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Azide-Modified Graphitic Surfaces for Covalent Attachment of Alkyne-Terminated Molecules by "Click" Chemistry

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Functionalization of graphitic surfaces is of fundamental and technological importance because carbon-based materials are used in the fields of energy conversion,[1] molecular electronics,[2] and sensors.[3] A method to graft aryl molecules onto graphitic surfaces by electrochemical reduction of the corresponding aryl diazonium ions is widely used.[4] Aryl radicals formed react with the graphene sheets to form direct C−C bonds.[5] However, the radical intermediate leads to formation of multilayer structures of aryl molecules ranging from 0.7 to 15 nm in height on the surface.[6] Such multilayers are not ideal for coupling redox molecules to the electrode because of the ill-defined electron-transfer path. Methods recently developed to couple alkynes[7] require high-temperature treatment of up to 400 °C, and alkenes[3] require photochemical treatment, limiting these methods to molecules stable to high temperature and radiation, respectively. Other general methods of coupling molecules to graphitic surfaces are oxidative in nature.[5,8] Oxidative methods form various oxygenated functional groups on graphite,[9] making it difficult to understand the exact nature of the linker between the surface and the molecule.

We explored the possibility of preparing azide-modified graphitic surfaces to couple molecules in a highly selective orientation and with a well-defined linker. Azides allow coupling of alkyne-terminated molecules via Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition,[10,11] popularly known as a "click" reaction. This reaction is extremely selective and high yielding while utilizing very mild reaction conditions. The product of the reaction is the stable heterocyclic linker, 1,4-disubstituted 1,2,3-triazole. Azides and alkynes are essentially inert to molecular oxygen, various solvents including water, and common reaction conditions in organic synthesis. These advantages are particularly useful for attaching multifunctional molecules to surfaces[12] and suggest that an azide-modified graphitic surface would be a highly versatile platform for attachment of a variety of functional molecules.

In this communication, a one-step chemical method to prepare azide-modified graphitic surfaces is reported using iodine azide as the reagent.[13,14] The azide groups are introduced at the graphitic edges, presumably via a Hassner-type addition of IN_3 to the double bonds and subsequent elimination of HI (Figure 1). X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry studies were used to characterize the azide-modified graphitic surface.

Pyrolyzed photoresist films formed on silicon substrates were used as graphitic surfaces.[15] The surfaces were modified with azides by immersing in an acetonitrile solution containing 10 mM iodine azide. An XPS survey scan of the iodine azide-treated graphitic surface showed nitrogen peaks corresponding to the presence of azides. Peaks due to iodine atoms corresponding to only 10% of the surface coverage of azides (vide infra) were also observed. These observations suggest that addition of iodine azide to the double bonds at the graphene sheets is followed by a spontaneous elimination of hydrogen iodide to form aromatic azides. The surface coverage of the azide groups was determined to be (4.4 ± 1.3) × 10^{13} molecules/cm^2 for an immersion time of 20 min. Extending the immersion time to 60 min gave an azide surface coverage of (7.3 ± 1.4) × 10^{13} molecules/cm^2. Further increase up to 16 h did not show any significant increase in the surface coverage. During the course of iodine azide treatment and subsequent reactions, the surface coverage of oxygen remained at the value obtained after pyrolysis of the photoresist, around 2.2 × 10^{14} atoms/cm^2.

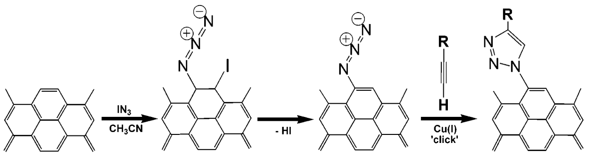

Figure 1. Scheme of the modification of graphene sheets with azides and coupling to terminal alkynes.

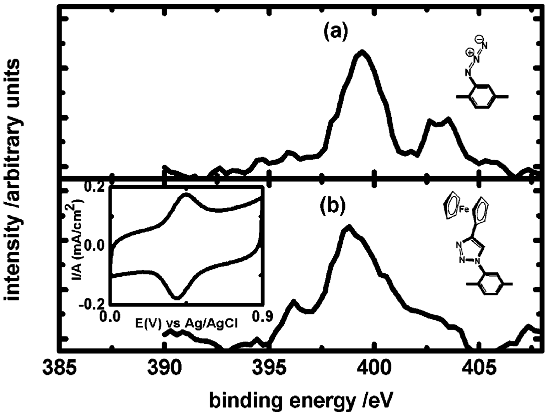

Figure 2. N1s XPS data obtained at a graphitic surface (a) before and (b) after click reaction with ethynylferrocene. The inset shows a cyclic voltammogram obtained at 5 V/s after attachment of ethynylferrocene.

Figure 2a shows the XPS N1s data obtained at an iodine azide-treated surface. There are peaks at 399 and 403 eV with a peak area ratio of 2:1 as expected for azide groups on the surface.[16] Figure 2b shows the XPS data obtained at the same surface after undergoing the click reaction with 20 μM ethynylferrocene in 3:1 DMSO/H_2O solution containing 400 μM Cu(I)(tris(benzyltriazolylmethyl)amine)(NO_3) as catalyst. The absence of the peak at 403 eV and broadening of the peak at 399 eV is consistent with formation of a 1,2,3-triazole. The area under the broader peak at 399 eV after the click reaction is equal to the area under the peaks at 403 and 399 eV before the click reaction. These observations suggest that the azide present on the surface forms the 1,2,3-triazole with 100% yield. The presence of ferrocene on the surface was confirmed by the XPS $2p_{3/2}$ and $2p_{1/2}$ peaks for iron at 706 and 720 eV, respectively (see Supporting Information). The azide was stable for several minutes of exposure to the Al Kα radiation. After 10 min, the ratio of the area of the 399 eV peak to the 403 eV

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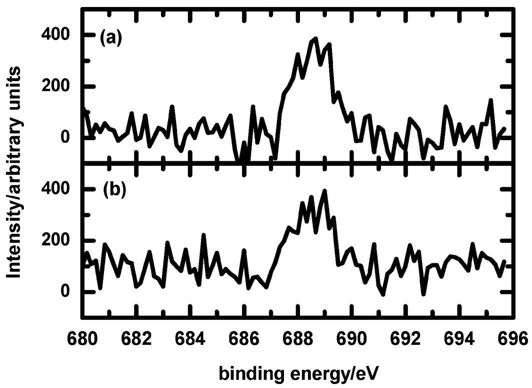

Figure 3. F1s XPS data (a) before and (b) after treating a 1-ethynyl-4-(trifluoromethyl)benzene-modified surface with 1 M HCl at 55 °C for 60 min.

peak decreased from 1:2 to 1:3. We presume that extensive exposure to X-radiation causes elimination of dinitrogen.

The inset of Figure 2b shows the cyclic voltammetric data obtained at a ferrocene-modified graphitic surface in 1 M aqueous perchloric acid. A well-defined redox peak ($E° = 0.42$ V vs Ag/AgCl/KCl) was observed. The peak current was found to vary linearly with scan rate from 1 to 10 V/s and is consistent with a surface-immobilized ferrocene. The full-width at half-maximum of the anodic and cathodic peaks were found to be roughly 0.15 V, approximately 50% greater than the ideal Nernstian width,[17] suggesting some heterogeneity or interaction among the ferrocenes. The charge under the reduction and oxidation peaks gave a surface coverage of 2.0×10^{13} molecules/cm^2. This surface coverage value agrees with the values obtained for azides using XPS analysis. No peaks corresponding to the ferrocene redox couple were observed when an azide-modified graphitic surface was treated with ethynylferrocene in the absence of the Cu(I) catalyst or when a bare graphitic surface was immersed in a solution containing ethynylferrocene and the Cu(I) catalyst. The voltammogram of the azide-modified surfaces was similar to bare surfaces, suggesting the residual iodine is not electrochemically oxidized. Edge-plane graphite has also been treated with iodine azide and subsequently coupled to ethynylferrocene by the click reaction. Higher coverages of up to 1.4×10^{14} molecules/cm^2 were obtained. Similar experiments on basal-plane graphite did not show a surface-immobilized ferrocene redox couple. These results support our model of azides attached at the edges of graphene sheets, as shown in Figure 1.

The azide-modified graphitic surfaces were treated with a solution of 20 μM 1-ethynyl-4-(trifluoromethyl)benzene in 3:1 DMSO/H_2O containing 400 μM Cu(I)(tris(benzyltriazolylmethyl)amine)(NO_3) as a catalyst to form a (trifluoromethyl)benzene-modified surface. Figure 3a shows the F1s XPS peak due to fluorine atoms present on this surface. A surface coverage of 1.5×10^{13} molecules/cm^2 was estimated for the (trifluoromethyl)benzene groups using the XPS peaks of fluorine and carbon (see Supporting Information). Figure 3b shows the fluorine peaks observed at the same surface after an acid hydrolysis treatment (1 M HCl for 60 min at 55 °C). No significant change in fluorine or oxygen surface coverage was observed, suggesting the triazole linker is stable to acid hydrolysis.

In conclusion, a method to couple functional molecules to graphitic carbon surfaces through click chemistry has been developed. The wide variety of functional groups that are orthogonal to the click reaction and the stability of the 1,2,3-triazole promise a wide range of applications for these surfaces.

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Supporting Information Available: Experimental procedures for preparing graphitic surfaces, azide-modified graphitic surfaces, and ethynylferrocene-modified and 1-ethynyl-4-(trifluoromethyl)benzene-modified graphitic surfaces. XPS data showing peaks due to iron on ferrocene-modified surface. XPS data showing the fluorine region before and after modifying the surface with (trifluoromethyl)benzene. XPS data showing the peaks due to C, N, O, and F before and after 1 M HCl hydrolysis. Surface coverage calculations for azide, I, O, and (trifluoromethyl)benzene groups. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Kinoshita, K. *Carbon: Electrochemical and Physicochemical Properties*; Wiley: New York, 1988.
(2) Ranganathan, S.; Steidel, I.; Anariba, F.; McCreery, R. L. *Nano Lett.* **2001**, *1*, 491−494.
(3) Sun, B.; Colavita, P. E.; Kim, H.; Lockett, M.; Marcus, M. S.; Smith, L. M.; Hamers, R. J. *Langmuir* **2006**, *22*, 9598−9605.
(4) Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 5883−5884.
(5) Downard, A. J. *Electroanalysis* **2000**, *12*, 1085−1096.
(6) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429−439.
(7) Ssenyange, S.; Anariba, F.; Bocian, D. F.; McCreery, R. L. *Langmuir* **2005**, *21*, 11105−11112.
(8) Yacynych, A. M.; Kuwana, T. *Anal. Chem.* **1978**, *50*, 640−645.
(9) Boehm, H. P. *Carbon* **2002**, *40*, 145−149.
(10) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596−2599.
(11) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057−3064.
(12) Devaraj, N. K.; Decreau, R. A.; Ebina, W.; Collman, J. P.; Chidsey, C. E. D. *J. Phys. Chem. B* **2006**, *110*, 15955−15962.
(13) Hassner, A. *Acc. Chem. Res.* **1971**, *4*, 9−16.
(14) Devadoss, A.; Devaraj, N. K.; Chidsey, C. E. D. U.S. Patent Application for Preparation of Azide-Modified Carbon Surfaces for Coupling to Various Species, 2007.
(15) Ranganathan, S.; McCreery, R.; Majji, S. M.; Madou, M. *J. Electrochem. Soc.* **2000**, *147*, 277−282.
(16) Collman, J. P.; Devaraj, N. K.; Eberspacher, T. P. A.; Chidsey, C. E. D. *Langmuir* **2006**, *22*, 2457−2464.
(17) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; Wiley: New York, 2001; p 591.

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