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Surface Chemistry

Permanent Pattern-Resolved Adjustment of the Surface Potential of Graphene-Like Carbon through Chemical Functionalization**

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The exceptional electronic and optical properties of graphene have caught the attention of physicists and materials scientists since the first effective preparation of this two-dimensional form of carbon by Novoselov et al. in 2004.[1] Much effort is currently being invested in the large-scale production of graphene surfaces[2,3] and in the investigation of its peculiar quantum effects.[4–6] Graphene is viewed as a potential alternative to silicon as a material for the construction of nanoscale electronic circuits. The use of graphene in this way would require control of its electronic band structure and the withdrawal or injection of electron density to adjust or tilt the Fermi level in a graphene sheet. Such pattern-resolved control of the energy level is the two-dimensional equivalent of n or p doping in classical semiconductors.[7] In contrast to silicon, graphene has a continuous band structure with zero band gap.[8] Thus, single adsorbed molecules modify the band structure and affect the electronic properties of graphene significantly,[9,10] which makes graphene difficult to handle. Device fabrication requires reliable and permanent control over the different electronic states and the Fermi energy of an air-stable material.[8] The adsorption of organic molecules[11] can result in p-type doping through a sandwichlike π-stacking arrangement on graphene. The injection of electrons is possible through n-type doping with potassium;[12] however, such materials are highly sensitive to air and water.

In the search for a robust and highly precise doping method, we investigated well-established protocols from organic radical chemistry[13–15] to attach an air-stable dopant covalently and thus permanently alter the electronic structure of graphene sheets. The relative surface charge levels were measured by Kelvin force microscopy (KFM). The application of the linear free-enthalpy relationship for substituted aromatic compounds enabled the direct prediction of the charge-withdrawing or charge-injecting effect of graphene modification. We therefore concluded that this approach should enable direct control of the surface potential, Ψ, of modified graphene. Furthermore, the Hammett concept[16] enabled a precise correlation between the observed change in the surface potential, $\Delta\Psi$, and the structure of the covalently bonded reagents. This concept was confirmed experimentally by using strongly electron withdrawing (*p*-nitrophenyl, $\sigma = 0.78$) and electron donating substituents (*p*-methoxyphenyl, $\sigma = -0.23$).[17]

For our experiments, we used the top graphene layer of highly ordered pyrolytic graphite (HOPG) as a model material. From a physical point of view, this model is not representative for detailed investigations on band structure or electronic effects. However, from a chemical point of view, the reactivity of the graphene stacks of HOPG is comparable to that of single-walled carbon nanotubes, which can be considered as rolls of graphene.[13,14] For additional experimental validation, we also carried out the graphene modifications described herein on carbon-coated nanoparticles (two or three layers of graphene on copper). Detailed structural evidence was then provided by diffuse reflectance FTIR to characterize the products and confirm the direct covalent attachment of the modifying groups to the top graphene layer. This functionalization approach extends p and n doping based on adsorbed molecules or ions to make it a systematic and robust method with which molecular electronics elements can be attached perpendicular to the graphene plane in a third dimension.

The experimental approach to covalent graphene modification is shown in Figure 1. The model material (top layer of a monocrystalline graphene stack) was first patterned by lithography, so that a plain (unfunctionalized) graphene surface would be preserved below the photoresist. The unmasked areas were functionalized by exposure to highly diluted diazonium reagents (see the Supporting Information). After removal of the photoresist, the graphene surface was investigated by scanning electron microscopy (SEM) and Kelvin force microscopy (KFM) in tapping mode to image the relative surface-potential levels of modified and native areas of the graphene surface. The chemical derivatization depends

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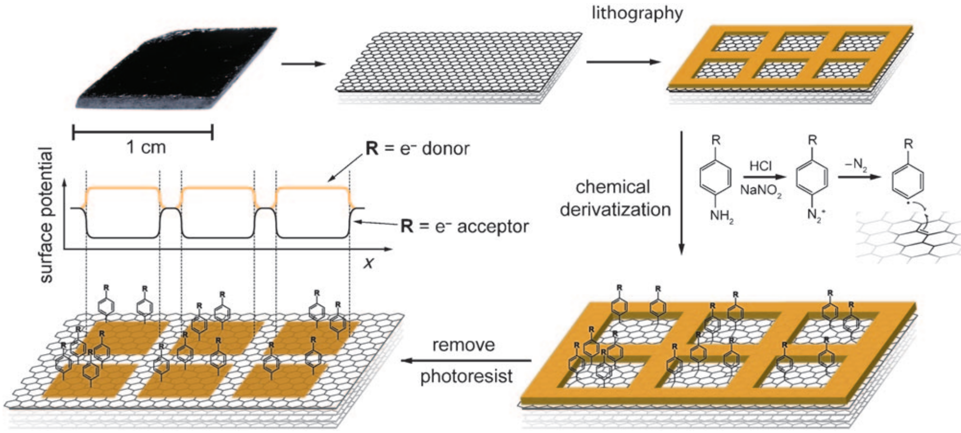

Figure 1. Patterned functionalization of an HOPG surface: First, a patterned mask is created by photolithography on the top graphene layer of a graphene stack. The unmasked regions are then exposed to a diazonium reagent. The photoresist is removed prior to analysis.

strongly on the reaction time, the concentration of the reactants, and a successful washing procedure. The reaction time and concentration control the amount of covalent derivatization of the graphene surface by dopants at a constant temperature. Overfunctionalization can result in the deposition of polymer layers of several nanometers in thickness as a result of nonspecific cross-linking of the phenyl radical.[13] Although such covalent bonds may enable the cross-linking of a graphene sheet with molecular wires, they are not desired for a controlled change in the surface potential. They might be eliminated through the use of sterically hindered diazonium salts.[18]

Our strategy to confirm the chemical identity of the attached phenyl units and their covalent attachment, and to determine the lithographic resolution and the change in surface potential, is based on a combination of analytical and chemical methods. SEM images were taken after chemical modification and washing. Figure 2 a,b shows areas of a graphene surface modified with electron-withdrawing (p-type) nitrophenyl or electron-donating (n-type) methoxyphenyl substituents. Since the SEM images were taken in a secondary electron-detection mode, they indicate the local emission properties,[19] and the contrast (dark/light) is inverted for the p- and n-type surface modification (dark/light squares in Figure 2 a,b). The patterning was also shown by locally resolved X-ray photoelectron spectroscopy and energy-resolved X-ray backscattering (see Figures S4 and S5 in the Supporting Information). The direct application of confocal Raman spectroscopy with spatial resolution down to about 400 nm[20] on the functionalized graphene stacks could not resolve the chemical structure of the derivatized surface areas owing to the extremely low concentration of the surface modifier and the high background noise from graphene sheets lying beneath the functionalized film. Atomic force microscopy (AFM) and KFM were used to determine the surface potential (Figure 2 c,d) and surface structure (see Figure S3 in the Supporting Information). Whereas no systematic height changes were observed beyond some bending of the graphene stacks, the surface potential changed distinctly between untreated and functionalized areas (along the line in Figure 2 c). The induced surface-potential difference of *p*-nitrophenyl-functionalized HOPG relative to HOPG is: $\Delta\Psi = (-74 \pm 16)$ mV. The lithographically applied mask frames the regions of higher potential precisely (squares). Potential and height measurements were made simultaneously to avoid sample shifts. A series of control experiments (individual reagents or types of treatment) confirmed that the potential changes were indeed caused by the substituted phenyl radicals.

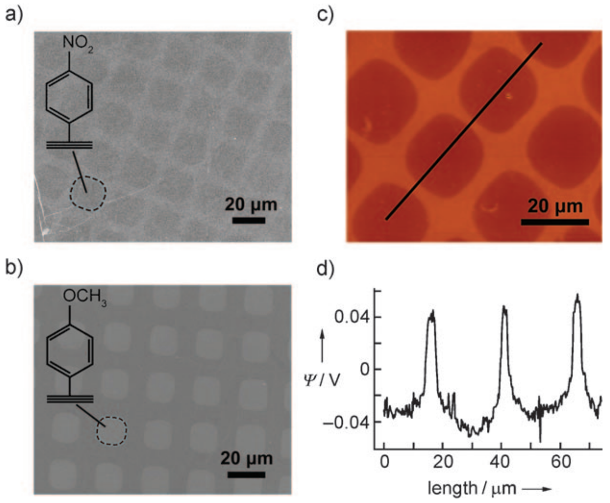

Figure 2. Scanning electron microscopy images of a) *p*-nitrophenyl- and b) *p*-methoxyphenyl-functionalized graphene stacks. The encircled areas are functionalized regions. c) Kelvin force microscopy image of *p*-nitrophenyl-modified HOPG. d) Profile of the surface potential along the black line in (c).

A closer look at the transition region between native and functionalized areas of the carbon surface revealed a change in height of about 1 nm (Figure 3), which is in agreement with the estimated height change corresponding to the attachment of a nitrobenzene moiety perpendicular to the graphene surface.[21] If the functionalization procedure is applied for too long, the formation of multilayered functionalized films can be observed as a result of a polymerization-like reaction between excess reagent and aromatic rings on the surface.[13] Such distinct changes in surface potential could serve as walls for quantum billiard-type devices, as suggested by Miao et al.,[22] or enable the printing of complex current devices, as suggested by Berger et al.[23] Furthermore, the ability to pattern a graphene layer permanently and thus shift its

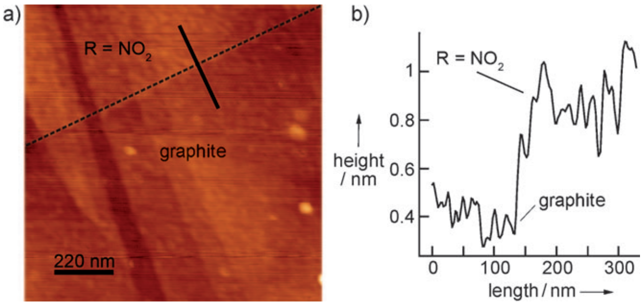

Figure 3. Height changes through patterned functionalization. a) AFM image of the transition region in *p*-nitrophenyl-functionalized HOPG (the dashed line shows the end of the functionalized area). b) Height profile along the solid line in (a).

surface potential could be useful for complex optoelectronic applications, as suggested by Wang et al.[24]

The chemical identity and covalent attachment of the nitrophenyl group was confirmed by the functionalization of copper-supported graphene bi- and trilayers, which were recently made accessible in gram quantities by Athanassiou et al.,[25] and the detection of surface-bound molecules by infrared spectroscopy.[15] The use of copper nanoparticles as a support for the graphene model material enables the simple handling of large graphene surfaces in a small volume (about 20 m^2 in 1 g of particles) and the application of classical chemical detection methods (with low detection limits). Thus, diffuse reflectance FTIR was used to demonstrate the attachment of a *p*-nitrophenyl moiety to the carbon surface (Figure 4). Whereas pure graphene showed no features between 1800 and 600 cm^{-1} (0.22–0.074 eV), peaks that corresponded to the molecular vibrations of the reference compound *p*-ethylnitrobenzene were observed for *p*-nitrophenyl-functionalized surfaces.

A systematic extension of the derivatization described herein is possible on the basis of the linear free-enthalpy relationship that was initially derived for kinetic and thermodynamic studies of benzene derivatives. An example is the Hammett substitution constant, which was derived by comparing different substituted benzoic acids (Figure 5 b) and is defined as the ratio of the acidity constant K_R of the substituted acid to the acidity constant K_H of unsubstituted benzoic acid. This concept has found broad application in organic chemistry,[17] as it provides a means of quantifying the electron-withdrawing (the anion of the acid is stabilized, stronger acids) or electron-donating nature (weak acids) of substituents experimentally.

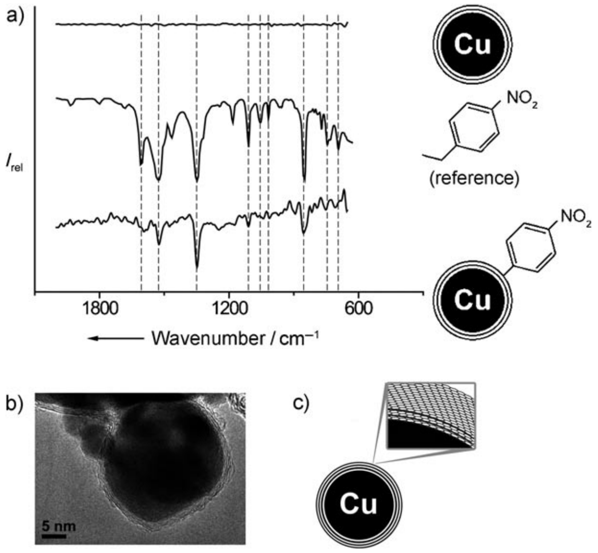

Figure 4. Chemical identity of graphene modifiers supported on metal nanoparticles. a) IR spectra of as-prepared graphene-coated copper nanoparticles (top), *p*-nitrophenyl-functionalized copper nanoparticles (bottom), and the reference compound 4-ethylnitrobenzene[15] (middle). b) Transition electron microscopy image of graphene-coated copper nanoparticles. c) A schematic representation.

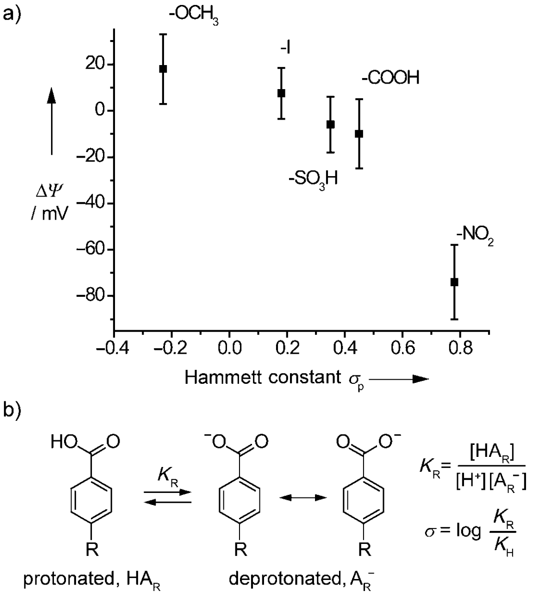

Figure 5. a) Correlation between the Hammett constant and the measured change in the surface potential on the graphene stack. b) Definition of the first Hammett correlation; K_R is the equilibrium constant for the protonation–deprotonation reaction. The subscript R describes the *para* substituent of the benzoic acid derivative. The Hammett constant, σ, is defined with respect benzoic acid (R = H).

When the substituent is itself a phenyl ring, the Hammett correlation applies both ways. Thus, graphene can be considered as a substituent or as the moiety under investigation. In this case, we used substituted phenyl units to adapt the electronic structure of a graphene sheet. To further test the validity of the Hammett correlation for graphene, we prepared derivatized graphene with *p*-methoxyphenyl (see the Supporting Information for details), *p*-iodophenyl, *p*-sulfophenyl, and *p*-carboxyphenyl substituents. The measured change in surface potential (Figure 5) was compared with literature values of the Hammett constant.[17] These initial studies clearly show a qualitative correlation; however, investigations on broader set of samples are necessary before a detailed quantitative statement can be made.

Our study reveals an astonishingly simple yet accurate method to adjust the surface potential in graphene layers. Besides the direct application of such patterning in device fabrication, the covalent attachment of groups to a graphene layer introduces a third dimension in the structure. The covalent attachment of molecular electronics, chemical sensors incorporated in circuitry, or actuators may ultimately be possible. This method offers an alternative to the solution of the contacting problem in the nanomolar range. The possibility of printing a pattern onto a bi- or trilayer graphene sheet was only shown conceptually herein, but this approach enables a permanent polarization of the graphene sheets (as in the case of gate-induced changes in conductivity). This feature will be of crucial importance if larger graphene sheets (3D analogue: native Si wafer), which are then doped and partially oxidized (3D analogue: insulating silicon oxide), are to be used as substrates in device fabrication. One might envision for graphene that doping or oxidation to an insulating state could be possible through a simple chemical process and classical or dip-pen lithography.

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[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
[2] M. J. McAllister et al., *Chem. Mater.* **2007**, *19*, 4396.
[3] J. Hass et al., *Appl. Phys. Lett.* **2006**, *89*, 143106.
[4] K. S. Novoselov et al., *Science* **2007**, *315*, 1379.
[5] L. A. Ponomarenko, F. Schedin, M. I. Katsnelson, R. Yang, E. W. Hill, K. S. Novoselov, A. K. Geim, *Science* **2008**, *320*, 356.
[6] C. Stampfer, J. Guttinger, F. Molitor, D. Graf, T. Ihn, K. Ensslin, *Appl. Phys. Lett.* **2008**, *92*, 012102.
[7] G. L. Pearson, J. Bardeen, *Phys. Rev.* **1949**, *75*, 865.
[8] T. O. Wehling, K. S. Novoselov, S. V. Morozov, E. E. Vdovin, M. I. Katsnelson, A. K. Geim, A. I. Lichtenstein, *Nano Lett.* **2008**, *8*, 173.
[9] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 652.
[10] I. Zanella, S. Guerini, S. B. Fagan, J. Mendes, A. G. Souza, *Phys. Rev. B* **2008**, *77*, 073404.
[11] W. Chen, S. Chen, D. C. Qi, X. Y. Gao, A. T. S. Wee, *J. Am. Chem. Soc.* **2007**, *129*, 10418.
[12] T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, *Science* **2006**, *313*, 951.
[13] J. K. Kariuki, M. T. McDermott, *Langmuir* **1999**, *15*, 6534.
[14] J. L. Bahr, J. M. Tour, *J. Mater. Chem.* **2002**, *12*, 1952.
[15] R. N. Grass, E. K. Athanassiou, W. J. Stark, *Angew. Chem.* **2007**, *119*, 4996; *Angew. Chem. Int. Ed.* **2007**, *46*, 4909.
[16] L. P. Hammett, *J. Am. Chem. Soc.* **1937**, *59*, 96.
[17] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165.
[18] C. Combellas, F. Kanoufi, J. Pinson, F. I. Podvorica, *J. Am. Chem. Soc.* **2008**, *130*, 8576.
[19] E. Lyman et al., *Scanning Electron Microscopy, X-Ray Microanalysis and Analytical Electron Microscopy*, Plenum, New York, **1990**.
[20] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, L. Wirtz, *Nano Lett.* **2007**, *7*, 238.
[21] D.-E. Jiang, B. G. Sumpter, S. Dai, *J. Phys. Chem. B* **2006**, *110*, 23628.
[22] F. Miao, S. Wijeratne, Y. Zhang, U. C. Coskun, W. Bao, C. N. Lau, *Science* **2007**, *317*, 1530.
[23] C. Berger et al., *Science* **2006**, *312*, 1191.
[24] F. Wang, Y. B. Zhang, C. S. Tian, C. Girit, A. Zettl, M. Crommie, Y. R. Shen, *Science* **2008**, *320*, 206.
[25] E. K. Athanassiou, R. N. Grass, W. J. Stark, *Nanotechnology* **2006**, *17*, 1668.