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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

The Electrochemical Transfer of CVD-Graphene Using Agarose Gel as Solid Electrolyte and Mechanical Support Layer

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

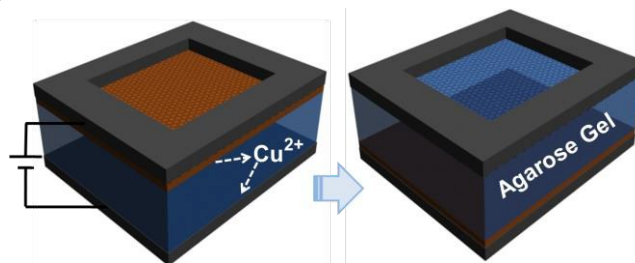
The transfer of chemical vapor deposition (CVD) grown graphene is the prerequisite for many applications. Here, we introduce a simple and eco-friendly electrochemical technique to transfer graphene by using agarose gel as the solid electrolyte and a mechanical support layer for graphene sheets. This transfer technique will be a perfect candidate for the industrial applications of graphene.

Graphene has attracted great interests because of its distinctive band structure and exciting physical and chemical properties.¹⁻⁵ Chemical vapor deposition (CVD) on copper foil as a low cost and scalable technique for obtaining large-area, high-quality and uniform graphene films has recently attracted great attentions.^{6,7} However, most applications require the graphene sheets be transferred from the copper foil surface to target substrates. For its weak mechanical strength, besides few complex methods by directly etching copper foils,⁸⁻⁹ most graphene transfer procedures would use a support layer to prevent destruction of the graphene sheets. The most widely investigated is the polymer-assisted process which use a polymer film such as polymethyl methacrylate,^{6,10-19} polydimethylsiloxane,²⁰⁻²¹ poly(bisphenol A carbonate)²² or self-release polymer²³ to provide mechanical support for the graphene. However, these transfer procedures are not suitable for preparing large-scale graphene films because the polymer/graphene composite films are difficult to handle for its weak mechanical strength. Moreover, the large amount of organic solvent consumption during the polymer coating and removing process make them are not eco-friendly. In addition, the target substrate was also used as a support layer for graphene sheets through closely contacting the graphene/copper composite films to substrate by electrostatic attraction force,²⁴ covalent bond,²⁵ hydrogen bond²⁶ or mechano-electro-thermal process,²⁷ subsequently etching the copper foil or direct dry transfer of the graphene. However, for its rough surface and the rigidity of the graphene/copper composite foils, it is difficulty to prepare large-area and complete graphene films using these procedures.

Safer solvents and renewable raw materials are two important principles of green chemistry.²⁸ Developing a simple and environmental-friendly approach to transfer CVD-grown graphene is a critical question for the large-scale applications of

graphene. In this work, we demonstrate an electrochemical technique by using agarose gel as a solid electrolyte and mechanical support layer to transfer graphene. This procedure not only avoids using any organic solvents, but also simultaneously realizes the recovery of copper during the transfer process.

The gel used in our experiments plays two roles. Firstly, it is a solid electrolyte during the electrochemical corrosion of copper foils. Secondly, it acts as a mechanical support layer for the graphene sheets. We chose agarose gel because itself and the solvent of water are friendly to the environment. Moreover, the agarose gel could turn into sol under high temperature, so it could be simply removed by hot water after the copper corrosion process.



Scheme 1. Schematic illustration of the electrochemical corrosion of copper foil.

The schematic illustration of the electrochemical corrosion of copper foil was shown in scheme 1. A piece of graphite flake with the size of 3 cm × 3 cm was used as the cathode. An 8 mm thick agarose gel with the size of 2 cm × 2 cm containing 0.4 M CuSO₄ solution was placed on it as the electrolyte, and the concentration of the gel is about 4% (wt). Then the as-grown graphene/Cu composite film prepared in a similar process reported previously with the size of 2.2 cm × 2.2 cm was placed on the agarose gel surface and make the copper intimately contact with the gel.²⁹ Another graphite electrode of 3 cm × 3 cm with a square hole of 1.2 cm × 1.2 cm in the center was carefully placed on the surface of the graphene/Cu composite film as the anode. Finally, a voltage was applied to the electrodes to electrochemically corrode the copper foil under the graphene sheets.

spectroscopy. Figure 2a shows the photograph of the transferred graphene film. The shape of the graphene film is almost a square and the length of the side is about 1.2 cm, which is similar with the hole in the center of the graphite electrode. For the strong π - π stacking interaction between the graphene and the graphite, the graphene sheet contacted with the graphite electrode would be removed when the electrode was taken away after the etching of the copper foil. It indicates that the size of the graphene film transferred on substrates is confined by the size of the hole in the graphite electrode. So this transfer method could be easily used to transfer large area graphene films through using graphite electrodes with a large size of hole. Figure 2b is the representative microscopy image of the transferred graphene sheet. The surface of the graphene film is clean without any residual copper fragments, but there are some wrinkles in the graphene film which also clearly shown in the SEM images (figure S1). These wrinkles may be come from the deformation of the agarose gel after the etching process of copper foil. When the rigid substrates with a flat surface completely contact with the flexible graphene/gel samples with a dome shape, the graphene/gel surface would distort and lead to the formation of folds in graphene sheets. AFM topographic imaging of a typical transferred graphene is presented in Figure 2c, which shows the graphene surface is very smooth. The height of the graphene sheet was measured to be 1.7 nm which is higher than that of a clean graphene sheet (~ 0.4 nm),¹ it is maybe due to the adsorption of agarose molecules on the graphene surface. In the Raman spectroscopy result shown in Figure 2d, the G and 2D bands were located at 1583 and 2712 cm^{-1} , respectively. And the negligible intensity of D band (at about 1352 cm^{-1}) indicates that the graphene sheet nearly not be oxidized when the copper foil under the graphene sheet is electrochemically oxidized.

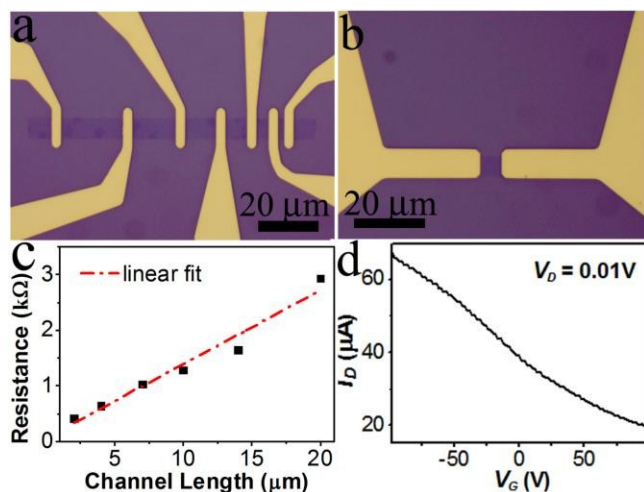


Figure 3. (a, b) Typical optical images of a TLM structure (a) and FET device (b). (c) The resistance with respect to the channel length obtained from the TLM pattern. The dash dot line is the linear fit. (d) The representative I_D - V_G curve from graphene FET device at drain voltage (V_D) = 10 mV. All the electrical measurements were carried out at room temperature under ambient condition.

The sheet resistance (R_S) of graphene was measured by a transmission line method (TLM), and the electronic transport

property of graphene was evaluated with back-gated field effect transistor (FET) devices. The TLM structures and the FET devices all were fabricated by standard optical lithography, and the detailed fabrication procedure has been published elsewhere.²⁹ In short, the graphene sheets transferred on SiO_2/Si substrate were etched by oxygen plasma through a resist mask into rectangular shape, and then the electrodes were fabricated by optical lithography and successively metallic electron beam evaporation of Ti and Au, respectively. The optical images of the TLM pattern and the FET device were shown in Figure 3a and b. The width of the graphene strip in the TLM structure is 7 μm , and the distance between adjacent electrodes is 2 μm , 4 μm , 7 μm , 10 μm , 14 μm and 20 μm , respectively. The graphene channel length and width of the FET device all are 6 μm .

Figure 3c shows the dependence of the total resistance (R_T) on the intercontact distance, which shows a distinct linear relationship between R_T and the interspacing of electrodes. The R_T is composed of the graphene sheet resistance and the contact resistance (R_C) between graphene and the electrode, which could be expressed in the following formula: $R_T = R_S(d/W_{\text{ch}}) + 2R_C$.³⁴ Where the W_{ch} and d are the graphene channel width and the space of adjacent electrodes, respectively. From the slope of the linear fit, the R_S value was evaluated to be 911 Ω/\square , which is smaller than previously reported results.¹⁰ It possibly is for the chemical doping of the graphene sheet by the adsorbed molecules on its surface. The typical curve of drain current (I_D) versus the gated voltage (V_G) for the FET device was shown in Figure 3d, which obviously indicates that the graphene shown p-type behavior reflected from the Dirac point moving to positive gate voltage beyond 100 V. It probably arisen from the adsorption of agarose molecules or photoresist introduced during the transfer process and device fabrication process.³⁵ The carrier field effect mobility μ is about 1851 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ which was extracted using the following formula of $\mu = (\Delta I_D / \Delta V_G)(L/W)(C V_D)$ from the I_D - V_G curve. Where L/W is the length-to-width ratio of the channel and C is the gate capacitance, respectively. This value is about 2 orders of magnitude below the intrinsic mobility of graphene at room temperature,³⁶ which could be due to the scattering of the adsorbed resist and agarose molecules or the wrinkles formed during the transfer process.

In summary, we introduce a simple electrochemical technique using the agarose gel as solid electrolyte and mechanical support layer for the transfer of graphene sheets to SiO_2 substrates. This method does not use any organic solvent and could simultaneously recover the copper during the electrochemical etching process. From the viewpoint of the copper recovery and without the use of organic solvent during the transfer process, this method described here provides an economical and eco-friendly way of preparing CVD graphene for large-scale applications. Therefore, it would has great application prospect for future industrial production of graphene.

The authors are grateful for the financial supports of the National Science and Technology Major Project (Grant NO. 2011ZX02707.3), the National Natural Science Foundation of China (Grant NO. 61136005, 61404167), and the Key Research Program of the Chinese Academy of Sciences (Grant NO. KGZD-EW-303). We also thank the help of all the members of the IMECAS compound semiconductor device department in our

device preparation.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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