

One-step transfer and integration of multifunctionality in CVD graphene by TiO₂/graphene oxide hybrid layer

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Introduction

For application in optoelectronic or electronic devices, graphene produced by CVD is to be transferred from the transition metal substrate to an insulating substrate. Poly(methylmethacrylate) (PMMA) has been widely used as the supporting material for graphene transfer. After the complete removal of copper, the graphene film coated with PMMA is placed on the desired substrate and the PMMA layer is removed using acetone. However, this process typically damages the graphene layer because of crack or ripple formation and tearing.¹ Moreover, it is difficult to completely remove the PMMA support layer.

Another crucial challenge in graphene-based optoelectronic devices is to reduce environmental stability. When graphene is exposed to moisture or other chemical molecules, the conductivity of graphene films is significantly decreased because the graphene can readily interact with adsorbents, resulting in reduced long term stability. To avoid this impurity scattering, additional treatments such as top coating of polymeric material, chemical welding, and thermal welding into the polymeric substrate have been introduced. The permeability of gas molecules is mostly inversely proportional to the thickness of the polymeric layer. However, if the thickness of the polymeric layer is increased for reducing the gas permeability, the conductivity of the graphene film may be significantly reduced because of the intrinsically insulating property of the polymeric layer. Thus, thin semiconducting metal oxides films with low gas permeabilities may be suitable candidates as protection layers for graphene-based optoelectronic devices.

Materials and methods

Monolayer graphene was grown by low pressure CVD of methane (99.96%) at 1050 °C on a 100 μm thick 3 × 5 cm polycrystalline copper foil. The as-grown graphene film was transferred onto the target substrate by a TiO₂ sol-mediated transfer method. A TiO₂ sol, which acted as a supporting layer, was prepared using titanium isopropoxide (TIP) / acetylacetonate (acac) (1:2 molar ratio), HCl, and water, which were stirring at 60 °C for 10 h.² 10 mL of the TiO₂ sol was spin-coated at 1000 rpm for 1 min. A 50 nm thick TiO₂ layer was finally obtained by curing the TiO₂ sol at various temperatures for 1 h. Next, the copper foil was etched away by soaking in a 0.2 M solution of ammonium persulfate for 3 h and then, the resulting graphene/TiO₂ film was transferred onto an arbitrary substrate.

Results and discussion

In order to examine the effect of the TiO₂ layer as a protective layer, we measured the changes in the sheet resistance of the graphene/GO/TiO₂ film with 30% GO coverage when exposed to conditions of high humidity (relative humidity of 80%) and temperature (80 °C) over a period of time, as shown in Figure 1. The environmental stability along with the transparency and conductivity are crucial for the application of graphene-based transparent electrodes. For comparison, the changes in the sheet

resistances of a graphene film without the GO/TiO₂ coating and a graphene film doped with gold were also measured. After 100 h, the sheet resistance of the undoped graphene film was increased by approximately 21% with respect to its initial value. This might have been caused by the selective adsorption of water molecules on the graphene domain boundaries, which acted as scattering centers in the carrier transport. Also, the adsorbed water molecules could open the band gap of the graphene film, which could have resulted in a decrease in the conductivity. Meanwhile, the sheet resistance of the Au-doped graphene film distinctively increased over time. Although the Au doping could effectively enhance the carrier density of graphene and thus, the electrical conductivity could be significantly increased, the marked increase in the sheet resistance might have resulted from the hygroscopic property of the Cl⁻ ions.

Conclusion

Electrical conductivity, environmental stability, and photocatalytic properties of graphene were significantly enhanced by simply introducing TiO₂ as a supporting layer for graphene transfer. TiO₂ also simultaneously acted as a passivation layer and a p-type doping layer. TiO₂ could efficiently support the GO-modified graphene layer during etching of the underlying copper and graphene transfer because TiO₂ strongly interacted with the oxygen functional groups of the graphene/GO film. The simple introduction of this multifunctional TiO₂ layer can make graphene suitable for application in a variety of devices including FETs, gas sensors, touch panels, photo detectors, and solar cells.

References

1. X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science*, 324 (2007) 1312.
2. J. T. Han, B. G. Kim, M. Yang, J. S. Kim, H. J. Jeong, S. Y. Jeong, S.-H. Hong, G.-W. Lee, *ACS Appl. Mater. Interfaces*, 3 (2011) 2671.

Figures

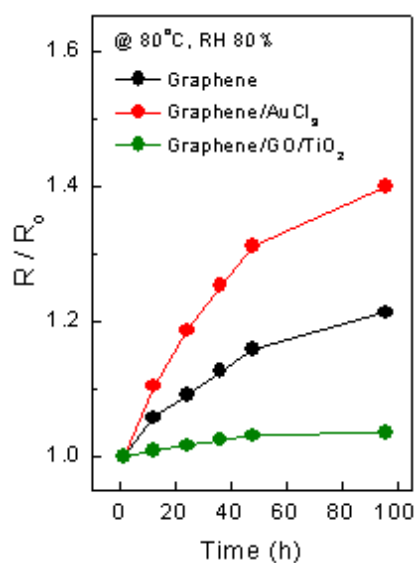


Figure 1. Long term environmental stability measured at 80 °C under a relative humidity of 80 % of bare graphene, Au-doped graphene, and the graphene/GO/TiO₂ film.