



Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Atom-scale covalent electrochemical modification of single-layer graphene on SiC substrates by diaryliodonium salts

Raluca I. Gearba^a, Kory M. Mueller^a, Peter A. Veneman^a, Bradley J. Holliday^a, Calvin K. Chan^b, Keith J. Stevenson^{a,*}

^aThe Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Department of Chemistry, 102E 24th Street, 78712 Austin, TX, USA

^bSandia National Laboratories, 1515 Eubank, 87123 Albuquerque, NM, USA

ARTICLE INFO

Article history:

Received 25 November 2014
Received in revised form 1 May 2015
Accepted 8 May 2015
Available online xxx

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 threefold symmetry, but occasional extended modifications (larger than 4 nm) were observed as well.

© 2015 Elsevier B.V. All rights reserved.

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 [4–6]. 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 [6,8–10]. 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

* Corresponding author.

E-mail address: stevenson@cm.utexas.edu (K.J. Stevenson).

powder), as well as electrochemically driven reactions at platinum surfaces [15–18]. 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 (3×) and dried in vacuum to yield product as off white solid (0.062 g, 50%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.49 (d, *J* = 9.0 Hz, 4H), 8.28 (d, *J* = 9.0 Hz, 4H). ¹⁹F NMR (376 MHz, DMSO-*d*₆): δ -148.28 (s). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆): δ 149.6, 136.8, 126.5, 123.0. HRMS (ESI): *m/z* calc'd for C₁₂H₈IN₂O₄ [M-BF₄]⁺ 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, ¹³C{¹H} 100 MHz, ¹⁹F 376 MHz) and were referenced to residual solvent peaks (¹H and ¹³C{¹H}) and CFCl₃ (¹⁹F). 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*-Bu)₄N][PF₆] (TBAPF), was recrystallized three times from hot ethanol, then dried for 3 days at 100 °C under active vacuum. All of the electrochemical experiments were carried out in a three-electrode cell with a Ag/AgNO₃ reference electrode (silver wire dipped in a 0.01 M silver nitrate solution in a 0.1 M Bu₄NPF₆ solution in CH₃CN), 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 Al₂O₃ 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 1 atm of 45% H₂: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 77 K 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 electro-generated 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. 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 [13,15–18]. 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 and d) starting at 1 mM **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 voltammetric signal.

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 -NO₂ moieties (Fig. 3a) [16, 21–24]. As shown in Fig. 3b, this highly reversible process is evidenced by a peak separation Δ*E*_p = 59 mV and an anodic peak current *i*_{p,a} = -15 μA 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 Eq. (1) [13]:

Download English Version:

<https://daneshyari.com/en/article/6662387>

Download Persian Version:

<https://daneshyari.com/article/6662387>

[Daneshyari.com](https://daneshyari.com)