Research Article

Covalent surface modification of graphene using photosensitive functional group

Deepshikha

Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, PR China
Email: deep.shikha80@rediffmail.com

Abstract

Graphene (GR) attracts increasing attention due to its unique physical and chemical properties, thus potential applications in optics and electronics. However the gapless band structure greatly limits its wide applications in optoelectronic devices. Surface functionalization proves to be an effective method to tune the properties of graphene. In this study, hybrid GR materials with enhanced properties were achieved through GR surface functionalization by using aryl diazonium salts of photosensitive azobenzene. We found that conformational transition from trans to cis states of azobenzenes induces hole-doping in graphene through charge transfer. Significantly different from the pristine graphene, the graphene-azobenzene hybrids exhibited strong photoisomerization of azobenzene between cis and trans forms under UV and visible light illumination. The large photoresponse obtained from the functionalized GR could be ascribed to the rigid chemical environment with azobenzene moieties chemically bonded onto the GR surface. Such surface-functionalized GR hybrids with unique optical properties position them as promising materials for optoelectronic devices.

Keywords: Graphene, photosensitive azobenzene, covalent modification, Raman spectroscopy.

Address for Correspondence
Deepshikha, Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing, PR China
Email: deep.shikha80@rediffmail.com

Received Date: 05/06/2014 Accepted Date: 10/06/2014

Access this article online

Quick Response Code:

Website:
www.statperson.com

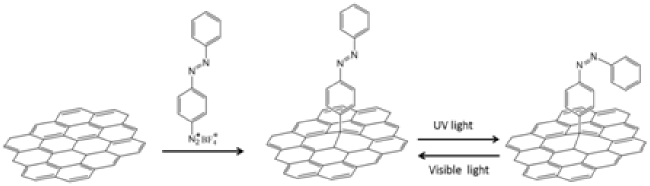
DOI: 10 June 2014

INTRODUCTION

Graphene, a single atomic layer of graphite consisting of sp^2 carbon atoms[1] has been attracting intense research due to its unique physical properties. The purely two dimensional nature in combination with its unusual electronic properties[2-7] including ultrahigh carrier mobility and half-integer quantum Hall effect etc places graphene as a promising material for a wide range of applications in nanoelectronics,[8] microelectronics,[9] macroelectronics,[10] and flexible electronics.[10,11] To realize graphene electronics, manipulating its electronic properties is critical.[12-14] Lots of approaches have been devoted to open bandgap in graphene without losing much of its high carrier mobility. Among them, chemical functionalization, either covalent[15,16] or non-covalent[17-19] is a common approach to control the electronic properties of graphene. Covalent carbon-carbon bond formation reactions can be used to change the hybridization of the graphitic atoms from sp^2 to sp^3 to modify the conjugation length of the delocalized carbon lattice while the backbone framework of graphene is preserved. Bekyarova *et al*[20] found that a bandgap had been opened in the electronic structure of diazonium functionalized epitaxial graphene, as revealed by temperature-dependent resistance measurements. In another study, Farmer *et al* [21] found a *p*-type doping effect using the same diazonium chemistry and they attributed their results to the noncovalent bonding between diazonium salts and graphene through partial charge transfer. In addition to doping effect in graphene, molecular functionalities such as conformational changes under photoexcitation might open up a new field of applications in graphene-based electronics and optoelectronic sensors. Azobenzene has been extensively studied for various applications such as light driven molecular switches,[22-25] reversible optical storage,[26] and micropatterning.[27] Upon UV irradiation, the trans configuration isomerizes to cis and the cis state will reversibly transform to trans under visible light.[22] As the trans configuration is more energetically favourable than the cis configuration,[28] the cis state will thermally be transformed to trans(Figure S1). Previously azobenzene-functionalized carbon nanotubes,[29] graphene oxide,[30] and graphene[31] have been reported, where they showed

How to site this article: Deepshikha. Covalent surface modification of graphene using photosensitive functional group. *International Journal of Recent Trends in Science and Technology* June 2014; 11(2): 218-221 http://www.statperson.com (accessed 11 June 2014).

modulated conductance by UV irradiation. Namphung Peimyoo *et al*. presented the strong doping effect of azobenzene noncovalently adsorbed on graphene layers and showed that the doping is thickness dependent.[32] Herein we report on the chemical functionalization of graphene (GR) covalently by benzenediazonium4-(phenylazo)-tetraflouroborate with an emphasis on doping characteristics and electrochemical properties of modified graphene. Chemical functionalization was carried out at different reaction conditions. Table S1 summarizes the synthesis conditions for the functionalization of both mechanically exfoliated (ME-GR) and chemical vapour deposition (CVD-GR) graphene. Scheme 1 shows the chemical functionalization of graphene with benzenediazonium4-(phenylazo)-tetraflouroborate. The trans–cis isomerization of azobenzene moieties on grapheme irradiated by ultraviolet and visible light was investigated by Raman spectroscopy and electrochemical measurements.



Scheme1: Chemical functionalization of graphene with benzenediazonium,4-(phenylazo)-tetraflouroborate

MATERIAL AND METHODS

CVD-grown monolayer graphene (CVD-GR) and mechanically-exfoliated graphene (ME-GR) flakes were transferred onto highly-doped Si substrates having 300 nm thick SiO_2 layer. The single layer nature of the flakes was confirmed by optical microscopy and Raman spectroscopy. Both CVD-GR and ME-GR were functionalized at room temperature by immersing the whole GR/SiO_2/Si substrates into a 10 mg/ml solution of water soluble azobenzene diazonium salt (Benzenediazonium,4-phenylazo-tetraflouroborate from Sigma Aldrich) for 30 min. Afterwards the diazonium treated substrates were cleaned in water and blown dry with nitrogen. Raman spectra were collected via a Renishaw system 1000 micro-Raman spectrometer with 514.5nm excitation. Atomic force microscopic (AFM) characterizations were performed using a Nanoscope IIIA using the tapping mode. Single layer ME and CVD graphene were located and identified by optical microscope (Olympus DX51, Olympus). XPS measurements were carried out using a Kratos Axis Ultra spectrometer with Al KR monochromated X-ray at low pressures of $5x10^{-9}$ to $1x 10^{-8}$ Torr.

RESULTS AND DISCUSSION

The functionalized graphene was characterized using multiple methods. Figure 1 shows the optical microscopic images and Raman spectra of graphene on silicon substrate before and after treatment with the diazonium salt. Both ME-GR and CVD-GR were monolayer which was confirmed by Raman spectroscopy. For both types of graphene, a symmetric single peak is observed for 2D band centred at 2684 cm^{-1} whose peak intensity is significantly higher than the G peak centred at 1582 cm^{-1}. These results confirm that the graphene investigated in this study is high-quality single layer.[33] For electrodes made of ME-GR no observable D peak was evident at ~1350 cm^{-1}, indicating that the graphene sheet is clean and defect-free. In comparison, a small D peak is observed for electrodes made of CVD-GR [34-36] indicating a less pristine layer. After functionalization a significant D band is observed at 1350 cm^{-1} for both types of graphene. The presence of the D band in the Raman spectra of graphene is attributed to the covalent attachment of functional group.[37-40] In particular we observed a strong D band for CVD-GR after functionalization, which is indicative of high concentration of structural defects in graphene.[41,42] The intensity of the D band was found to increase over time (Figure 2a,2b and Table S2) and in the presence of higher concentrations of the diazonium salt (Figure 2c,2d and Table S3). This result is consistent with the transformation of sp^2 to sp^3 bonding of some of the graphene's carbon atoms.[43-46] Control experiment is also carried out in order to check the physical adsorption of functional group on to the surface of graphene (Figure S2). It is confirmed from this experiment that the functional group is adsorbed physically and not covalently on the surface of graphene. As shown in Figure 1b and 1d G band is upshifted after functionalization with azobenzene, indicating p-type doping of graphene by azobenzene. Similar to G band position, 2D band is also upshifted after functionalization with azobenzene.

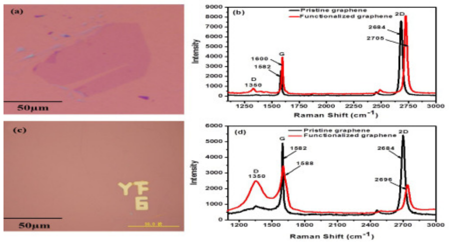


Figure 1: (a) Optical microscope image of ME-graphene (b) Raman spectrum of pristine ME-graphene and azobenzene-functionalized ME-graphene (c) Optical microscope image of CVD- graphene (d) Raman spectrum of pristine CVD-graphene and azobenzene-functionalized CVD-graphene.

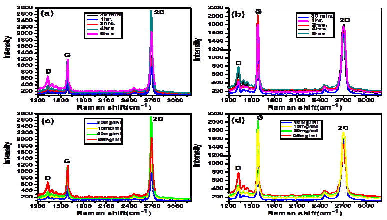


Figure 2: Raman spectra of (a) CVD-GR functionalization for different reaction times (b) ME-GR functionalization for different reaction times (c) CVD-GR functionalization using different diazonium salt concentrations (d) ME-GR functionalization using different diazonium salt concentrations

The Atomic force microscopy is one of the foremost tools for imaging, measuring and manipulating matter at the nanoscale. AFM is used to measure the height profiles of pristine graphene and functionalized graphene. The heights measured by AFM for pristine single-layer ME-GR was 0.5 nm (Figure3a). After chemical reaction with azobenzene diazonium solution, the heights of single-layer graphene increased to 1.75 nm (Figure3b). It shows that azobenzene groups are attached on the surface of graphene.

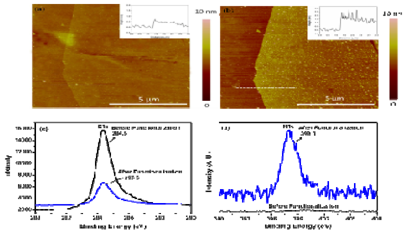


Figure 3: AFM height images of (a) Pristine ME-GR (b) Functionalized ME-GR (c) C1s XPS spectra of graphene before and after functionalization (d) N1s XPS spectra of graphene before and after functionalization.

The covalent bonding of azobenzene with graphene was further assessed with XPS and the key results are summarized in Figure 3c and 3d. The C1s signal observed at ca. 284.5 eV broadened and decreased in intensity after exposure to diazonium solution. The signal observed at ca. 285.5 eV was attributed to the C–N bond of the azobenzene group while the decrease in the intensity of the peak at 284.5 eV was attributed to the decreased number of sp^2 carbons in the lattice due to the change in hybridization.[47-49] The signals observed at ca. 399.3 (Figure 3d) was assigned to the azo (–N=N–) group. No significant signals from B or F were detected. The AFM and XPS studies of pristine and functionalized graphene directly demonstrated that the azobenzene groups were attached to one side of the single-layer graphene basal plane.To induce photoisomerization of azobenzene between trans and cis forms, 500 µW/cm^2 hand-held UV lamp with 365 nm wavelength and 150 W tungsten lamp were used as UV and white light sources, respectively. As shown in Figure 4a, G band is upshifted by 8.0 cm^{-1} after functionalization with azobenzene diazonium salt, indicating that graphene is doped by azobenzene. UV illumination of azobenzene-graphene induced a clear downshift (6.0 cm^{-1}) in G band (Figure4a). This shift in G band was reversed upon white light illumination (Figure4b). UV illumination induces isomerization of azobenzene from trans to cis form, leading to increase in the dipole moment.[50,51] Increase in dipole moment can alter the extent of doping and change the charge carrier concentration in graphene which is reflected in the shifts of G band. Subsequent illumination with white light isomerizes the cis back to the trans form. Similar trends were also observed in the position of 2D band (Figure4c and 4d). Figure 5 summarizes the shifts in G band and 2D band for azobenzene-graphene hybrid after UV and white light illumination.

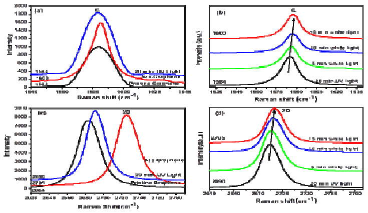


Figure 4: Raman spectra of (a) pristine graphene, azobenzene-graphene and UV illuminated Azo-graphene showing the changes in the G band position (b) UV illuminated azobenzene-graphene samples showing changes in G band upon white light illumination (c) pristine graphene, azobenzene-graphene and UV illuminated azobenzene-graphene showing the changes in the 2D band position and (d) UV illuminated azobenzene-graphene samples showing changes in 2D band upon white light illumination.

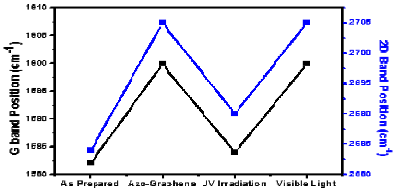


Figure 5: Plots showing the changes in G band and 2D band position for azobenzene-graphene upon illumination with UV and white light.

CONCLUSION

In summary the chemical functionalization of graphene (GR) covalently by benzenediazonium4-(phenylazo)-tetraflouroborate with an emphasis on doping characteristics has been demonstrated. Under illumination with UV and white lights, the azobenzene undergoes reversible photoisomerization which leads to reversible doping modulation as evidenced by the shift of the G and 2D peaks in Raman spectra. However, the formation of covalent carbon–carbon bonds involving the basal plane carbon atoms offers key advantages, such as greater stability of the hybrid material, controllability over the degree of functionalization and reproducibility. It is a facile route for band gap engineering of graphene and patterning of electronic circuits on graphene.

Experimental Section

CVD-grown monolayer graphene (CVD-GR) and mechanically-exfoliated graphene (ME-GR) flakes were transferred onto highly-doped Si substrates having 300 nm thick SiO_2 layer. The single layer nature of the flakes was confirmed by optical microscopy and Raman spectroscopy. Both CVD-GR and ME-GR were functionalized at room temperature by immersing the whole GR/SiO_2/Si substrates into a 10 mg/ml solution of water soluble azobenzene diazonium salt (Benzenediazonium,4-phenylazo-tetraflouroborate from Sigma Aldrich) for 30 min. Afterwards the diazonium treated substrates were cleaned in water and blown dry with nitrogen.

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Source of Support: None Declared
Conflict of Interest: None Declared