

# Transmission Electron Microscopy Specimen Preparation for Layer-area Graphene by a Direct Transfer Method

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We suggest a facile transmission electron microscopy (TEM) specimen preparation method for the direct (polymer-free) transfer of layer-area graphene from Cu substrates to a TEM grid. The standard (polymer-based) method and direct transfer method were by TEM, high-resolution TEM, and energy dispersive X-ray spectroscopy (EDS). The folds and crystalline particles were formed in a graphene specimen by the standard method, while the graphene specimen by the direct method with a new etchant solution exhibited clean and full coverage of the graphene surface, which reduced several wet chemical steps and accompanying mechanical stresses and avoided formation of the oxide metal.

**Key Words:** Graphene, Transmission electron microscopy, Specimen preparation

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## INTRODUCTION

Graphene is a monolayer of carbon atoms arranged in a honeycomb lattice and is a basic building block for graphitic materials of all other dimensionalities. It can be wrapped up into zero-dimensional fullerenes, rolled into one-dimensional nanotubes or stacked into three-dimensional graphite. Graphene has unusual electrical, mechanical, and thermal properties, so it presents new opportunities in fundamental research and practical applications (Zhang et al., 2005; Geim & Novoselov, 2007; Geim, 2009). Recently, large-area synthesis methods for graphene have been advanced epitaxial growth on SiC (Brar et al., 2007; Qi et al., 2010) and chemical vapor deposition on metal substrates such as Ni (Dedkov et al., 2008) and Cu (Li et al., 2009). Particularly, Cu is a considerably attractive substrate because it can be produce layer-area graphene.

Transmission electron microscopy (TEM) is a direct and

relatively fast imaging tool ideally suited for suspended atomically thin membranes, so it has been successfully applied to study adsorbates on graphene and the atomic structure of graphene (Huang et al., 2011). To observe graphene by TEM, the graphene must transfer from metallic Cu substrates to a TEM grid. Standard transfer of layer graphene has been carried out using a polymer coating such as polymethyl methacrylate (PMMA) or polydimethylsiloxane as a temporary support during etching of the metal substrate to prevent tearing of the graphene (Reina et al., 2009). However, the standard transfer method using these polymers can contaminate and mechanically damage the graphene because it includes several wet chemical steps. Thus, a simple and gentle method is necessary for good TEM images of graphene. Direct transfer method doesn't include polymer coating process. So it is expected simple and effective method to make graphene specimen by avoiding wet chemical steps (Regan, 2010).

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This study describes a simple method for the direct transfer of layer-area graphene from Cu growth substrates to the TEM grid.

## MATERIALS AND METHODS

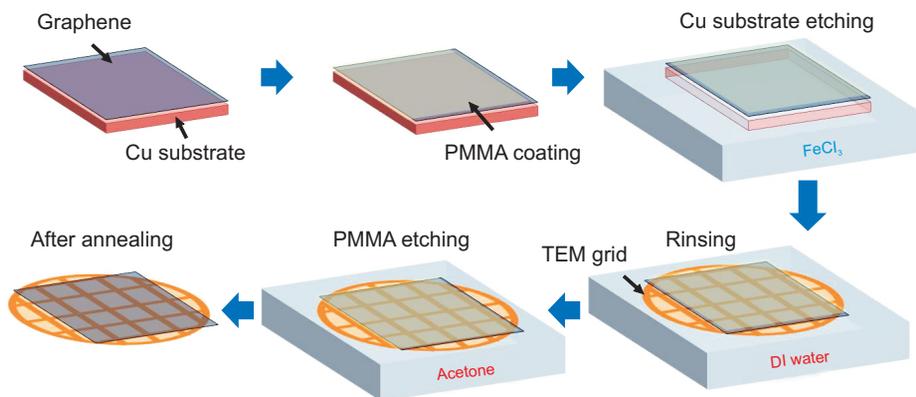
### Synthesis of Graphene on Copper

Cu foils (25- $\mu\text{m}$  thick, 99.8%, No. 13382; Alfa Aesar, Korea) were inserted into a 2 inch quartz tube, which was loaded inside a horizontal furnace. The tube was pumped to 600 mTorr, then heated up to 1,000°C with 50 sccm Ar and 20 sccm  $\text{H}_2$  mixture flow. It took around 50 minutes for both heating up and annealing. Subsequently, graphene growth was carried out in 30 minutes under the mixture flow of 30 sccm  $\text{CH}_4$  and 20 sccm  $\text{H}_2$ . To induce slow cooling and prevent the tube from cracking, the furnace lid was kept closed until the temperature reached 800°C. Then, the sample was rapidly cooled by opening the lid of the furnace and blowing air.

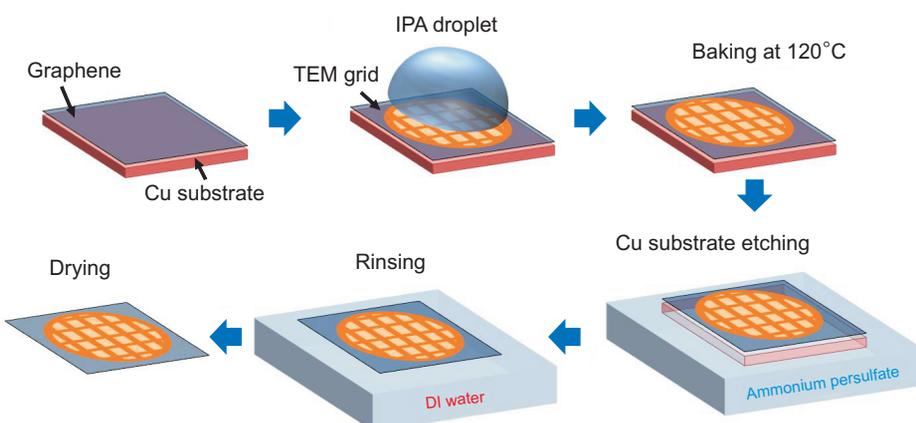
### Standard Transfer Method

Fig. 1 illustrates a standard polymer-based method. PMMA

(950 A4; Micro-Chem Inc., USA) was used as a scarified layer by spin coating on the top of graphene at 2,500 rpm in 30 seconds. The samples were then put onto a 80°C hot plate for 2 minutes to harden the PMMA layer. Since graphene was grown on both sides of the samples, the unused graphene was etched away by oxygen plasma at chamber pressure 0.3 torr for 10 seconds. To etch Cu, the PMMA coated samples were placed floating on  $\text{FeCl}_3$  for 2 hours. The floating PMMA/graphene films were transferred to a flat beaker and rinsed with deionized water several times. The graphene/PMMA films were pulled out of the deionized water onto a holey carbon film coated TEM grid (Au Quantifoil, Germany). The samples were naturally dried in air for 2 hours and baked on a hot plate of 110°C for 1 hour to enhance the adhesion of graphene with the TEM grid. Subsequently, the samples were submerged in a beaker of warm acetone (60°C) for 1 hour to remove the polymer layer. To minimize the effects of polymer residues, the graphene transferred to the TEM grid were annealed in 500 sccm Ar flow at 350°C for 1 hour.



**Fig. 1.** Standard transfer method of layer-area graphene to TEM grids. TEM, transmission electron microscopy; PMMA, polymethyl methacrylate, DI, deionized.



**Fig. 2.** Direct transfer method of layer-area graphene to TEM grids. IPA, isopropanol; TEM, transmission electron microscopy; DI, deionized.

### Direct Transfer Method

Fig. 2 illustrates the direct method. The Au Quantifoil TEM grid was placed in contact with a small piece of graphene/Cu and heated to 100°C on a hot plate. A droplet of isopropanol ( $C_3H_8O$ , IPA, 99.7%; Sigma-Aldrich, USA) was dropped onto the surface of the TEM grid and graphene/Cu. After IPA was completely evaporated, the TEM grid was strongly attached to the graphene/Cu sample. Subsequently, the sample was placed floating on an ammonium persulfate ( $(NH_4)_2S_2O_8$ , APS, 0.1 M) solution for 2 hours. Normally, it takes around 5 hours to etch Cu completely. The sample was then moved to a new APS solution to ensure that the unused graphene on the other side of the Cu foil was washed away. The graphene/TEM grid was then rinsed in deionized water several times and dried naturally.

### Low Voltage Transmission Electron Microscopy

Conventional TEM operates at an accelerating voltage up to 200 kV. However, the knock-on damage by high electron beam energy makes it difficult to observe the graphene. For successful TEM analysis of graphene, the graphene needs to be observed at a low acceleration voltage of less than 100 kV, which minimizes the damage (Meyer et al., 2013). In this study, graphene specimens were observed using by a JEM-ARM 200F (JEOL, Japan) microscope operated at a 80 kV acceleration voltage. To characterize the graphene, selected area diffraction (SAD) and TEM energy dispersive X-ray spectroscopy (TEM-EDS) mapping were performed.

## RESULTS AND DISCUSSION

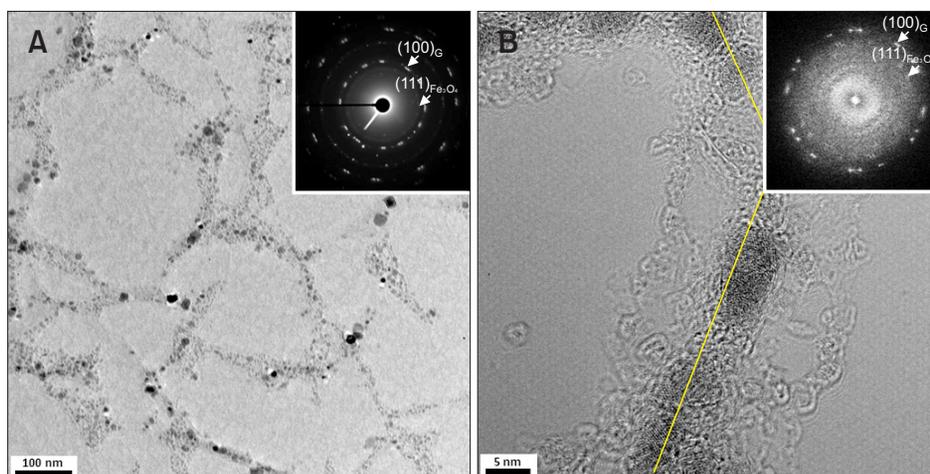
Fig. 3A shows the TEM image of a graphene specimen made by the standard direct method. The residue and the crystalline particles were formed on a graphene sheet. It also reveals folds that are commonly seen in metal-based layer-area graphene growth, possibly forming to relieve stress during the cooling of

the graphene and metal from the high synthesis temperature down to room temperature or scooping during the graphene transfer process (Han et al., 2011). The corresponding SAD in the inset reveals the characteristic graphene structure of this region. The separation of the diffraction spots resulted from the grain boundaries, folded graphene sheets of overlapped graphene sheets with various directions. Fig. 3B shows the high-resolution TEM (HRTEM) image with a fast Fourier-transform (FFT) image in the inset. The FFT images were different and were obtained at each region divided by the yellow line. Therefore the yellow line is seen as the grain boundary. Furthermore, the SAD and FFT images in Fig. 3A and B reveals that the particles are not related to Cu but FeO (111) patterns (JCPDS 77-2355).

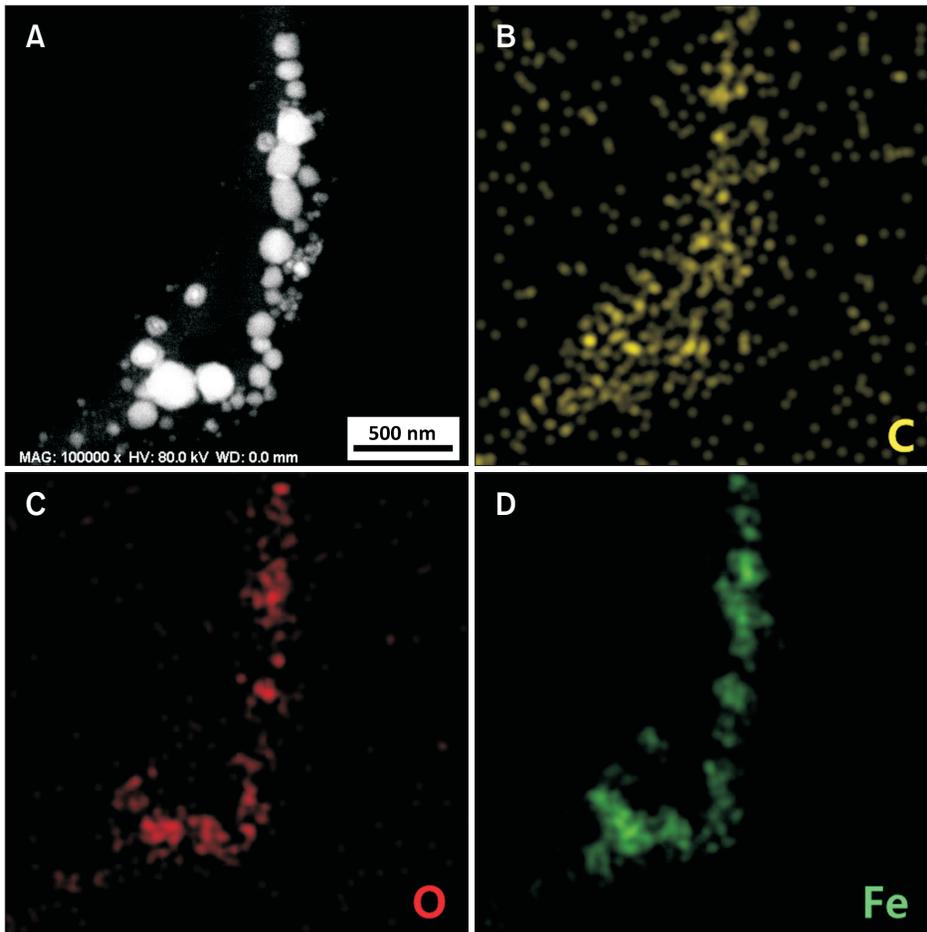
Fig. 4A shows the image of dark-field scanning transmission electron microscopy and Fig. 4B-D shows EDS mapping for C, O and Fe elements, respectively. In Fig. 4B, the C element was detected weekly overall, but higher intensity was detected at the residue region. O and Fe were detected at the region of crystalline particles, which indicates that the particles are FeO. The FeO particles were formed by  $FeCl_3$ , which is the etchant of the Cu substrate. Furthermore, they were formed on PMMA residues which were formed at grain boundaries. These formed particles can be a problem for the TEM analysis of graphene. Moreover, the big problem of using the standard method is that the transfer process is complex and difficult, so it is easy to lose or damage the graphene sheet. Therefore, we used the direct transfer method with a relatively simple process, and we perform the Cu substrate etching by a new etchant of ammonium persulfate (APS:  $(NH_4)_2S_2O_8$ ).

Fig. 5 shows the TEM image and HRTEM image of the graphene specimen by the direct method. In Fig. 5A, the graphene sheet has a clear surface with no metallic oxide particles, which is unlike using  $FeCl_3$  solution, and no folds like the ones that formed in the standard transfer method.

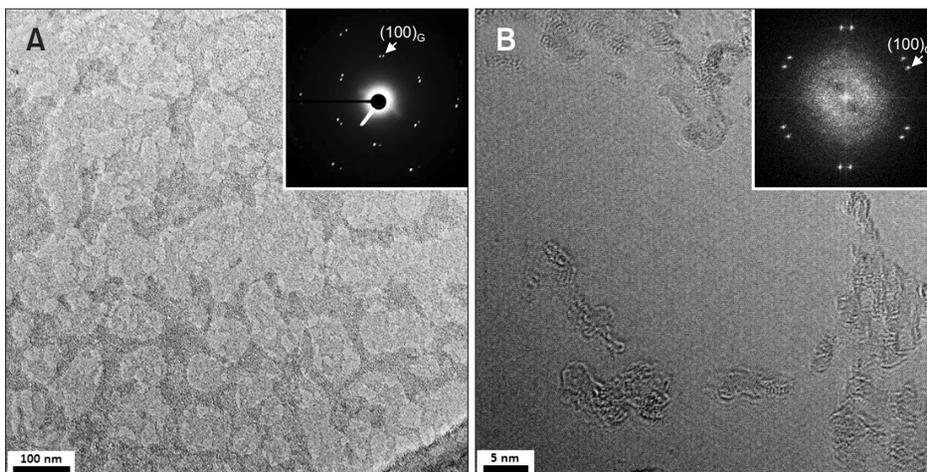
As shown in the TEM image, our direct transfer method



**Fig. 3.** A typical transmission electron microscopy (TEM) image with the diffraction pattern (inset) (A) and a high-resolution TEM image with fast Fourier-transforms (inset) (B) of the graphene layer using a polymethyl methacrylate transfer method. The yellow solid line indicates the grain boundary.



**Fig. 4.** (A) Dark-field scanning transmission electron microscopy image of the graphene layer using the standard transfer method and energy dispersive X-ray spectroscopy element maps of C (B), O (C), and Fe (D).



**Fig. 5.** A typical transmission electron microscopy (TEM) image with the diffraction pattern (inset) (A) and a high-resolution TEM image with fast Fourier transforms (inset) (B) of the graphene layer using the direct transfer method.

results in a strong bond between the grid support film and the graphene with no damage and a clear surface with no particles. Therefore, this is a suitable method to make graphene specimens for TEM measurement.

## CONCLUSIONS

We proposed a direct graphene transfer method with APS as a new substrate etchant for making TEM specimens. The graphene specimens were made by the standard transfer method with a FeCl etchant and direct transfer method

by an APS etchant for the comparison. In the TEM results, the surface of the graphene specimen by the direct transfer method was clear while the graphene specimen by standard transfer had some FeO particles on the surface. Thus, the direct transfer method can be a useful method to make graphene specimens for TEM measurement.

## CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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