PAPER

Semiconducting properties of perchlorate-doped graphene using an electrochemical method†

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We report a band gap opening and p-type doping for single layer graphene by an electrochemical method. The chlorine oxide doping to graphene was carried out in 0.1 M $LiClO_4$/acetonitrile solution. The temperature dependent conductivity of the p-type doped graphene at an applied potential of 1.5 V during the electrochemical doping process showed the band gap of 0.094 eV.

Graphene, a two-dimensional carbon material, has attracted much attention due to its unique electrical and physical properties[1] which can promise a variety of fundamental research opportunities and applications. However, graphene is a semimetal with a linear energy-momentum dispersion relation[1] without a band gap. Recently, several researchers have tried to open a band gap in graphene by means of symmetry breaking, which induces a change in band structure. For instance, defect generation,[2] molecular doping,[3,4] applied bias,[5–7] and nano ribbon,[8] have shown band gap opening in graphene. More recently, boron-doped graphene by reactive microwave plasma showed tunable band gap engineering up to 0.54 eV.[4] Even though the above mentioned result is close to adequate values for device applications, a more facile and precise control for the band gap tuning of the graphene is still desired to realize device applications. In general, the carbon atoms in the carbon nanotubes (CNTs) or in graphene are sp^2 hybridized and they also have an unsaturated dangling bond, which can promise various surface modifications. Herein, we report a band gap opening and p-type semiconducting property of graphene using electrochemical doping on the graphene surface. Among electrolytes, $LiClO_4$ is decomposed into Li^+ + ClO_4^- by applied bias. Then, chlorine oxide (perchlorate) can easily combine with the unsaturated dangling bond in graphene during electrochemical doping. Furthermore, the amounts of doping can be controlled by electric potential. The perchlorate nanoparticles adsorbed on graphene were used as the dopants in an electrolyte, which induces the band gap opening and the change in the electronic structure.

The graphene used in this study was synthesized by chemical vapour deposition (see ESI†), and the graphene film for the working electrode was prepared to carry out the electrochemical redox reaction in the electrolyte solution (Fig. S1†). In general, the core of the experimental setup used in electrochemical doping is a typical 3-electrode electrochemical cell. The components of the cell include a working electrode, an auxiliary or counter electrode, and a reference electrode all submerged in the electrolyte solution. The 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 ClO_4^- for the doping was controlled using an electric potential between the reference and the working electrode. The higher the potential, the more concentration was adsorbed on graphene.[9] In this study, we chose an optimized condition, where we used an applied potential of 1.5 V for perchlorate adsorption, and ClO_4^- ions were simultaneously doped on the surface of graphene. The film was rinsed in DI-water and outgassed at 80 °C in a vacuum oven after electrochemical doping in solution. The electronic structure was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS spectrometer, VG Scientifics). Raman spectra of the graphene film were measured for excitation of 514.5 nm at room temperature using a Jobin-Yvon HR800UV spectrometer. The electrical transport was measured in order to confirm the semiconductor properties using a cryostat with He displex (Sumitomo).

Fig. 1 shows the Raman spectra of the pristine single layer graphene film on Si after synthesis. All the areas of the sample showed a uniform Raman signal like that in Fig. 1. Two dominant peaks clearly appeared, including the G peak at ~1592 cm^{-1} and the 2D peak at ~2703 cm^{-1}. The peak intensity ratios (I_{2D}/I_G) of pristine graphene are approximately less than 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.[10]

Fig. 2a shows representative C 1s spectra for graphene doped with perchlorate molecules. Detailed analysis of the XPS spectra provides clear evidence that graphene has been chemically

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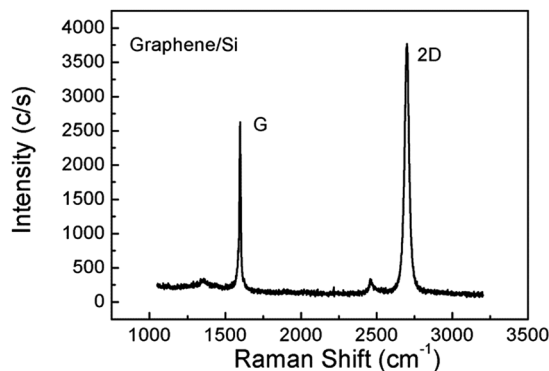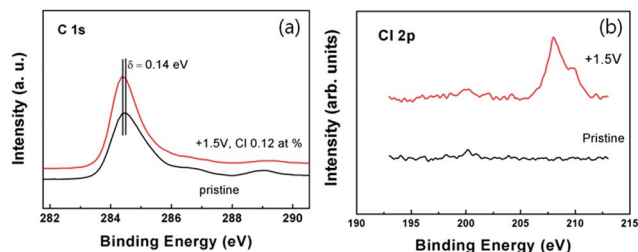
Fig. 1 Raman spectrum of a pristine graphene film.

Fig. 2 XPS C 1s spectra of graphene doped with ClO_4^- ion at 1.5 V (a) and Cl 2p spectra of graphene doped at 1.5 V (b).

Fig. 3 Temperature dependent conductivity of graphene doped with ClO_4^- ion. The inset shows the metallic behavior of undoped graphene.

Fig. 4 (a) I–V characteristics of the perchlorate doped graphene FET device with various gate voltages. (b) I–V characteristics of the perchlorate doped graphene FET device with various V_{DS}.

modified. The peak position at 284.7 eV for pristine graphene without immersion in electrolyte is very close to the value for the pure sp² C–C bonding in the pristine highly oriented pyrolytic graphite (HOPG), indicating that carbon atoms are almost exclusively sp² hybridized in non-doped graphene.[11] The perchlorate nanoparticles were adsorbed on graphene in a chemical bond by an unsaturated dangling bond or defect. The downshift of the 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 the ClO_4^- ion adsorbe.[12,13] The chlorine Cl 2p core level spectrum in graphene doped at 1.5 V, depicted in Fig. 2b, reveals clear doping. The atomic composition of doped graphene follows that of Cl, C, O, and Si at 0.12%, 68.9%, 24.5%, and 6.48%, respectively.

To obtain the transport properties of graphene, we measured the temperature dependence of conductivity. Fig. 3 shows the conductivity *versus* temperature plot of the perchlorate-doped graphene. The temperature-dependent conductivity was measured in the range from 150 to 300 K. The conductivity of the perchlorate-doped graphene increases with increasing temperature like a usual semiconductor and then can be fitted by the conductivity equation. However, the inset of Fig. 3 shows that the undoped graphene has a metallic behaviour. According to the previous study, the temperature-dependent conductivity of graphene at very low temperatures can be well explained by the variable range hopping (VRH) mechanism. However, thermally activated (TA) conduction is the main transport mechanism at high temperature, over 100 K. The TA model can be described as $\sigma = \sigma_0 \exp(-E_g/2kT)$ for high temperature regions
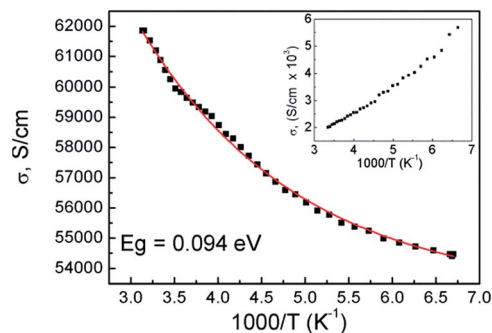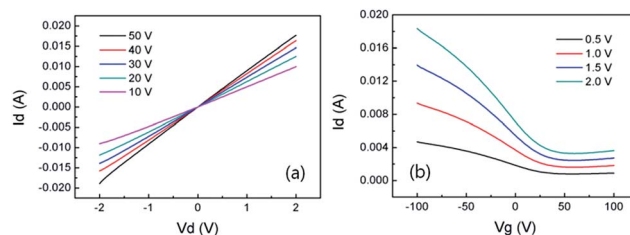
over 100 K.[14,15] The observed band gap energy of the perchlorate doped graphene is determined to be 94 meV as shown in Fig. 3. Hence it induces the change of the electronic properties of materials. Therefore, the transition of electronic properties of graphene from semimetal to semiconductor in Fig. 3 is one of the strong evidences of chemical adsorption.

We fabricated back-gate FETs using the perchlorate-doped single layer graphene. Single layer graphene was formed after transfer onto a 300 nm-thick SiO_2/Si substrate and used 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. Fig. 4a shows I–V characteristics of the graphene FET device with various gate voltages. Fig. 4b shows I–V characteristics of the graphene FET device with various V_{DS} at room temperatures. Herein, the I–V curve from the graphene FET clearly indicates a p-type semiconductor behavior. The field effect mobility of holes was determined by estimating the linear region of I–V curves using the equation $\mu = (L/WC_{ox}V_d)(\Delta I_d/\Delta V_g)$ where, L and W are the channel length and width, respectively, and C_{ox} is the gate capacitance for the 300 nm-thick SiO_2. The field effect mobility was calculated to be 2406 cm² V⁻¹ s⁻¹ for the perchlorate-doped graphene.

Conclusions

In conclusion, we demonstrated the band gap opening and p-type graphene field effect transistor. The perchlorate-doped

graphene has a shift of 0.14 eV in binding energy of XPS after doping. The temperature dependent conductivity indicates that the perchlorate doped graphene has a band gap of 94 meV. The fabricated back-gate graphene FET revealed a p-type semiconducting behavior. These results suggest a boosting of the band gap modulation for future graphene electronics.

Acknowledgements

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