Article type: invited

Atom-Scale Covalent Electrochemical Modification of Single-Layer Graphene on SiC Substrates by Diaryliodonium Salts

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Keywords: epitaxial graphene, electrochemical modification, functionalization, iodonium salts, STM

Abstract

Owing to its high conductivity, graphene holds promise as an electrode for energy devices such as batteries and photovoltaics. However, to this end, the work function and doping levels in graphene need to be precisely tuned. One promising route for modifying graphene's electronic properties is via controlled covalent electrochemical grafting of molecules. We show that by employing diaryliodonium salts instead of the commonly used diazonium salts, spontaneous functionalization is avoided. This allows for precise tuning of the grafting density. By employing *bis*(4-nitrophenyl)iodonium(III) tetrafluoroborate (DNP) salt calibration curves, the surface functionalization density (coverage) of glassy carbon was controlled using cyclic voltammetry in varying salt concentrations. These electro-grafting conditions and calibration curves translated directly over to modifying single layer epitaxial graphene substrates (grown on insulating 6H-SiC (0001)). In addition to quantifying the functionalization densities using electrochemical methods, samples with low grafting densities were characterized by low-temperature scanning tunneling microscopy (LT-STM). We show that the use of buffer-layer free graphene substrates is required for clear observation of the nitrophenyl modifications. Atomically-resolved STM images of single site modifications were obtained, showing no preferential grafting at defect sites or SiC step edges as supposed previously in the literature. Most of the grafts exhibit three-fold symmetry, but occasional extended modifications (larger than 4 nm) were observed as well.

1. Introduction

Graphene has shown impressive physical and chemical properties, including high electron mobility ($2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),[1] broadband optical transparency (98%),[2] excellent thermal conductivity ($3000 \text{ W m}^{-1} \text{ K}^{-1}$), and high elastic modulus (1 TPa).[3] Because of this versatility, graphene is promising for a wide array of applications, including supercapacitors, batteries, transistors, photonics, sensors, and flexible electronics.[4],[5],[6] Further tuning of the chemical and electronic properties of graphene via chemical functionalization is desired to enhance its usefulness in specific applications. For example, electronic structure modifications are required for transistors and photonics, and chemical modifications are desired for interfaces and processing.[7] A large number of functionalization strategies have been investigated that include non-covalent functionalization through π -stacking, condensation reactions with graphene oxide, cycloaddition reactions, and covalent functionalization via free radical grafting. Recent reviews have been dedicated to compiling these varied techniques.[6],[8],[9],[10] Covalent modification offers a robust method to locally modify the electronic properties in graphene.[11],[12] However the attachment of molecules induces local disruptions in the graphene structure and locally alters the electronic properties of the graphene. Therefore a precise control of the grafting density must be achieved. For instance, in order to use graphene as transparent conductor in photovoltaics one needs to locally modify the work function while preserving conductivity and transparency.

Diaryliodonium salts are an emerging class of compounds for the modification of graphene.[13],[14] Unlike the commonly employed diazonium salts, spontaneous functionalization is avoided by the more negative reduction potential associated with the diaryliodonium salts. Electron transfer to the iodonium salt leads to the heteroleptic cleavage of the carbon–iodine bond leaving an iodoarene and an aryl radical capable of grafting to the working electrode surface. Diaryliodonium salts have been studied in their reactions with

several carbon substrates (highly ordered pyrolytic graphite (HOPG), glassy carbon (GC), and carbon powder), as well as electrochemically driven reactions at platinum surfaces.[15],[16],[17],[18] Studies on graphene, however, are very limited. In the present contribution, we reveal the precise tunability in graphene functionalization densities using cyclic voltammetric activation of a symmetric iodonium salt, *bis*(4-nitrophenyl)iodonium(III) tetrafluoroborate (**DNP**). In addition we show that choosing a model single layer graphene allows us to address controversial questions related to the electron transfer (ET) kinetics behavior.

2. Experimental Section

All solvents were dried using an Innovative Technology Pure Solv solvent purifier with double purifying column. 3-Chloroperbenzoic acid (*m*-CPBA) >77% (Sigma Aldrich), 4-nitrobenzeneboronic acid (Alfa Aesar) and 1-iodo-4-nitrobenzene (Alfa Aesar) were used as received. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. Preparation of *bis*(4-nitrophenyl)iodonium tetrafluoroborate (**DNP**) was achieved using methods outlined by Olofsson *et al.*[19] In a 5 mL round bottom flask, 1-iodo-4-nitrobenzene (0.068 g, 0.273 mmol) is dissolved in 1 mL of CH₂Cl₂ followed by the addition of *m*-CPBA (> 77%, 0.065 g, 0.290 mmol). BF₃·Et₂O (81 μL, 0.656 mmol) is added to the reaction mixture via syringe. The solution is stirred vigorously for 1 h and then cooled to 0°C in an ice bath. 4-nitrophenylboronic acid (0.050 g, 0.300 mmol) is added to the reaction mixture and the resulting mixture is allowed to warm to r. t. over the course of 0.5 h. The reaction mixture is then subjected directly to a silica column. Impurities are eluted using CH₂Cl₂ and the product is collected using a CH₂Cl₂:CH₃OH (20:1) solution. The solution containing product is concentrated under a N₂ stream and the product is crashed out using Et₂O. Product is washed with Et₂O (3x) and dried in vacuum to yield product as off white solid (0.062 g, 50%). ¹H NMR (400 MHz, DMSO-d₆): δ 8.49 (d, *J* = 9.0 Hz, 4H), 8.28 (d, *J* =

9.0 Hz, 4H). ^{19}F NMR (376 MHz, DMSO- d_6): δ -148.28 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 149.6, 136.8, 126.5, 123.0. HRMS (ESI): m/z calc'd for $\text{C}_{12}\text{H}_8\text{IN}_2\text{O}_4[\text{M-BF}_4^-]^\dagger$ 370.95230; found 370.95180.

The product was stored under nitrogen at 0°C. NMR spectra were recorded with a Varian DirectDrive 400 (^1H 400 MHz, $^{13}\text{C}\{^1\text{H}\}$ 100 MHz, ^{19}F 376 MHz) and were referenced to residual solvent peaks (^1H and $^{13}\text{C}\{^1\text{H}\}$) and CFCl_3 (^{19}F). Electrospray ionization was collected on an Agilent 6530 quadrupole time of flight mass spectrometer.

Electrochemical studies were performed under a nitrogen atmosphere in a dry-box with previously dried solvents using a GPES system from Eco. Chemie. B. V. The supporting electrolyte, $[(n\text{-Bu})_4\text{N}][\text{PF}_6]$ (TBAPF), was recrystallized three times from hot ethanol, then dried for three days at 100 °C under active vacuum. All of the electrochemical experiments were carried out in a three-electrode cell with a Ag/AgNO_3 reference electrode (silver wire dipped in a 0.01 M silver nitrate solution in a 0.1 M Bu_4NPF_6 solution in CH_3CN), a glassy carbon button working electrode (3.0 mm diameter), and a Pt wire coil counter electrode unless otherwise noted. The glassy carbon buttons were polished successively using 0.3 μm and 0.05 μm Al_2O_3 and rinsed with distilled water and acetone. Blank scans were performed to confirm a clean surface prior to grafting.

Epitaxial graphene on SiC was prepared using previously reported methods.[20]. The 6H-SiC(0001) substrates were first etched and annealed in 1atm of 45% H_2 : Ar at 1450°C. This procedure induces the formation of atomically flat surfaces by removing the defects produced by crystal polishing. The graphene was subsequently grown at 1550°C in ultrahigh purity Ar atmosphere at atmospheric pressure. Modification was accomplished in a similar fashion as described for the glassy carbon electrodes except that the graphene sample was used as the working electrode. Contact to the graphene sheet on insulating SiC was accomplished by pinching a gold sheet to the graphene with an alligator clip. The sample was dipped into the solution of **DNP** with great care being taken to avoid submerging the contact in the solution.

Grafting was accomplished by two successive sweeps from 0 to -0.85 V vs Ag/Ag⁺. The sample was then thoroughly rinsed with acetonitrile before being transferred to a blank solution. Surface functionalization was measured using two successive sweeps from 0 to -2.1 V vs Ag/Ag⁺. The reduction peak of the nitro moiety on the second scan is integrated to determine the surface coverage.

The STM images were acquired using an Omicron LT-STM system operated at 77K using PtIr probes.

3. Results and discussion

3.1. Surface modification of glassy carbon

Before electrochemically functionalizing epitaxial graphene, preliminary grafting and mechanistic studies with **DNP** were performed on glassy carbon (GC) electrodes in order to better understand and control the modification of graphene samples. Nitro functionalities are placed at the *para*-position to the iodine in order to maximize electronic effects to the surface of graphene and to provide a redox handle to quantify the degree of surface functionalization by electrochemical means. A schematic representation of the grafting mechanism is presented in Fig. 1a. Electron injection from the GC electrode induces the reduction and dissociation of the **DNP** salt. Subsequently, the resulting nitrophenyl radical binds covalently to the GC electrode, while the iodide compound stays in the electrolyte solution. *For simplicity we imply that the electrogenerated Nitro-aryl radical will attach with the nitro-group para to the carbon surface. However, it cannot be ruled out that the nitro-aryl group can attach to the graphene lattice in other ring positions (orientations).*

Fig. 1. (a) Schematic showing the covalent grafting of **DNP** to a glassy carbon (GC) surface. (b) Sequential cyclic voltammograms of the reduction of a 1.0 mM solution of **DNP** in CH₃CN containing 0.1 M TBAPF₆ using a GC working electrode. The scan rate is 50 mV s⁻¹.

Fig. 1b shows a representative sequential voltammetric response for the reduction of **DNP** when using a GC working electrode in a 1.0 mM solution of DNP in CH₃CN containing 0.1 M TBAPF₆. The scan rate is 50 mV s⁻¹. The first scan shows an irreversible wave at $E_{p,c} = -0.72$ V vs Ag/Ag⁺ quasi-reference corresponding to the reduction and concomitant decomposition of the **DNP** salt into 1-iodo-4-nitrobenzene and a nitrophenyl radical (Fig. 1a). Subsequent attenuation of the faradaic signal in the following cycles is attributed to the passivation of the GC electrode surface by the covalently grafted nitrophenyl molecules.[13],[15],[16],[17],[18] Further confirmation of this passivation layer on the surface of the GC electrode can be seen in Fig. 2, where a marked decrease in the intensity of the ferrocene redox couple shows the presence of an insulating blocking layer on the electrode surface.[15], [21],[22] A significant ferrocene voltammetric signal is still observed on the nitrobenzene modified surface (red curve in Fig. 2). As discussed below (Figs. 4c, d) starting at 1mM DNP salt concentration the grafting results in the formation of multilayers. It is expected however that the layers have pinholes therefore explaining the presence of the ferrocene volammetric signal.

Fig. 2. Electrochemical response of a pristine GC electrode (black curve) and a nitrobenzene surface modified GC electrode (red curve) to a ferrocene solution at 100 mV s^{-1} . The surface functionalized GC electrode was modified by 10 voltammetric cycles as shown in Figure 1b.

Quantitative determination of the surface concentration of nitrophenyl grafts (after 2 voltammetry cycles) was determined electrochemically through the integration of the peak associated with the one electron reduction of the $-\text{NO}_2$ moieties (Fig. 3a).[16],[21],[22],[23], [24] As shown in Fig. 3b, this highly reversible process is evidenced by a peak separation $\Delta E_p = 59 \text{ mV}$ and an anodic peak current $i_{p,a} = -15 \text{ } \mu\text{A}$ at -1.50 V , which allows for the determination of charge passed (Q) during the reduction event. The charge can be directly related to the surface density (Γ) using equation (1):[13]

$$\Gamma = \frac{QN_A}{nFA} \quad (1)$$

where N_A is Avogadro's constant, n is the number of electrons associated with the redox event ($n = 1$ for this case), F is Faraday's constant, and A is the electroactive surface area of the electrode in cm^2 . The electroactive surface area (A) was determined experimentally from the $i_{p,a}$ of ferrocene, as shown in Figure 2 for example, using equation (2):[25]

$$i_{p,a} = 0.4463(nF)^{3/2}(RTDv)^{1/2}AC \quad (2)$$

where R is $8.314 \text{ C V mol}^{-1} \text{ K}^{-1}$, T is the temperature in Kelvin, ν is the scan rate in V s^{-1} , C is the concentration in mol cm^3 , D is the diffusion coefficient and was taken as $2.24 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and $n = 1$ for ferrocene. Coulometric integration revealed a surface coverage of $(3.0 \pm 0.6) \times 10^{14} \text{ molecules cm}^{-2}$ at saturation.[25]

Fig. 3. (a) Schematic of the reversible reduction of the grafted *para*-nitrophenyl moiety. (b) Representative background corrected cyclic voltammogram showing the reversible one-electron redox couple of the grafted *para*-nitrophenyl groups on the electrode surface. The GC electrode here was modified by 10 scans from 0 to -0.85 V with 1.0 mM DNP.

Reproducible control over the degree of functionalization (surface coverage) can be achieved in principle by using chronoamperometry (CA) by varying the time at a constant reduction potential for a given solution concentration,[13] or by cyclic voltammetry (CV) by varying the salt concentration and cycled potential (Fig. 4a). Using the previously described method for quantifying the surface functionalization density by the electrochemical reduction of NO₂ (Fig. 4b), calibration curves of the surface functionalization were obtained (Fig. 4d). A calibration curve was also obtained by monitoring the peak current from the reduction of the iodonium salt (Fig. 4c). Both calibration curves scale linearly with solution concentration

up to approximately 0.8 mM **DNP**. In a similar study by Vase *et al.* *bis*(3-nitrophenyl)iodonium bisulfate showed the cathodic peak current $i_{p,c}$ that similarly varied linearly with concentration between 0.2 - 1.0 mM.[16]

Fig. 4. (a) First CV scan for the grafting of the **DNP** on GC electrodes performed at 50 mV s⁻¹. (b) The corresponding voltammetric response of the grafted *para*-nitrophenyl moieties. Calibration curves obtained from (c) $i_{p,c}$ of **DNP** electrolysis, and (d) grafting density Γ .

While the two calibration curves shown in Figs. 4c, d are in excellent agreement to each other, generation of the calibration curve through monitoring of the $i_{p,c}$ revealed an interesting trend: the shift in $E_{p,c}$ to more positive potentials (-795 mV to -680 mV) with iodonium salt concentrations exceeding ~1.0 mM is accompanied with a concurrent increase in the prominence of a prewave that forms approximately +200 mV before the $E_{p,c}$. The origin of the prewave during the reduction of iodonium salts has been unclear in the literature. In the closely related family of diazonium salts, it has been speculated that the origin of a prewave is due to differences in the potential of zero charge of the electrode surface.[16] However, the concentration dependence of the prewave, as well as the observed anodic shift in $E_{p,c}$ indicates the possibility of the formation of a preadsorbed layer of unreduced *bis*(4-

nitrophenyl)iodonium(III) tetrafluoroborate. To test this hypothesis, solutions of **DNP** were prepared with varied concentrations within the range of linear control, and were subjected to two reductive scans from 0 to -0.450 V versus Ag/Ag⁺ (approximate E_{p,c} for the prewave event). The resulting surface coverage was monitored. Results showed an extremely low degree of surface functionalization with weak, distorted signals and no observable linear trend. The results are in agreement with the hypothesis of a physisorbed layer of **DNP** that is electronically affected by the interaction with the electrode. This interaction subsequently causes the anodic shift that is observed in the CV at high concentrations. As reported previously,[16] starting at 1 mM **DNP** concentration (blue line) grafting results in the formation of multilayers where additional grafts occur at the activated sites in the covalently attached nitrophenyls.

3. 2. Graphene electrochemistry

Epitaxial graphene samples on insulating H-intercalated SiC were functionalized using the procedure as described above for the GC electrodes. The electro-grafting conditions and calibration curves for **DNP** on GC translated directly over to single layer epitaxial graphene substrates with excellent agreement. [14] Given that the GC electrode is highly defective compared to the graphene these data indicate that the graphene basal plane is highly reactive (see discussion below).

Fig. 5. (a) First and second CV sweeps showing the grafting of 0.15 mM **DNP** at 50 mV s⁻¹ on epitaxially grown graphene on insulating SiC. (b) Voltammetric response of nitrophenyl surface modified graphene on insulating H-intercalated SiC (100 mV s⁻¹). The surface coverage was determined to be 4.0×10^{13} molecules cm⁻² using the geometric area of the graphene electrode.

For Low Temperature Scanning Tunneling Microscopy (LT-STM) studies, a low concentration of surface functionalities was desired to obtain a clear view of the graphene surface, and to evaluate the effects of surface functionalization on the graphene substrate. A concentration of 0.15 mM **DNP** was targeted to achieve an anticipated surface coverage of $(3.7 \pm 0.6) \times 10^{13}$ molecules cm⁻². Fig. 5a shows the first and second sweeps of CV-initiated functionalization of epitaxial graphene on insulating SiC from a 0.15 mM **DNP** solution at 50 mV s⁻¹. As evidenced by the reduction wave in the second scan, graphene is not fully functionalized at these dilute **DNP** concentrations. Fig. 5b plots the voltammetric response of surface modified graphene on insulating SiC at a scan rate of 100 mV s⁻¹. On both insulating and conductive substrates graphene grafting show excellent agreement with the results obtained from the GC calibration studies (0.14 mM curves in Figs. 4a,b). The surface coverage of nitrophenyl on graphene under these functionalization conditions was determined to be 4×10^{13} molecules cm⁻².

3.3. Characterization of the covalently modified graphene using LT-STM

To understand the impact of nitrophenyl functionalization on graphene, the pristine epitaxially grown graphene on 6H-SiC(0001) were characterized first using STM. As reported previously, graphene film growth on SiC is mediated by the formation of the so-called buffer layer (BL), or otherwise known as zero-layer graphene.[26],[27],[28] This buffer layer is a graphene-like layer composed of C-atoms partially linked to the underlying SiC substrate rendering the film insulating and locally charged.[26],[29] This charge in the BL is responsible for the n-type doping in epitaxial graphene grown on SiC.[30],[31] Although the graphene layer is structurally nearly perfect, it is electronically coupled with the underlying BL.[28],[32],[33] The spatial variation in the electronic properties of graphene due to the presence of the defective BL has been shown by employing scanning tunneling spectroscopy by us[14] and others.[32] Because of this electronic coupling, isolating the effects of covalent graphene modifications from those induced by changes in the BL is not possible in these “graphene on buffer layer” samples. Removal of the buffer layer by H-intercalation[34],[35] produces quasi-free standing graphene films. Fig. 6a shows a $5 \times 5 \text{ nm}^2$ STM image of a single graphene layer that was epitaxially grown on insulating 6H-SiC(0001). As predicted by theory[36] and measured experimentally[27] the electronic structure of single layer graphene on the H-intercalated SiC surface is minimally perturbed near the Dirac point. No local variation in the density of states was observed by dI/dV spectroscopy (Fig. 6b). The BL-free substrates are ideal for the studying the electronic changes induced in graphene by covalent modification.

Fig. 6. (a) STM image of graphene on H-intercalated insulating 6H-SiC(0001) at $V_{\text{bias}} = 30$ mV, $I_{\text{setpoint}} = 40$ pA and (b) the corresponding dI/dV spectra. No local variation in the density of states is observed.

As previously mentioned, the calibration curves (Figs. 4c, d) allowed for a controlled low-density modification of the graphene samples. Fig. 7a shows a $50 \times 50 \text{ nm}^2$ large area STM image of a graphene sample modified using CV in 0.15 mM **DNP**. The image shows the presence of ~ 1 nm diameter bright globular structures, as well as extended structures (larger than 4 nm) that likely consist of aggregated molecular grafts (Fig. 7b). The nitrophenyl modifications appear as bright spots (high electronic density of states) since the $-\text{NO}_2$ group is electron withdrawing. Grafting seems to occur randomly on the graphene surface, with no preference for attachment at SiC step edges (see Fig. 7a) or defect sites (see Fig. 7c). These observations are in contrast to suggestions in the literature, which assume that electron transfer (ET) kinetics are faster at graphene step edges and defect sites.[37],[38] Rather, the results here support recent reports that defect free basal surfaces of sp^2 carbon materials exhibit fast ET kinetics,[39] and therefore are expected to exhibit increased reactivity. The most common defects we observe in the graphene samples grown on H-intercalated SiC are single vacancies.[40],[41] By analyzing different areas of a pristine sample, an average single

vacancy density (estimated over more than 30 STM images) of $(2 \pm 0.5) \times 10^{12}$ defects. cm^{-2} was measured.

Fig. 7. (a) Large area STM image of **DNP** modified graphene at $V_{\text{bias}} = 30$ mV, $I_{\text{setpoint}} = 40$ pA. The ~ 1 nm globular structures represent covalent nitrophenyl modifications. No preferential grafting at the SiC step edge is observed. Occasional extended area modifications can be observed (b). (c) STM image at $V_{\text{bias}} = 30$ mV, $I_{\text{setpoint}} = 40$ pA showing the presence of several single point defects (vacancies, white circles) along with a modification. (d) High resolution 7×7 nm² STM image at $V_{\text{bias}} = -450$ mV reveal that some modifications exhibit a threefold symmetry indicative of structural or electronic perturbations that are oriented with the graphene lattice.

Since the grafting density varies linearly with the salt concentration, it is clear that the grafting does not selectively target these single vacancies. In addition, in Fig. 7c, one can clearly see four distinct vacancies but only one modification (bright spot). Given that the grafting density is equal to the defect density in the sample shown in Fig. 7, if vacancy defects were preferentially active, then they would not be visible in Fig. 7c. These observations are indicative that the grafting does not occur preferentially at the defect (vacancy) sites. In addition, electron transfer kinetics performed on graphene samples with low (graphene on BL SiC) and high (graphene on BL-free SiC) density of single point defects showed that the grafting densities are similar which implies that there is no preferential attachment at the defect sites and the electron kinetics at the basal plane are fast. [14]

Fig. 7d shows another high-resolution image of the most commonly observed grafts. Many images taken in different regions of the sample showed that one can find at least one such sub-nanometer size modification in a $7 \times 7 \text{ nm}^2$ area from where an effective grafting density of 2×10^{12} modifications per cm^2 can be estimated. In contrast to the modification in Fig. 7c, this modification appears as a bright spot with threefold symmetry. Ongoing computational work is aimed at elucidating the structure of these particular modifications.

4. Conclusion

We demonstrated controlled modification of epitaxial graphene using diaryliodonium salts. The grafting density calculated from the electrochemistry data can be reproducibly tuned from 4×10^{13} molecules cm^{-2} up to 3×10^{14} molecules cm^{-2} . Using buffer layer-free graphene substrates, we obtained atomically resolved STM images of single site functionalization on graphene. The nitrophenyl grafting from iodonium compounds was found to occur preferentially in the defect free areas of graphene films suggesting that the basal plane of the graphene is highly reactive. Most of the grafts present three-fold symmetry, but both elongated as well as extended (larger than 4 nm) structures were observed. Reproducible

controlled modifications of graphene are expected to have a major impact in tuning the doping level and work function in graphene, enabling its deployment in photovoltaic and battery applications.

Acknowledgements

The authors thank T. Ohta, G. Copeland, and L. Brunke for providing the graphene/(BL)/SiC substrates. This work was supported by an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences on “Understanding Charge Separation and Transfer at Interfaces in Energy Materials” (EFRC:CST, Award Number DE-SC0001091). C.K.C. also acknowledges support from Sandia National Laboratories’ Laboratory Directed Research and Development Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000. KJS acknowledges additional funding by the Welch Foundation (Grant F-1529).

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Graphical Abstract

Graphene on buffer layer free SiC

Covalently modified graphene