

# Band gap opening and p-type transport of Cl-oxide doped graphene by electrochemical doping

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The graphene, a monolayered carbon material, has attracted much attention due to its unique, electrical, and physical properties which can promise a variety of applications. However, the graphene has a semimetallic property with a linear energy-momentum dispersion relation without a band gap.[1] Recently, many researchers have tried to open a band gap in a graphene in terms of symmetry breaking, which induces a change of a band structure. For instance, defect generation,[2] molecular doping,[3, 4] applied bias,[5-7] and nano ribbon,[8] have showed the band gap opening in graphene. More recently, the boron doped graphene by reactive microwave plasma showed the tunable bandgap engineering ranging from 0.19 eV to 0.54 eV.[4] Even though the above result is close to the adequate values for device applications, the more facile and exact control of the band gap tuning of the graphene is still desired. In general, the carbon atoms in the carbon nanotubes (CNTs) or in the graphene are  $sp^2$  hybridized and they also have an unsaturated dangling bond which can promise various surface modifications. Here, we report a band gap opening in the graphene by using an electrochemical doping on the graphene surface. The Cl-oxide nanopartilces adsorbed on the graphene were used as the dopants in an electrolyte, which induces the band gap opening and the changed electronic structure.

The graphene film for a working electrode has been prepared for the electrochemical redox reaction in electrolyte solution. The components of the cell include a working electrode, a counter electrode, and a reference electrode all submerged in electrolyte solution. Electrochemical experiment was carried out using WPG potentiostats with Pt counter electrode and Ag/AgCl reference electrode. The electrochemical cell was equipped with a common glass beaker. The electrochemical doping was carried out in a 0.1 M  $LiClO_4$ /Acetonitrile solution, and the amount of adsorption of the  $ClO_4^-$  for the doping was controlled using an electric potential between the reference and the working electrode. The applied potential was a 1.5 V, and  $ClO_4^-$  ions are simultaneously doped on the surface of graphene. The film was rinsed in DI-water and outgassed at 80 °C in a vacuum oven after the electrochemical doping in a solution.

From the Raman spectra of the Cl doped single layer graphene film, two dominant peaks clearly appeared, including the G peak at  $\sim 1592\text{ cm}^{-1}$ , and the 2D peak at  $\sim 2698\text{ cm}^{-1}$ . The peak intensity ratios ( $I_{2D}/I_G$ ) of pristine graphene are approximately below two, while the full widths at half-maximum (FWHM) of the 2D peaks are about 32, indicating that this sample is, in fact, single layer graphene.[9] Besides, detailed analysis of the XPS spectra provides clear evidence that the graphene has been chemically modified after doping. The peak position at 284.7 eV for the pristine graphene without immersing in electrolyte is very close to the value for the pure  $sp^2$  C-C bonding in the pristine highly oriented pyrolytic graphite (HOPG).[10] The downshift of carbon core level of 0.14 eV in the binding energy for graphene doped at 1.5 V evidences the p-type doping with the Fermi level change as  $ClO_4^-$  ions adsorb. The chlorine Cl 2p core level spectrum in graphene doped at 1.5 V reveals a clear doping.

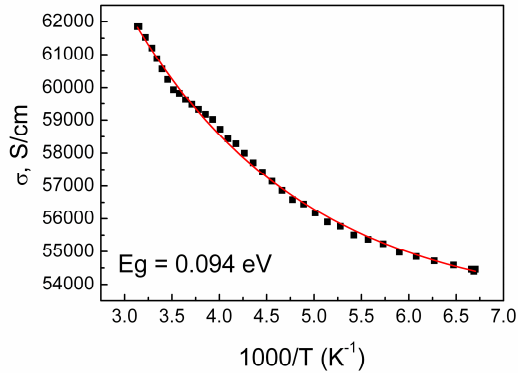


Figure 1. Temperature-dependent conductivity of the Cl-oxide doped graphene film.

To obtain the transport properties of graphene, we have measured the temperature dependence of conductivity. Figure 1 shows the conductivity versus temperature of the Cl doped graphene. The temperature-dependent conductivity was measured in the temperature range from 150 to 300 K. The conductivity of the Cl doped graphene increases with increasing temperature like a usual semiconductor, and then can be fitted by the conductivity equation. The thermally activated conduction is the main transport mechanism at high temperature, over 100K. The observed band gap energy of the Cl doped graphene is determined to be 94 meV as shown in Figure 1.

We fabricated back-gate FETs using the Cl doped single layer graphene. The single layer graphene was formed after transfer onto a 300-nm-thick SiO<sub>2</sub>/Si substrate as a channel. A 50-nm gold layer deposited by e-beam evaporation was used as source and drain electrodes. The channel length was 10 μm, and the channel width was 100 μm. Here, the I-V curve from the graphene FET clearly showed a semiconductor behavior with p-type.

In conclusion, we demonstrated the band gap opening and p-type graphene field effect transistor. The Cl doped graphene has a shift of 0.14 eV in binding energy of XPS after doping. The temperature dependent conductivity indicates that the Cl doped graphene has a band gap of 94 meV. A fabricated back-gate graphene FET revealed the p-type semiconducting behavior. These results suggest a boosting of the band gap modulation for future graphene electronics.

## References

- [1] K.S. Novoselov et al., Nature 438 (2005) 197.
- [2] X. Dong et al., Physical Review Letters 102 (2009) 135501.
- [3] T. Ohta et al., Science 313 (2006) 951.
- [4] Y.-B. Tang et al., ACS Nano 6 (2012) 1970.
- [5] E. Rudberg et al., Nano Letters 7 (2007) 2211.
- [6] Y.-W. Son et al., Nature 444 (2006) 347.
- [7] Y. Zhang et al., Nature 459 (2009) 820.
- [8] M.Y. Han et al., Physical Review Letters 98 (2007) 206805.
- [9] A.C.M. Ferrari et al., Phys. Rev. Lett., 97 (2006) 187401.
- [10] S. Maldonado et al., Carbon 44 (2006) 1429.
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