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All carbon materials pn diode

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Semiconductor pn junctions are elementary building blocks of many electronic devices such as transistors, solar cells, photodetectors, and integrated circuits. Due to the absence of an energy bandgap and massless Dirac-like behaviour of charge carriers, graphene pn junction with electrical current rectification characteristics is hardly achieved. Here we show a graphene pn junction diode can be made exclusively from carbon materials by laminating two layers of positively and negatively charged graphene oxides. As the interdiffusion of oppositely charged mobile counterions, a built-in potential is created to rectify the current by changing the tunnelling probability of electrons across the junction. This graphene diode is semi-transparent, can perform simple logic operations, and since it has carbon nanotubes electrodes, we demonstrate an all carbon materials pn diode. We expect this graphene diode will expand material choices and provide functionalities (e.g. grafting recognition units on graphene oxides) beyond that of traditional semiconductor pn junctions.
Graphene, an atomically-thin hexagonal lattice, has currently attracted enormous research interest because of its great promising use for a wide range including electronic devices, energy conversion and storage, sensors, optics, as well as biomedical applications. In contrast to conventional semiconductors, its conduction and valence bands meet at Brillouin zone corners and, therefore, fabricating electronic components from this zero-gap semiconductor should find an unusual way. Techniques such as cutting graphene into nanoribbons, placing bias on bilayer graphenes, and applying mechanical strains were developed to open a bandgap and turn off the current of graphene field-effect transistors. In addition, graphene diodes have received particular attention because diodes are the basic building blocks in a wide variety of electronic/photonic systems. Since graphene is metallic at a sufficient large Fermi energy, Schottky diodes were fabricated by bringing metallic graphenes and semiconductor materials into contact. With a gate modulation of localized energy levels, tunable light-emitting diode was demonstrated by using a semi-reduced graphene oxide. Although pn junctions with a planar geometry could be realized by multiple electrostatic gating, local chemical doping, and engineering of substrates, no current rectifying effect was observed owing to the Klein tunnelling of relativistic Dirac fermions. In the vertical structure pn junctions, current rectifying was achieved by inserting/forming a thin layer of insulating or semiconducting barrier material between p and n graphene layers, showing behaviours of a typical resonant tunnelling diode. So far, there is still lack of robust technique in making graphene diodes especially the diode as a similar structure to semiconductor pn junction. On the other hand, graphene oxide (GO) contains various reactive oxygen groups (–COOH, –OH, and –C–O–C), which provide possibility for chemical modification and produce functional materials for a variety of applications.

Here, the graphene pn junction diode was fabricated by laminating two layers of such chemically functionalized positively (p) and negatively (n) charged graphene oxides on the transparent substrates. As the contact of two layers, mobile counterions diffused across the interface while the anchored charges on graphene oxides frame were immobile. An equilibrium condition was reached in which an internal electric field was established to tune the electron tunnelling probability through the junction. The coupled movement of ions and electrons as well as the current rectification were modelled by using a combination of Nernst–Planck diffusion and Poisson’s equations. Since carbon nanotubes were used as conductive electrodes, we demonstrated an all carbon materials pn diode. To evaluate the utility of these graphene diodes to build the processing units needed for simple computation, in combination with graphene resistors, all carbon materials AND and OR logic gates were constructed.

Results

All carbon materials pn diode fabrication. The key components of the graphene pn junction diode are a layer of negatively charged GO and a layer of positively charged GO (see Fig. 1a and Methods). Before anchoring negative and/or positive charges onto the graphene oxides, the GO was further oxidized to produce more –COOH groups which would then increase the ionic charge density in the subsequent GO layers (Supplementary Fig. 1). Negatively charged GO was synthesized by deprotonating the GO with Tetrathylammonium hydroxide solution ((CH₃)₄N+OH–, TMAH, pH = 10), while the positively charged GO was synthesized via a two-step procedure (see Methods and Supplementary Fig. 2a). The chemical functionalization was verified by the change of Zeta potential from −34.66 mV to +48.17 mV for negatively charged GO and to +39.37 mV for positively charged GO (Supplementary Table 1). Moreover, the positive modification was further demonstrated by the Fourier-transform infra-red spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) characterization. In FTIR, the intensities of C=O (1734 cm⁻¹) and O–H (3415 cm⁻¹) stretching peak were greatly suppressed while amide-I band, amide-II band, and amide-III band appeared at 1631 cm⁻¹, 1460 cm⁻¹, and 1384 cm⁻¹, respectively, which were attributed to C=O stretching vibrations in RNH–CO and the coupling of C–N stretching vibration to N–H bending vibration (Supplementary Fig. 3). In XPS, the peaks correlated to amidation...
interfaced high precision electrometers. was conducted under ambient condition with the computer-ﬁnal con-duction of charged 20 nm-thick CNT electrodes was over-formation at the interface between CNT and GO layers; (2) the-procedures to the GOs (see Methods) to eliminate possible dipole-electrodes were also chemically functionalized by the similar-(0.01 V/0.1 s) and slow (0.05 V/5 s) sweep rates, the current rec-tification ratios (r = IþV/I–V) were stabilized at approximately 6. This current rectification phenomenon was not observed in a series of control devices: (1) a device comprising of two layers of positively charged GOs, (2) a device comprising of two layers of negatively charged GOs, and (3) several other devices (see Fig. 2b and Supplementary Fig. 7 for details), which ruled out possible interface effect (e.g. Schottky barrier or dipole) between CNT electrode and GOs, and therefore, we surmised that the interface between positively and negatively charged GOs should be the key feature for the current rectiﬁcation.

The current rectification effect was further veriﬁed when a bias was constantly applied (Fig. 2c). The current transients were recorded for up to 100 s by switching the bias from 0 to +1 V or −1 V. The currents were found to reach the steady state and stabilized at approximately 600 nA (+1 V) or approximately 100 nA (−1 V) shortly with application of the bias at both polarities. This demonstrated that (1) the recorded current is not dominated by the transient currents of ionic species but electrons,
The current rectification (blue curve, right axis of Fig. 2c), plotted in real time and stabilized at a ratio of approximately 6, is the intrinsic characteristics of the graphene pn diode where the electron tunnelling and/or hopping probability varied at forward and reverse bias.

In the GO layers, the charges anchored onto the GO frames are jammed and restricted to migration, but the counterions (Cl\(^-\) and (CH\(_3\))\(_4\)N\(^+\), see Fig. 1b) are not. As the laminating of two oppositely charged GO layers, counterions diffused across the interface since it is entropically favourable. Chloride anions diffused into n region while ammonia cations diffused into p region (see p and n region in Fig. 1a), which was manifested as a transient current recorded immediately after lamination of two GO layers in the absence of an applied bias (Fig. 2d). Such interdiffusion created a potential and then transformed to an internal electric field at the junction pointing from p to n layer. This field subsequently rectified the current by facilitating or impeding the transport of electrons, depending on the polarity of external bias.

**Modelling of the pn diode.** The current rectification of graphene pn junction diode was explained by using a continuum charge-transport model (see details in the sections Methods and References\(^{28,29}\)). This model combined Nernst–Planck diffusion and Poisson’s equations, in which both counterions and electrons could diffuse in response to concentration gradients and migrate due to local electric fields. The interdiffusion of counterions (n\(_i\), Fig. 3a), spatial evolving distribution of conduction electrons (n\(_e\), Supplementary Fig. 8c, black curve), potential (\(u\), Supplementary Fig. 8d, black curve), and the internal electric field (\(E\), Fig. 3b) were firstly reproduced in the absence of applied bias. By applying a forward bias, the counterions and electrons redistributed (see Supplementary Figs. 8a and 8c, red curve) and a stronger electric field (Supplementary Fig. 8e, red curve) was generated to help the electrons tunnelling from negative to positive GO layer; however, with a reverse bias, the field, on the other hand, impeded the electrons transport. Importantly, this model qualitatively reproduced (1) the current–voltage (I–V) characteristics (Figs. 2a and 3c), (2) the transient current responses at either positive or negative bias (Figs. 2c and 3d), and (3) the transient current as the lamination of two layers in the absence of applied bias (Fig. 2d and Supplementary Fig. 8f).

**Logic gates.** To demonstrate the utility of the graphene pn junction diode to build the processing units needed for simple computation, AND and OR logic gates were constructed (Fig. 4). For the AND logic gate (Fig. 4a), only when a positive potential was applied to switches A and B (represented by 1), a high output potential was produced. A different circuit design allowed an OR logic gate to be realized (Fig. 4b). In contrast to the AND gate, when either of the switches A and B was activated by a high potential, the output was a high potential. It must be noted that the cutting-off capability of the AND gate (black, red, and green curves in Fig. 4a) could not compete with the circuits based on semiconductor diodes because the graphene pn diode has a substantial internal resistance (approximately MΩ) even when a forward bias was applied (Fig. 2a, the current is in the range of sub micro-Ampere). This resistance also influenced the output of OR gate where the high potentials were less than the applied 2 V (approximately 1.7 V). Apparently,
integrating a resistor with much higher resistance could improve the circuit performance. For example, with a GΩ resistor the output of the low potential in the AND gate could be less than 0.01 V and the high potential in the OR gate could be higher than 1.99 V.

**Discussion**

The construction of graphene pn diode from charged GOs results in a different physical description from previous junction diodes. In a typical semiconductor pn junction, for example, the charge carriers (both holes and electrons) diffuse/drift across the interface and at the equilibrium condition, a depletion region was created and an internal electric field is established pointing from n region to p region in the absence of an external applied bias. In the graphene pn diode, however, (1) the interdiffusion happened at the mixing zone rather than the depletion region in semiconductor pn diode, (2) the formation of internal electric field was entropically driven, unlike in semiconductor pn junctions where the voltage arose from equilibration of the electron chemical potential, (3) the internal electric field of graphene diode increased the probability of electron tunnelling/hopping from n to p layer, in contrast to a semiconductor pn diode where the band alignment allowed electrons to flow from n type region to p type region, but not in the reverse direction, and (4) the interdiffusion-created electric field was pointing from p to n layer while in the depletion region of a semiconductor pn diode, this field was reversed from n to p region. On the other hand, diodes based on pure ionic charge transport are often labelled as P or N based on the sign of mobile charge carriers: mobile cations are given as P while electrons are given as N. The observation of current rectification and an internal electric field was found in graphene graphene pn junctions greatly expands the class of materials and devices where the current rectification ratio is dependent on the degree of ions mixing at the junction.

In summary, we have demonstrated a semi-transparent all carbon materials pn junction diode by laminating two layers of oppositely charged GO layers. This diode is distinct from previous devices where the current rectification happens because an internal field controls the tunnelling and/or hopping probability of conduction electrons. The observation of current rectification in graphene pn junctions greatly expands the class of materials and physical phenomena that can be used to build electronic components. Looking forward, we envision our graphene pn diode being inkjet-printed from aqueous carbon inks on flexible, transparent, and even stretchable substrates in a wide range of applications. These applications could be skin-like electronics to monitor the physiological conditions, systems for recording and manipulating tissue behaviours, and even smart self-powered devices with multi-functionalities. Also, we wish to integrate functions of GOs (energy, sensing, catalytic, medical etc.) into our graphene circuit which is hard to achieve in semiconductor electronics.

**Methods**

**The synthesis of GO**. In a typical synthesis, 35 mL sulphuric acid (98 wt%) and 2.60 g potassium permanganate were carefully added into an ice-bath-cooled flask with 50 mL commercially available GO solution (4 mg mL$^{-1}$, Graphenea Inc.) under constant stirring. 5 min later, the mixture solution was heated to 35 °C and kept reacting for 3 h. 63 mL DI water was then poured into the mixture. 15 min later, additional 200 mL DI water and 3.5 mL hydrogen peroxide (30 wt%) were added to stop the reaction. The yellowish product was thoroughly washed with...
The synthesis of GO(−). A two-step procedure was employed to synthesize positively charged GOs.26,27 (Supplementary Fig. 2a). 60 mg protonated GO (the above re-oxidized), 6 mL N,N-Dimethyl-1,3-propanediamine (99%), and 60 mg HATU (O-(7-Aza-1H-benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate) was mixed and reacted at room temperature for 6 h in a 60 mL N,N-Dimethylformamide (DMF). This step was repeated for three times to ensure the majority of −COOH groups were amidated. Next, 500 μL hydrochloric acid (36.5%) and 5.5 g 3-Chloro-1,2-propanadiol (98 wt%) were added into an aqueous solution of above amidated GOs (50 mL, 1 mg mL−1). The mixture was heated to 85 °C and kept reacting for 30 min under stirring and refluxing. The grayscale products were then washed with DI water for 4 times and then finally dispersed into DI water (0.25 mg mL−1).

The synthesis of CNT(−) and CNT(+). 100 mg carboxyl functionalized CNTs powder (single-walled carbon nanotubes, 2/3 semiconducting and 1/3 metallic, Chengdu Organic Chemicals Co. Ltd) was added into 100 mL mixed acid solution (3 M H2SO4 and 3 M HNO3 with 3 to 1 volume ratio) and refluxed for 2 h at 80 °C under stirring. This step produces CNTs with more −COOH groups. The products were collected through DI water for 5 times and then re-dried using DI water by the assistance of Sodium deoxycholate and sonication (0.1 mg mL−1, pH = 6). To produce negatively charged CNTs, the procedure with GO(+) was employed, while Hexadecyltrimethylammonium bromide (CTAB) was added to improve their dispersity.

Graphene pn diode fabrication. The graphene pn diode was fabricated by lamination two layers of oppositely charged GO layers. To prepare GO layers, all of the carbon solutions were sonicated using a probe sonicator (150 W) for 1 h. Gradient centrifugation was then used to collect highly dispersed carbon solutions. The concentration of all carbon materials is approximately 0.03 mg mL−1. 15 mL CNT (−) was firstly vacuum filtered through a mixed cellulose membrane (MCE, 0.22 μm in pore size and 50 mm in diameter) and thoroughly washed with 20 mL DI water to remove any surfactants. 10 mL GO(+) was subsequently added. The MCE, carbons film was peeled off and cut into desired pieces (15 mm × 10 mm) while all the carbons were dried. The MCE was then removed by floating the film onto DMF solvent for approximately 120 min and the negatively charged GO layer was transferred onto the transparent glass slide (20 mm × 14 mm). The layer was finally dried by using nitrogen gas. This produces a layer of approximately 20 nm CNTs and approximately 40 nm GOs (Supplementary Fig. 16). The same procedure was employed for preparing positively charged GO layer. Before laminating two GO layers, 50 μm diameter platinum wires were connected to the end of CNT electrodes. These are used as the leads for later electrical measurements. The two GO layers were subsequently laminated with a face-to-face configuration with a face-to-face configuration. This device was then wrapped by using a transparent tape and pressed by using two pieces of permanent magnet (5 mm in diameter and 1 mm in thickness) on the back sides of two substrates. To prevent atmospheric humidity from influencing the device performance, the device was encased in polydimethylsiloxane. (Note: every step should be operated carefully).

Characterization and measurement. The structure of carbon materials was characterized by using scanning electron microscopy (SEM, Hitachi SU8030) and transmission electron microscopy (TEM, Tecnai G2 F20 U-TWIN). The composition of GOs was evaluated by using X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) and Fourier-transform infra-red spectroscopy (FTIR, Spectrum One). Ultraviolet-visible spectroscopy (UV-vis, Lambda 950) was used to evaluate the light transmission capability. Zeta potential is tested on Zetasizer Nano ZS. The surface roughness and thickness of carbon layers were measured by using Dektak XT Surface Profiling System. The conductivity of carbon layers was characterized by a four-probe technique (MST 4145-B). The measurement of graphene pn diode was conducted under ambient condition with a computer-interfaced high precision electrometer (Keithley 6517). To drive logic circuits, an additional 6517 electrometer was applied.

Theory details. The graphene pn junction diode was simulated by using a continuum charge-transport model, which combined Nernst-Planck diffusion and Poisson’s equations. The details of this model was presented in references28,29. For simplicity, we considered one dimensional domain which contain four regions: CNT(−), GO(−), GO(+) and CNT(+). We assumed that the CNT electrode layer (either CNT(−) or CNT(+)) is equipotential27 and the electrons are free to move out or into the layers. The accumulation of mobile counterions in CNT layers was neglected. The flow of electrons as well as the rearrangement of ionic charges throughout the layers produced the electric current J. The dimensionless electric current density (J) is given by equation (1)
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Acknowledgements
This work was supported by the National Natural Science Foundation of China (21571039) and the Chinese Academy of Sciences. The authors thank B. Tu and B. Lu for their helpful discussions and supports on modelling.

Author contributions
X.F. and X.Z. carried out the experiments and, along with M.L., Y.Z. performed the data analysis. L.Y. modelled the experimental results. F.Q and J.G. assisted the synthesis of the charged GOs. All authors wrote the manuscript. Y.Y. conceived and supervised the project.

Additional information
Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-06150-z.

Competing interests: The authors declare no competing interests.

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