Covalent Modification of Graphene and Graphite Using Diazonium Chemistry: Tunable Grafting and Nano-Manipulation

John Greenwood, Thanh Hai Phan, Yasuhiko Fujita, Zhi Li, Oleksandr Ivasenko, Willem Vanderlinden, Hans Van Gorp, Wout Frederickx, Gang Lu, Kazukuni Tahara, Yoshito Tobe, Hiroshi Ujii, Stijn F. L. Mertens, Steven De Feyter

Supplementary Information

Electrochemical response

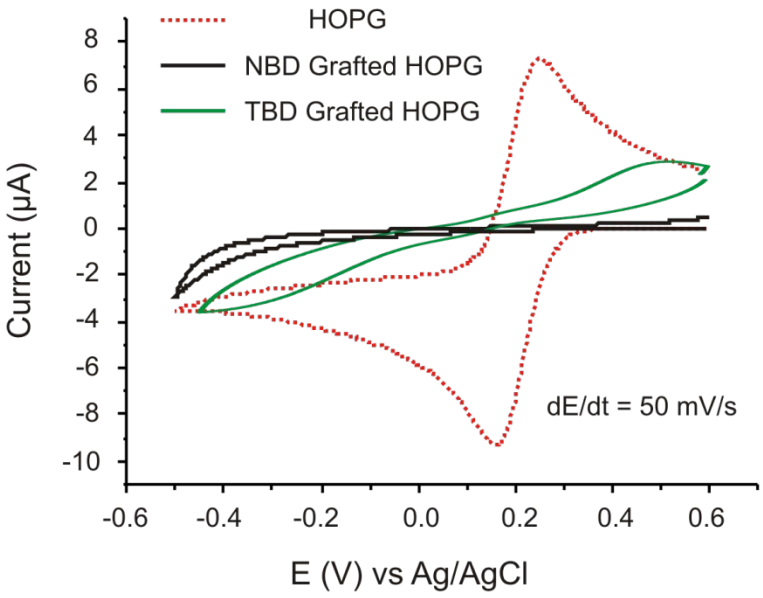


Figure S1. Cyclic voltammograms of bare HOPG (red dotted curve), modified HOPG after 4-NBD grafting (1mM) (black curve), and 3,5-TBD grafting (1mM) (green curve), in 1 mM $K_3Fe(CN)_6$ + 0.2 M Na_2SO_4 electrolyte.

We have employed the charge transfer properties of a suitable redox probe, $K_3Fe(CN)_6$, to analyze the quality of the grafted film on HOPG. Figure S1 shows the CVs of bare HOPG, and of HOPG after grafting of 4-NBD and of 3,5-TBD in 1 mM $K_3Fe(CN)_6$. For bare HOPG, quasi-reversible redox behavior is observed (red dotted curve), with peaks centering around E_f = + 0.2 V *vs* Ag/AgCl and a peak separation of 80 mV. After grafting of 4-NBD, the redox current is almost completely blocked (black curve), in accordance with surface coverage by a non-conducting polyaryl layer.[1-2] For 3,5-TBD-grafted HOPG (green curve), an intermediate degree of blocking is observed, characterized by strongly suppressed redox peaks with large separation. This behavior points at a blocking layer with point defects, in accordance with the structure observed in STM.

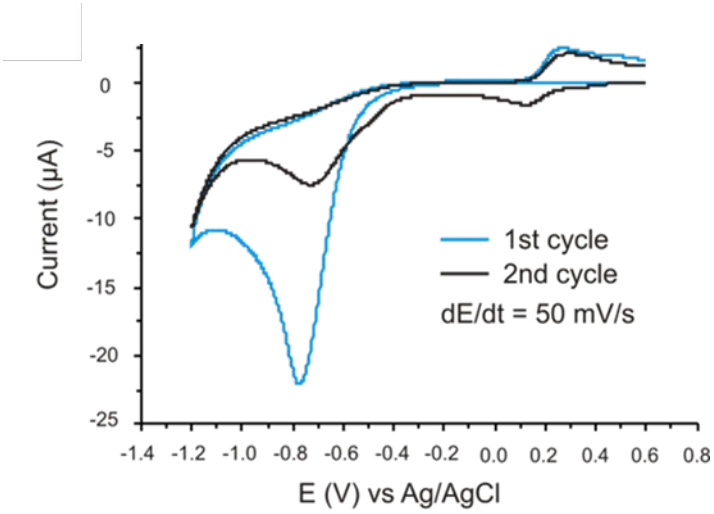


Figure S2. Cyclic voltammetry (first two cycles) of 4-NBD (1mM) grafted on HOPG in 0.1 mM $HClO_4$**.** Scan rate 50 mV s^{-1}.

Electrochemical characterization of the modified surface has been often used to estimate the number of adsorbed molecules, in cases where a redox label is present. In the case of 4-NBD, the

electroactivity of the nitrophenyl group allows such estimation. To this end, after grafting, 4-NBD modified HOPG was washed with Milli-Q water to remove physisorbed material and then transferred to 0.1 M $HClO_4$. The two first cyclic voltammetric cycles in perchloric acid are shown in Figure S2. During the first cycle, an irreversible reduction peak is observed at E = –0.78 V *vs* Ag/AgCl. Following this reduction, a quasi-reversible pair of redox peaks appears, centered around +0.22 V. In accordance with previous studies,[3-6] the irreversible reduction peak originates from the reduction of the grafted nitrophenyl groups to the corresponding aminophenyl and/or hydroxylaminophenyl groups. The quasi-reversible pair of redox peaks is attributed to the hydroxylaminophenyl/nitrosophenyl redox couple. Based on the charges involved, a surface coverage of 11 x 10^{-10} mol cm^{-2} can be estimated, which implies that a multilayer is formed.

Raman Spectroscopy and Scanning Tunneling Microscopy

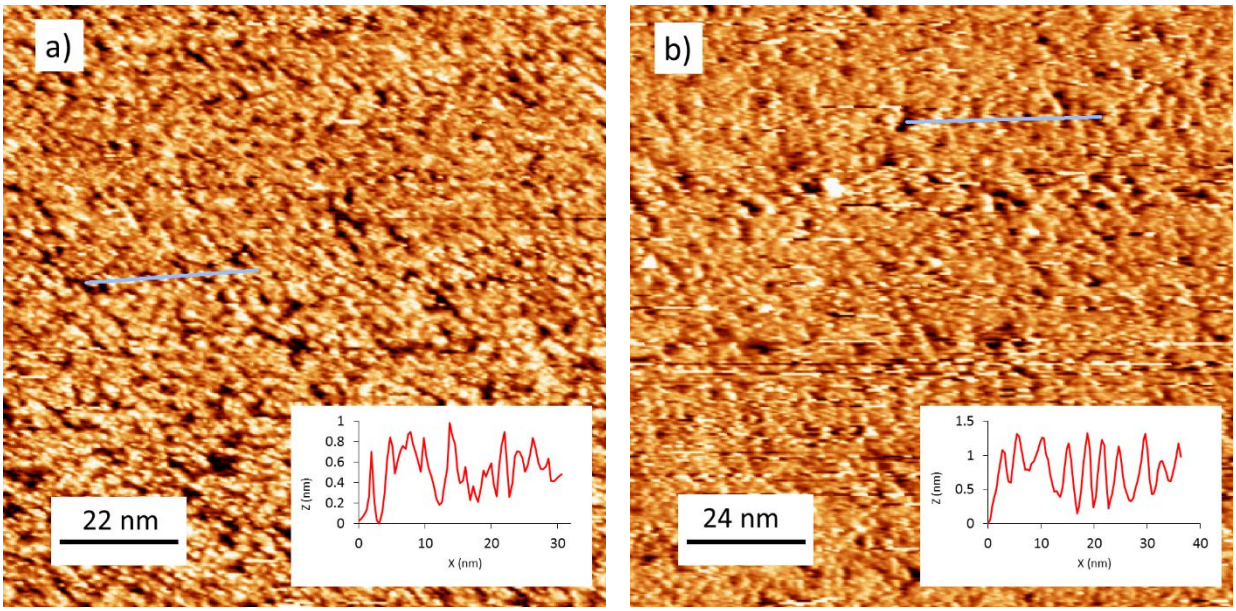
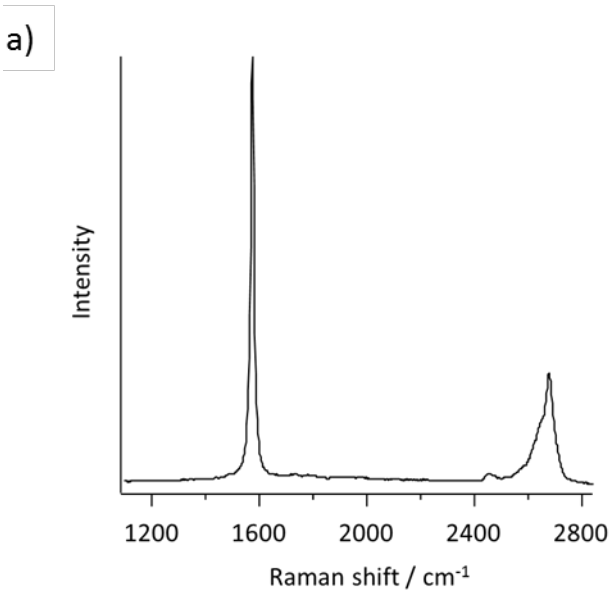
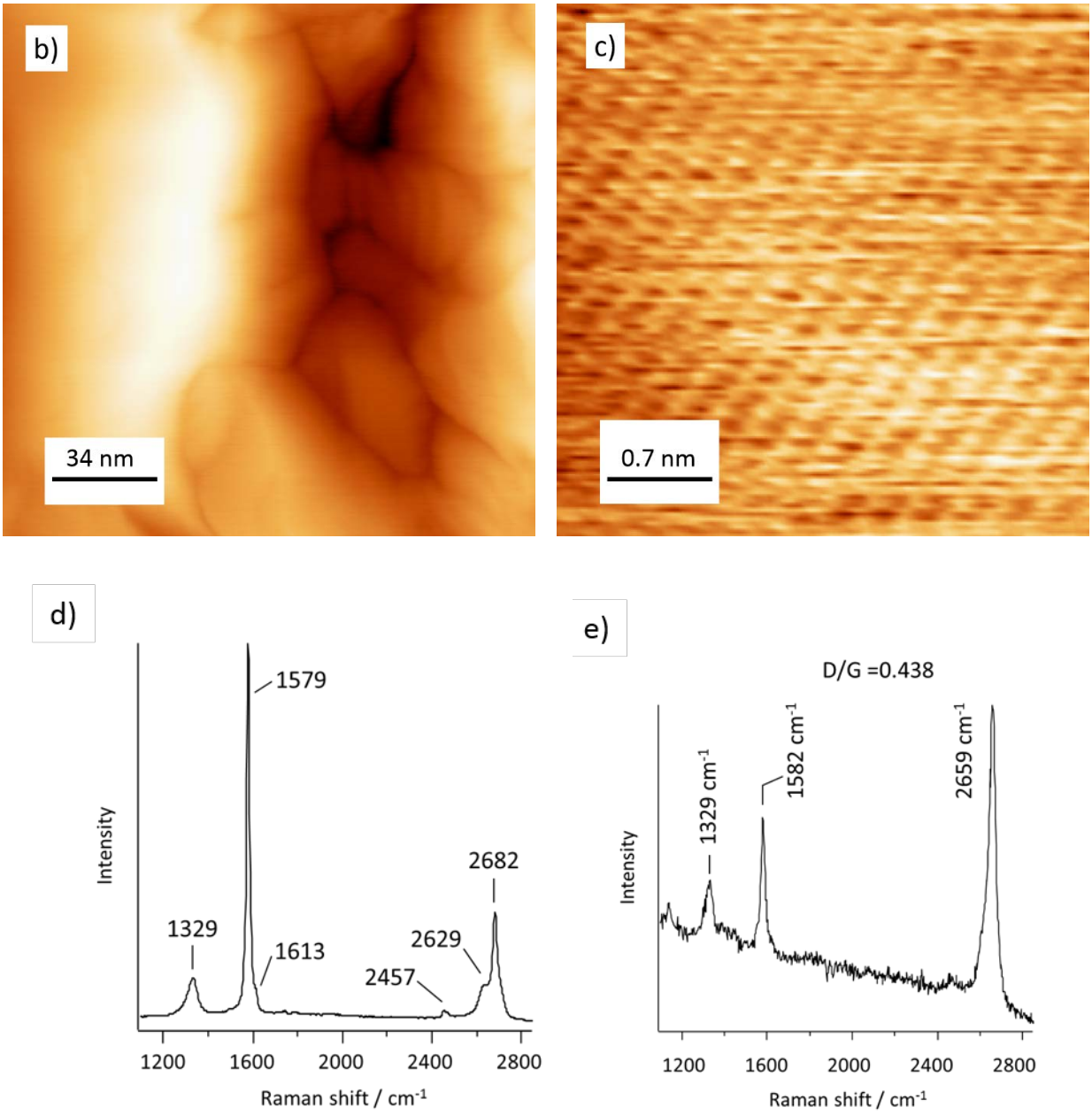


Figure S3. STM images of HOPG after grafting of 3,5-TBD from (a) 5 mM (I_{set} = 0.08 nA and V_{bias} = –0.4 V) and (b) 10 mM solutions (I_{set} = 0.08 nA and V_{bias} = –0.4 V).




b)
34 nm
c)
0.7 nm
d)
1579
1329
1613
2629
2457
2682
Intensity
1200
1600
2000
2400
2800
Raman shift / cm-1
e)
D/G =0.438
1329 cm-1
1582 cm-1
2659 cm-1
Intensity
1200
1600
2000
2400
2800
Raman shift / cm-1

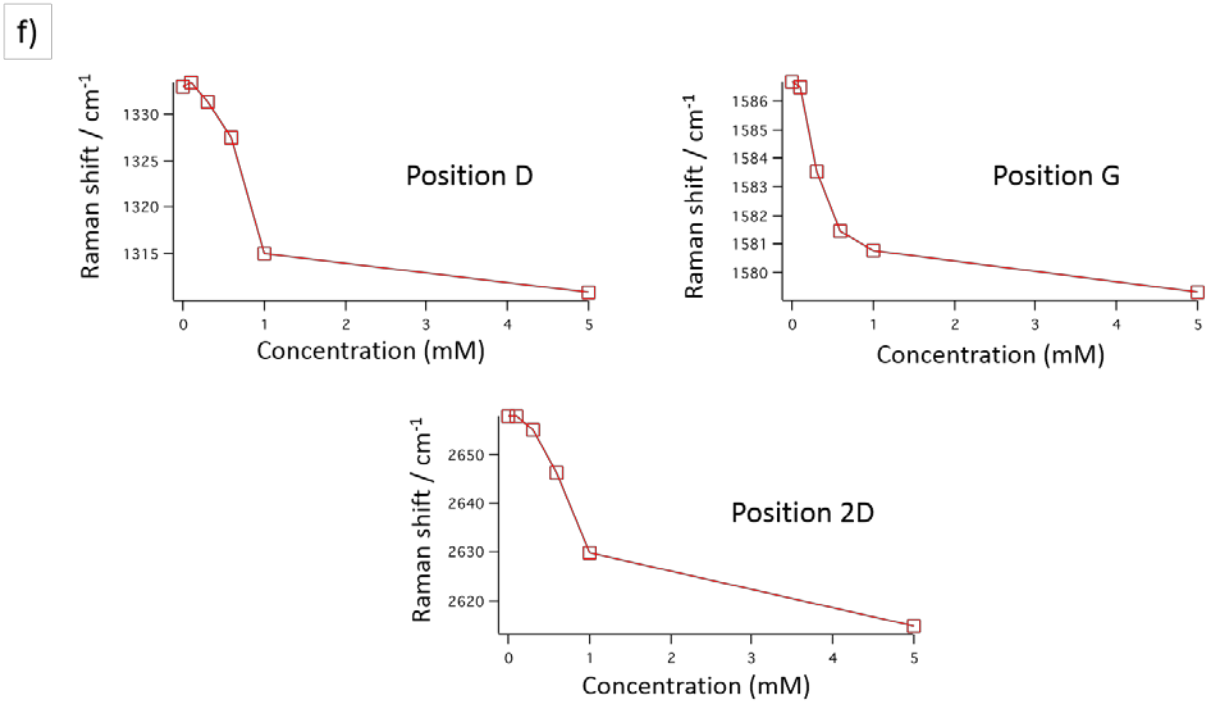


Figure S4. (a) Raman spectra for the bare HOPG used. The absence of a significant D-band indicates good sample quality. (b) Large scale (I_{set} = 0.08 nA, V_{bias} = 0.7 V) and (c) high resolution (I_{set} = 0.2 nA, V_{bias} = 0.01 V) STM images of graphene on Cu. (d) Raman spectrum of 3,5-TBD (10 mM) on HOPG and of (e) 4-NBD (5 mM) on graphene on Cu. (f) Relative Raman shift of the D-, G-, and 2D-bands as a function of 3,5-TBD concentration.

Height profile analysis

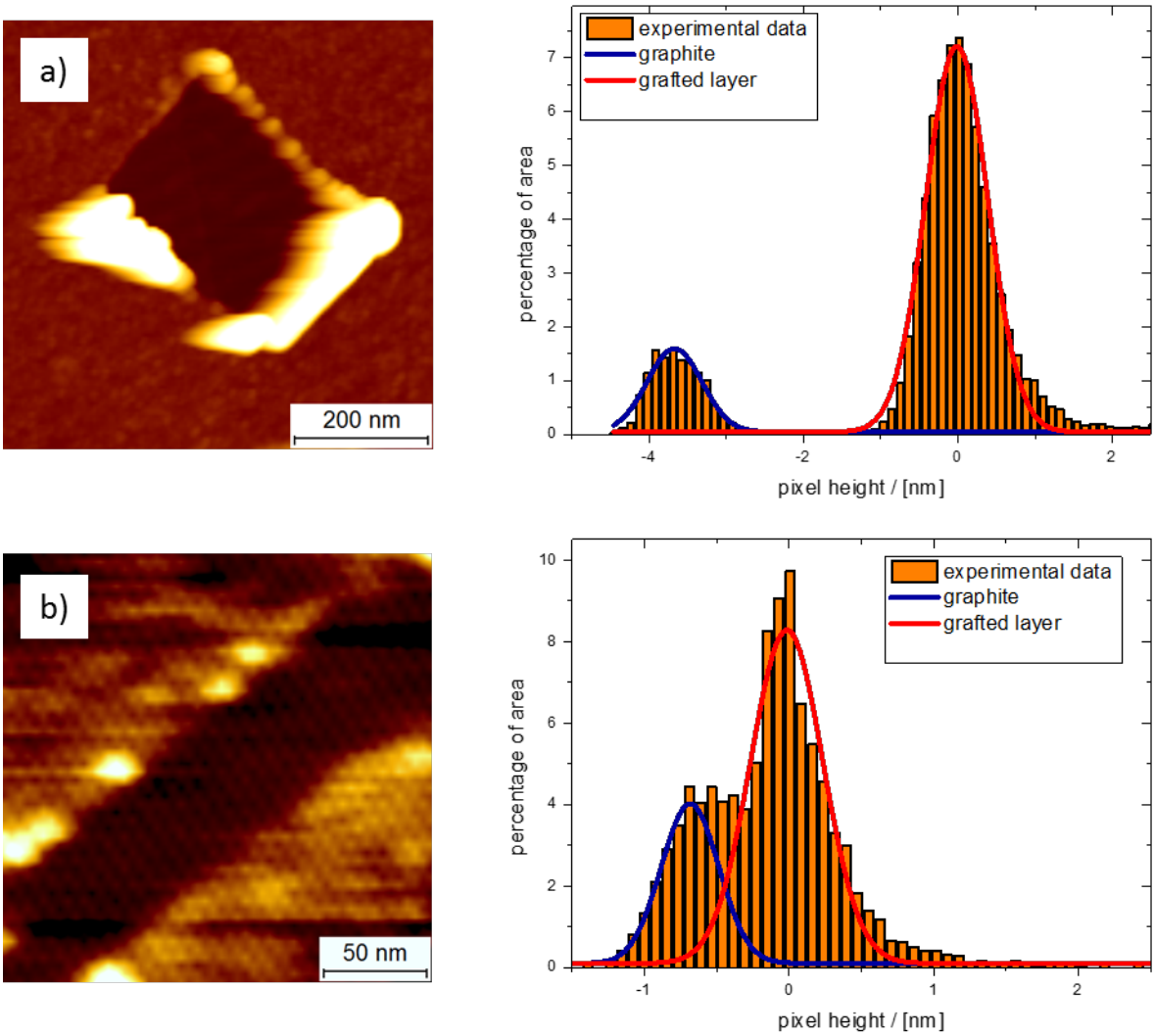


Figure S5. AFM tip scratching image and histogram plot for (a) 4-NBD (1 mM) and (b) 3,5-TBD (1 mM) modified HOPG.

References

1. Lehr, J.; Williamson, B. E.; Downard, A. J., Spontaneous Grafting of Nitrophenyl Groups to Planar Glassy Carbon Substrates: Evidence for Two Mechanisms. *J. Phys. Chem. C* **2011,** *115*, 6629-6634.
2. Hossain, M. Z.; Walsh, M. A.; Hersam, M. C., Scanning Tunneling Microscopy, Spectroscopy, and Nanolithography of Epitaxial Graphene Chemically Modified with Aryl Moieties. *J. Am. Chem. Soc.* **2010,** *132*, 15399-15403.
3. Barriere, F.; Downard, A. J., Covalent Modification of Graphitic Carbon Substrates by Non-Electrochemical Methods. *J. Solid State Electrochem.* **2008,** *12*, 1231-1244.
4. Pinson, J.; Podvorica, F., Attachment of Organic Layers to Conductive or Semiconductive Surfaces by Reduction of Diazonium Salts. *Chem. Soc. Rev.* **2005,** *34*, 429-439.
5. Stewart, M. P.; Maya, F.; Kosynkin, D. V.; Dirk, S. M.; Stapleton, J. J.; McGuiness, C. L.; Allara, D. L.; Tour, J. M., Direct Covalent Grafting of Conjugated Molecules onto Si, GaAs, and Pd Surfaces from Aryidiazonium Salts. *J. Am. Chem. Soc.* **2004,** *126*, 370-378.
6. Malmos, K.; Dong, M. D.; Pillai, S.; Kingshott, P.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K., Using a Hydrazone-Protected Benzenediazonium Salt to Introduce a near-Monolayer of Benzaldehyde on Glassy Carbon Surfaces. *J. Am. Chem. Soc.* **2009,** *131*, 4928-4936.