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Scanning Tunneling Microscopy, Spectroscopy, and Nanolithography of Epitaxial Graphene Chemically Modified with Aryl Moieties

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Abstract: The reduction of diazonium salts has recently been proposed as a robust covalent modification scheme for graphene surfaces. While preliminary studies have provided indirect evidence that this strategy decorates graphene with aryl moieties, the molecular ordering and conformation of the resulting adlayer have not been directly measured. In this Article, we report molecular-resolution characterization of the adlayer formed via the spontaneous reduction of 4-nitrophenyl diazonium (4-NPD) tetrafluoroborate on epitaxial graphene on SiC(0001) using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) and spectroscopy (STS). An atomically flat inhomogeneous layer of covalently bonded organic molecules is observed after annealing the chemically treated surface at ~500 °C in UHV. STM and STS results indicate that the adlayer consists predominantly of aryl oligomers that sterically prevent uniform and complete covalent modification of the graphene surface. The adsorbed species can be selectively desorbed by the STM tip above a threshold sample bias of −5 V and tunneling current of 1 nA, thus enabling the fabrication of a diverse range of graphene nanopatterns at the sub-5 nm length scale.

Introduction

Graphene, a one-atom thick planar sheet of sp^2-bonded carbon atoms in a honeycomb lattice, has attracted substantial attention due to its unique electronic, thermal, and physical properties.[1−10] Furthermore, a wide range of applications including electronic devices, sensors, and composite materials have been anticipated for graphene.[5] In most of these applications, graphene will need to be integrated with other materials, thus necessitating surface functionalization strategies that will provide robust and well-defined interfaces. Chemical functionalization also holds promise for tailoring the chemical specificity and electronic properties of graphene via doping and bandgap engineering.[11−17] However, as compared to the vast overall recent literature on graphene, relatively few studies have focused on strategies for chemically modifying graphene surfaces.[18−29]

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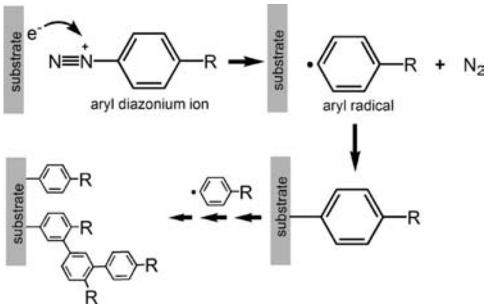
Scheme 1. Reduction of Aryl Diazonium Salts[a]



[a] The aryl diazonium cation accepts one electron from the substrate and forms an aryl radical through the release of a nitrogen molecule. The aryl radical can then covalently react with the surface or with other surface mounted aryls leading to aryl oligomers.

The surface chemistry of graphene is expected to be similar to that of graphite and related carbonaceous materials such as carbon nanotubes. One of the most versatile and facile methods of covalently grafting organic molecules onto these carbonaceous materials is the reduction of aryl diazonium salts ($Ar{-}N{\equiv}N^+X^-$) through either electrochemical or spontaneous reduction with the substrate.[30−33] In this reduction process, the aryl diazonium cation accepts an electron from the substrate and generates an aryl radical by releasing a nitrogen molecule. The highly reactive aryl radical can then covalently react with graphitic substrates and possibly with other surface mounted aryls leading to aryl oligomers as shown in Scheme 1.[32,33] Recently, this covalent modification strategy has been applied to both epitaxial graphene on silicon carbide[12,19] and mechanically exfoliated graphene.[27] In particular, on the basis of infrared spectroscopy and electrochemical characterization, it was suggested that the reduction of 4-nitrophenyl diazonium tetrafluoroborate led to a fully ordered close-packed monolayer of vertically oriented nitrophenyl groups on graphene.[12,19]

Herein, we report a molecular-resolution ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) and spectroscopy (STS) investigation of the spontaneous reduction of 4-nitrophenyldiazoium (4-NPD) tetrafluoroborate on epitaxial graphene on SiC(0001). Following annealing of the surface at ~500 °C in UHV, STM imaging reveals an atomically flat inhomogeneous layer of covalently bonded organic molecules across the graphene surface. In particular, the adsorbed molecules possess a chain-like appearance in STM that is indicative of aryl oligomerization. The aryl oligomers appear to sterically inhibit full covalent modification of the surface, as determined by STM imaging and STS spectra. Although the adsorbed species are stable under normal scanning conditions, STM-induced desorption does occur above a threshold sample bias of -5 V and tunneling current of 1 nA, which allows for the controlled fabrication of graphene nanostructures at the sub-5 nm length scale. Overall, this molecular-resolution UHV STM study provides an unprecedented perspective and direct insight into the chemical and electronic structure of covalently grafted graphene, thus informing ongoing and future efforts to realize graphene-based chemical and electronic device applications.

Experimental Details

Epitaxial graphene was formed on the SiC(0001) surface by repeated annealing at 1350 °C for 30 s in UHV conditions (maximum pressure during annealing was $\sim 5 \times 10^{-9}$ Torr). Following UHV STM verification of successful graphitization, the substrate was directly transferred into a nitrogen glovebox for subsequent chemical modification. Molecular grafting was then accomplished by submersing the epitaxial graphene sample into 10 mM of 4-NPD tetrafluoroborate and 0.1 M of tetrabutylammonium hexafluorophosphate ($[Bu_4N]PF_6$) solution in acetonitrile for 20 h. Following chemical modification, the substrate was sonicated for 10 min in acetonitrile before reintroduction to the UHV chamber. Attempts to obtain atomically resolved STM images of the chemically modified graphene surface without degassing were unsuccessful. Consequently, the sample was annealed at ~500 °C in UHV for 5 min to remove physisorbed contamination, subsequently resulting in stable STM imaging. Temperature-dependent STM measurements (see Supporting Information) reveal no thermal decomposition of the organic adlayer at this degassing temperature, which is consistent with previous Auger spectroscopy annealing studies of arylated graphite.[34] All STM and STS measurements were performed at room temperature with electrochemically etched tungsten tips using a home-built UHV STM system operating at a base pressure of $\sim 5 \times 10^{-11}$ Torr.[35] The voltage was applied to the sample with respect to the tip that was grounded through a current preamplifier.

Results and Discussion

A characteristic STM image of epitaxial graphene on SiC(0001) is shown in Figure 1a. The sample is fully graphitized and consists of a mixture of bilayer (BL) and monolayer (ML) domains, showing atomic structures (Figure 1b and c) that agree with previous reports.[36] Because the graphitized SiC(0001) surface is stable under atmospheric pressure conditions, it can be safely removed from UHV for ex situ chemical modification.[18,37] In particular, the reduction of 4-NPD tetrafluoroborate with epitaxial graphene in aprotic medium is accomplished in a nitrogen glovebox for 20 h. The substrate is then reintroduced into UHV where degassing at ~500 °C allows for the selective removal of physisorbed contamination.

Figure 2a shows a representative STM image of the chemically modified graphene surface. The image shows that an atomically flat inhomogeneous layer of adsorbed molecules was formed on epitaxial graphene. Similar STM images were obtained at several points across the surface and on separately prepared samples, including samples where the ex situ reaction time was doubled to 40 h. Consequently, the image shown in Figure 2a represents the maximum obtainable molecular coverage for covalently grafted organic molecules resulting from 4-NPD tetrafluoroborate reduction on epitaxial graphene. Even at this maximum coverage, the molecules are not densely packed with small patches of underlying graphene observable within the adsorbed layer. High-resolution STM imaging (Figure 2b) provides further insight into the morphology of the chemically modified graphene surface. Careful inspection reveals that most

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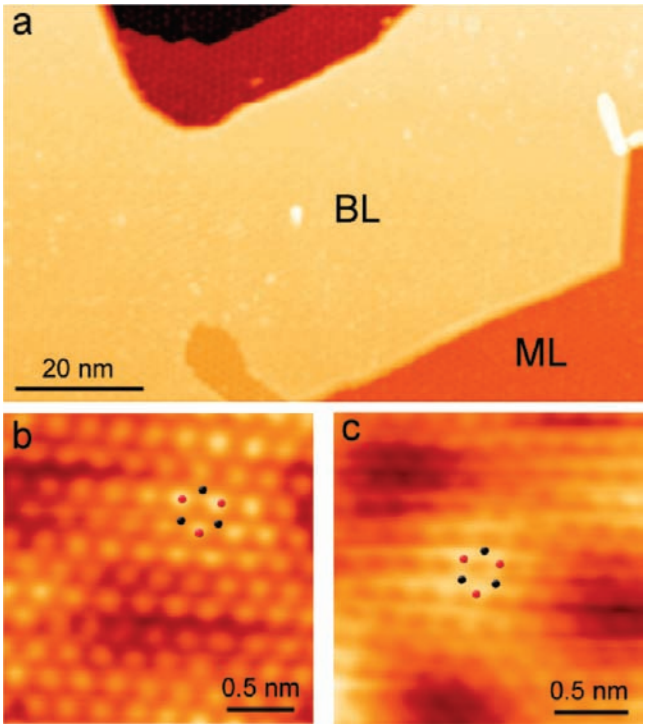

Figure 1. STM images of epitaxial graphene on SiC(0001). (a) Large area STM image (sample bias = −2.6 V; tunneling current = 0.05 nA) where both bilayer (BL) and monolayer (ML) domains are present. (b) Atomic resolution STM image (sample bias = −0.25 V; tunneling current = 0.1 nA) of bilayer graphene. (c) Atomic resolution STM image (sample bias = −0.25 V; tunneling current = 0.1 nA) of monolayer graphene. A schematic representation of the atomic lattice of graphene is indicated by the hexagon.

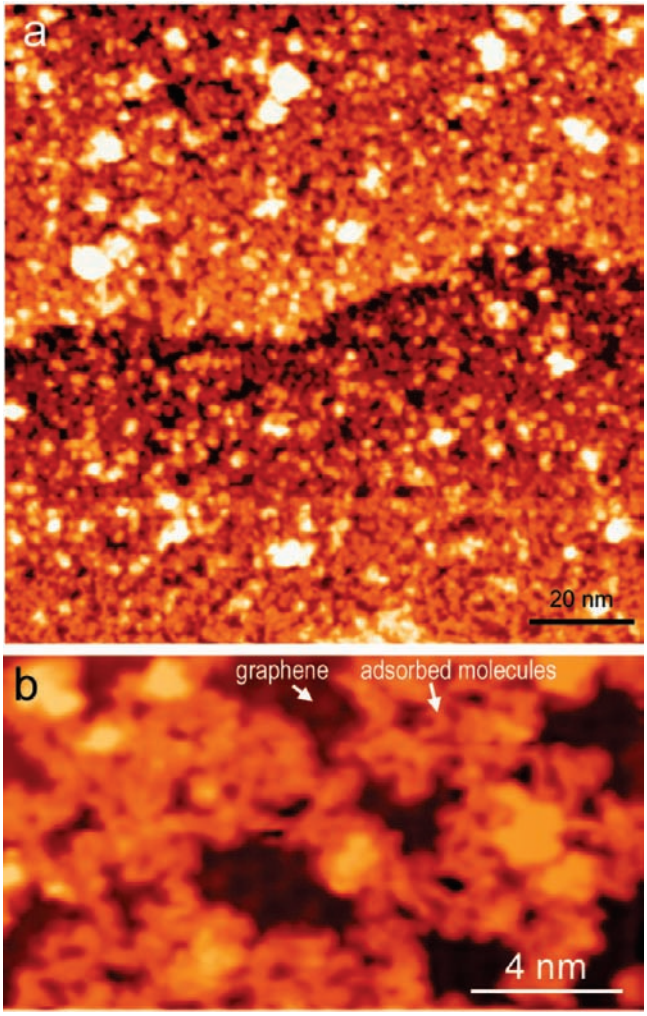

Figure 2. (a) Large area STM image (sample bias = +2.0 V; tunneling current = 0.05 nA) of epitaxial graphene on SiC(0001) modified with 4-NPD tetrafluoroborate. (b) High-resolution STM image (sample bias = −2.0 V; tunneling current = 0.05 nA) of epitaxial graphene on SiC(0001) modified with 4-NPD tetrafluoroborate.

of the adsorbed molecules appear as irregularly shaped chain-like features, which are reminiscent of pseudorandom walk organic chain reactions on silicon surfaces.[38] This observation provides initial experimental evidence for the aryl oligomers on the surface that were suggested in Scheme 1. While the first step in the reaction likely leads to covalent attachment of an aryl moiety on the surface, the bulk of the aryl oligomer appears to be physisorbed to the surface, thus yielding a random, irregular shape. An oligomer may also stand off the surface, perhaps explaining the relatively large protrusions that are also observed on the chemically modified graphene surface. However, these large protrusions may also be attributed to large molecular weight contamination introduced during ex situ processing that is not removed via in situ degassing.

The existence of adsorbed species on the chemically modified graphene surface following annealing at ~500 °C strongly suggests covalent attachment to the substrate, which agrees with earlier studies.[12,19,27] On the other hand, the low packing density and inhomogeneity of the adsorbed layer can be attributed to aryl oligmerization as predicted in previous reports on semiconductor and metal surfaces.[32,33] Similar to graphitized SiC(0001), the chemically modified graphene surface is also robust and stable in atmospheric pressure conditions as determined by STM imaging following ambient exposure. Furthermore, under normal STM imaging conditions (i.e., sample bias = ±2 V; tunneling current = 0.05 nA), we do not observe any morphological change in the adsorbed layer. However, under more aggressive scanning conditions such as higher negative sample biases and/or higher tunneling currents, the adsorbed molecules can be desorbed, thus uncovering bare graphene. This observation suggests the possibility of controlled STM-induced nanopatterning of chemically modified graphene.

Figure 3a shows an STM image of the initial region of chemically modified graphene preceding STM-induced nanopatterning. The result of bias-dependent nanopatterning of line structures at a constant tunneling current (1.0 nA) and tip velocity (100 Å/s) is shown in Figure 3b. The adsorbed molecules are cleanly desorbed revealing ribbons of pristine graphene with widths of ~5 nm. Extensive exploration of the nanopatterning phase space allowed identification of the threshold sample bias and tunneling current of −5 V and 1.0 nA, respectively. This relatively high threshold nanopatterning voltage coupled with the inhomogeneity of the adlayer likely limits the width of the nanopatterned structures. Nanopatterning was not achieved at positive sample bias, thus suggesting that desorption occurs via inelastic scattering of the tunneling hole with a σ hole resonance.[39] It should also be noted that

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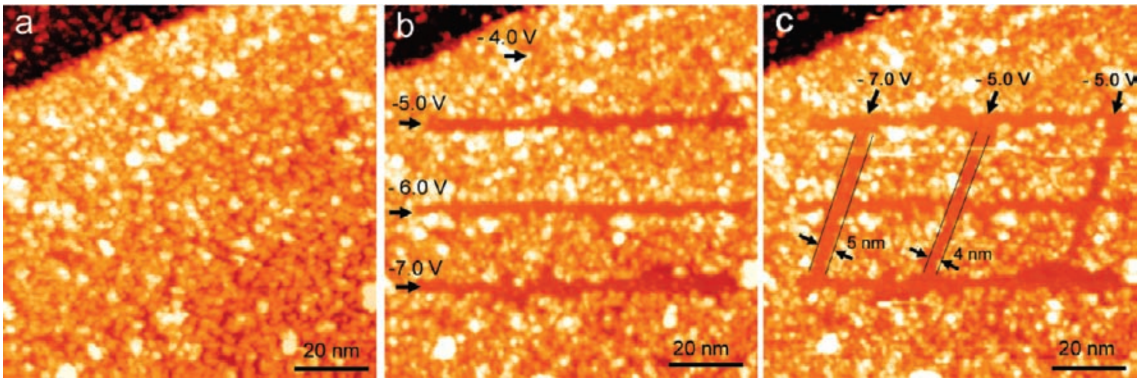

Figure 3. (a) Initial STM image of the chemically modified graphene surface preceding nanopatterning. (b) STM image following bias-dependent nanopatterning of three horizontal lines at a constant tunneling current (1.0 nA) and tip velocity (100 Å/s). (c) Additional nanopatterning of three vertical lines, showing linewidths at the sub-5 nm length scale. All STM images were acquired at a sample bias of +1.85 V and tunneling current of 0.06 nA.

nanopatterning is independent of tip velocity over the range of 50−400 Å/s. Nanopatterning above the threshold bias and current is reproducible and independent of geometric direction as indicated in Figure 3c. Furthermore, the nanopatterning line width is independent of the sample bias, tunneling current, and tip velocity. However, because the adsorbed organic layer is inhomogeneous with low packing density, the graphene nanopatterns possess edge roughness at the 1 nm scale. Graphene nanopatterns of larger widths can be achieved by writing multiple overlapping lines.

STS measurements were performed to probe the electronic structure of the chemically modified graphene surface compared to adjacently nanopatterned pristine graphene domains. Representative d*I*/d*V* spectra of chemically modified and clean graphene on the same atomically flat terrace are shown in Figure 4a(i) and (ii), respectively. In addition to the minimum at zero bias, the clean graphene spectrum shows typical characteristics of bilayer graphene with a local minimum at approximately −0.3 V, which corresponds to the Dirac point, as shown in the schematic band structure in the inset of Figure 4a.[24,40] Based on hundreds of measured STS spectra, the majority (∼70%) of the spectra on chemically modified graphene appear featureless at negative sample bias as shown in Figure 4a(i), while a minority (∼25%) of the spectra appear similar to clean graphene. These minority spectra can likely be attributed to the submonolayer packing density of aryl groups on the chemically modified graphene surface. It should be noted that the majority spectra (Figure 4a(i)) show nonzero d*I*/d*V* at all biases similar to that of clean bilayer graphene. In rare cases (∼5%), the spectra possess d*I*/d*V* approaching zero over a range of ∼0.5 V at low bias, which is indicative of the opening of a band gap (Figure 4b). Recently, photoelectron spectroscopy has suggested a minimum gap opening of ∼0.35 eV for arylated graphene.[41]

As discussed earlier, the formation of aryl oligomers likely explains the inhomogeneous and loosely packed adsorbed layer on the chemically modified graphene surface. Because the bulk of the oligomer is physisorbed and thus weakly interacting with the surface, the underlying graphene electronic structure is unlikely to be significantly perturbed for the vast majority of sites on chemically modified graphene, thus explaining the d*I*/d*V* spectra shown in Figure 4a. However, the stability of the adsorbed layer at temperatures up to ∼500 °C suggests that there is at least one covalent attachment site per oligomer. These covalent attachment sites locally disrupt the sp^2 hybridization of the underlying graphene, leading to the infrequently observed spectra shown in Figure 4b. Indeed, covalent modification of the graphene surface is expected to break its zero-gap characteristics.[12,14,42]

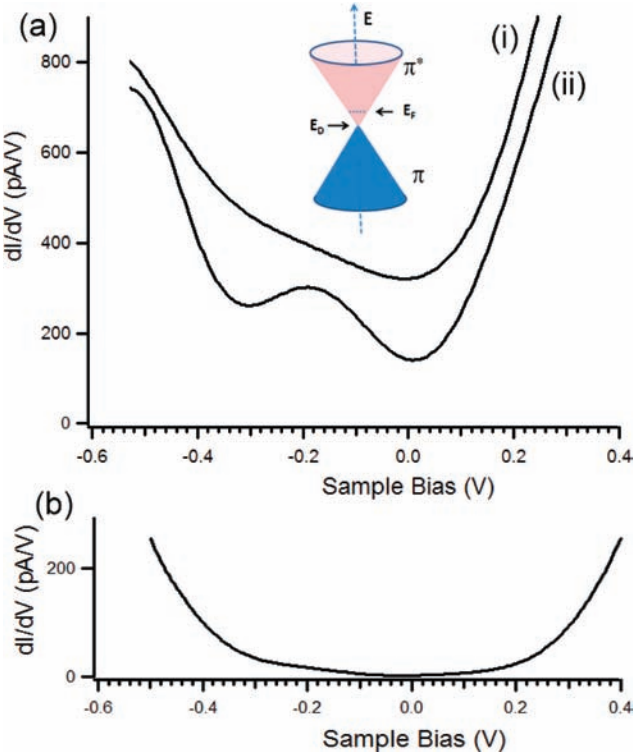

Figure 4. (a) Representative d*I*/d*V* spectra for (i) chemically modified graphene and (ii) clean graphene regions. Spectrum (i) has been offset by 250 pA/V for clarity. Inset: Schematic band structure of pristine graphene.[40] (b) The rare example of a d*I*/d*V* spectrum showing the opening of band gap on chemically modified graphene. The feedback set point for all spectra is sample bias = 0.3 V and tunneling current = 0.1 nA.

Recently, it has been reported that graphene nanoribbons with sub-10 nm widths should have a measurable band gap in their electronic structure.[43] However, we did not observe a band gap

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in STS spectra taken on the sub-5 nm graphene nanopatterns shown in Figure 3. Because of the low concentration of covalent binding sites on the chemically modified graphene surface, the nanopatterned region apparently does not possess a large enough electronic structure contrast to show quantum confinement effects. This observation is consistent with theoretical calculations that suggest that the concentration of covalent modification sites needs to approach ∼25% to open a bulk band gap in the electronic structure of graphene.[12] Future efforts to tune the electronic structure of graphene via grafting of organic molecules will thus need to avoid conditions under which oligomerization sterically hinders complete covalent modification.

Conclusions

Covalent grafting of aryl moieties through the reduction of 4-nitrophenyl diazonium (4-NPD) tetrafluoroborate on epitaxial graphene on SiC(0001) has been studied at the molecular scale using UHV STM and STS. STM images of chemically modified graphene following annealing at ∼500 °C in UHV indicate that the adsorbed layer is covalently bound to the surface and contains a significant fraction of aryl oligomers. STM nanolithography is achievable above a threshold sample bias (−5 V) and tunneling current (0.1 nA), leading to sub-5 nm nanopatterns of pristine graphene. STS measurements reveal that the physisorbed portions of the aryl oligomers do not significantly perturb the electronic structure of the underlying graphene. Consequently, the sub-5 nm nanopatterns do not show quantum confinement effects. On the other hand, at covalent attachment sites, a band gap is observed in the STS spectra, thus suggesting that high density organic covalent modification schemes can be used to tune the bulk electronic structure of graphene. Overall, this study provides unique, molecular-resolution insight into graphene surfaces covalently modified via diazonium chemistry, thus informing future efforts to utilize this popular functionalization pathway for graphene-based electronic and sensing applications.

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Supporting Information Available: Temperature-dependent STM images and complete citations for refs 9, 16, and 29. This material is available free of charge via the Internet at http://pubs.acs.org.

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