Applied Surface Science 463 (2019) 900–906

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Tunable Fermi level of graphene modified by azobenzene molecules

Jiaojiao Yu[a,b,1], Mingjia Zhang[a,1], Jianjiang He[a], Chunfang Zhang[c], Weiwei Cui[d], Ning Wang[a], Changshui Huang[a,*]

[a] Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No. 189 Songling Road, Qingdao 266101, PR China
[b] University of Chinese Academy of Sciences, Beijing 100190, PR China
[c] Department of Chemistry and Environmental Science, Hebei University, Baoding 071002, PR China
[d] Department of Physics, Qingdao University, Qingdao 266071, PR China

ARTICLE INFO

Keywords:
Graphene
Raman spectroscopy
Field-effect transistor
Fermi level
Carrier concentration

ABSTRACT

Carbon-based nanomaterials, especially graphene, are considered to be the most hopeful alternatives to silicon in the near future of pushing to its limits. However, the zero band gap of graphene suppresses its application, it needs to develop a convenient method to modulate its Fermi level and band gap. Herein, we report a general approach to regulate Fermi level of graphene precisely by designed azobenzene molecules with different dipole moment and dipole orientation. The Raman spectra results demonstrate the π-π interaction between the azobenzene molecules and graphene, which result in the modulation of the Fermi level of graphene. Besides, based on the field effect transistor characteristic measurement, we also observe the Fermi level adjustment for the hole/electron doping to graphene from the spontaneous polarization effect of the azobenzene molecules, further speculating the regulation of electronic structure and providing a new route for changing the electrical properties of graphene.

1. Introduction

The foundation of modern information technology is the integrated circuit chip, 90% of which is silicon-based complementary metal-oxidesemiconductor (CMOS) technology. Silicon-based CMOS technology is about to enter the 14 nm node after half a century rapid development and will reach its performance limit [1]. With the increasingly critical research in the post-Moore era of nanoelectronics science, many researchers count on the development of non-silicon-based electronics and abandon the use of silicon as a supporting material to be up against the 8 nm technology node. Among the few possible candidate materials [1–3], carbon-based nanomaterials, especially graphene [4,5], are considered to be the most hopeful alternatives [6] to silicon due to its extremely small thickness and extraordinary carrier mobility [7] and will likely profoundly affect the future development of chips and related industries. Since the discovery of graphene in 2004 [8], it becomes a fascinating material [5] applying to the field of high-frequency transistors, sensors, flexible electronics for its great mechanical strength [9], excellent chemical and thermal stability [10], and brilliant flexibility [11,12]. Nevertheless, the zero band gap severely limits its application in the semiconductor field.

Graphene has four half-filled degenerate states at the intrinsic Fermi level which consisting of two degenerate states at two nonequivalent Dirac points (K and K'), comes from the crystal symmetry of graphene's honeycomb lattice. Band gap opening in graphene thus implies breaking of the symmetry [13]. Hence, many efforts have been dedicated to open the band gap of graphene by modulating the Dirac point or Fermi level [14]. It is reported that the graphene Fermi level is modulated by electrical field effect which would result in hole or electron doping [15]. Graphene nanoribbons and atom-doped graphene are also investigated for the application in field effect transistors which demonstrate high on-off ratios [16]. Just recently, the molecules (including gas, molecular acceptor, self-assembled monolayers) adsorbed on graphene are considered to be an effective way to tune the electronic structure of intrinsic graphene because of its harmlessness, simpleness and effectivity [17–20]. However, general rules for the adjustment of graphene Fermi level by adsorbed molecules have not yet been established.

Herein, we modify the surface of graphene with the azobenzene molecules with different dipole moments and dipole orientations to realize the n- and p- doping and regulate its Fermi level. Raman spectrum and field effect transistor (FET) are used to characterize the

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[*] Corresponding author.
E-mail address: huangcs@qibebt.ac.cn (C. Huang).
[1] These authors contributed equally.

https://doi.org/10.1016/j.apsusc.2018.09.021
Received 10 February 2018; Received in revised form 30 August 2018; Accepted 3 September 2018

interaction between the azobenzene molecules and graphene and the modulation in the Fermi level of graphene. The results demonstrate that the tactic achieves the regulation for the Fermi energy and carrier concentration of graphene, and maintains the lattice structure of graphene at the same time. This research offers a general approach to the rational design of dipole molecules adsorbed on graphene for modulating its band gap.

2. Materials and methods

2.1. Preparation of the materials

The three molecules (DR1P, DR1P', and DRSP) with different dipole moments and orientations for the diverse functional groups of azobenzene can be attached on graphene via π-π interaction between the end pyrene and graphene. DR1P, DR1P', and DRSP were synthesized as reported in previous literature [21]. All chemicals were purchased from Sigma-Aldrich and used as received. 4-R-aniline was dispersed in water yielding a suspension. A certain volume of aqueous HCl was added in the suspension to make a clear solution. A cold aqueous $NaNO_2$ was added dropwise to the mixture and stirred in the ice bath. The resulting mixture was added to the solution of 2-(N-ethylanilino)ethanol in glacial acetic acid and water in an ice bath and then the aqueous Na_2CO_3 solution was added to adjust the pH to 6. The mid product was filtered and washed with hexane. The mid product, 1-pyrenebutryic acid, N,N′-dicyclohexylcarbodiimide (DCC), and 4-(dimethylamino)pyridine (DMAP) (5:5:5:1) were mixed and stirred in anhydrous $CHCl_3$. The crude solution was collected and concentrated with a rotary evaporator after the precipitate was filtered. The resulting liquid was further passed through a silica gel column with a $CHCl_3$/hexane mixture as the eluent, collecting the resultant product (see Supporting Information Fig. S1).

The single layer graphene for Raman spectroscopy was obtained by using scotch tape we started repeatedly peeling flakes of graphite off the mesas. When a Si wafer adheres to the scotch tape with the single layer graphene, some flakes became captured on the wafer's surface. The Raman spectroscopy is performed on the Thermo Scientific DXRxi at 532 nm with the spot size of 5 μm and laser power of 10 mW. The peak position and intensity of Raman spectra is calibrated by SiO_2 peak at 520 cm^{-1}. So that it can be used in the comparison between different samples. Due to the small-scale graphene from mechanical exfoliation, the monolayer graphene prepared on copper foils (99.8%, 0.025 mm thick, Alfa Aesar) by chemical vapor deposition is used to fabricate field effect transistor for electrical measurements. Graphene growing on copper is deposited a protective poly(methyl methacrylate) (PMMA) and the original copper substrate is etched off by soaking in iron chloride ($FeCl_3$, 0.2 M). The SiO_2/Si substrate was subsequently cleaned by sonication in isopropanol, ethyl alcohol and acetone. Then the monolayer graphene is successfully transferred onto the insulating SiO_2/Si substrate. The protective layer was removed by dissolving in acetone.

2.2. Computational details

The following calculations were performed using the DFTB + package [22]. The geometric and electronic structure properties were studied with the dispersion-corrected self-consistent charge density functional tight-binding (SCC-DFTB-D) method [23,24]. The 3OB parameters set was chosen for the O, N, C, S and H elements contained in the organic molecules, and dispersion was included via a Lennard-Jones potential between each pair of atoms.

2.3. Fabrication procedure of graphene-based field effect transistors

The field effect transistors based monolayer graphene were fabricated on the SiO_2/Si substrate by UV photolithography process. The surface was cleaned by UV/ozone treatment to remove the contamination from the surface of the wafer and graphene. The photoresist (AR-P 3740) was spin-coated on the surface of graphene at high-speed (1500 rpm) for 30 s to result in a uniform thin layer between 2 and 3 μm thick. Preparation of the resist is concluded prebaking over a hot plate at 100 °C for 30 s to evaporate the photoresist solvent. After prebaking, the sample coated photoresist was exposed to a pattern of intense ultraviolet light within the intensity of 100 mJ/cm^2 through photolithographic masks. The samples were developed in developer for 30 s and rinsed using deionized water. The sample was then post-baked to drive off excess water at 120 °C for 60 s on a hotplate. Silver (80 nm) electrode was deposited on the graphene by evaporation. And lift-off process was performed in toluene with immersion times typically of several hours (see Supporting Information Fig. S2).

2.4. Physical and electrical characterization

The layer number of graphene was determined by Raman spectrum. The azobenzene molecules (DR1P', DR1P, and DRSP) were respectively dissolved in dichloromethane with concentrations ranging from 5×10^{-10} M to 5×10^{-5} M. A 20 μL of the azobenzene molecules solution from low concentration to high concentration were sequentially spin-coated on graphene at 3000 rpm for 30 s. The higher the concentration of azobenzene molecules solution spin-coated on the surface is, the more the azobenzene molecules on the surface of graphene kept. Raman spectra of azobenzene molecule/graphene samples were gained by Thermo Scientific DXR Raman microscope. Wavenumber and intensity were calibrated based on a Si peak at 520 cm^{-1}.

The electrical measurements were performed on the Keithley 4200 SCS and Signatone H100 series probe station. The graphene spin-coated with the azobenzene molecules is investigated its FET characteristics.

3. Results

Fig. 1a–c show the structure of the three azobenzene molecules with distinct dipole moments and dipole orientations. They are all azobenzene derivatives attached various groups with the discrepant capacities of donating and withdrawing electron. The dipole moments of the DR1P', DR1P and DRSP were calculated and defined to be −10.61 D, 13.55 D and −13.56 D, respectively. And the related calculated results are list in SI. The schematic diagram of the azobenzene molecules anchored to graphene via the π-π interaction between pyrene and graphene can be found in Fig. 1d. The Raman spectrum of the pristine single layer graphene in our study is measured and showed in Fig. 1e. The high ratio between 2D band and G band reveal that graphene is single layer and indistinct D band suggests the few defects. Meantime, the reproducibility of Raman spectrum for graphene was also conducted. As shown in Fig. S3, it can be observed that the peak positions as well as peak intensities are similar with each other at different regions on graphene. The standard deviation (σ) of peak shift on pristine graphene from different regions is 0.237 cm^{-1} (Table S1) which is far less than the shift from different modification (1.5–3 cm^{-1}). Moreover, the experiments were operated in the same ambient atmosphere to the great extent. Hence, the small shift on the Raman peak for modified graphene can be clearly observed.

Fig. 2a–c show the comparison between Raman intensity of the azobenzene molecules on graphene and that of azobenzene molecules on Si with the excitation wavelength of 532 nm. The three azobenzene molecules (DR1P', DR1P and DRSP) were uniformly spin-coated at 3000 rpm for 30 s upon graphene attached on the Si wafer. The Raman intensity of the azobenzene molecules on graphene is several tens of times stronger than the corresponding value on the Si wafer regardless of its dipole moments and dipole orientations. As shown in Fig. 2d–f, the effect of the surface coverage on the Raman enhancement is investigated by changing the concentration (ranging from 5×10^{-10} to 5×10^{-5} M) of the three azobenzene molecules spin-coated on the