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The role of copper on the restoration of graphene oxide by chemical vapor deposition

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Abstract

High-quality reduced graphene oxide (rGO) sheets can be accessible through Langmuir–Blodgett self-assembly (LBSA) on copper foil and dielectric substrate under high temperature ethanol vapors via chemical vapor deposition (CVD) process. Through the LBSA forming method, a uniform and smooth graphene oxide (GO) film can be obtained on the target substrate, which is more economical and efficient compared to the traditional growth strategy. Moreover, the GO-derived graphene film repaired on copper was nearly defect-free with a negligible defect density (I_D/I_G ratio of < 0.1) and manifested a strong 2D peak, indicating high efficiency of defects restoration. The obtained rGO sheets exhibited excellent electrical properties (1.2 kΩ/sq prepared on SiO₂/Si, 0.2 kΩ/sq prepared on copper and subsequently transferred to SiO₂/Si) that had surpassed other GO-derived graphene ever reported. Meanwhile, we demonstrate that Cu-vapor will degrade the restoration efficiency when introduced remotely, which is quite different from previous studies on graphene growth.

1. Introduction

Graphene has attracted enormous attentions due to its fascinating performance like outstanding mechanical, optical and electrical properties [1–6] which have been applied in wide range of fields [7–12]. The preparation of graphene has been invested a lot, including mechanical exfoliation [13], epitaxial growth [14, 15], chemical vapor deposition (CVD) [16–18] and graphite oxide reduction [19–21]. Among these methods, the most promising and accessible process to obtain high-quality graphene is through CVD on copper substrate due to its catalytic and self-limited to a monolayer of graphene growth [22]. In addition, the synthesis of graphene by reducing graphene oxide is becoming a relatively efficient way according to its large scale and low cost. However, many vacancies and oxygen-containing functional groups on graphene oxide (GO) are mainly derived from the liquid-phase stripping preparation [23], which restrain the recovery of the structure. Many attempts have illustrated that thermal annealing turned out to be efficient but still remained large number of vacancies which is generally far inferior to the traditional graphene growth on metal substrate [24–26]. It is demonstrated that with the presence of precursor (CH₄, ethanol, isopropanol, etc.), thermal annealing has been a more promising method to recover GO sheet and improve its crystallinity and conductivity [27–30]. Generally, the defects restoration of reduced graphene oxide (rGO) is unsatisfactory with strong intensity of the Raman D peak, especially on dielectric substrate owing to its weak catalysis comparing to the copper [31]. Therefore, it is essential to find an efficient and controllable approach to prepare rGO film with excellent quality and electrical performance, which can meet the requirements of both electronic devices and industry. Herein we apply a low-cost CVD-assisted annealing in hydrogen/ethanol atmosphere to restore the LBSA-made GO film on copper,
which is efficient and controllable to repair the defects and has the lowest $I_{D}/I_{G}$ ratios ($<0.1$) and sheet resistance ($0.2 \, \Omega/\text{sq}$) compared to other reported GO-derived graphene. Furthermore, we demonstrate that copper has played a different role on the rGO when introduced in another form as the remote Cu-vapor when repairing on the SiO$_2$/Si substrate.

2. Methods

2.1. Synthesis of the GO-derived graphene film

We used graphene oxide from GaoxiTech. In order to form a single layer of GO-covered film on the substrate, we adopted Langmuir-Blodgett self-assembly (LBSA) \[^{25, 32}\]. Disperse 1 ml GO solution with a concentration of 1 mg/ml onto the surface of deionized (DI) water with a dropper. Then, the mixture solution was allowed to stand for 1 min, at which time the GO solution gradually dispersed evenly and a uniform film with approximately 2 nm thickness was formed on the water-air interface. At this point we used the target substrate (copper foil or SiO$_2$/Si) to pull out the GO film slowly and dried it at 90 °C for 3 min to evaporate the ethanol and DI water (figure 1(b)). For the LPCVD treatment, samples were introduced in a quartz tube furnace while being fed a flow of mixture comprising 10 sccm of H$_2$ and ethanol (99.9%) for 60 min at 1000 °C. After this process, the sample was cooled to room temperature under the protection of H$_2$.

2.2. rGO transferred

Due to subsequent characterization of Raman, XPS and electrical measurements, the treated rGO on copper should be transferred to a SiO$_2$/Si substrate by wet etching. First prepared an anisole solution of PMMA (polymethyl methacrylate) with a mass fraction of 8wt%. The PMMA solution was spin-coated onto the side of the rGO/copper surface and then heated two minutes to form a protective layer of moderate thickness. In order to remove the graphene grown on the back of copper during CVD, the other side of the sample was exposed to O$_2$ plasma for 3 min. Then, the copper foil was placed on the solution of 1M FeCl$_3$ to separate the rGO from the substrate. After the metal was totally etched, only PMMA/rGO film remained. PMMA/rGO film was washed several times in deionized water and transferred to the target substrate. After removing the PMMA on the rGO film surface with acetone solvent, the film was finally dried in protective gas. Similar to the transfer process of rGO/copper, we used hydrofluoric acid instead of FeCl$_3$ to etch SiO$_2$/Si substrate, and subsequently transferred rGO film onto quartz glass for UV characterization.

2.3. Characterization

The morphology of rGO film on the copper and SiO$_2$/Si substrate was analyzed by the scanning electron microscope (SEM). The Raman spectrum of transferred rGO on the SiO$_2$/Si substrate was tested by HR Evolution Raman spectrometer. The laser wavelength was 532 nm and the quality of rGO was initially measured. Elemental composition analysis was carried out with x-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) and Energy Dispersive Spectrometer (EDS). The optical Transmittance was carried out by UV–visible spectrophotometer (Shimadzu UV–2700). Sheet resistance measurements were measured with the four-point probe method using a PROBES TECH RTS-8.
3. Results and discussions

3.1. Restoration of GO film on Cu substrate

Through the LBSA forming method, a uniform and smooth GO film can be obtained on the dielectric substrate and copper foil (figure 1(b)). It is worth noting that, due to the self-limiting characteristic, the graphene films growing on copper are predominantly single-layer [9, 33]. Resulting from the low carbon solubility in copper and poor carbon saturation, graphene surface coverage will play a role in preventing the growth process [34]. During our experiment, the copper substrate can be completely covered with a uniform GO film without exposing any area of copper. According to this self-limiting theory, barely new graphene will grow on our sample and affect the characterization of GO. In our experiment, the original defects in GO were mainly vacancies and poor carbon saturation, graphene surface coverage will play a role in preventing the growth process.

3.2. Restoration of GO film on dielectric substrate with Cu–vapor introduced

In order to explore the role of copper played during the process, we introduced copper in another way, that is, remote Cu–vapor. As we know copper foil evaporates easily at high temperature and releases Cu atoms due to its high vapor pressure. As is vividly showed in the figure 4(a), we introduced Cu–vapor from the copper foil suspended 5mm away from the SiO₂/Si substrate without any physical contact. Meanwhile, there was no Cu detected by Energy Dispersive Spectrometer (EDS) which means the as-made rGO film was confirmed to be free of Cu deposition (figure 4(c)). The XPS analysis also proved there was no Cu residue on the surface of the sample.

We carried out the CVD restoration experiment with precursor of ethanol and H₂ at various concentrations, that is, different amounts of C atoms. In Raman spectra, the intensity ratio $I_D/I_G$ (1D, intensity of the D peak; $I_G$, intensity of the G peak; $I_D$, intensity of the D peak) of Cu deposition was due to the presence of the covalent C–O bonds at both top and bottom surfaces and absorbed contaminations [44, 45]. After restoration, the thickness of single GO domains was determined to be 1.8 nm (figure 3(b)), indicating that functional groups and absorbed contaminations were removed by the H₂ and hydroxyl species. Therefore, our restoration approach can effectively remove the functional groups of GO and recover the lattice structure.
intensity of the G peak) has been found to be related to the defect density of graphene. We can vividly find the linear relationship between \( I_D/I_G \) and partial pressure of ethanol, which prove that the restoration of lattice defect based on the content of precursor (figure 5(a)). It can be found from the figure 5 that as the amount of precursor ethanol increased, the intensity of the D peak significantly decreased and the 2D peak became stronger at the same time implying less defects of rGO remained. In detail, the average \( I_D/I_G \) peak ratios decreased from 2.05 to 1.84 then to 1.30, finally to 1.04 of the regular CVD process on SiO\(_2\)/Si, while the average intensity ratios were 2.44, 2.06, 1.36 and 1.05 for Cu-vapor participation CVD reaction. However, contrary to the previous results and expectations, the introduction of Cu-vapor did not promote the repair, but even reduced the efficiency of defect restoration (figure 5(b)). Therefore, we put forward a conjecture that copper and Cu-vapor
Figure 4. (a) Langmuir-Blodgett self-assembly GO film on SiO$_2$/Si substrate treated via CVD process on SiO$_2$/Si substrate with remote introduction of Cu-vapor, (b) Scanning electron microscopy of LBSA rGO film on SiO$_2$/Si substrate repaired with Cu-vapor, and (c) corresponding EDS element distribution map.

Figure 5. Raman spectra of (a) GO-derived graphene film under different partial pressure of ethanol at 1000 °C, (b) GO-derived graphene film under different partial pressure of ethanol with Cu-vapor introduced at 1000 °C and (c) corresponding average $I_D/I_G$ intensity ratios, (d) GO-derived graphene film repaired at 1040 °C with or without Cu-vapor under 50Pa partial pressure of ethanol.
have totally different influence on the rGO during thermal annealing. When the ethanol content was insufficient (50Pa), only a small amount of carbon atoms generated. At this time, the negative effect of Cu-vapor played a leading role and a considerable number of carbon atoms on the rGO film were adsorbed and taken away, which significantly hindered the structure restoration. With more precursor of ethanol introduced, the carbon atoms that required for restoration gradually became sufficient and the influence of Cu-vapor gradually weakened. In order to confirm our hypothesis about the Cu-vapor, we further raised the temperature up to 1040 °C in which condition copper foil evaporated more violently and produced more Cu-vapor. The ratio of \( \frac{I_D}{I_G} \) even reached a value of 2.49 compared to 1.8 (figure 5(d)) in parallel to the increase of temperature when Cu was not involved indicating more defects remained due to the adsorption of Cu-vapor, which powerfully proving our assumption.

We further investigated the influence of Cu-vapor on the structural modification of GO by removing the precursor of ethanol and applied a thermal annealing only in hydrogen at temperature of 1000 °C with Cu-vapor involved for a comparison. From the Raman spectra (figure 6(a)), we can intuitively find that, annealed GO film on the dielectric substrate with hydrogen modified \( \frac{I_D}{I_G} \) ratio to 1.1 with no improvement to 2D peaks. It is worth noticing that when Cu-vapor was introduced, the \( \frac{I_D}{I_G} \) ratio slightly increased to 1.4 (figure 6(a)), which means Cu-vapor took a small amount of carbon atoms away and caused some damages to the rGO structure as well. In addition, percentage transmittance of the GO film after annealing (subsequently transferred onto to quartz glass) was determined by UV–visible spectroscopy (figure 5(b)). With the restoration of sp2 and \( \pi \)-electron system in the rGO, the transmittance tends to decrease in general, which was observed previously [46–48]. As expected, we found the transparency of the rGO film increased when Cu-vapor was involved in the reaction which is another evidence proved that Cu absorbed carbon atoms and hindered the restoration of the lattice structure.

3.3. Electrical measurements

The conductivity of graphene mainly depends on the carrier mobility and the functional groups attached to GO are the most important factors to degrade it. Thermal annealing process could effectively remove the oxygen-containing functional groups on the GO but resulting in a large number of vacancies and lattice defects left, which mainly prevented the electrical property recovery of rGO (150 kΩ/sq) [25]. Therefore, if these defects can be repaired, the performance of rGO will be highly improved even comparable to the pristine graphene. Note that, rGO deposited on quartz substrate under 30 min thermal annealing assisted by ethanol at 1000 °C was developed by Su, CY et al with sheet resistance of 15 kΩ/sq [27]. Subsequently, K. Kanishka et al carried out a similar method to reach sheet resistance of 9 kΩ/sq and reduced the temperature to 800 °C [29]. Furthermore, plasma is also a significant approach to further reduce the temperature and consume less time to obtain high-quality rGO(9 kΩ/sq) [28]. In this work, our restoration approach can effectively prepare high-quality rGO film with excellent electrical properties even on dielectric substrate when compared with other methods of GO derived graphene reported (figure 7) and its sheet resistance is even close to the pristine graphene (1.2 kΩ/sq repaired on SiO2/Si, 0.2 kΩ/sq repaired on copper and subsequently transferred to SiO2/Si).
4. Conclusion

In summary, we have demonstrated that copper and Cu vapor introduced have totally different influences on the rGO restoration for the first time. Cu could effectively catalyze the decomposition of precursors to help repair almost all the defects when restored on the copper. On the contrary, when Cu-vapor was introduced remotely, it would adsorb a portion of carbon atoms on the GO and even degrade the restoration efficiency. Meanwhile, high-quality rGO film could be accessible through Langmuir-Blodgett self-assembly GO film deposited on copper under high temperature ethanol vapors. Raman spectroscopic and XPS spectra studies revealed that functional groups of the original GO could be effectively removed and the lattice structure was successfully restored via this simple method. The as-made rGO sheets exhibited excellent electrical properties (1.2 kΩ/sq prepared on SiO2/Si, 0.2 kΩ/sq prepared on copper and subsequently transferred to SiO2/Si), which is promising for scalable graphene production and its practical applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit authorship contribution statement

Xinliang Yang: Conceptualization, Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. Zijian Zhang and Sifan He: Writing - review & editing. Yenan Song: Validation. Yenan Song: Project administration, Supervision, Funding acquisition, Writing - review & editing. Wenjie Wu, Xiangfeng Shu and Yijun Chen: Resources. Zhaokai Zhang, Kai Jiang and Jianlong Liu: Data curation.

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