

Chemical Modification of Epitaxial Graphene: Spontaneous Grafting of Aryl Groups

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1. Chemical Modification of Epitaxial Graphene

The epitaxial graphene used in this study was grown on single crystal SiC by vacuum graphitization. [(a) Berger, C.; Song, Z. M.; Li, X. B.; Wu, X. S.; Brown, N.; Naud, C.; Mayo, D.; Li, T. B.; Hass, J.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A., Electronic Confinement and Coherence in Patterned Epitaxial Graphene. *Science* **2006**, 312, 1191-1196.; (b) de Heer, W. A.; Berger, C.; Wu, X. S.; First, P. N.; Conrad, E. H.; Li, X. B.; Li, T. B.; Sprinkle, M.; Hass, J.; Sadowski, M. L.; Potemski, M.; Martinez, G., Epitaxial Graphene. *Solid State Commun.* **2007**, 143, 92-100.]

This technique produces a material with an electronic structure indistinguishable from an isolated single graphene sheet in the vicinity of the Dirac point. Theory and experiment have shown that the planes in epitaxially-grown multilayer graphene are rotationally disordered and thus they are electronically decoupled and this preserves the

electronic properties of an isolated graphene sheet.[Hass, J.; Varchon, F.; Millan-Otoya, J. E.; Sprinkle, M.; Sharma, N.; De Heer, W. A.; Berger, C.; First, P. N.; Magaud, L.; Conrad, E. H., Why Multilayer Graphene on 4H-SiC(000(1)over-bar) Behaves Like a Single Sheet of Graphene. *Phys. Rev. Lett.* **2008**, 100, 125504-4.]

The epitaxial graphene (EG) was grown on the C-face of a SiC wafer (Cree Inc, High purity R grade 4H SiC) by hydrogen etching to produce atomically flat surfaces and vacuum graphitization at $\sim 1450^{\circ}\text{C}$ (UHV; base pressure 1×10^{-10} Torr). [(a) Berger, C.; Song, Z.; Li, T.; Li, X.; Ogbazghi, A. Y.; Feng, R.; Dai, Z.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A., Ultrathin Epitaxial Graphite: 2d Electron Gas Properties and a Route Toward Graphene-Based Nanoelectronics. *J. Phys. Chem. B* **2004**, 108, 19912-19916.; (b) Berger, C.; Song, Z. M.; Li, X. B.; Wu, X. S.; Brown, N.; Naud, C.; Mayo, D.; Li, T. B.; Hass, J.; Marchenkov, A. N.; Conrad, E. H.; First, P. N.; de Heer, W. A., Electronic Confinement and Coherence in Patterned Epitaxial Graphene. *Science* **2006**, 312, 1191-1196.]

Ellipsometry measurements show that the sample consists of 9 graphene layers. AFM analysis indicated that the RMS roughness of the graphene is less than 4 Å.

For the functionalization, the EG substrate was immersed in a solution of 10 mM 4-nitrophenyl diazonium (NPD) tetrafluoroborate and 0.1 M tetrabutylammonium hexafluorophosphate ($[\text{Bu}_4\text{N}]\text{PF}_6$) in degassed acetonitrile (ACN) in a glove box in the absence of light for 20 h, after which it was removed and washed with ACN and acetone.

2. Cyclic Voltammetry

The electrochemical experiments were carried out with a computer-controlled CH Instruments Electrochemical Analyzer. The pristine EG or nitrophenyl (NP) - functionalized EG served as the working electrode, Pt-wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The electrochemical cell was purged with argon for 2 hours before measurements, which were conducted at a scan rate of 100 mV/s. To estimate the nitrophenyl surface coverage, cyclic voltammograms were

recorded in an 0.1 M solution of tetrabutylammonium tetrafluoroborate in acetonitrile (ACN). The surface coverage (Γ) was calculated from the formula: $\Gamma = Q/nFA$, where Q is the area of the reduction peak, n is the number of electrons transferred in the reduction process ($n=2$), F is the Faraday constant ($9.648 \times 10^4 \text{ C.mol}^{-1}$), and A is the area of the substrate exposed to the solution. From these measurements the concentration of the nitrophenyl groups on the graphene surface was found to be $\sim 1 \times 10^{15}$ molecules/cm², which is in agreement with previous studies of nitrophenyl-grafted carbon surfaces.

[(a) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J. M., Covalent Modification of Carbon Surfaces by Aryl Radicals Generated from the Electrochemical Reduction of Diazonium Salts. *J. Am. Chem. Soc.* **1997**, *119*, 201-207.; (b) Saby, C.; Ortiz, B.; Champagne, G. Y.; Belanger, D., Electrochemical Modification of Glassy Carbon Electrode Using Aromatic Diazonium Salts .1. Blocking Effect of 4-Nitrophenyl and 4-Carboxyphenyl Groups. *Langmuir* **1997**, *13*, 6805-6813.; (c) Zhong, Y. L.; Loh, K. P.; Midya, A.; Chen, Z. K., Suzuki Coupling of Aryl Organics on Diamond. *Chem. Mater.* **2008**, *20*, 3137-3144.]

3. X-ray Photoelectron Spectroscopy

The XPS measurements were performed at the University of California – Santa Barbara with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) using Al K α monochromated radiation at 1486 eV at base pressure between 5.10^{-9} and 1.10^{-8} Torr. The survey spectra were recorded using 270 watts of X-ray power, 80 pass energy, 0.5 eV step size. The high-resolution scans were run using power of 300 watts, 20 pass energy and step size of 0.05 eV. A low-energy electron flood from a filament was used for charge neutralization. The spectra are shown without energy-scale correction and the peak fits consist of Lorentzian and Gaussian distributions.

Figure 1S illustrates the XPS spectra of pristine and functionalized epitaxial graphene. The spectra were recorded on the epitaxial graphene (EG) layer grown on the C-face of the SiC substrate. The survey scan of pristine EG (Figure 1S-a) reveals a strong C-peak accompanied with Si2s and Si2p peaks arising from the SiC substrate and a weak O1s peak presumably due to oxygen atoms bound to carbon at the graphene edges.

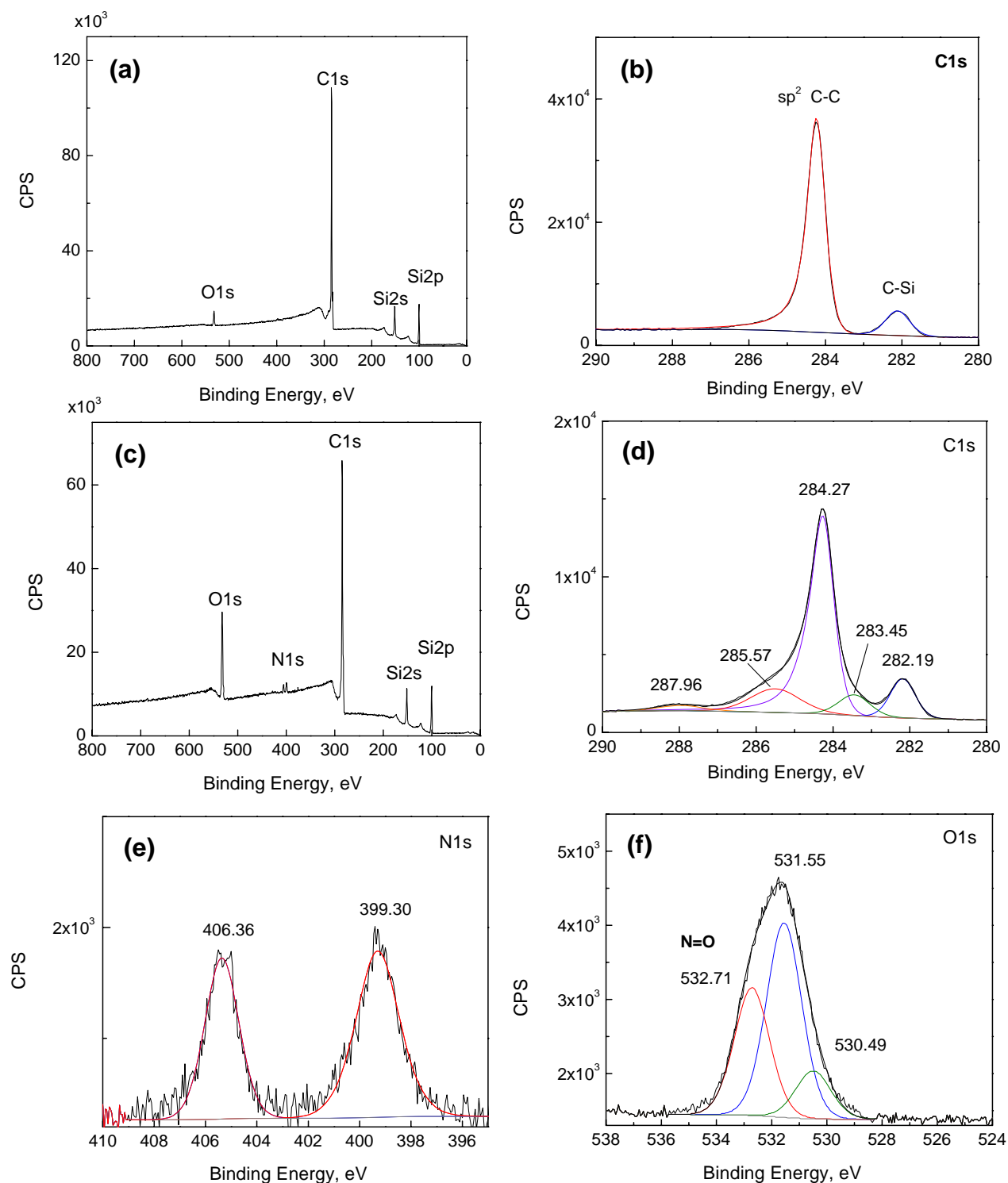


Figure 1S. XPS spectra of epitaxial graphene grown on the C-face of a SiC substrate. Before functionalization: (a) low resolution survey, (b) C1s core level spectra. After functionalization with nitrophenyl: (c) survey, and core level spectra of (d) C1s, (e) N1s and (f) O1s.

The C1s core level signal for the pristine graphene (Figure 1S-b) exhibits a sharp peak at a binding energy of 284.2 eV as expected for sp^2 hybridized C atoms.

The XPS survey spectrum of the nitrophenyl (NP) functionalized EG, shown in Figure S1-c, reveals N1s peaks. The high resolution N1s and C1s spectra are discussed in the manuscript. The C1s peak at binding energy of 287.96 eV in C1s (Figure 1S-d) and the O1s peak at 531.55 eV (Figure 1S-f) are associated with C=O functionality; the origin of these functional groups is unclear.

The NO_2 -groups in the functionalized EG were electrochemically reduced in aqueous solution ($H_2O : EtOH = 90 : 10$, and 0.1 M KCl) at a scan rate of 100 mV/s. The substrate was rinsed with ethanol and dried. The recorded XPS N1s spectra showed a single peak centered at 399.30 eV (Figure S2), assigned to the amino group nitrogen.

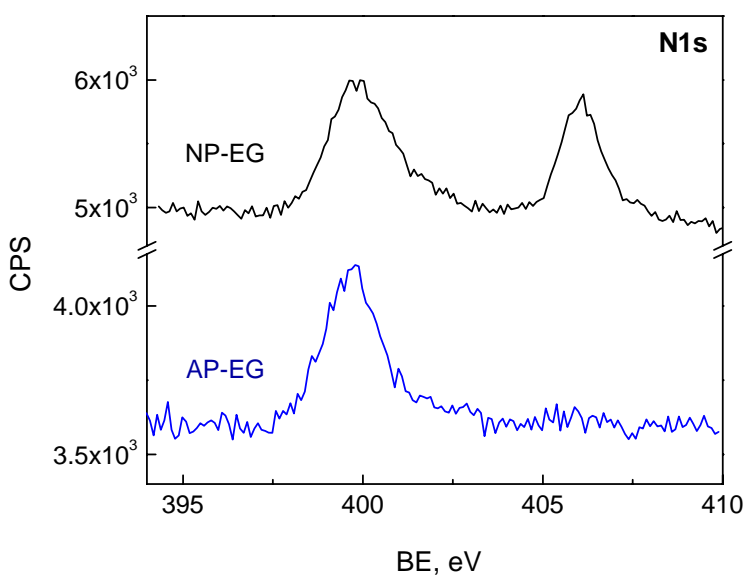


Figure 2S. XPS N1s spectra of nitrophenyl-functionalized EG (NP-EG, black line) and aminophenyl-functionalized EG (AP-EG, blue line), prepared by electrochemical reduction of NP-EG.

4. Effect of Chemical Species on Resistance

Theoretical and experimental studies show that the transport properties of graphene are sensitive to charged impurities and adsorbed chemical species. [(a) Ando, T., Screening Effect and Impurity Scattering in Monolayer Graphene. *J. Phys. Soc. Jpn* **2006**, *75*, 074716-4.; (b) Chen, Z. H.; Lin, Y. M.; Rooks, M. J.; Avouris, P., Graphene Nano-Ribbon Electronics. *Physica E* **2007**, *40*, 228-232.; (c) Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S., Detection of Individual Gas Molecules Adsorbed on Graphene. *Nat. Mater.* **2007**, *6*, 652-655.; (d) Lin, Y. M.; Avouris, P., Strong Suppression of Electrical Noise in Bilayer Graphene Nanodevices. *Nano Lett.* **2008**, *8*, 2119-2125.; (e) Chen, J. H.; Jang, C.; Adam, S.; Fuhrer, M. S.; Williams, E. D.; Ishigami, M., Charged-Impurity Scattering in Graphene. *Nat. Phys.* **2008**, *4*, 377-381.]

To examine the effect of the chemical species used in the chemical treatment on the graphene sheet resistance, we measured the resistance of an as-grown graphene sample before and after treatment with acetonitrile and acetone and compared these values with the resistance of nitrophenyl (NP)-functionalized graphene. For these measurements four in-line gold contacts (5 nm Pd, 200 nm Au) were deposited by e-beam evaporation on a graphene substrate. The substrate was subjected to vacuum ($<10^{-6}$ Torr) at room temperature for several hours before measurement. The four-point resistance at room temperature of the as-grown EG increased by less than 2% after exposure to liquid acetone and acetonitrile.