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A review of doping modulation in graphene

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Keywords:	Graphene is one of the most promising materials for post-silicon electronics and has outstanding physical and
Graphene	electronic properties. In particular, its unique 2D sp^2 -hybridized networks of carbon atoms arranged in a hon-
Doping Fermi level engineering Lattice substitution Surface adsorption Stimuli-responsiveness	eycomb lattice make graphene potential for exceptional electronic quality. However, in order to use graphene in possible applications such as photodetector, photovoltaics, sensors, organic light-emitting diodes, organic thin- film transistors, supercapacitor, and catalytic applications, it is essential to precisely modulate its electronic properties, i.e. doping. In this review, we present various strategies for engineering the Fermi level in graphene, including heteroatom substitution, molecular adsorption, introducing functional molecules for external stimuli
	responsiveness. We anticipate that the current review provides a concise information on the methods to probe doping level, effective doping approaches, and achievable doping type and charge carrier concentration ranges

so that an appropriate doping approach can be readily designed.

1. Introduction

Since A. Geim and K. Novoselov were awarded the 2010 Novel Prize in physics with their works on graphene, the material has attracted tremendous interests throughout a wide scientific community. Due to its unique two-dimensional honeycomb structure, it exhibits extraordinary electronic properties, i.e. an extremely long pathway for charge carriers and phonons, and hence ultrahigh charge carrier mobility and thermal conductivity [1-4]. Theoretically predicted highest mobility in graphene reaches $\sim 200,000 \text{ cm}^2/\text{V}^{-1} \cdot \text{s}^{-1}$ when charge carrier scatterings by disorders, defects, and other components in the extrinsic environment are minimized [5,6]. This value is much higher than that of silicon, $\sim 1,000 \text{ cm}^2/\text{V}^{-1} \text{ s}^{-1}$, resulting in tremendous attentions in the field of semiconducting materials. In addition, graphene's intrinsic mechanical strength, predicted to exceed that of any other materials, and high transparency can open up a feasible route toward flexible electronics and transparent electrodes [7]. Consequently, graphene is considered as a promising material for a wide range of applications such as nanoelectronics and flexible electronics [8,9].

However, graphene is a semimetal which intrinsically does not provide high conductance with zero band gap compared to other metallic or semiconducting materials. Therefore, in order to exploit this promising material to desired applications, it is required to control the electronic structures and properties of graphene. To do so, the control of charge carrier concentration by tuning Fermi level ($E_{\rm F}$), i.e. doping, has been extensively investigated. Since graphene itself is an atomically thin electronically active surface, its Fermi level can be disturbed upon any contacts with arbitrary matter, even underlying substrates, as well as trace environmental changes, leading to undesirable and uncontrollable doping. However, the capability for the precise and effective control of n-type or p-type doping in graphene with desired charge carrier concentration, a number of applications such as photodetector, photovoltaics [10,11], sensors [12], organic light-emitting diodes [13,14], organic thin-film transistors (OTFTs) [15], supercapacitor [16,17], and catalytic applications [18–20], can be possible.

Fermi level engineering typically occurs when electrons are either injected or extracted into or from graphene, referred to as n-type or ptype doping (Fig. 1a) [21]. Generally, two approaches have been developed: i) substitution of carbon atoms with heteroatoms and ii) incorporation of dopants through physical or chemical adsorption on the graphene surface. Substitution with heteroatom is inherently stable due to the covalent bond linkage of the dopant in the graphene lattice; however, it inevitably disturbs graphene's unique honeycomb structure, inducing defects and disorder (Fig. 1b) [22]. This induces a decrease of electronic mobility and hence degradation in the performance of electrical devices. In contrast, adsorption of electronically interacting dopants with graphene leads to a local perturbation of graphene, resulting in desired doping (Fig. 1c) [23,24]. The structural integrity of the

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Fig. 1. (a) Schematic showing p- or n-type doping in graphene. [Adapted with permission from Ref. [21]. Copyright (2015) American Chemical Society.] (b) Illustration of doping by heteroatom substitution into the graphene lattice. [Adapted with permission from Ref. [22]. Copyright (2009) American Chemical Society.] (c) Illustration showing doping by adsorption of functional molecules on graphene. [Adapted with permission from Ref. [24]. Copyright (2012) American Chemical Society.] .

lattice is expected to be preserved; however, it does not guarantee a stable doping system. In addition, it should be important to understand how wide the range of hole or electron concentration can be controlled with the methods.

The aim of this review is to provide what doping methods have been developed since the graphene researches became rapidly expanded, and to give a concise information on highly effective approaches, doping types, and achievable charge carrier concentration ranges, so that appropriate doping methods for desired applications can be carefully and readily selected. In order to analyze and interpret the results in literature, we begin with an introduction on experimental and theoretical methods to explore and characterize doping in graphene in details. Then we will describe the approaches to modulate the $E_{\rm F}$ in two categories aforementioned. We further focus on dynamic doping modulation using external stimuli such as light and chemical cues, which have been of importance in fundamental aspects as well as in applications to smart electrical devices and sensors. Ultimately, we envision that this review will help to further extend the doping approach to hybrid carbon materials and functional molecules, enabling the realization of ultrahigh performance in related applications.

2. Methods to probe doping modulation in graphene

Raman spectroscopy and electrical measurements in a FET geometry are generally used to investigate doping behaviors of graphene [25-27]. The most common method to estimate charge carrier concentration (*n*) is an electrical measurements to characterize graphene FET device. In the curve of the conductance as a function of gate voltage, the Dirac point, the gate voltage at the minimum conductance, can be simply converted to charge carrier concentration. In a back-gate geometry with a SiO₂/Si substrate, n can be extracted with the equation of n = $\epsilon_0 \epsilon_r V_{Dirac} / eT_{OX}$, where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of SiO₂, $V_{\rm Dirac}$ is the Dirac point in voltage, $T_{\rm OX}$ is the thickness of SiO_2 , and *e* is the elemental charge. In Raman spectroscopy, it is known that an increase of the charge carrier concentration systematically changes the positions of the G and 2D bands, the intensity ratio of G to 2D, and the full width at half maximum (FWHM) of the G band [26,27]. Specifically, the G band scattering is due to the degeneracy of E_{2g} phonon at the center of the Brillouin zone in reciprocal lattice of graphene, which is highly sensitive to the change of the charge carrier concentration. Das et al. [27]. monitored the changes of doping in the graphene FET device. (Fig. 2a) They showed that the shifts of G band position can be correlated with hole concentration: the shift of approximately $1-3 \text{ cm}^{-1}$ per 10^{12} cm^{-2} of hole concentration. Plus, the type of doping can be probed by examining 2D band. Upshift and downshift of 2D band relative to neutral point where G band position is at minimum indicate p-doping and n-doping, respectively, though quantitative analysis using 2D band is not recommended due to the charge carrier concentration range where the position of 2D band does not change much even when actual carrier concentration changes.

With this method, Kim et al. [28] determined charge carrier concentration in single layer graphene doped by an organic molecule exhibiting a large dipole moment. The dipolar molecule highly p-dopes graphene, resulting in upshifts of both Raman G and 2D bands. By further careful quantitative analyses with the position of G band and electrical measurements, they showed that charge carrier concentration values estimated by FET device characterization and Raman spectra were in good agreement, confirming an excellent correlation between two different methods.

UV photoemission spectroscopy (UPS) can also be used to probe doping in graphene. It measures the kinetic energy of photoelectrons emitted by molecules upon their absorption of UV light to determine molecular orbital energies in the valence band. Luo et al. [29] investigated the electronic structure of C–N bonding configurations in nitrogen doped graphene by determining its valence band structure with UPS. They found that pyridinic C–N effectively modified the valence band structure in graphene; as a result, the density of p-doping states near the Fermi level was increased and the work function was reduced.

The theoretical approach is also useful to explore doped graphene [30]. One of widely utilized method is density functional theory (DFT) which enables to predict the band structure of graphene modified in various approaches [31]. For example, Nakada et al. used the DFT to investigate the adsorptions of different atoms on graphene [32]. They calculated theoretical adsorption migration energies in the adsorption site on a graphene sheet for many atomic species, ranging from atomic number 1 to 83. Marquez et al. [33] specifically calculated the binding energy of Li⁺ ions on hydrogen terminated graphene using DFT calculation, finding that Li⁺ ions are preferentially bound outside the graphene. Wong and Gopalan et al. [34] explored electronic structures of graphene interacting with organic molecules exhibiting controlled dipole moments with DFT calculation. (Fig. 2b) They showed that their theoretical approach allowed deeper understanding on the enhancement of Raman signal occurring due to significant electronic coupling between highly polarizable organic dipolar molecules and graphene, which also led to hole doping in graphene.

3. Doping by substitution of dopants in the lattice of graphene

A carbon lattice in graphene is a great and effective pathway of charge carriers. In the lattice, an introduction of heteroatom leads to a modulation of charge carrier concentration. In other words, the graphene lattice is disrupted by the substitution of carbon atoms in the graphene with heteroatoms such as nitrogen and boron [35]. An introduction of B or N in the graphene lattice creates strong polarization in the carbon network due to differences in the electronegativities of B

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