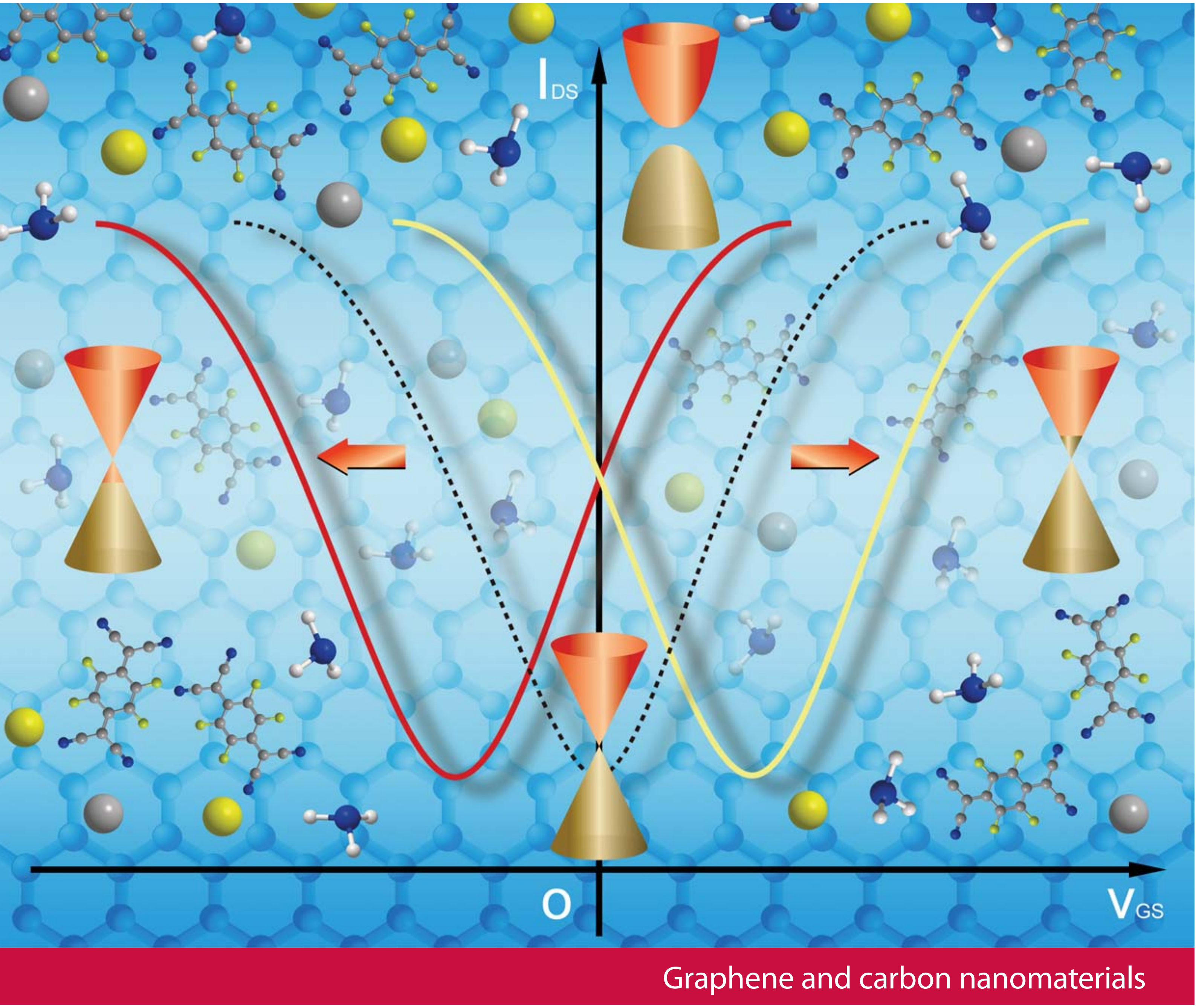
Journal of Materials Chemistry

www.rsc.org/materials

Volume 21 | Number 10 | 14 March 2011 | Pages 3253–3496



Graphene and carbon nanomaterials

ISSN 0959-9428

RSC Publishing

FEATURE ARTICLE
H. Liu *et al.*
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FEATURE ARTICLE www.rsc.org/materials | Journal of Materials Chemistry

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Received 2nd September 2010, Accepted 14th October 2010
DOI: 10.1039/c0jm02922j

Recently, a lot of effort has been focused on improving the performance and exploring the electric properties of graphene. This article presents a summary of chemical doping of graphene aimed at tuning the electronic properties of graphene. p-Type and n-type doping of graphene achieved through surface transfer doping or substitutional doping and their applications based on doping are reviewed. Chemical doping for band gap tuning in graphene is also presented. It will be beneficial to designing high performance electronic devices based on chemically doped graphene.

1. Introduction

Graphene, a single layer of sp^2-bonded carbon atoms, has many unique physical properties such as ambipolar electric field effect,[1] high mobility of charge carriers (200,000 cm^2 V^{-1} s^{-1}),[2,3] anomalous quantum Hall effect (QHE)[4–6] and massless relativistic carriers,[5] all of which make graphene appropriate for many potential applications including graphene nanoribbon (GNR) transistors, single molecule gas detectors, supercapacitors and transparent conducting electrodes. Moreover, field-effect transistors (FETs) based on graphene are now considered a candidate for post-silicon electronics.[7] Modern logic circuits are based on silicon complementary metal oxide semiconductor (CMOS) technology. Both p-type and n-type conductions are desired to construct complex logic circuits. Chemical doping is an effective method to tailor the electrical properties of graphene. Although pristine graphene exhibits ambipolar field effect, it is not air stable and sensitive to unintentional doping by species absorbed from the surroundings[8] or residual polymers used during device fabrication. Most graphene based transistors with ambipolar field effect are measured in a vacuum, nitrogen or argon and/or by annealing treatment. There is no water and other species easily affecting the electrical properties of graphene[1,9–12] under those conditions. So, it is important to modulate the electronic properties of graphene by controlled doping with holes or electrons and reduce unnecessary contamination. This paper is concerned with a review of experimental studies of the chemical doping of graphene. p-Type and n-type doped graphene through surface transfer doping and substitutional doping will be discussed, and doping for band gap tuning in graphene is also presented. For a thorough discussion focused on synthesis, chemistry of graphene or graphene oxide and applications, see several excellent reviews.[7,13–20]

2. Mechanisms and characterization of chemical doping

Graphene is made out of sp^2 hybrid carbon atoms with the s, p_x and p_y atomic orbitals on each carbon atom forming three strong σ bonds with other three surrounding atoms. Overlap of the remaining p_z orbital on each carbon atom with neighboring carbon atoms produces a filled band of π orbitals, called the valence band and a empty band of π^* orbitals known as the conduction band. The valence and conduction bands touch at the Brillouin zone corners thus making graphene a zero-band-gap semiconductor.[24] Fig. 1A shows the energy spectrum of

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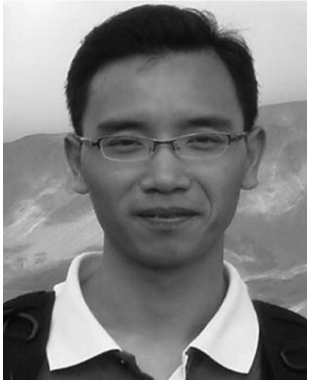

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graphene and zoom-in of the energy bands at one of the Dirac point (at the K or K′ points in the Brillouin zone or the intersection of the valence band and the conduction band).[21] Graphene can be doped by electric field (Fig. 1B),[22] by adsorption of metal atoms and by substrate (Fig. 1C).[23]

The mechanism of chemical doping in graphene would resemble that of carbon nanotubes, however the latter is still controversial.[25–29] From a large amount of literature, doping of graphene may be briefly classified as electrical doping,[1,30,31] achieved by changing gate voltage, and chemical doping,[22,32] obtained by using chemical species. It can be seen in Fig. 1B that pristine graphene exhibits strong ambipolar field effect indicating the doping of electrostatic potential. Fig. 1C shows the shift of the Dirac point relative to the Fermi level induced by chemical doping. In this review, we focus on the chemical doping of graphene. It is discussed in the following categories: surface transfer doping and substitutional doping.[14,20] For surface transfer doping,[33,34] doping is achieved by electron exchange between a semiconductor and dopants which adsorb on the surface of a semiconductor. Consequently, surface transfer doping is also called adsorbate-induced doping. In general, surface transfer doping does not disrupt the structure of graphene and most cases of chemical doping can be reversible. However, substitutional doping refers to the substitution of carbon atoms in the honeycomb lattice of graphene by atoms with different number of valence electrons such as nitrogen and boron. The incorporation of foreign atoms would disrupt sp^2 hybridization of carbon atoms. Furthermore, substrate, residual chemical species and ambient air can induce involuntary doping.[5,35–37]

Surface transfer doping occurs through charge transfer from the adsorbed dopant (or graphene) to graphene (or dopant).[23,29,33] Charge transfer is determined by the relative position of density of states (DOS) of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the dopant and the Fermi level of graphene. If the HOMO of a dopant is above the Fermi level of graphene, charge transfers from dopant to the graphene layer, and the dopant acts as a donor; if the LUMO is below the Fermi level of graphene, there is a charge transfer from graphene layer to dopant,[21,38] and the dopant acts as an acceptor. Graphene can be p-type or n-type doped *via* chemical doping.[32,38–40] p-Type doping drives the Dirac points of graphene above the Fermi level, and n-type doping drives the Dirac points below the Fermi level. Generally speaking, molecules with electron withdrawing groups adsorbed on the surface of graphene will lead to p-type doping of graphene, and molecules with donating groups will lead to n-type doping. In contrast, the mechanism of substitutional doping still remains uncertain. p-Type doping is generally achieved by adding atoms with fewer valence electrons than carbon like boron, while n-type doping is generally achieved by adding atoms with more valence electrons than carbon like nitrogen.

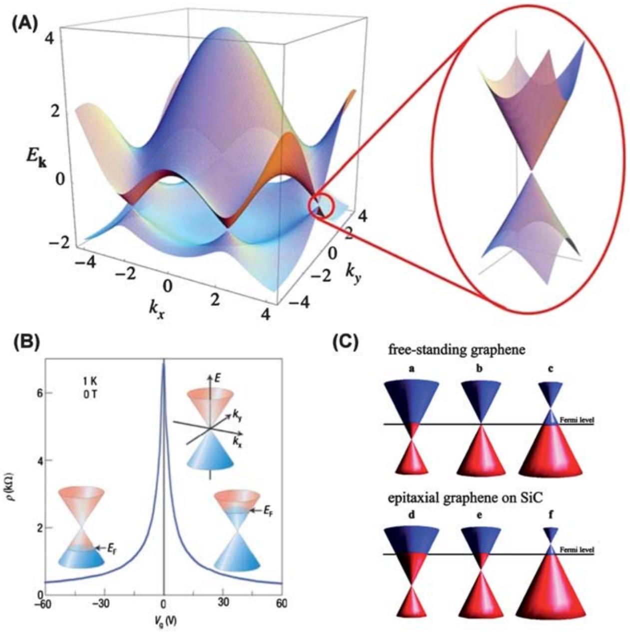

Fig. 1 (A) Left: the band structure of graphene in the honeycomb lattice. Right: zoom-in of the energy bands close to one of the Dirac points. Reprinted with permission from ref. 21, copyright (2009) by the American Physical Society. (B) Ambipolar electric field effect in single-layer graphene. The insets show the position of the Dirac point and the Fermi energy E_F of graphene as a function of gate voltage. Reprinted with permission from ref. 22, copyright 2007, Nature Publishing Group. (C) A schematic diagram of the position of the Dirac point and the Fermi level as a function of doping. The upper panel is n-type doped, pristine and p-type doped free standing graphene (a to c). The lower panel is n-type doped, pristine and p-type doped epitaxial graphene grown on silicon carbide (SiC) (d to f). Reprinted with permission from ref. 23, Copyright 2008, American Chemical Society.

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Chemical doping of graphene has so far been extensively characterized by these three main kinds of methods: photoemission spectroscopy (PES), especially X-ray photoelectron spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES), Raman spectroscopy and transport measurement. From spectrum of XPS, we can find whether the dopant exists by the characteristic peak of element contained in the dopant. The doping level can be determined by areas of the peak. The chemical states and electric states of the element could be obtained by analyzing the high resolution spectra of the element. ARPES is widely used to probe the electronic structure of graphene.[41–43] The band structure of graphene at Fermi level near the K point in the Brillouin zone can be obtained from the energy dispersions as a function of momentum along high-symmetry directions measured by ARPES. Fermi level locates at zero bonding energy, while the Dirac point is near, below or above the Fermi level depending on whether the graphene is pristine or doped.

Raman spectroscopy is a powerful tool for monitoring the number of layers, disorder and doping of graphene.[44,45] Due to relatively easy identification of single- and few-layer graphene flakes by optical microscopy on silicon substrates with typically 300 nm SiO_2, most of Raman studies are performed on graphene deposited on standard Si/SiO_2 (300 nm).[22] For electrically doped graphene, it is well known that the G band stiffens and upshifts for both electron and hole doping.[31,46] The full-width at half-maximum (FWHM) of G band also decreases for both kind of doping. Raman G peak is also sensitive to chemical doping and there is a useful empirical rule used to determine the doping type for surface transfer doping of graphene. n-Type doped graphene, or adsorption of molecules with electron-donating groups, the G band downshifts and stiffens; p-type doped graphene, or adsorption of molecules with electron-withdrawing groups, it upshifts and softens (Fig. 2).[14,47–49] The ratio of the density of the 2D band and the G band (I_{2D}/I_G), is sensitive to both kinds of doping. The asymmetry of the G band or the G band splitting induced by adsorption of aromatic molecules has also been reported.[50] For substitutional doping, it would be different. It has been reported that both nitrogen and boron substitutionally doped graphene have an upshift of the G band.[51]

Electrical conductivity or resistance of n-type and/or p-type doped graphene can be measured by field effect devices. The relationship between the conductivity or resistivity and gate voltage of pristine undoped graphene is a characteristic V-shaped curve. Typically, the minimum conductivity (or maximum resistivity) point or the Dirac point of pristine undoped graphene is at the zero gate voltage, and the point shifts toward positive (negative) gate voltage as a consequence of p-type (n-type) doping of graphene. If the band gap opens, graphene-based transistors will have higher on/off current ratio.

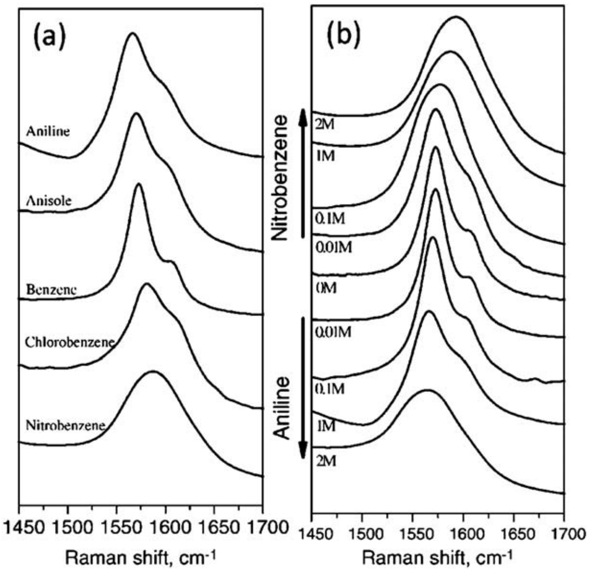

Fig. 2 Raman shift of the G band of graphene on interaction with (a) 1 M solutions of monosubstituted benzenes and (b) with varying concentrations of aniline and nitrobenzene. Reprinted with permission from ref. 47, copyright 2008, the Royal Society of Chemistry.

3. Surface transfer doping

3.1 p-Type doping

In 2004, Novoselov *et al.*[1] showed for the first time that free-standing 2D atomic crystal graphene stably exits with strong ambipolar field effect and they also found that it can be doped by electric field or chemical species. The electric field doping transforms the zero-band-gap semiconductor into completely electron or completely hole conductor (Fig. 1B). Water vapor and ammonia lead to p-type and n-type doping of graphene respectively. During water vapor exposure, the resistance decreases and recovers to its original state when water vapor is removed.[1,29]

The resistance of graphene decreases rapidly when the device is exposed to NO_2 gas (Fig. 3b).[29] NO_2 dopes holes into graphene and the minimum conductivity point shifts toward positive gate voltage without limiting carrier mobility (Fig. 3c) and changing the shape of the transfer characteristic of graphene-based FET. The doped graphene can be recovered by annealing at 150 °C. Those observations have been interpreted by calculations.[32] The adsorbed molecules neutralize the charged impurities in the substrate, thereby enhancing the carrier mobility. The mechanism of NO_2 doping has been theoretically and experimentally investigated by Wehling *et al.*[40] The Fermi level of NO_2, exactly at the partially occupied molecular orbital (POMO), is about 0.4 eV below the Dirac point of graphene independent of adsorption configuration. Therefore, the NO_2 molecule is a strong electron acceptor and accepts one electron from graphene. Adsorbed Br_2 and I_2 on one

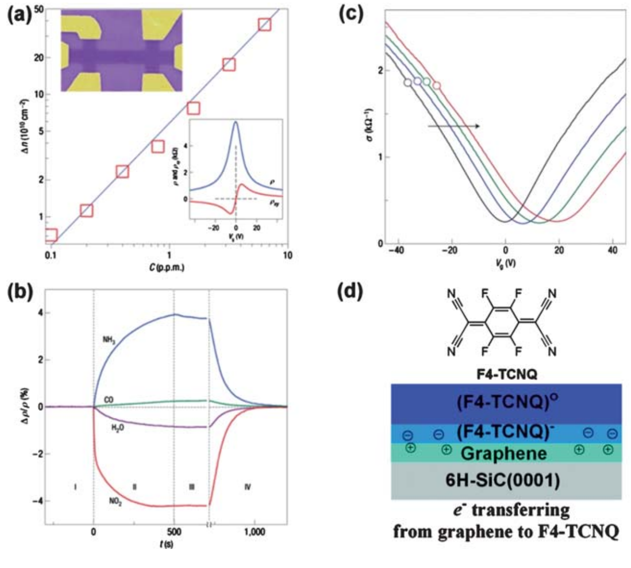

Fig. 3 (a) Concentration, $\triangle n$, of chemically induced charge carriers in single-layer graphene exposed to different concentrations, C, of NO_2. Lower inset: characterization of the graphene device by using the electric field effect. (b) Changes in resistivity, ρ, at zero B caused by graphene's exposure to various gases diluted in concentration to 1 ppm. The positive (negative) sign of changes is chosen here to indicate electron (hole) doping. (c) Constant mobility of charge carriers in graphene with increasing chemical doping. The parallel shift implies a negligible scattering effect of the charged impurities induced by chemical doping. Reprinted with permission from ref. 29, copyright 2007, Nature Publishing Group. (d) Schematic drawings of the charge transfer at the F_4-TCNQ/graphene interface. Reprinted with permission from ref. 52, copyright 2007, American Chemical Society.

layer of graphene inject high density of holes in graphene through charge transfer leading to p-type doping of graphene.[53]

Surface adsorbed molecules with electron-withdrawing groups can induce p-type doping effect of graphene. Tetrafluoro-tetracyanoquinodimethane (F_4-TCNQ) is a strong electron acceptor and widely used to improve the device performance of organic light-emitting diodes (OLEDs) and carbon nanotubes.[54–59] Chen *et al.*[52] demonstrated that epitaxial graphene (EG) can be p-type doped by adsorbing F_4-TCNQ on its surface (Fig. 3d). Synchrotron-based high-resolution photoemission spectroscopy (PES) reveals that electrons transfer from EG to F_4-TCNQ and it only occurs at the F_4-TCNQ/EG interface. So, an electron accumulation layer in F_4-TCNQ and a depletion layer in EG form at the interface and a p-type doping of EG is obtained. The hole density in EG can be controlled by the coverage of F_4-TCNQ. Later theory and experiment confirm that it is a simple and effective method to obtain p-type doped graphene.[60,61] Other organic molecules with electron withdrawing groups can also lead to p-type doping of graphene, such as tetracyanoethylene (TCNE),[62] tetrasodium 1,3,6,8-pyrenetetrasulfonic acid (TPA).[49] However, there is no significant charge transfer between EG and C_{60}, which is an electron acceptor too, partially due to the lower electron affinity of C_{60}, and hence the absence of p-type doping of EG.[52]

Under laser illumination, graphene reacts with benzoyl peroxide (BPO), leaving phenyl groups covalently bonded to basal plane of graphene.[63] Electrons in graphene are excited by laser illumination and accepted by surface adsorbed BPO. The BPO radical anion decomposes leaving holes in graphene. Single layer and double layer graphene react with oxygen at low temperature leading to hole doped graphene.[64] The doping effect might be caused by electron transferring from graphene to acceptors produced by the reaction, such as endoperoxides, hydroperoxides, and/or charge-transfer complexes, bound on the basal plane. Diazonium salts with electron acceptor groups dope graphene with holes.[65] The electron conduction is suppressed by doping *via* producing potential barrier preventing electron injection from the graphene electrodes beneath the metal electrodes to the graphene in channel. A self-assembled monolayer (SAM) of fluoroalkyltrichlorosilane (FTS) on graphene introduces ultra high level hole doping with hole density $>10^{13}$ cm^{-2}.[66] As the SAM is growing, the Dirac point of pristine graphene moves towards more positive gate voltage and the mobility (μ) decreases. The SAM of FTS extracts electrons from graphene and the SAM serves as negative charged scatters at the interface of SAM and graphene. For long-range charged scatters, the mobility inversely depends on the density of charged impurities (n_{imp}), $1/\mu \propto n_{imp}$.[67] This is why the mobility decreases with SAM growth.

Besides organic molecules, metal atoms with high electron affinity like bismuth, antimony and gold, adsorbed on the surface of graphene also lead to a similar shift of the Dirac point of EG.[23,68] EG on silicon carbide (SiC) is n-doped by the substrate, as a result of this, the Dirac point of graphene shifts below the Fermi level (panel e in Fig. 1C). Surface adsorbed bismuth and antimony atoms extract electrons from EG, and the Dirac point shifts toward the Fermi level but not coincide with it, but in contrast, gold, with higher electron affinity, shifts the Dirac point into the unoccupied states inducing p-type doping of EG (panel f in Fig. 1C).

Density functional theory (DFT) shows that charge transfer is driven by work function difference as well as the chemical interactions between metal substrate and graphene.[69] It is expected that graphene will be doped with holes if the metal work function (W_M) is higher than the graphene work function (W_G) and doped with electrons if $W_G > W_M$. The crossover points from n-type to p-type doping is then at $W_G = W_M$. The chemical interactions are strongly dependent on the distance between graphene and metal surfaces. For metals with weak interactions such as Al, Cu, Ag, Au and Pt, the Fermi level of graphene shifts without perturbing the graphene band structure when graphene adsorbs on the metal surface due to the work function differences and there is a crossover from n-type to p-type doping. At larger distance, *i.e.* about 5.0 Å, the chemical interaction is very weak and the crossover would then be at $W_M = W_G$. While at equilibrium distance, *i.e.* about 3.3 Å, the chemical interaction is strong and the crossover point locates at about 5.4 eV. In other words, metals with work function 0.9 eV higher than graphene work function can just induce holes in graphene and lower W_M induces electrons in graphene.

3.2. n-Type doping

Four-probe resistance measurement of graphene finds that the resistance of graphene changes when it is exposed to various gases such as water, ethanol and ammonia (Fig. 3b).[1] Among those, ethanol and ammonia, both donors, dope graphene with electrons, that is, n-type doping. Conduction of this electron doped graphene decreases and the original state recovers when the dopants are removed. Ammonia is more difficult to remove than ethanol because of the strong interaction with graphene. Later experiments show that chemical doping of graphene by donors or acceptors doesn't deteriorate graphene's mobility but shifts the position of the Dirac points of graphene without any significant changes in their shape of $\sigma(V_g)$ curves (Fig. 3c).[29] However, the curves become broader around the minimum conductivity points. The doping effect may be due to charge transfer from adsorbed ammonia to graphene.[70]

The similar results were also found in potassium doped graphene.[67,71] Additionally, as doping concentrations increase, the mobility of potassium doped graphene decreases and the asymmetry for electron *versus* holes increases (Fig. 4). These observations are most likely due to the high quality of samples, well-controlled environmental conditions with little unintentional charged impurities and high concentration doping.[67] The doped potassium atoms are charged-impurity scatterers which limit carrier mobility. However, potassium is highly reactive, so this doping method is difficult to implement in device technology.

Carbon nanotubes can be efficiently doped by poly(ethylene imine) (PEI), an electron-donating polymer.[72] Similarly, graphene can also be doped with PEI, which results in n-type behavior.[65] The conduction asymmetry for holes and electrons is observed. Hole conduction is suppressed and electron conduction is preserved in graphene when it is doped by PEI as the result of imbalanced carriers injection from the graphene electrodes beneath the metal electrodes like the diazonium salts.

Aromatic molecules with donating groups also lead to electron-doped graphene.[49] The electron-doped graphene can be simply distinguished by Raman spectroscopy based on

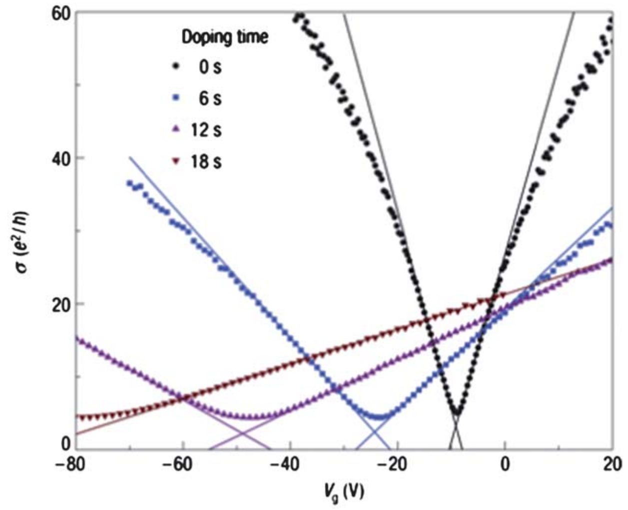

Fig. 4 The conductivity (σ) *versus* gate voltage (V_g) curves for the pristine sample and three different concentrations of potassium doped graphene taken at 20 K in ultrahigh vacuum (UHV). Reprinted with permission from ref. 67, copyright 2008, Nature Publishing Group.

downshifting of the 2D and G bands without using expensive ARPES. It has been reported that adsorption of free radicals results in n-type doping of graphene.[73]

Graphene could also be n-doped by the substrate of SiO_2[36,74] or silicon carbide (SiC)[21,41] on which epitaxial graphene were grown. And the doping effect may be dependent on the interaction with the substrate.[75] So that it is important to choose the proper substrate for graphene devices.[76]

4. Substitutional doping

4.1. p-Type doping

It is worth recalling that one route for modifying the electronic properties of materials is the addition of electron donors or acceptors, which is a well known procedure in semiconductor technology. Compared to carbon, nitrogen has one additional electron and boron lacks one. When nitrogen atoms are incorporated into the basal plane of graphene, they denote electrons into graphene leading to n-type doping of graphene, which will be discussed later. As expected, graphene doped with boron would exhibit p-type behavior[39] and boron doped GNRs would be a semiconductor.[77] Boron doped graphene has been synthesized by Panchokarla *et al.*[51] using arc discharge of graphite electrodes in the presence of H_2, He, and diborane (B_2H_6). XPS demonstrates that B is bonded to the sp^2 carbon network and the doping level is about 1.2–3.1%, slightly different to 1.0–2.4%, confirmed by electron energy loss spectroscopy (EELS). The intensity ratio of the Raman D band and G band (I_D/I_G) is higher than undoped graphene and the G band shifts to higher frequency as a result of B doping. The B-doped graphene exhibits higher conductivity and the Fermi level shifts 0.65 eV below the Dirac point by calculations indication the p-type doping of graphene.

Recently, a large-area atomic thick film of h-BNC consisting of hybridized hexagonal-BN (h-BN) and C (graphene) domains has been prepared by a CVD method using methane and ammonia borane (NH_3–BH_3) as precursors and a copper substrate as a catalyst.[78] Pure h-BN and pure graphene domains randomly distributes in h-BNC and their compositions can be tuned by changing the ratio of the gas concentration, therefore, h-BNC with different band gaps are obtained. Because of its unique properties, it will have many potential applications in electronics.

4.2. n-Type doping

Single-layer and few-layer nitrogen doped graphene sheets have been synthesized by a chemical vapor deposition (CVD) method with NH_3 as the nitrogen source and their electrical properties were investigated.[79] The nitrogen atoms are substitutionally incorporated into the basal plane of graphene in the forms of "pyridinic", "pyrolic" and "graphitic" nitrogen bonding configurations revealed by X-ray photoelectron spectroscopy (XPS), which is illustrated in Fig. 5a. The "pyridinic" and "pyrolic" nitrogen may lie at the edge or the defect sites and the "graphitic" nitrogen refers to the nitrogen replacing carbon in graphene plane. The "graphitic" nitrogen is dominating and the doping level is about 8.9%, which can be controlled by the ratio of NH_3 and CH_4 in the feedstock. As a result of nitrogen doping, there are many ripples in the graphene sheets and high density of D bands in Raman spectra in most samples.

Field-effect transistors based on pristine graphene and N-doped have been fabricated. Compared with pristine graphene, N-doped graphene behaves like an n-type doped semiconductor with lower conductivity, lower mobility (about 200–450 $cm^2\ V^{-1}\ s^{-1}$) and larger on/off current ratio (Fig. 5b to 5d). The foreign nitrogen atoms may release electrons into graphene and modify the electronic structure of it, leading to n-type doping of graphene and opening the band gap.

Nitrogen species can also be incorporated into the graphene plane through thermal annealing of graphene oxide (GO) in ammonia (Fig. 6a).[10] It is demonstrated that ammonia reacts with oxygen functional groups in GO, giving rise to pyridinic and quaternary N-doped graphene during annealing (Fig. 6b), and GO is reduced simultaneously. The highest doping level is about

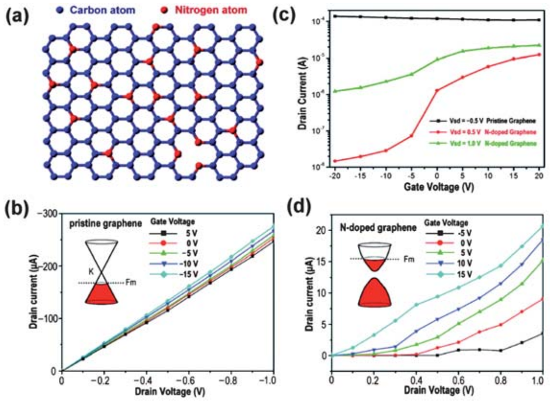

Fig. 5 (a) A schematic representation of the N-doped graphene. (b) Transfer characteristics of the pristine graphene and the N-doped graphene. (c) and (d) I_{ds}/V_{ds} characteristics at various V_g for the pristine graphene and the N-doped graphene FET device, respectively. The insets are the presumed band structures. Reprinted with permission from ref. 79, copyright 2009, American Chemical Society.

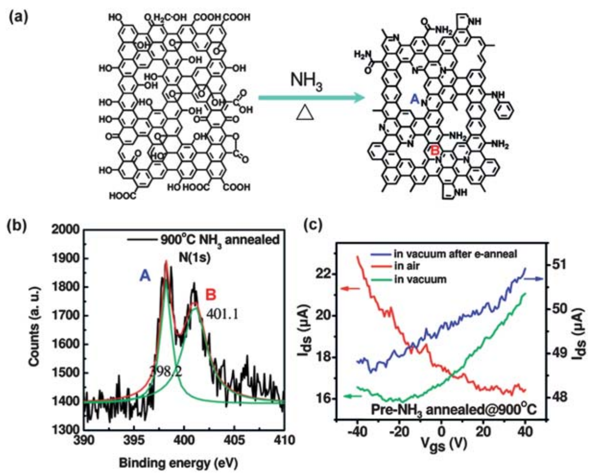

Fig. 6 (a) A schematic of the structure of GO and its reaction with ammonia through thermal annealing. (b) High resolution N (1s) spectra of GO annealed in NH_3 at 900 °C. The peak is fitted into low and high energy A and B components centered at 398.2 and 401.1 eV respectively. Letter A and letter B in (a) show the two predominant binding conditions of nitrogen in graphene annealed at high temperatures ≥900 °C. (c) Current-gate voltage (I_{ds}–V_{gs}) curves of a single GO device fabricated with an NH_3-annealed (900 °C) GO sheet. Reprinted with permission from ref. 10, copyright 2009, American Chemical Society.

5% with 500 °C annealing. The doping level is stable with no significant decrease when the N-doped reduced GO is annealed up to 900 °C. Electrical measurements confirm that the conductivity of N-doped reduced GO is higher than GO annealed in H_2. The minimum conductivity point (the Dirac point) of N-doped graphene is at negative gate voltage in vacuum and it shifts more negative after electrical annealing indicating the n-type doped effect (Fig. 6c). This method has also been used by others.[80]

The substitutional N-doping of graphene nanoribbons have been obtained by electrical joule heating (e-annealing) of GNRs in ammonia gas.[11] During e-annealing, the GNR is self-heated up to about 300 °C and the more reactive carbon atoms at the edge of the GNR can react with ammonia producing C–N bonds. When the GNR is annealed in vacuum, the Dirac point of it is at positive gate voltage, typically at 5 to 20 V partially due to p-type doping of remaining oxygen groups at the edge. However, when it is e-annealed in ammonia and the excess and physisorbed ammonia is removed by a pump overnight, the Dirac point shifts about 20 voltages to negative gate voltage comparing with that e-annealed in vacuum indicating the n-type doping of the covalently bonded nitrogen atoms. Because the main doping sites locate at the edge of the GNR, and there are no charged impurities in the plane of it, the carrier mobility is almost the same as it of the sample without doping.

The N-doped graphene has also been synthesized by arc-discharge method[51,81] and ammonia plasma[82] treatment of graphene. Atomic layer graphene with boron nitride domains has been prepared by CVD method and the band gap of graphene opens up.[78] Bottom-up synthesis of nitrogen doped GNRs has also been reported (Fig. 7a),[83–86] which will be a prospective way to synthesize n-type doped graphene with precise structure.

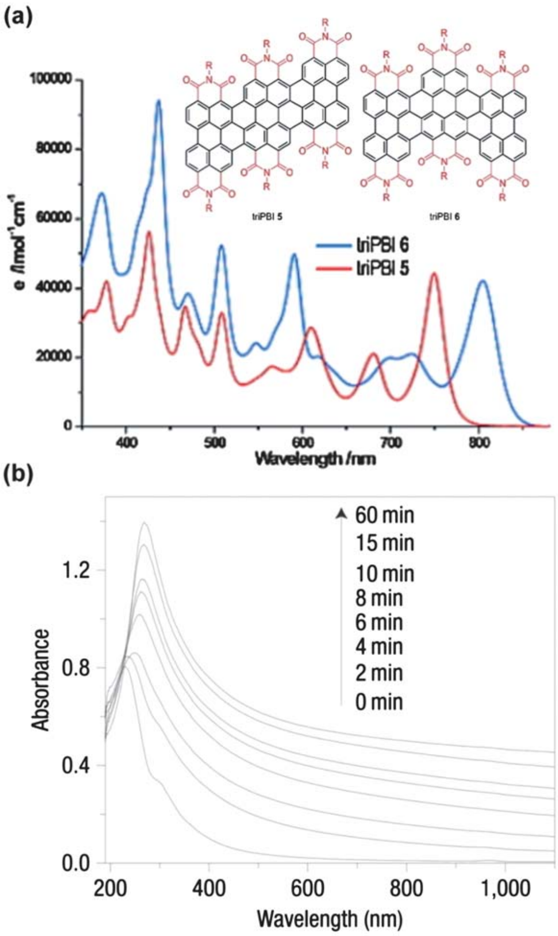

Fig. 7 (a) Two tri(perylene bisimides) (triPBIs) isomers and their UV-vis absorption spectra. Reprinted with permission from ref. 83, copyright 2008, American Chemical Society. (b) UV-vis absorption spectra showing the change of GO dispersions as a function of reaction time. Reprinted with permission from ref. 87, copyright 2008, Nature Publishing Group.

5. Doping for band gap tuning in graphene

Graphene is a zero-band-gap semiconductor, so it is highly desired for inducing a gap in graphene for device applications. Many methods have been proposed to open the band gap in graphene such as substrate-induced band gap,[75,88–90] bilayer graphene[91–95] and confinement and edge effects induced band gap such as graphene quantum dots[96] and nanoribbons.[97–101] Some methods of opening the gaps can be found in another review.[7] Chemical modification, like partially oxidation of graphite or controlled reduction of GO,[102,103] hydrogenation,[104] fluorination,[105] and chemical doping,[42] is an alternate strategy to open a gap in graphene.

There has been any amount of research on the synthesis, structures and properties of GO and reduced GO.[16] It is well known that GO behaves like an insulator, while the electrical properties of reduced GO are similar to perfect graphene but with lower conductivity and mobility partly because of the residual oxygen functional groups and vacancy defects.[35,106,107] Controlled oxidation of graphite or reduction of GO can induce band gap in graphene.[108] Fig. 7b is a typical UV-vis adsorption spectra of GO and reduce GO.[87] There is no clear leading edge in the adsorption spectra, which indicates the absence of a well-defined band gap.[16] However the defects in reduced GO can be used to tune the electrical properties of it,[102] and the conductivity of GO can be controlled by reduction level.[109] During reduction, the transitions from insulator to semiconductor then to semi-metal have been observed.[103] and reduced GO with semiconductor behavior has also been reported.[110]

Calculations have been demonstrated that adsorption of atomic hydrogen on graphene can open a substantial gap in graphene.[111] Graphene reacts with hydrogen atoms forming C–H bonds on the basal plane of graphene. Hydrogenation of graphene changes sp^2-bonded carbon atoms into sp^3-bonded ones and the conducting π-bands are eliminated thus opening the band-gap. The hydrogenated graphene can be restored by thermal annealing at 100–200 °C.[112] It indicates that the electronic properties of graphene can be tailored by reversible hydrogenation of graphene. Graphane, hydrogenated graphene has been synthesized by Elias *et al.*[104] Before hydrogenation, the device exhibits an ambipolar field effect with the neutral point near zero gate voltage and QHE at low temperature (Fig. 8A and 8B) while the hydrogenated graphene behaves like an insulator (Fig. 8C and 8D). By thermal annealing in argon at 450 °C, graphane converts back into graphene with its characteristic electrical properties (Fig. 8E and 8F), all of which are in line with the calculations. However, the recovery is not complete and the neutral point is not at the zero gate voltage but shifts to positive gate voltage indicating p-type doping of graphene (Fig. 8E). All the changes have been confirmed by Raman and TEM. It is easy to imagine that the band gap of hydrogenated graphene would be modulated by finely tuning the dosage of hydrogen atoms. The hydrogen atoms have also been detached by electron-stimulated desorption using a scanning tunneling microscope (STM) tip.[113]

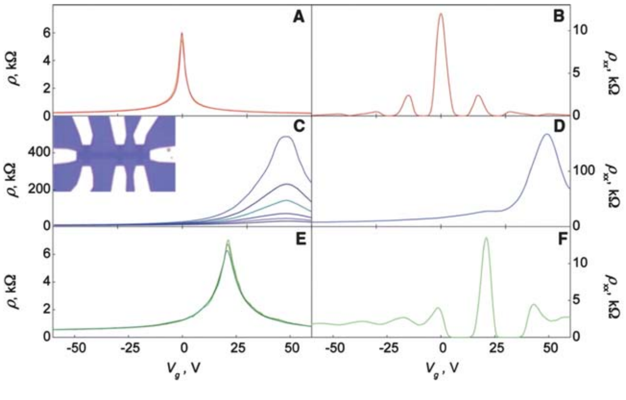

Fig. 8 Control of the electronic properties of graphene by hydrogenation. The electric field effect for a device at zero *B* at various temperatures *T* (left column) and in *B* = 14, *T* at 4 K (right). (A and B) The sample before its exposure to atomic hydrogen. (C and D) After atomic hydrogen treatment. (E and F) The same sample after annealing. Reprinted with permission from ref. 104, copyright 2009, the American Association for the Advancement of Science.

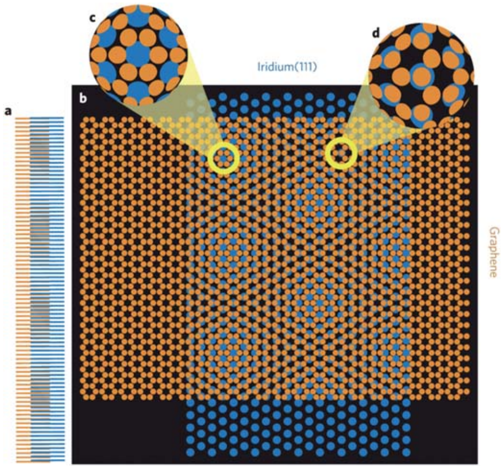

Fig. 9 a, the Moiré pattern formed by two sets of parallel lines. b, the Moiré pattern formed by graphene's honeycomb lattice on top of a triangular iridium (111) surface and two high-symmetry carbon–iridium configurations: c, a carbon ring is centered above an iridium atom. d, a carbon atom sits on top of iridium. Hydrogenation preferentially takes place at carbon sites such as d, closest to peaks in the iridium landscape. Reprinted with permission from ref. 115, copyright 2010, Nature Publishing Group.

The band gap does open by patterned hydrogenation of graphene.[114] This is achieved by iridium catalyzed hydrogen chemisorption. The iridium lattice constant is different to graphene and a Moiré pattern (Fig. 9), which has a much larger periodicity, is generated when graphene grows on the top of Ir (111).[115] The carbon atoms which are located nearest the top center surface of the iridium atom surface are preferentially hydrogenated giving rise to graphane-like islands and other spots remain clean (Fig. 9d). The hydrogen-free graphene regions become narrower as hydrogenation progresses and the band gap in hydrogenated graphene opens due to confinement effect like graphene antidot lattices[116,117] and graphene nanomesh.[118–120] The band gap is dependent of the hydrogen coverage or the dosage of atomic hydrogen. A band gap of at least 0.45 eV is observed by ARPES. The patterned hydrogenation of graphene has also been obtained by other methods.[113]

Like hydrogenation, fluorination of graphene may also induce a gap. Theoretical calculation shows that only hydrogen and fluorine can completely covalently cover the basal plane of graphene.[105] Graphene fluoride can be synthesized and exhibits insulator behaviors with large band gap while the reduced graphene fluoride has low resistance.[121] The gap may be tailored by different fluorination level.[122]

Covalent attachment of aryl groups to the basal plane of graphene might induce band gap in graphene.[123] The nitrophenyl groups modified epitaxial graphene is prepared by spontaneous reaction of the diazonium salt with the graphene layer. It is confirmed by Fourier transform infrared (FTIR) spectroscopy and XPS that the nitrophenyl groups are sp^3-bonded to the surface of graphene. The coverage of nitrophenyl groups, estimated by cyclic voltammetry is about 1×10^{15} molecules cm^{-2} on the graphene sheet. The resistance of the modified graphene increases and is dependent on the temperature suggesting the transform from a near-metallic conductor to a semiconductor.

The band structure near the Dirac point of bilayer epitaxial graphene grown on the surface of SiC can be easily tuned by potassium doping.[41] Fig. 10 is the energy-momentum curves and schematic illustrations of the evolution of band gap closing and reopening induced by potassium doping. The band structure is sensitive to the symmetry of the two layers. If the individual

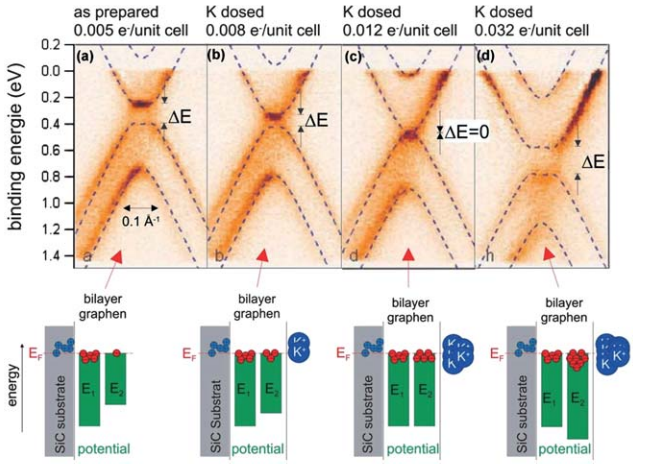

Fig. 10 Upper panel: closing and opening of the band gap in bilayer graphene induced by potassium adsorption on top of the bilayer stack. Lower panel: the Coulomb potential changes corresponding to the doping process.[124] Reprinted with permission from ref. 41, copyright 2006, the American Association for the Advancement of Science.

layers in bilayer graphene are rendered inequivalent, then a gap opens. The as-prepared graphene is naturally n-type doped by the SiC substrate. The bottom layer is charged by electrons from the SiC substrate and then the electron concentration is different in the two layers. The Coulomb potential (E_i in Fig. 10) difference generates between the two layers. So the electronic structures of bilayer graphene possess a gap at the K point, which is observed in ARPES (Fig. 10a). The gap closes when adsorbed potassium donates electrons into the top layer and balances the charges in the bottom layer (Fig. 10c). It reopens when the charges of the top layer outweigh the charges of the bottom layer (Fig. 10d).

Gaps can also be formed in graphene by molecular doping, such as NO_2,[42] Br_2 and I_2 adsorption.[53] NO_2 dopes graphene with holes as discussed above, and simultaneously induces a reversible metal to insulator transition in one layer and bilayer EG conformed by AREPS with a depletion of density of states at the Fermi level. For few-layer graphene, Br_2 adsorbs and intercalates into graphene layers, in contrast I_2 only adsorbs on the surface of graphene introducing different doping levels between surface and interior layers then creating symmetric potential (from two surfaces to the center) thus opening the band gap.

Compared with other proposals for tuning band gaps, chemical doping is a simple and effective method to open a band gap in graphene. The gaps induced by chemical doping can be controlled by doping levels. Moreover, the original state of graphene can be restored by annealing.

6. Doping, dedoping and their applications

Graphene is very sensitive to surface transfer doping and most doping processes are reversible. It is a two-dimensional material with large surface areas and ultra high conductivity which changes rapidly when gas molecules adsorb on the surface of it. All of them make graphene an excellent candidate for sensors with high sensitivity. It has been reported that its conductivity responses linearly to the concentrations of NO_2, (Fig. 3a) which would greatly simplify the use of graphene based sensors and even individual NO_2 molecules can be detected.[29] High performance sensors based on chemically derived graphene have been demonstrated.[125–129] Graphene-based biosensors for detecting bacteria,[130] glucose,[131] pH and proteins[132,133] have also been fabricated. Detection of DNA targets based on GO has also been reported.[134,135] And graphene may be an ideal material for DNA sequencing.[136–140]

Experimental and theoretical studies have shown that graphene based p–n junctions have many novel properties.[141–145] In most heterojunctions, the p-type and/or n-type region is formed by local top gate control. By selective chemical doping, p–n junctions have been created and their properties have been investigated.[146]

One aim of chemical doping is to obtain controllable, air stable and high performance n-type, p-type or even ambipolar field effect. As mentioned above, pristine graphene and reduced GO always show p-type behavior at ambient conditions because of unintentional doping caused by residual species or oxygen molecules in air, which is still not fully understood. However, when graphene is embedded in a insulating polymer matrix like polystyrene (PS), it is weakly sensitive to ambient doping and exhibits ambipolar field effect.[147] Although very high mobility is obtained in suspended graphene devices,[2,3] graphene supported on chemically modified substrates, especially on hydrophobic substrates,[148,149] or in aqueous solutions[150,151] performs considerably well *via* screening the charged-impurity scatterings and reduction of doping.

Graphene can be used as buffer layers between the electrodes and the organic semiconductors to enhance the performance of organic field effect transistors (OFETs).[152,153] The work function of graphene is similar to Ag or Cu electrode. Moreover, the molecular structure of graphene is similar to organic semiconductors like pentacene and the π–π interactions between graphene and pentacene are very strong. All of those result in low carrier injection barrier and high performance of the device.

Other applications have also been reported such as nitrogen-doped graphene can be used as an efficient metal-free electrocatalyst for oxygen reduction in fuel cells[80] and be doped with $SOCl_2$ for high electrical conductivity.[35] Because of the rapid progress on graphene, we believe other practical applications would emerge soon.

7. Conclusions and perspectives

Herein, we have highlighted the important methods for modulating the electrical properties of graphene *via* chemical doping. p-Type and n-type doped graphene can be obtained through surface transfer doping and/or substitutional doping by different dopants. Some typical strategies to tune the band gap of graphene are illustrated, such as adsorption of chemical species *i.e.* atomic hydrogen, potassium, NO_2, Br_2 I_2 and O_2, controlled oxidation or controlled reduction and covalent modification. And the applications based on chemical doping are also mentioned.

There are many challenges remaining at present. Most cases of surface transfer doping are obtained by adsorption of strong electron-donating or withdrawing chemical species. Because the adsorbed chemical species could desorb from graphene surface and the chemical species may react with reactive molecules such as oxygen or water from surroundings, doping of graphene would not have long-term stability. The substitutionally doped graphene would be more stable in that the foreign atoms are covalently bonded to the carbon network of graphene. The surface coverage of the chemical species or the number of foreign atoms incorporated into the basal plane of graphene is difficult to control and the doping of graphene would be difficult to reproduce. We need exact methods to homogenously and reproducibly dope graphene p-type/n-type for different applications and to control the doping level. And the doping mechanism is not fully understood, the relation between doping and mobility and band gap opening induced by chemical doping being among them. Doping caused by contaminations and the ambient air need to be investigated. However, tailoring the properties of graphene by chemical doping is considerably simple and high throughput doping of graphene is possible.

Acknowledgements

We acknowledge financial support from the National Natural Science Foundation of China (60736004, 20721061), the National Major State Basic Research Development Program (2006CB806203, 2006CB932103, 2009CB623603), and the Chinese Academy of Sciences.

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