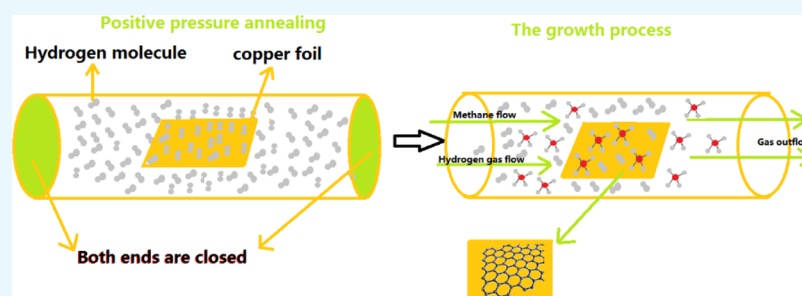


# Growth of Large-Area High-Quality Graphene on Different Types of Copper Foil Preannealed under Positive Pressure H<sub>2</sub> Ambience

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## Supporting Information



**ABSTRACT:** Large-area high-quality graphene was synthesized on different types of copper foils preannealed under positive pressure H<sub>2</sub> atmosphere between 1 and 2 standard atmospheres. The prepared graphene showed good electrical conductivity, transmittance, and uniformity. The sheet resistance values of the grown monolayer graphene film were all about 500 Ω/□, and the transmittance was as high as 97.24%. The carrier mobility of the monolayer graphene film was around 2000–3000 cm<sup>2</sup>/(V s). Furthermore, the monolayer coverage could be more than 95.00% controlled by adjusting the process parameters. The properties of the four layer-superposed graphene film nearly reached that of the commercialized indium tin oxide (ITO) glasses, which showed that the prepared graphene could be well applied to the transparent conductive electrode. The obtained graphene film has been used to construct Si/graphene solar cells without an antireflection film, which showed energy conversion efficiency among 4.99–5.62%.

## 1. INTRODUCTION

Graphene, the one-atom-thick 2D planar structure carbon material, has been a hot spot for long time because of its unique properties.<sup>1–4</sup> The prerequisite for these excellent properties to be fully utilized is to prepare high-quality graphene. It is known that graphene can be prepared by micromechanical exfoliation<sup>5</sup> method, chemical vapor deposition (CVD),<sup>6–9</sup> oxidation reduction<sup>10</sup> method, solvothermal<sup>11</sup> method, and so on. Among these preparation methods, only CVD method can meet the requirements of large-scale preparation of high-quality, large-area, and uniform graphene films. So far, graphene has been grown on a number of metals<sup>7–9,12–17</sup> by a surface-catalyzed process. Among these metals, copper foil has obvious advantages, such as high melting point, low absorption rate of carbon atoms, low price, and reusability. However, it is well known that the surface condition of copper foil has a great influence on the growth of graphene. To grow high-quality graphene films, prior to the preparation of graphene, many pretreatment methods have been applied on the copper foil substrates to optimize their surface conditions, such as pickling, electrochemical polishing, oxidation, long-time annealing, melting-resolidifying, smoothing, and so forth.<sup>18–22</sup> In addition, in the past 2 years, single-crystal copper foil substrates could be prepared by adjusting the annealing process of polycrystalline copper foil. Thus, high-

quality and flat substrates could be provided for the subsequent preparation of large-scale single-crystal graphene films.<sup>23,24</sup> As reported previously, Alfa Aesar copper foil (abbreviated as  $\alpha$  copper foil) was generally used as substrates for the growth of high-quality graphene.<sup>9,20,25</sup> It is also noted that low-pressure H<sub>2</sub> gas was usually used in the pretreatment (preannealing) of copper substrates.<sup>18</sup> In this work, we proposed to use, instead, positive H<sub>2</sub> pressure in preannealing of the copper foil substrate, under which more H<sub>2</sub> molecules would take part in modifying the surface condition of the foil. It was expected that thus treated foils would be more suitable for growing high-quality graphene, regardless of the type of the copper foil.

To verify this idea, four types of copper foils were used as the substrates in our investigation. They were first preannealed under positive H<sub>2</sub> pressure of 1–2 standard atmospheric pressure, and then, the graphene were synthesized on them under the condition used conventionally. The experiments demonstrated that high-quality graphene films could be deposited on all these four types copper foils preannealed under positive pressure H<sub>2</sub> ambient. The prepared graphene films have good electrical conductivity (the sheet resistance are

Received: December 29, 2018

Accepted: February 14, 2019

Published: March 12, 2019

all about  $500 \Omega/\square$ ) and carrier mobility (around 2000–3000  $\text{cm}^2/(\text{V} \cdot \text{s})$ ). The coverage of the monolayer graphene could reach more than 95.00%. Besides, to demonstrate its good uniformity and quality, different parts of a thus prepared graphene film were used respectively to construct Si/graphene solar cells. For all of the constructed cells, the energy conversion efficiencies (PCE) were within 4.99–5.62%. Our results showed that the proposed positive  $\text{H}_2$  pressure preannealing technique is promising and suitable for different types of copper foil substrates for high-quality graphene preparation.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of Copper Foil Substrates.** Four kinds of commercial copper foils were used in the work, which were as follows: T<sub>2</sub> copper foil (25  $\mu\text{m}$  thick, 99.8%, named “A”), electrolytic copper foil (25  $\mu\text{m}$  thick, 99.8%, named “B”), oxygen-free copper foil (40  $\mu\text{m}$  thick, 99.8%, named “C”), and  $\alpha$  (Alfa Aesar) copper foil (25  $\mu\text{m}$  thick, 99.8%, named “D”). All of the reagents used in the experiment are of analytical grade.

The purchased copper foils (A–D) were cut into pieces of size 2 cm  $\times$  2 cm. In addition, the copper foil pieces were dipped into acetic acid solution (the volume ratio of acetic acid to water is 1:1) for 60 min at room temperature to remove the oxide layer and impurities on their surface. Then, they were cleaned with deionized water repeatedly for getting rid of acetic acid. To remove the organic compounds on the foil surface, the copper foil pieces were then sequentially soaked in acetone and ethanol for ultrasonic cleaning for 10–20 min. At last, the cleaned copper foil pieces were kept in acetone solution or dried out for using as the substrate of graphene synthesizing immediately.

**2.2. Synthesis of Graphene Films.** A tubular furnace with a CVD system was used in our experiment. A few pieces of the four kinds of cleaned copper foils were put on the quartz boat, and the boat was put onto the middle of the furnace tube. A mechanical pump was used to vacuum the tube until the inner pressure was lower than 10 Pa. During vacuuming, hydrogen was brought into the tube at least three times to exhaust the air inside for ensuring a clean growth environment. Then, the foil pretreatment and graphene deposition were started.

Figure 1 shows schematically the growth processes. A certain amount of  $\text{H}_2$  was injected into the furnace tube. Then, both ends of the furnace tube were sealed, insuring that no air would leak into the tube. The amount of the injected  $\text{H}_2$  gas was controlled to provide a positive pressure between 1 and 2 standard atmospheres inside the tube, when the tube temperature reached the annealing temperature (9). After the  $\text{H}_2$  infection, the substrates were heated up to 980  $^\circ\text{C}$  within 60 min (with the heating rate of about 20  $^\circ\text{C}/\text{min}$ ). Then, the copper foil substrate was preannealed at the temperature for about 30 min. Afterward, the  $\text{H}_2$  gas flow was introduced into the tube with the flow rate of 300 sccm. In addition at the same time, 1.4 sccm  $\text{CH}_4$  was brought in for the growth of the graphene film. The time for the growth of graphene was about 140 min.

When the growth step was over, the heating system and gas source were turned off and the lid of the tubular furnace was opened to cool the tube to room temperature. The size of the prepared graphene film could be adjusted with the size of the

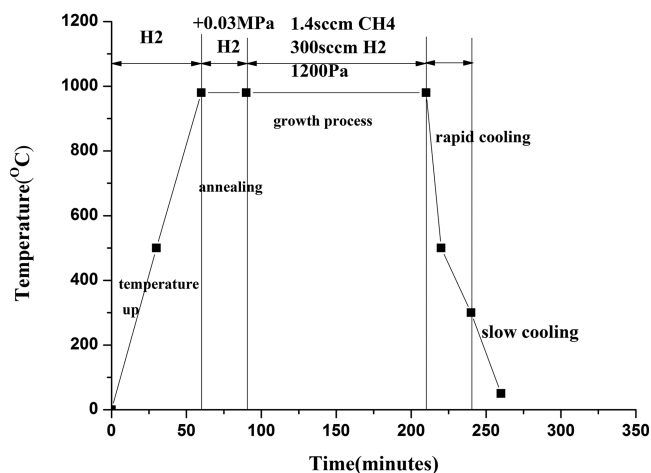


Figure 1. Flow diagram for the growth of graphene.

oven’s hearth. In addition, the graphene film with an area of 20  $\times$  30 cm was produced in our work.

The wet transfer method<sup>26</sup> was used to transfer the prepared graphene films onto  $\text{SiO}_2/\text{Si}$  and Quartz glass sheets for measuring the sheet resistance, carrier mobility, and transmittance. The size of the  $\text{SiO}_2/\text{Si}$  and quartz glass sheets was 1.5 cm  $\times$  1.5 cm, and the transferred graphene films covered the entire substrate surface.

**2.3. Fabrication of the Graphene/Si Solar Cells.** To demonstrate the quality of the graphene films prepared with our method, the graphene/Si (G/Si) solar cells were fabricated with the prepared monolayer graphene grown on oxygen-free copper foils. The structure of the cell is shown in Figure 2, in

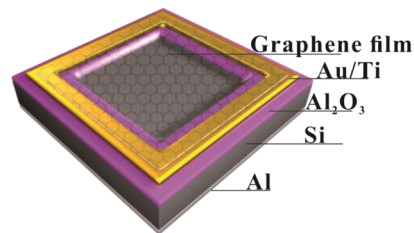


Figure 2. Model of the solar device.

which the layers, from the top to bottom, are graphene film, gold/titanium (Au/Ti), alumina ( $\text{Al}_2\text{O}_3$ ), silicon (Si), and aluminum (Al). The cell fabrication process was briefly as follows. A mask plate of 25  $\text{mm}^2$  (5 mm  $\times$  5 mm) was first put on the middle of the front surface of an n-type doped silicon wafer ((100), 0.5 mm, resistivity: 1–10  $\Omega \cdot \text{cm}$ ) of a size of 1 cm  $\times$  1 cm. Then, the front surface of the wafer was coated with a 100 nm alumina ( $\text{Al}_2\text{O}_3$ ) layer by using a high vacuum multitarget magnetron sputtering coating machine. Subsequently, gold/titanium (Au/Ti) and aluminum (Al) electrodes were evaporated to provide Ohmic contacts on the front and back sides, respectively. Next, the mask plate was removed, leaving a square window, and the produced monolayer graphene film was transferred onto the Si substrate, covering the entire window and tightly contacting with the Si wafer. To demonstrate the uniformity of the prepared graphene films at the same time, six Gr/Si solar cells were fabricated with their graphene layers intercepted from the produced graphene film of large size deposited on the large size copper foil substrate.

**2.4. Characterization.** The pretreated foil substrate surface, prepared graphene films, and fabricated Si/graphene solar cells were characterized using appropriate methods as follows. A horizontal high power X-ray powder diffractometer (XRD) (model: TTR-III) was used to analyze the structure of the copper foil surface after negative and positive pressure annealing.

A field-emission scanning electron microscope (model: JEOL JSM-6700F) was used to observe the microstructure of the synthesized graphene.

Raman spectra of the prepared films were measured using HORIBA Jobin Yvon micro-Raman spectrometer (model: LabRAM 800HR). The layer number and large-scale uniformity of graphene samples could be determined by the spectral characteristics.

Visible spectrophotometer (Shanghai Shunyu constant company, Instrument model 723PC) was used to measure the light transmittance of the graphene film transferred from the copper substrate to Quartz glass sheet.

The hall Effect measurement system (ECOPIA Co., Ltd., model: HMS-5000) was used to measure sheet resistance and carrier mobility of the prepared graphene in the van der Pauw configuration with a 0.56 T magnetic field.

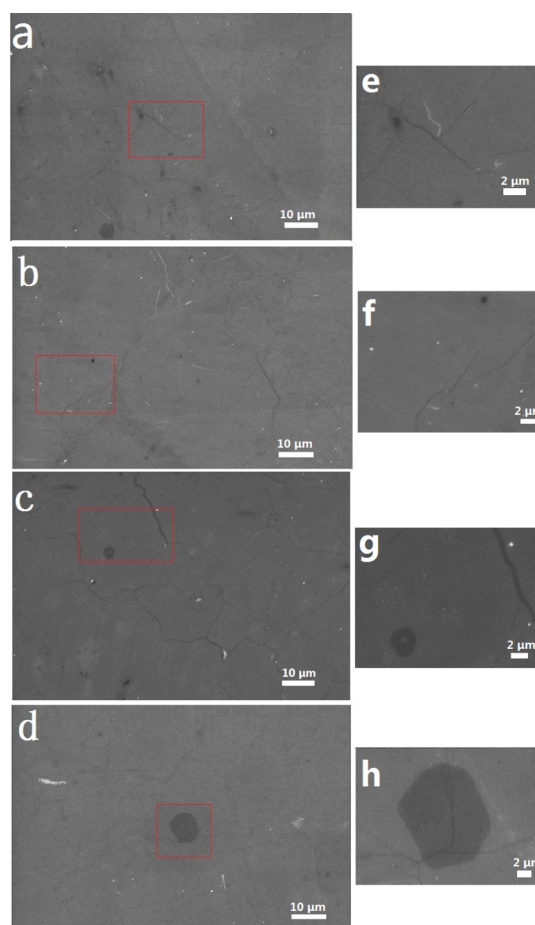
Zolix SS150 Solar Simulator is used to test the performance parameters of the solar cells, such as photoelectric conversion efficiency, open circuit voltage, short circuit current, and filling factor.

### 3. RESULTS AND DISCUSSION

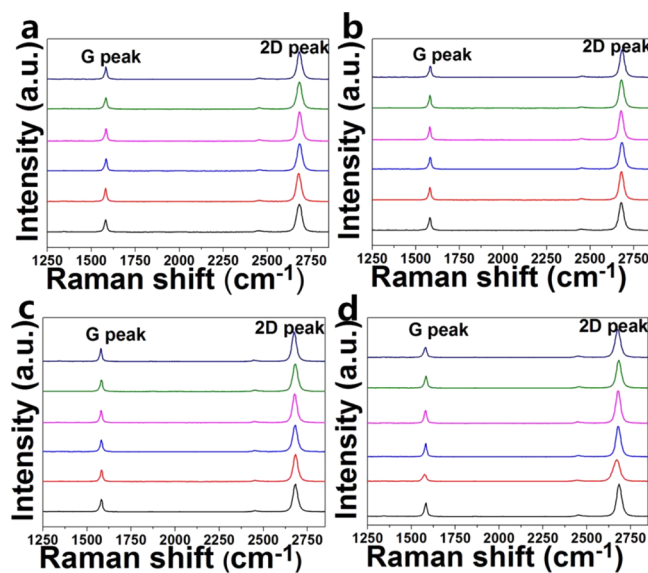
We examined systematically the Graphene films deposited on the copper foils annealed under positive pressure. Figure 3a–d shows the SEM images of the graphene films (on the silicon substrates), which were respectively grown on copper foils A–D under the conditions of an optimizing the gas ratio and growth time. The images indicated that thus deposited graphene films covered the entire surface of substrates, and films were continuous and their uniformity was good. In this case, we could prepare graphene films with a monolayer proportion of 95% or more. Figure 3e,f shows partial enlarged views corresponding to images a–d. From the images, we could see that the graphene films have less dark area (dark areas are multilayered) and have almost uniform color. The number of the carbon atom layer of the graphene film was characterized by Raman.

Figure 4a–d displays the Raman spectra of the graphene films grown on the four kinds of copper foils (A–D), each of which contain six spectra corresponding to arbitrarily selected 6 areas of the same graphene film. In each chart, six color curves represent the spectra at six different locations in the graphene. It is known that Raman spectra of graphene materials generally show three major peaks (D peaks:  $\sim 1350\text{ cm}^{-1}$ , G peaks:  $\sim 1580\text{ cm}^{-1}$ , and 2D peaks:  $\sim 2700\text{ cm}^{-1}$ ),<sup>27</sup> and the D peak was thought to be responsible for the existence of the defects in the sample. Figure 4a–d shows that the spectra nearly has no D peak, which means the prepared graphene film nearly has no defect. The ratio of  $I_{2D}/I_G$  in the spectra measured on different areas of the sample are nearly the same (Table S1 in the Supporting Information), reflecting that the films are uniform, consisting of monolayer regions.

Monolayer graphene films grown on the four copper foils (A–D) were transferred to the  $\text{SiO}_2/\text{Si}$  substrates to test the sheet resistance and carrier mobility. The statistical histogram of the measured sheet resistances are shown in Figure 5a–d,

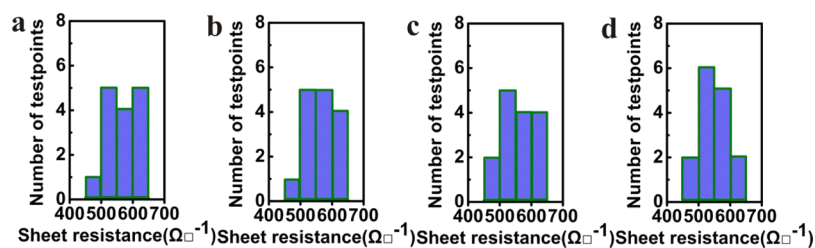


**Figure 3.** SEM image of monolayer graphene prepared on four copper foils (transferred to Silica wafer). (a) A copper foil, (b) B copper foil, (c) C copper foil, (d) D copper foil; (e–h) Partial enlarged images corresponding to (a–d).

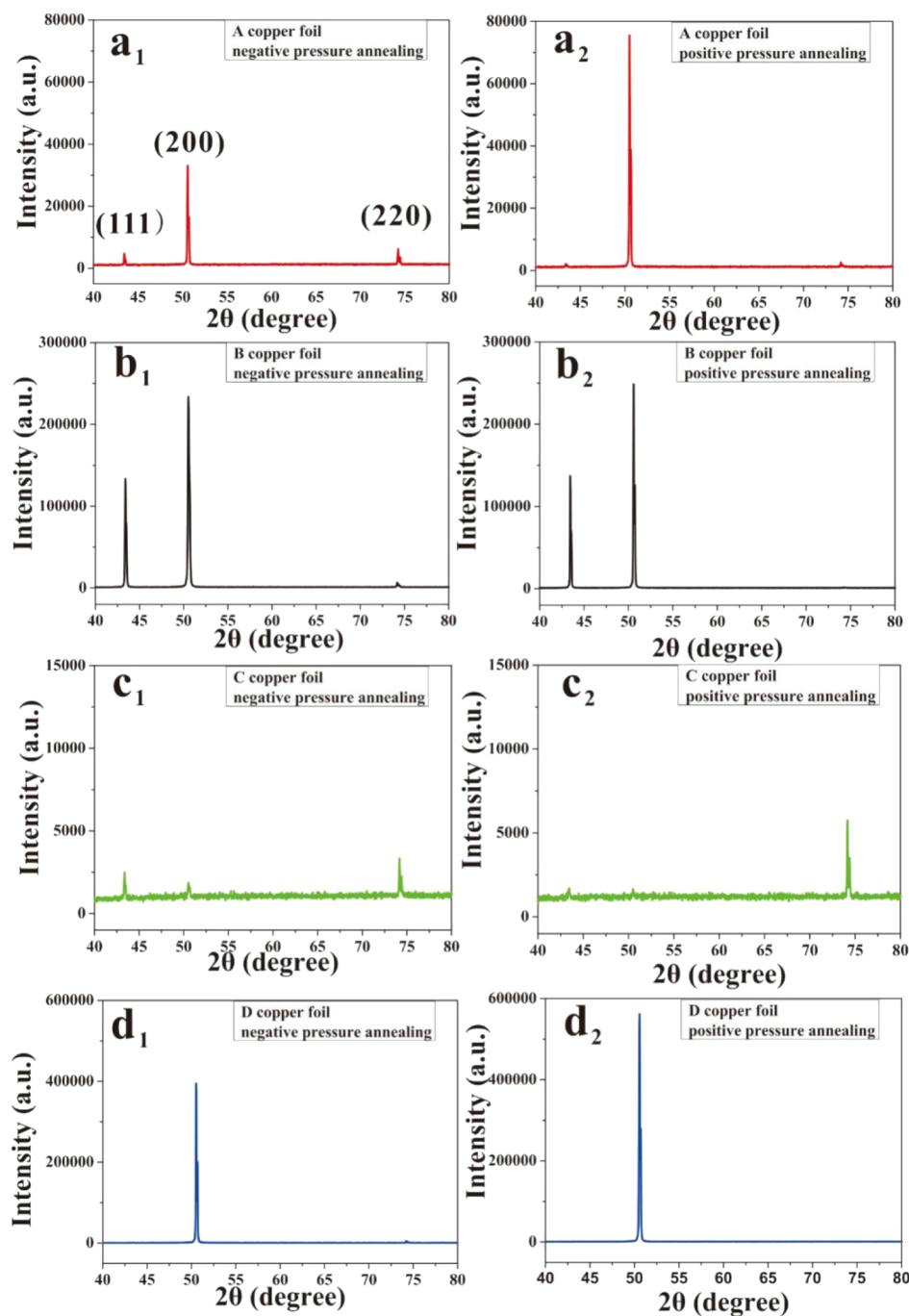


**Figure 4.** Raman spectra of graphene films grown on (a) “A”, (b) “B”, (c) “C” and (d) “D” copper foils.

where the data were recorded from randomly selected 15 test points on each sample. The results show that the sheet resistance are mainly among  $500\text{--}600\ \Omega/\square$ . In addition, the



**Figure 5.** Sheet resistance of the monolayer graphene grown on the four kinds of copper foils: (a) A substrate; (b) B substrate; (c) C substrate; and (d) D substrate.



**Figure 6.** XRD spectra of the four kinds of copper foils pretreated with N-A and P-A: (a–d) denote the foil types A–D, respectively, and the subscripts 1 and 2 denote the corresponding foils that underwent negative and positive H<sub>2</sub> pressure annealing, respectively.

Hall measurement showed that the values of the carrier mobility of these samples were 2000–3000 cm<sup>2</sup>/(V s). The uniformity of sheet resistance and carrier mobility over the whole layer implies higher lattice quality of the prepared graphene films.

However, it was found that the growth conditions of graphene for the four kinds of copper foils, preannealed under positive H<sub>2</sub> pressure (less than 2 atm), were wider than negative preannealed substrates to produce high-quality graphene films, which would be very conducive to the industrial production. In particular, the suitable annealing time is around 30–120 min, which is as that used for low-pressure annealing. The growth results are not good when the annealing time is too short or too long. This may be explained as follows: the recrystallization of the copper foil has not yet been completed, if the annealing time is too short; to the opposite, if the annealing time is too long, then the evaporation of copper foil will be too serious, leading to production of more defects in copper.

Our results demonstrated that the positive pressure annealing of the copper substrates is more favorable for graphene deposition. To understand the mechanism, the surface crystalline structures of the four types of copper substrates annealed under positive and negative H<sub>2</sub> pressure were compared. Figure 6 shows the XRD spectra of the four kinds of copper foils, where Figure 6a–d is respectively for foils A–D, and the subscripts 1 and 2 indicate the foils were annealed respectively under the ambient of negative H<sub>2</sub> pressure (N-A) and positive H<sub>2</sub> pressure (P-A). For all four kinds of foils, the spectra show three peaks (111), (200), and (220), but their intensities differ considerably for foils treated with N-A and P-A. Figure 6a<sub>1</sub>,a<sub>2</sub> shows the recorded XRD spectra of “A” copper foils after N-A and P-A, respectively. It is found that, different from the spectra of the N-A-treated sample, for the sample after P-A treatment, the intensities of (220) and (111) peaks were weakened, whereas the intensity of (200) peak was enhanced considerably. The results for “B” copper foil (Figure 6b<sub>1</sub>,b<sub>2</sub>) show that for the XRD spectra (Figure 6b<sub>2</sub>) of the foil treated through P-A, the intensities of (111) and (200) peaks were enhanced, and the (220) peak disappeared in comparison with that of N-A-treated foil B. The results for the “C” copper foil (Figure 6c<sub>1</sub>,c<sub>2</sub>) display that after P-A, the (111) and (200) peaks nearly disappeared, and the (220) peak was enhanced a lot. In addition, the results for “D” copper foil (Figure 6d<sub>1</sub>,d<sub>2</sub>) show that after P-A, the (220) peak disappeared, and the (200) peak was enhanced with respect to the N-A-treated foil. The results mentioned above demonstrated that the P-A-treated copper foil, compared with the N-A-treated foil, exhibited better crystallinity and the preferential orientation, which would be more favorable for the growth of graphene (large area and single crystalline).

Figure 7 shows the optical photographs of the graphene-copper foil (copper foil annealed under negative pressure). In Figure 7a–c, the places that are not covered with graphene were oxidized and showed the color of copper oxide. In Figure 7d, the copper foil is  $\alpha$  copper foil, which could prepare large area and continuous films under negative pressure and certain parameters as has been reported in many papers. Figure 8 shows the optical photographs of the graphene/copper foil (copper foil annealed under positive pressure). As could be seen from the pictures, graphene grown on four kinds of copper foils have very good continuity, and graphene film completely covered the surface of the copper foil substrate. By

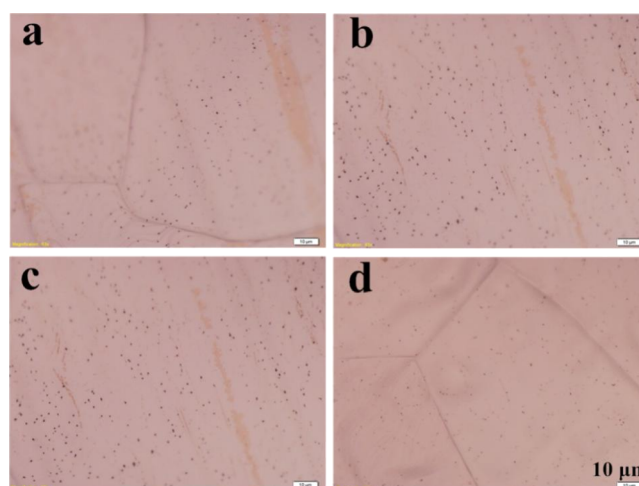


Figure 7. Graphene grown on (a) A copper foil; (b) B copper foil; (c) C copper foil; and (d) D copper foil. (The scale of four pictures is 10  $\mu\text{m}$ ).

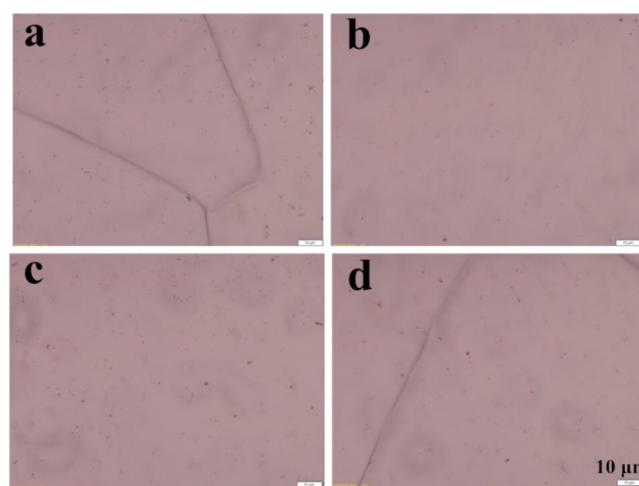
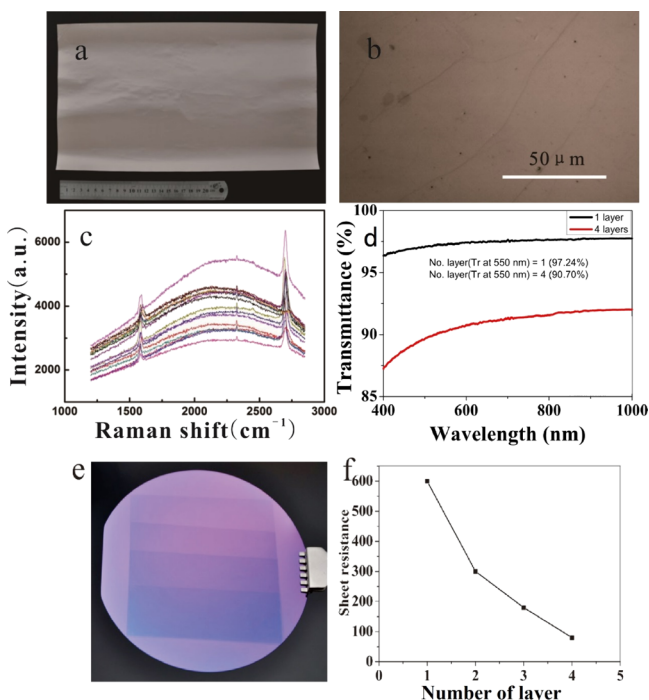


Figure 8. Graphene grown on (a) A copper foil; (b) B copper foil; (c) C copper foil; and (d) D copper foil. (The scale of four pictures is 10  $\mu\text{m}$ ).

comparison, graphene films with better quality could be prepared on copper foil substrates under positive pressure annealing.

Figure 9a displays the picture of a 20 cm  $\times$  30 cm oxygen-free copper foil (type C) with a graphene layer deposited on its surface. Figure 9b is the optical microscope photograph of the graphene layer (shown in the picture (a)) transferred to a silicon substrate. From the picture, it is seen that the whole grown graphene is continuous and exhibits the same color, implying that almost no multilayer region exists in the grown film. Figure 9c is the Raman spectra recorded from randomly selected 16 sites of the as-grown graphene film on the oxygen-free copper foil. These spectra clearly demonstrate that the grown graphene is basically in monolayer form and the amount of defects is very small. The transmittance of the deposited monolayer graphene film is 97.24% ( $\lambda = 550 \text{ nm}$ ) as shown in Figure 9d. With the method of wet transfer<sup>26</sup> and layer superposition, a four layer-superposed graphene film was prepared, of which the sheet resistance was about 80  $\Omega/\text{sq}$  and the light transmittance was 90.70%. Through the same method, 1–4 layers graphene film were transferred to silicon

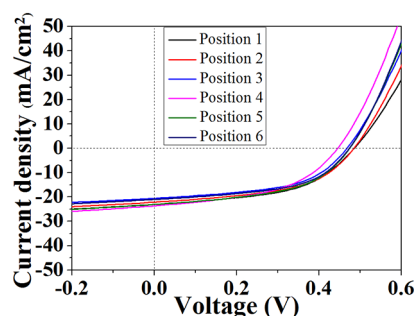


**Figure 9.** (a) Optical photograph of an as-grown graphene on a oxygen-free copper foil. (b) Microscope photograph of the graphene [the same as in picture (a)] transferred to a silicon substrate. (c) Raman spectra of graphene on a oxygen-free copper foil as shown in figure (a). (d) Transmittance of the monolayer and superposed four layers of graphene film transferred onto the quartz glass sheets. (e) 1–4 layers of graphene film transferred to silicon oxide substrate. (f) Sheet resistance of 1–4 layers graphene film.

oxide substrates, as shown in Figure 9e, and the surface resistance was tested. The results are shown in Figure 9f. It could be seen that the surface resistance of 1–4 layers of graphene was reduced from 500 to 80  $\Omega/\text{sq}$ . These properties of graphene films nearly reached that of the commercialized indium tin oxide (ITO) glasses. The surface resistance of the commercialized ITO glass is in the range of several tens of ohms to several hundred ohms, and the light transmittance is 80% or more. The higher the light transmittance, the larger the sheet resistance is. These results show that the graphene we prepared could be well applied to the transparent conductive electrode.

It was possible to synthesize single-crystal graphene domains by controlling the growth condition. We prepared single-crystal graphene by adjusting the growth condition parameters. As shown in the Figure S1, the diameter of the prepared single-crystal graphene was about 500  $\mu\text{m}$ .

Figure 10 shows the current density ( $J$ )–voltage ( $V$ ) characteristics of the Gr/Si solar cells. As seen from the figure, the curves for the six solar cells are similar to each other and with only a small dispersion. From the figure, the performances of the cells were derived, and the results are summarized in Table 1. It can be seen that all of the cells have similar performances. These results evidenced qualities of different parts of the graphene film that were nearly the same, which indicated that the graphene film prepared in this work was quite uniform.



**Figure 10.**  $J$ – $V$  characteristics of as-fabricated G/Si solar cells.

**Table 1.** Open-Circuit Voltage ( $V_{oc}$ ), Short-Circuit Current ( $J_{sc}$ ), Fill Factor, and Energy Conversion Efficiency (PCE) of the Six Solar Cells Fabricated in the Work

	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	fill factor (%)	PCE (%)
position 1	0.48	22.91	51.08	5.62
position 2	0.48	21.96	51.57	5.43
position 3	0.46	20.44	53.07	4.99
position 4	0.44	23.47	48.63	5.02
position 5	0.47	22.94	51.13	5.51
position 6	0.47	20.93	53.07	5.22

## 4. CONCLUSIONS

The positive pressure  $\text{H}_2$  ambience annealing method was proposed and used to pretreat the copper foil substrates for graphene deposition. The results demonstrated that high-quality, large-area graphene films could be deposited on different types of copper foil substrates by using the proposed substrate preannealing method. The sheet resistances of the obtained graphene films are all about 500  $\Omega/\square$ . In addition, the coverage of the monolayer graphene film on the substrates could be more than 95.00%. The transmittance of the produced monolayer graphene film is as high as 97.24%. The electron mobility of the graphene films grown on the four types of copper foils was in the range of 2000–3000  $\text{cm}^2/(\text{V s})$ . The prepared graphene films were used to fabricate graphene/silicon solar cells. The energy conversion efficiencies of all of the fabricated cells were between 4.99 and 5.62%, which also illustrated the continuity and uniformity of the prepared graphene films. The advantage of the proposed method was preliminarily analyzed, which could be attributed to the better crystallization orientation of the copper foils under positive pressure  $\text{H}_2$  ambience annealing.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02538.

Ratio of  $I_{2D}/I_G$  for each Raman spectrum and single-crystal graphene domain image (PDF)

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank Professor Li-Ren Lou for his help in the preparation of this paper. This work was supported by the National Natural Science Foundation of China (grant nos. 11374280, 50772110).

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