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Graphene

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# Reversible Grafting of α-Naphthylmethyl Radicals to Epitaxial Graphene**

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Chemical functionalization is a promising approach for the modification of the electronic and magnetic properties of graphene.[1–8] From a chemical standpoint, graphene is a particularly intriguing material;[9–12] although graphene constitutes the thermodynamic ground state of carbon and is solely comprised of $sp^2$-hybridized carbon atoms, the unique electronic structure of graphene allows it to participate in surprisingly mild reaction processes.[13,14]

Herein we show that graphene readily undergoes the Kolbe reaction [Eq. (1)],[15–17] which involves the electrochemical oxidation of carboxylates with subsequent grafting of the derived carbon radicals (Figure 1 and Scheme 1).

$$RCOOH + OH^- \rightarrow RCOO^- \rightarrow R^{\bullet} + CO_2 + e^- \qquad (1)$$

We demonstrate the reversible grafting of α-naphthylmethyl groups to epitaxial graphene (EG) as a versatile approach for engineering the electronic band structure of graphene. The advantages of the Kolbe electrooxidation in the chemical modification of graphene are: 1) reversibility of the reaction, as the grafted functionality can be electrochemically erased; 2) α-naphthylmethyl (α-NM) groups are found to offer well-ordered structures on graphite surfaces,[18] and thus the resulting graphene derivative is anticipated to exhibit interesting magnetic and electronic behavior; and 3) simplicity, versatility, and efficiency of the reaction that makes possible the covalent binding of a wide variety of arylmethyl groups with appropriate substituents on the phenyl rings.[18]

The grafting of α-NM groups to the EG surface was performed by anodic oxidation of a α-naphthylacetate (Figure 1 a, process 1 in Scheme 1); this process produces α-naphthylmethyl (α-NM) radicals in the vicinity of the graphene surface, which rapidly leads to the covalent attachment of the α-NM functionality to the graphene lattice via C−C bond formation and the creation of an $sp^3$ carbon center in the graphene lattice (processes 2 and 3 in Scheme 1).

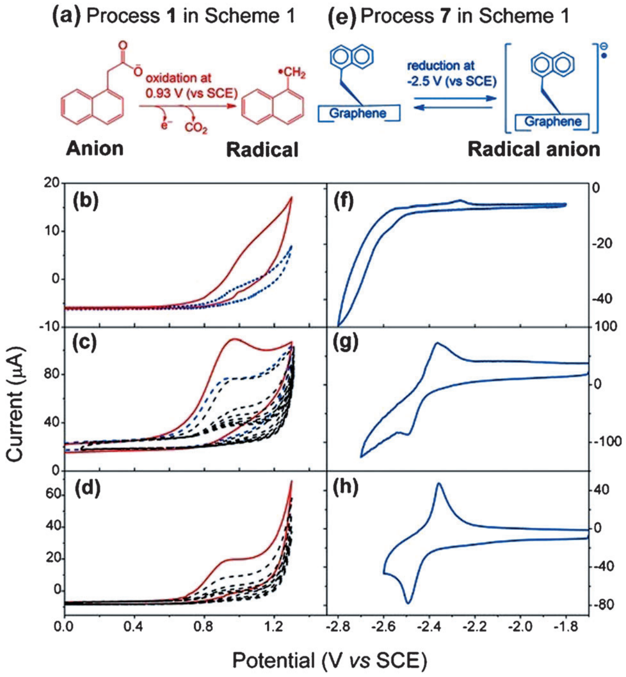

**Figure 1.** a) Generation of an α-naphthylmethyl radical by oxidation of α-naphthylacetate. b)–d) Oxidative cyclic voltammetry of b) the EG electrode in 2 mм α-naphthylacetic acid (α-NAA), c) HOPG in ca. 2 mм α-NAA, and d) HOPG in ca. 4 mм α-NAA; the solutions were prepared with $CH_3CN$ and contained $n$$Bu_4NOH$ and ca. 0.1 м $n$$Bu_4NPF_6$. —— first scan, ----- successive scans; scan rate = 0.2 $Vs^{-1}$. e) Reduction of the α-naphthylmethyl group attached to graphene. f)–h) Reductive cyclic voltammetry of f) α-NM-EG and g, h) α-NM-HOPG electrodes (derivatized using the electrochemical processes in the left frames) with ca. 0.1 м $n$$Bu_4NPF_6$ in $CH_3CN$.

The experiments were performed using a 3.5 × 4.5 $mm^2$ EG wafer (or HOPG pieces of similar size) as the working electrode immersed in a solution of α-naphthylacetic acid and $n$$Bu_4NOH$ in acetonitrile, to which about 0.1 м $n$$Bu_4NPF_6$ was added as an electrolyte (see Supporting Information for details). Figure 1 b,c, and d show successive cyclic voltammograms recorded at EG and HOPG electrodes; the oxidation of the α-naphthylacetate occurs at about 0.93 V vs SCE. During the derivatization of EG with α-NM groups, the anodic current (oxidation peak) in the cyclic voltammetry curve vanishes almost completely after the first scan (Figure 1 b; scan rate = 0.2 $Vs^{-1}$), irrespective of the concentration of the α-naphthylacetate solution. The decrease in current is indicative of the passivation of the EG surface, which becomes coated with the attached layer of α-NM groups.

The efficient passivation of EG is in contrast to the passivation of HOPG, which occurs progressively and depends on the concentration of the arylacetate (Figure 1 c,d).

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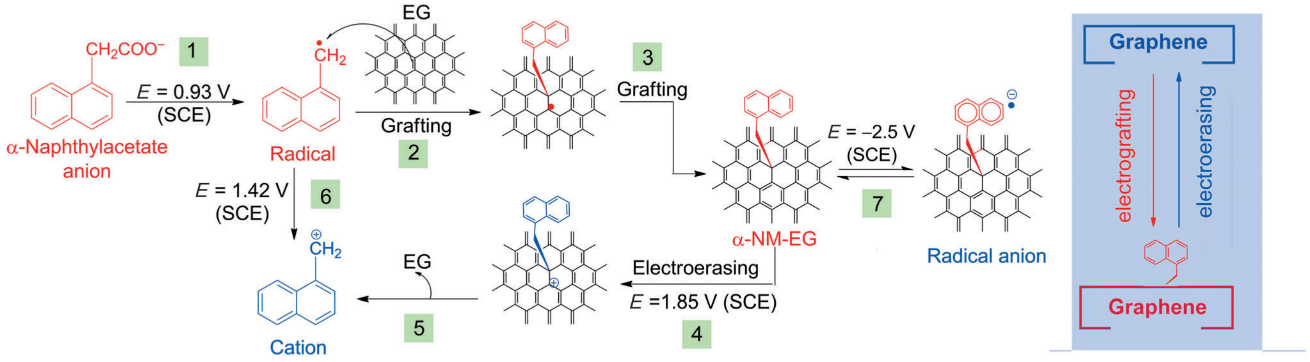

***Scheme 1.*** Mechanistic pathways associated with the grafting of α-naphthylmethyl (α-NM) groups to epitaxial graphene (EG). SCE = standard calomel electrode.

Thus, in case of a 2 mm α-naphthylacetate solution, the number of cycles required for the passivation of HOPG at a scan rate of 0.2 V s$^{-1}$ was 11 (Figure 1 c), whereas four cycles were necessary when a 4 mm solution was used (Figure 1 d). This phenomenon is attributed to the competing dimerization of the α-NM radicals, which is operative only in the presence of the less-reactive graphite (HOPG) surface, and not on the graphene (EG) surface.[11,19,20]

The covalent attachment of the α-NM radical to the epitaxial graphene (processes 2 and 3 in Scheme 1) creates a new sp$^3$ carbon center in place of an sp$^2$ carbon atom in the graphene lattice and this is readily detected by Raman spectroscopy with the development of a D band at about 1345 cm$^{-1}$ (Figure 2 a). The Raman spectrum of the pristine EG shows the characteristic G, G′, 2D, and 2D′ bands (Figure 2 a), whereas the D, D*, and D + D′ bands appear in the spectra of the α-NM-EG product; the intensity of the 2D band is reduced by functionalization, as observed in the addition of nitrophenyl groups to graphene.[4,5]

The Raman intensity map of the D band in the graphene samples is shown in Figure 2; the map of pristine EG (Figure 2 b) shows that the selected area of the wafer is defect-free, whereas covalent functionalization of the same EG surface leads to the appearance of a prominent D peak (Figure 2 c).

The attachment of α-NM group to EG was further confirmed by attenuated total reflectance (ATR)-IR spectroscopy (Figure 2 d). The spectrum of α-NM-EG shows the characteristic intense band at about 792 cm$^{-1}$, which is ascribed to the in-phase C-H wagging vibrations of aryl groups; similar peaks in α-naphthylacetic acid and naphthalene appear at about 778 and 774 cm$^{-1}$, respectively (Supporting Information, Figure S7).[21,22]

The oxidation waves of the grafted groups (process 4 in Scheme 1) were irreversible at low scan rates in a pure electrolyte solution, and these waves disappeared after the second anodic scan (Figure 3 a,b), showing the erasure of the grafted functionalities under electrooxidative conditions (process 5 in Scheme 1). Thus, electroerasing of the α-NM-EG films was achieved by running two cycles of an oxidative CV between 1 and 2.5 V vs SCE, which is illustrated in Figure 3 a for α-NM-EG and Figure 3 b for α-NM-HOPG.

After electrochemical erasure, the resulting EG or HOPG electrode behaved like a clean EG or HOPG electrode, as

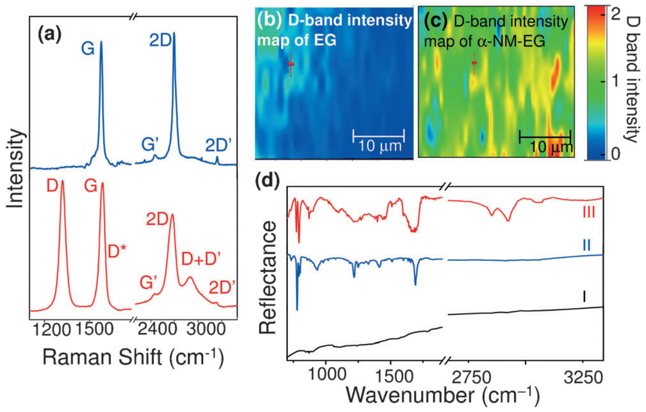

***Figure 2.*** a) Raman spectra ($\lambda_{ex}$ = 532 nm) showing the D and G bands before (blue; $I_D/I_G$ = 0) and after (red; $I_D/I_G$ = 1.1) electrochemical grafting of an α-naphthylmethyl group to EG. α-NM-EG was prepared by complete passivation as shown in Figure 1 b. b), c) Raman intensity maps of the D band in b) pristine EG and c) α-NM-EG for a selected area of the wafer; d) ATR-IR spectra of I) pristine EG, II) α-naphthylacetic acid, and III) α-NM-EG.

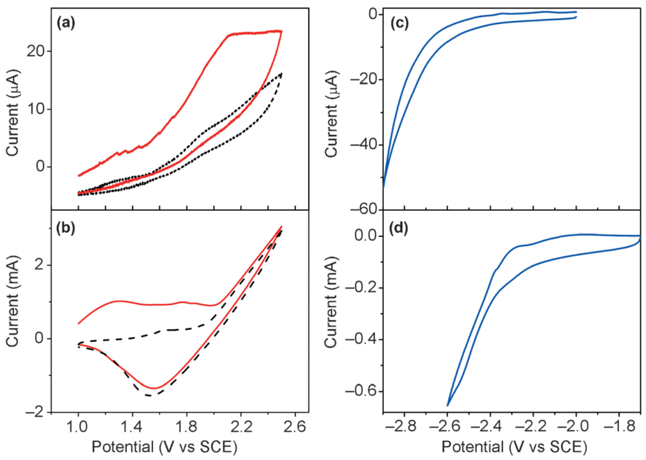

***Figure 3.*** Electrochemical erasure (Scheme 1, process 4,5) of the α-NM-groups from a) the α-NM-EG electrode and b) the α-NM-HOPG electrode by oxidative cleavage. —— first cycle, ----- second cycle. c), d) Reductive cyclic voltammetry of electroerased c) α-NM-EG and d) α-NM-HOPG electrodes (scan rate = 0.2 V s$^{-1}$).

may be seen by running the reductive CV of the electroerased electrodes, which are essentially featureless (Figure 3 c,d). After electroerasing of the α-NM-groups from the α-NM-EG electrode, the surface can be refunctionalized under the oxidative CV conditions shown in Figure 1 b, and the electrode exhibited the same behavior towards passivation by α-naphthylacetate as the pristine EG electrode.

The fidelity of the electrografting (process 2,3) and electroerasing steps (process 4,5) is apparent in the evolution of the D band in the Raman spectrum as a function of the electrochemical treatment (Figure 4). Alternatively, the α-NM groups can be electrochemically erased by transferring the α-NM-EG electrode to a pure electrolyte solution and setting the potential at the level of the oxidation wave. Thus potentiostatic electrolysis of the α-NM-EG electrode at 1.85 V versus SCE for 240 s in a pure electrolyte solution produces a subsequent CV that is essentially featureless, suggesting the efficient erasure of the grafted functionality and the restoration of the initial structure of the epitaxial graphene.

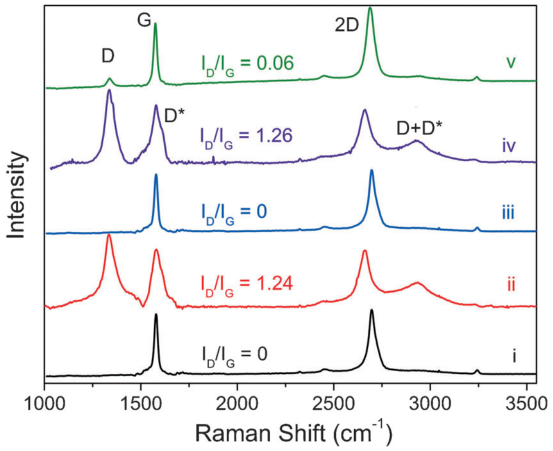

***Figure 4.*** Evolution of the EG Raman spectrum ($\lambda_{ex} = 532$ nm) following multiple electrochemical grafting and erasing steps of the α-naphthylmethyl group: i) pristine EG, ii) after first grafting of α-NM (α-NM-EG), iii) after first electrochemical erasing of α-NM functional group from α-NM-EG, iv) after second grafting of α-NM to electroerased α-NM-EG, and v) second electrochemical erasing.

The derivatized surfaces were further characterized by analyzing the reductive cyclic voltammetry, which was conducted in a pure electrolyte solution. The one-electron reduction of the attached α-NM groups (Figure 1 e, process 7 in Scheme 1) gives rise to a reduction wave (Figure 1 f–h) and the surface coverage $\Gamma$ of the α-NM groups can be estimated from the charge by $\Gamma = Q/nFA$, where $Q$ is the integrated area of the reduction peak (Coulombs of charge), $n$ is the number of electrons ($n = 1$), $F$ is the Faraday constant ($9.648 \times 10^4$ C mol$^{-1}$), and $A$ is the area of the electrode. The functionalized α-NM-EG samples, obtained by complete passivation of the EG surface in a α-naphthylacetate solution (Figure 1 b) were found to have an approximate surface coverage of $1 \times 10^{-9}$ mol cm$^{-2}$ (Figure 1 f), which corresponds to a densely packed layer of α-NM groups. For the EG substrate, the surface coverage was found to be independent of the concentration of the α-naphthylacetate, while for the HOPG functionalization the surface coverage was found to be $4.5 \times 10^{-10}$ mol cm$^{-2}$ (Figure 1 c, 1 g, 2 mM) and $8.1 \times 10^{-10}$ mol cm$^{-2}$ (Figure 1 d, 1 h, 4 mM).[19,20]

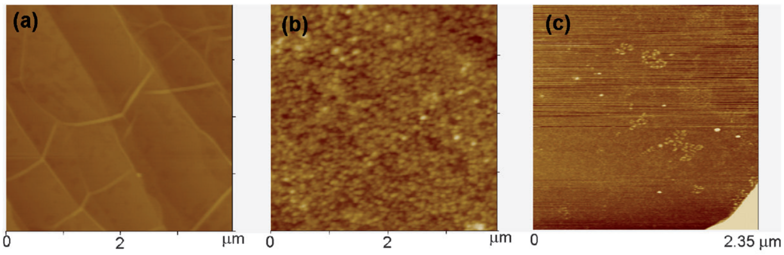

***Figure 5.*** AFM images of a) pristine EG, b) completely passivated α-NM-EG obtained by oxidative CV runs in 2 mM α-naphthylacetate between 0 and 1.3 V vs SCE, and c) sparsely functionalized α-NM-EG obtained by controlled potentiostatic electrolysis of 2 mM α-naphthylacetate at 0.8 V vs SCE for 2.5 seconds.

AFM images of the α-NM-EG surface, which were recorded after cleaning the substrate by ultrasonication in isopropanol, confirmed the formation of a dense layer on the EG surface (Figure 5 b), which suggests that these layers may function as dielectric films. In another experiment, the EG was functionalized by potentiostatic electrolysis in a 2 mM α-naphthylacetate at 0.8 V vs SCE for 2.5 seconds; a subsequent reductive CV gave a reduction peak at −2.5 V vs SCE, corresponding to a surface coverage of about $0.49 \times 10^{-10}$ mol cm$^{-2}$ (Supporting Information). The AFM image confirmed a sparse coverage of the EG surface (Figure 5 c). Control experiments on HOPG substrates show that the film thickness can be controlled by the applied potential and the scan duration.

In conclusion, our present work demonstrates that arylmethyl groups can be grafted electrochemically to the surface of epitaxial graphene, which shows higher reactivity than HOPG, and the EG grafting was found to be independent on the concentration of the α-naphthylacetic acid used in this study (2–4 mM). The surface coverage of naphthylmethyl groups can be controlled by adjusting the electrochemical conditions for functionalization of EG; the control of the layer structure and packing of the functional groups over the graphene surface is an essential issue in the development of graphene chemistry.[14,23–25] The functionalization is readily reversed and may be repeated in a simple, efficient, and reproducible manner, suggesting the potential of this approach for reversible engineering of the band structure of graphene. The versatility of this method offers new routes for the post-grafting modification and well-ordered structural patterning of graphene wafers for advanced electronic, magnetic, and electro-optical applications.

## Experimental Section

Epitaxial graphene (EG) samples, grown on single-crystal SiC (0001) by vacuum graphitization, were provided by Professor Walt de Heer

(Georgia Institute of Technology). All experiments were performed on the C face of the EG. HOPG samples were obtained from Union Carbide Corporation. α-Naphthylacetic acid (FW = 186.21), tetrabutylammonium hexafluorophosphate ($n\mathrm{Bu_4NPF_6}$, FW = 387.43), tetrabutylammonium hydroxide ($n\mathrm{Bu_4NOH{\cdot}30\,H_2O}$, FW = 259.47), and acetonitrile (anhydrous, 99.9 %) were obtained from Sigma–Aldrich. Electrochemical experiments were carried out with a computer-controlled CH Instruments Electrochemical Analyzer. Raman spectra were collected in a Nicolet Almega XR Dispersive Raman microscope with a 0.7 μm spot size and 532 nm laser excitation. The ATR-IR spectra were taken using a Thermo Nicolet Nexus 670 FTIR instrument equipped with an ATR sampling accessory.

The EG and HOPG samples for electrochemical surface functionalization reactions were fixed on a glass substrate with prepatterned gold contacts. The graphene samples were electrically contacted with silver paint and the contacts were isolated with epoxy resin. The EG (or HOPG) substrate served as the working electrode, while the platinum (Pt) wire and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The solutions of α-naphthylacetate were prepared in a glove box (see Supporting Information for details). The electrochemical cell with the substrate and solution was purged with argon prior to use.

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**Keywords:** aryl acetates · graphene · Kolbe oxidation · quasireversible grafting · surface chemistry

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