - 0.43 \text{ V} \tag{1}
\]

with ohmic contacts at both the anode and cathode side.\(^{23}\)

Using 1.08 eV as the \( E_g \) value of annealed P3HT:PCBM layer,\(^{23}\)
the estimated \( V_{oc} \) from Equation (1) is ≈0.65 V. It is quite close to the \( V_{oc} \) value (0.59 V) measured from the MoO3+PEDOT:PSS-modified graphene device.

We observe that the double interfacial layer of MoO3 and PEDOT:PSS is beneficial for the performance of the device. The MoO3 islands can improve the hydrophilicity of graphene and thus assist PEDOT:PSS to wet the surface. The significance of this feature is verified by the performance of the graphene device using only PEDOT:PSS. Without the underlying MoO3, the structural inhomogeneity of PEDOT:PSS causes uneven charge extraction and results in a low PCE (0.12%). The photoactive layer deposited on non-uniform PEDOT:PSS will create a current leakage path and reduce the shunt resistance. Atomic force microscopy (AFM) shows that MoO3 forms nanoislands on the graphene surface (see Supporting Information), so the device improvement should result from a combined work function improvement by MoO3 and surface planarization effect on the deposited PEDOT:PSS. This planarization effect yields an improvement of both \( FF \) and \( J_{sc} \).

not spread well on the as-grown graphene due to its low surface free energy.\(^{16}\) To improve the hydrophillicity of graphene, a thin layer of (≈20 Å) molybdenum oxide (MoO3) is evaporated on the graphene. The presence of the hydroxyl group on MoO3,\(^{17}\) allows the spreading of PEDOT:PSS on MoO3-coated graphene effectively. Ultraviolet photoelectron spectroscopy (UPS) measurements indicate that MoO3-coated graphene has a much higher work function (5.47 eV) than that of as-grown graphene (4.36 eV) (Figure 3b). The large increment in the work function of graphene is attributed to the high work function of MoO3 (6.1–6.6 eV).\(^{18,19}\) As shown in the energy level diagram (Figure 3c), the work function of PEDOT:PSS\(^{20}\) and highest occupied molecular orbital (HOMO) level of P3HT\(^{21}\) is 5.2 eV, whilst the work function of MoO3-coated graphene is 5.47 eV. Thus the energy offset is favorable for barrierless hole extraction. In contrast, the large energy difference between the work function of as-grown graphene (4.36 eV) and the HOMO of P3HT (5.2 eV) introduces a barrier height of 0.84 eV for hole extraction.

The beneficial role of the MoO3+PEDOT:PSS interfacial layer in improving device performance of graphene anode was experimentally verified in solar devices using P3HT:PCBM as the photoactive layer. The device configuration is shown in Figure 3a. The performance of the LBL stacked (4 layers) graphene anodes, and the same but modified with either PEDOT:PSS only, MoO3 only, or MoO3+PEDOT:PSS were compared to identify the best interface engineering methods. Figure 3d and Table I (Supporting Information) indicates that the as-grown graphene device shows poor performance, with an open-circuit voltage (\( V_{oc} \)) of 0.5 V, short-circuit current density (\( J_{sc} \)) of 2.4 mA cm\(^{-2}\) and fill factor (\( FF \)) of 0.29, which yielded a low PCE of 0.35%. After modifying the graphene with MoO3+PEDOT:PSS double interfacial layer, a high \( V_{oc} \) value of 0.59 V was attained. Both \( J_{sc} \) (4.8 mA cm\(^{-2}\)) and \( FF \) (0.43) was also dramatically increased and produced an over threefold increment in PCE (1.23%).

\[ J_{sc} = \frac{2.4 \text{ mA cm}^{-2}}{2.4 \text{ mA cm}^{-2}} \]
Further improvement in PCE can be achieved by acid-doping the graphene layer-by-layer to improve the extrinsic conductivity. Figure 3c and Table 2 (Supporting Information) show the PV effect of the devices with 3-layer, 4-layer, and 5-layer LBL-stacked graphene anode. The MoO$_3$+PEDOT:PSS double interlayer was applied to modify the graphene surface. As shown in Figure 3c, 4-layer acid-doped graphene solar cells exhibited the best PV performance in this work with PCE of 2.5%. A stable $V_{oc}$ of 0.59 V, high $J_{sc}$ of 7.8 mA cm$^{-2}$, and high $FF$ of 0.45–0.51 could be obtained. Figure 3f compares the PV performance of this 4-layer graphene with a control device fabricated on ITO; the PCE of graphene is about 83.3% that of ITO. The control ITO device tested in our measurement conditions has a $V_{oc}$ of 0.38 V, $J_{sc}$ of 9.2 mA cm$^{-2}$, $FF$ of 0.57, and PCE of 3%.  

In principle, increasing the thickness of the film while not sacrificing transparency should produce a higher PCE due to its lower sheet resistance. However, the PCE decreases when we used 5-layer acid-doped graphene. In order to provide a deeper insight into the number of graphene films on the PV effects, series resistances ($R_s$) are analyzed. As reported by Choi et al.,[24] $R_s$ arises from the power loss of various resistive layers in solar cells and is given by

$$R_s A = \frac{P_R}{J_{max}^2}$$  \hspace{1cm} (2)

where $A$ is the active area, $P_R$ is the total resistive power loss density, and $J_{max}$ is the current density at the maximum power point while

$$P_R = P_{Al} + P_{MoO_3+PEDOT:PSS} + P_{P3HT:PCBM} + P_{interfacial contacts} + P_{Al}$$  \hspace{1cm} (3)

where $P_{Al}$, $P_{MoO_3+PEDOT:PSS}$, $P_{P3HT:PCBM}$, $P_{interfacial contacts}$, $P_{Al}$ are the resistive power loss densities of the interfacial contacts and different layers in the devices. Assuming good interfacial morphology is achieved between various layers in the devices, $P_{interfacial contacts}$ will become negligible. $P_{Al}$ can also be neglected because of the high conductivity of the Al cathode. Equation (3) can be further interpreted as

$$P_R = J_{max}^2 (R_{sheet_{anode}}/3 + J_{max}^2 (p)_{MoO_3+PEDOT:PSS} + J_{max}^2 (p)_{P3HT:PCBM})$$  \hspace{1cm} (4)

where $R_{sheet_{anode}}$ is the sheet resistance of anode, $L$ is the length of solar cell, $p$ and $t$ are the resistivity and thickness of the organic layers, respectively.

By combining Equations (2) and (4), $R_s$ can be calculated as shown in Equation (5)

$$R_s A = (L^2 R_{sheet_{anode}}/3 + (p)_{MoO_3+PEDOT:PSS} + (p)_{P3HT:PCBM})$$  \hspace{1cm} (5)

The results indicate that the values of $R_{sheet}$ based on power loss are 14.9, 14.1, and 13.9 $\Omega$ cm$^2$ for 3, 4, and 5 layers of acid-doped graphene films, respectively. With the exception of the 5-layer graphene films, these $R_s$ values are quite consistent with the values evaluated from the inverse slope of dark current density–voltage ($J_D$–$V$) characteristics of the real devices (see Supporting Information). The $R_s$ values extracted from the inverse slope of $J_D$–$V$ data are 15.5 and 14.6 $\Omega$ cm$^2$ for 3 and 4 layers graphene devices. Similar $R_s$ values determined from two approaches further supports our initial hypothesis, i.e., good interfacial contacts exist in the devices. However, this assumption is invalid for graphene films that are >5 layers thick. The $R_s$ values attained from $J_D$–$V$ data of devices (21.5 $\Omega$ cm$^2$) are much larger than that calculated from the power loss equations. The mismatched $R_s$ values suggest that the total resistive power loss in the 5-layer graphene device is governed by the poor interfacial contact. In fact, we believe there is a trade-off between the sheet resistance and morphology in device performance. We have also investigated the PV effect of devices by replacing MoO$_3$ with pyrene bau-noic acid succidymyl ester (PBASE). 4-layer graphene anodes modified with PBASE also exhibited the highest PCE (2%) among other numbers of layers.

In conclusion, we demonstrate that the device efficiency of graphene-anode-based devices (2.5%) modified by MoO$_3$/PEDOT:PSS is very close to that of ITO-based devices (3%). Using 4-layer acid-doped graphene as the anode in organic solar cells, we have attained 83.3% of the PCE of ITO. In fact, all key photovoltaic parameters for solar devices fabricated using the graphene anode are quite similar to those of the ITO anode (Figure 3f). For further improvements to the PCE, the sheet resistance of graphene should be reduced. This can be accomplished either by more effective doping or by increasing the carrier mobility via interface control. One ongoing effort is to increase the size of the single crystal domain of CVD-grown graphene.[25] The layer-by-layer stacking process of the graphene also needs to be improved. The main limitation at the present moment is the increasing roughness with the number of stacked layers in our film preparation process, which results in increased series resistance. Interface engineering of the graphene in terms of modifying its work function and surface free energy is also an important aspect in any charge or energy transfer device. By optimizing these processes, it is highly possible that the PCE of graphene will exceed that of ITO in organic or inorganic solar cell in due course. Finally, the unique advantages of graphene in terms of its flexibility, chemical robustness, and roll-to-roll processability can open a wide range of applications in flexible solar cell panels and display electronics that is not amenable to ITO.

**Experimental Section**

**CVD Graphene:** CVD graphene films were produced in a thermal CVD furnace using copper foil as substrate, similar to methods reported previously (see Supporting Information).[13,26] Fabrication of PV Devices: Sheet resistance values of graphene films were evaluated using four-point-probe method. The poly(3, 4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) film was first spin-coated on top of the anode ($\sim$30 $\Omega$ sq$^{-1}$ ITO or MoO$_3$-coated graphene) and dried at 100°C for 15 min. A 1000 Å P3HT:PCBM blend layer (1:0.8 w/w, 30 mg mL$^{-1}$) was then spin-coated from chlorobenzene on the PEDOT:PSS layer. LiF (10 Å) and Al metal (600 Å) were thermally evaporated through a shadow mask giving an active device area of 0.04 cm$^2$. To prepare MoO$_3$-modified graphene anode, 20 Å of MoO$_3$ was thermally evaporated through a shadow mask on the graphene film. After this, the devices were annealed on a hot plate at 120 °C for 10 min in the dry box. The fabricated solar cells were characterized with
a 150 W solar simulator with AM 1.5G filter from Newport Corporation at an intensity of 100 mW cm\(^{-2}\). Previously, Shrotriya et al. reported the importance of selecting an appropriate reference cell for illumination intensity calibration.\(^{[27]}\) In order to report a reliable device efficiency value, we used a thermal detector with same spectral responsivity profile as that used in the work of Shrotriya et al. and the spectral mismatch was corrected.

**Supporting Information**

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

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Supporting Information


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**Supporting Information**

*CVD growth of graphene:* In a typical experiment, the CVD growth of graphene was carried out in a quartz tube at reduced pressure. Before the growth of graphene, copper foil (25µm thick, 99.999% purity) was pretreated at 1000°C for 30min under a combined flow of Ar:H$_2$=50:10 in order to obtain the copper crystal with larger grain size. After that, Ar gas is replaced into high purity of methane (99.999%). A gas mixture of CH$_4$ (110 sccm) and H$_2$ (10 sccm) was used for the growth of graphene at ~5.0 Torr. After 30 min of growth, the system was cooled down to room temperature under H$_2$.

*Characterization:* The Raman spectra were measured using a WITEC CRM200 Raman system at room temperature. The excitation source is 532 nm laser (2.33 eV) with a laser power below 0.1 mW to avoid laser induced heating of the sample.

For resistance measurement, we apply a small AC current (10 nA) through the samples and measure longitudinal and transverse voltage using Stanford 830 lock-in amplifier. The samples were made into Hall bar geometry by standard e-beam lithography technique with the length of 3.5 micrometer between source and drain. A highly doped silicon wafer is used as the gate electrode with a 300nm silicon oxide as the dielectric layer. The room temperature resistance is measured in a probe station (Alessi REL-4800). Low temperature magnetoresistance is measured in Cryogenic 9T High Field System with a temperature range from 1.6 to 300K.

**TABLE 1.** Performance of graphene-based photovoltaic cells. Device configuration is anode/P3HT:PCBM/LiF/Al (anode is as-grown graphene, MoO$_3$-coated, PEDOT:PSS-coated graphene and MoO$_3$+PEDOT:PSS-coated graphene).

<table>
<thead>
<tr>
<th>Layer number</th>
<th>MoO$_3$</th>
<th>PEDOT:PSS</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>--</td>
<td>--</td>
<td>0.50</td>
<td>2.4</td>
<td>0.29</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>√</td>
<td>--</td>
<td>0.59</td>
<td>4.2</td>
<td>0.40</td>
<td>1.01</td>
</tr>
<tr>
<td>4</td>
<td>--</td>
<td>√</td>
<td>0.42</td>
<td>1.2</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>4</td>
<td>√</td>
<td>√</td>
<td>0.59</td>
<td>4.8</td>
<td>0.43</td>
<td>1.23</td>
</tr>
</tbody>
</table>
TABLE 2. Performance of photovoltaic cells with acid-doped graphene. Device configuration is graphene/MoO$_3$+PEDOT:PSS/P3HT:PCBM/LiF/Al.

<table>
<thead>
<tr>
<th>Layer number</th>
<th>Interlayer doping</th>
<th>Surface doping</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>HCl</td>
<td>HNO$_3$</td>
<td>0.59</td>
<td>7.0</td>
<td>0.45</td>
<td>1.9</td>
</tr>
<tr>
<td>4</td>
<td>HCl</td>
<td>HNO$_3$</td>
<td>0.59</td>
<td>8.5</td>
<td>0.51</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>HCl</td>
<td>HNO$_3$</td>
<td>0.59</td>
<td>6.4</td>
<td>0.44</td>
<td>1.6</td>
</tr>
</tbody>
</table>

TABLE 3. Performance of photovoltaic cells with ITO anode or graphene anode. Device configuration is anode/PEDOT:PSS/P3HT:PCBM/LiF/Al.

<table>
<thead>
<tr>
<th>Anode</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>0.58</td>
<td>9.2</td>
<td>0.57</td>
<td>3.0</td>
</tr>
<tr>
<td>Graphene</td>
<td>0.59</td>
<td>8.5</td>
<td>0.51</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Figure S1. $J$-$V$ characteristics of devices under dark condition (a) anode/P3HT:PCBM/LiF/Al (anode is 4 layers as-grown graphene, PEDOT:PSS coated or MoO$_3$ coated or MoO$_3$+PEDOT:PSS coated 4 layers as-grown graphene), (b) 3-5 layers of HCl+HNO$_3$-doped graphene/MoO$_3$+PEDOT:PSS/P3HT:PCBM/LiF/Al; (c) anode/PEDOT:PSS/P3HT:PCBM/LiF/Al (anode is ITO or MoO$_3$-coated graphene).
Figure S2. AFM sectional analysis of MoO$_3$-coated graphene. The MoO$_3$ forms nanoislands on graphene with the size of $\sim$4nm.
Figure S3. XPS Mo3d core-level spectrum of MoO$_3$-coated graphene. Peaks at the binding energy of 232.7 eV indicates that Mo ion exists as the (+6) form in MoO$_3$ film.

Figure S4. AFM images of graphene film with different layer number, (a) 2 layers, (b) 3 layers, (c) 4 layers, (d) 5 layers. Scale bar is 2µm.

TABLE 4. Root Mean Square (RMS) roughness vs. layer number of graphene film, showing the roughness increases with layer number of graphene.

<table>
<thead>
<tr>
<th>Layer Number</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.22</td>
</tr>
<tr>
<td>3</td>
<td>2.31</td>
</tr>
<tr>
<td>4</td>
<td>3.88</td>
</tr>
<tr>
<td>5</td>
<td>5.62</td>
</tr>
</tbody>
</table>
Figure S5. Optical transmittance spectrum of MoO$_3$ layer. The transmittance is over 99% between 300 to 850 nm.

Figure S6. The Raman spectra of graphene films before and after HNO$_3$ doping. The $p$-doping results in a blueshift (~13 cm$^{-1}$) of both G and 2D peaks.