Facile preparation of an n-type reduced graphene oxide field effect transistor at room temperature†

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We introduce a facile method to prepare an n-type reduced graphene oxide field effect transistor at room temperature via a typical Benkeser reduction using lithium and ethylenediamine.

Graphene is a popular material which has attracted considerable attention for its unique properties and applications in transparent electronics, drug delivery, and in the catalysis of organic chiral reactions. In modern electronics, the doping of graphene transistors is a promising process for realistic applications. Both n-type and p-type doped graphene field effect transistors (FETs) are necessary for a complete electronic circuit. It is easy to prepare p-type graphene FETs under ambient conditions. Oxygen is spontaneously adsorbed on the graphene FET surface, leading to typical p-type doping via both chemisorption and physisorption. In the fabrication of n-type doped graphene FETs, both substitutional doping and surface doping methods are effective. When considering industrial production, nucleophilic substitution doping is preferable to volatile surface doping, the latter can affect the physical properties of graphene materials.

A combination of chemical oxidation, exfoliation, and reduction is ideal for the mass production of graphene. W. Gao et al. tried various methods to convert graphene oxide (GO) into the original graphene honeycomb structure by chemical reduction. The conventional method for producing rGO is to treat GO with a strong reducing agent and commonly used in the Benkeser reduction to open aromatic rings and hydrogenate carbon atoms covalently. However, the hydrazine reductant requires specific heating conditions to reduce most of the epoxy and hydroxyl groups of GO and intensively promote the mobility of chemically converted graphene (CCG). Recently, I. K. Moon et al. developed an HI/weak acid method that provides high mobility and low sheet resistance CCG at room temperature and even lower temperatures. Although this was an excellent achievement, researchers continue to develop new GO reduction methods at low temperature with low boiling point solvents, such as an alkali metal and liquid ammonia (Birch reduction). S. Some et al. have developed in situ nitrogen doped graphene during GO reduction with various chemicals and reducing methods. The doped nitrogen atoms are added to the graphene backbone with chemical bonding during GO reduction to rGO. In addition, this concept was used to fabricate an n-type reduced graphene oxide field effect transistor (rGOFET), however heating was required with hydrazine. Thus, the development of a low temperature process for the fabrication of n-type rGOFETs is necessary. A novel and facile method for producing an n-type rGOFET at room temperature has not yet been reported.

Herein, we demonstrate a facile method to produce highly N-doped rGO and in situ n-type doped graphene FETs. Ethylenediamine (EDA) was meticulously chosen as the solvent for the reduction system because it is in the liquid phase at room temperature, is a strong base with di-amine terminal groups to accept the solvated electrons, and acts as a nucleophile in the substitution reaction. With Li and EDA, Li–rGO and n-type doped rGOFETs were easily prepared at room temperature by dipping the pre-made GO channel device into the reductant solution for a short amount of time. After the dipping process, both Li and EDA were easily removed from the surface by quenching and rinsing with de-ionized (DI) water and ethanol. Li pieces were dissolved in EDA at room temperature, forming Li⁺ cations and free solvated electrons. This blue solution is a very strong reducing agent and commonly used in the Benkeser reduction to open aromatic rings and hydrogenate carbon atoms in organic reactions. Benkeser reduction using the Li–EDA system was much more powerful than Birch reduction using the Na–NH₃ system because the final product (rGO) obtained via the Benkeser reduction was reduced further than that of obtained by the Birch reduction. The work up process after the Li–EDA reaction is more
convenient for purification at room temperature than that of the Birch reduction.

X-ray diffraction (XRD) is an efficient and convenient method to quantify the reducing degree of rGO. The Li–rGO preparation was characterized by XRD, as shown in Fig. 1a. A typical GO peak near 10.89° (d-spacing ~ 8.11 Å) and different from the graphite peak (26.34°, d-spacing ~ 3.38 Å) was observed, indicating that the interlayer spacing increased during oxidation. The Li–rGO peak showed an obvious shift to higher 2θ angles (23.39°; d-spacing ~ 3.80 Å) compared to GO, suggesting that the Li–rGO was well ordered in a two-dimensional plane by the removal of surface functional oxygen groups during reduction. The quality of the Li–rGO was directly related to the reaction time (ESI†, Fig. S1). The GO peak in XRD was completely eliminated when the reaction time was more than 60 min.

Raman spectroscopy is a universal method used to for the non-destructively characterization of graphene. The main Raman features bands of graphene are the G-band, D-band, and 2D-band, each of which has individual physical origins. Raman spectra of GO and Li–rGO powder are shown in Fig. 1b. The \( I_D/I_G \) ratio of Li–rGO notably increased from 0.86 (in GO) to 1.06, indicating that the reduction process changed and repaired the structure of GO. The 2D band of Li–rGO was stronger than that of GO, supporting the idea of better graphitization in the reduced product.

X-ray photoemission spectroscopy (XPS) was used to investigate the elemental composition and amount of samples. Fig. 1c shows the C 1s spectra of GO and Li–rGO samples. GO generally showed bimodal XPS peaks since the oxidation process generated many carbon–oxygen functional groups. In contrast, the XPS of Li–rGO exhibited a spectrum similar to that of natural graphite (ESI†, Fig. S2a). The C—C bonding domain showed a single peak around 284.5 eV, confirming suitable reconstruction of pi-conjugation in Li–rGO during the reduction process. Interestingly, the amount of N could not be detected when the amount of Li was less than 1.67 mg ml\(^{-1}\) (Fig. S2b, ESI†). After doubling the concentration of Li in EDA (from 3.33 mg ml\(^{-1}\) to 6.67 mg ml\(^{-1}\)), the amount of N increased linearly as the Li concentration increased from 1.1% to 2.1% (Table S1, ESI†).

Thermogravimetric analysis (TGA) was used to characterize the level of reduction of GO powder by measuring the weight loss. The TGA thermograms in Fig. 1d shows the weight loss at different temperatures for GO and Li–rGO (nitrogen atmosphere, heating rate of 10 °C min\(^{-1}\)). The elimination of interlayer water in GO was observed in the curve at around 100 °C. Further intensive weight loss of the GO sample occurred around 150 °C to 200 °C. This was attributed to the loss of oxygen groups. The same elimination of interlayer water did not occur in the Li–rGO curve since common rGO is hydrophobic. Li–rGO demonstrated thermal stability because the Li–EDA reduction removed most of the oxygen functional groups and resulted in suitable graphitization of the rGO layer.

Atomic force microscopy (AFM) was used to characterize and investigate the topographic surface of GO (Fig. S7, ESI†) and Li–rGO (Fig. 2a). A graph of the height profile shows the restacking and aggregation of Li–rGO (Fig. 2a). Scanning electron microscopy (SEM) also revealed the surface morphology of Li–rGO in which the restacking could be easily observed after the reduction (Fig. 2b). To demonstrate the distribution of N atoms on the Li–rGO surface, the element mapping in the selected area is shown in Fig. S6 (ESI†). From the element mapping, we could clearly observe the distribution of C, O and N atoms. Transmission electron microscopy (TEM) also confirmed the morphology of Li–rGO. Fig. 2c clearly shows the mono-sheet-like structure of the material. During reduction, a portion of the Li–rGO restacked, which contributed to the well-reduced pi-conjugation (Fig. 2d). To characterize the electronic properties of Li–rGO, Li–rGO FETs were fabricated from GO FETs. GO was spin-coated on the device to fabricate top channels using the same method as reported in our previous paper.19
After reducing the device in a solution of Li–EDA, a constant source-drain bias at 0.5 V was applied while the gate voltage was swept from −40 V to 40 V. Under ambient conditions, all channels exhibited p-type doping behaviour because oxygen could spontaneously adsorb onto the graphene surface. After removing oxygen and moisture at 10−4 Torr for 2 h, the Li–rGO changed to n-type doping behaviour with a typical Dirac point shift to −23.8 V (Fig. 3). This proved that Li–EDA effectively reduced GO to rGO and supplied suitable electronic properties to induce n-type doping during the reduction. Most gaps in the Li–rGO FET showed typical n-type doping behaviour, which confirmed the reproducibility of this method.

To compare Li–rGO FET to other FETs reduced by the hydrazine and HI methods, rGO FET devices were prepared under different reducing conditions. As shown in Fig. S5a and b (ESI†), rGO FETs reduced from HI and hydrazine showed ambipolar states with a threshold voltage at around 0 V in the vacuum. This common phenomenon indicates that graphene is a zero bandgap semiconductor and moisture at 10−4 Torr for 2 h, the Li–rGO changed to n-type doping behaviour with a typical Dirac point shift to −23.8 V (Fig. 3). This proved that Li–EDA effectively reduced GO to rGO and supplied suitable electronic properties to induce n-type doping during the reduction. Most gaps in the Li–rGO FET showed typical n-type doping behaviour, which confirmed the reproducibility of this method.

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