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High resolution imaging of functional group distributions on carbon surfaces by tapping mode atomic force microscopy

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Here we report, for the first time, the high resolution imaging of hydrophilic, polar functional group distributions on flat carbon surfaces by phase contrast in noncontact tapping mode AFM.

The presence of chemical functional groups, particularly oxygen groups, on the surface of carbon materials (from graphite to carbon nanofibres and nanotubes) plays a crucial role in their interfacial behaviour, thus determining their applicability and performance in fields such as electrochemistry[1–4] or heterogeneous catalysis.[5–7] In this context, the detection of the mentioned groups and, most significantly, the visualization of their lateral spatial distribution with very high resolution (of the order of just a few nm or below) becomes of the utmost importance. However, the latter task lies beyond the capabilities of most surface characterization techniques (*e.g.*, infrared or X-ray photoelectron spectroscopies), which are only able to provide spatially averaged information.[1] An alternative approach potentially suitable for this purpose would be the use of scanning probe microscopies, for instance, atomic force microscopy (AFM). Nevertheless, the attempts undertaken to date in this regard for the detection of functional groups/chemically active sites on carbon surfaces have been unsuccessful,[8] or have relied on the selective growth of metal or semiconductor nanoparticles, which are readily observable by AFM topographic imaging, at the surface functionalities, as two recent examples on carbon nanotubes demonstrate.[9,10]

In the present work, we report for the first time a more direct approach to the imaging of oxygen functional group distributions on flat carbon surfaces with very high resolution by phase contrast in tapping mode AFM. The method is based on the detection of the local physicochemical changes that the presence of the polar, hydrophilic surface oxygen groups induce in their vicinity. Results are presented for highly oriented pyrolytic graphite (HOPG) with oxygenated multiatom vacancies produced in a controlled fashion by oxygen plasma etching.

To create the oxygenated sites, freshly cleaved HOPG surfaces were exposed to a microwave oxygen plasma for a few seconds.[11] Scanning tunneling microscopy (STM) was employed to verify that surface defects were developed. Subsequently, tapping mode AFM measurements were conducted on the plasma-oxidized samples. Height and phase images were acquired simultaneously in constant amplitude mode and under different tip-sample interaction regimes (noncontact and intermittent contact), which were established by first recording phase-distance curves and settting the free and setpoint amplitudes of cantilever oscillation appropriately.[12] The STM/AFM observations were carried out under ambient conditions with a Nanoscope Multimode IIIa (Digital Instruments).

Fig. 1 demonstrates by means of STM the production of atomic-sized defects on the HOPG surface following very short plasma treatments. As expected, the untreated sample appears completely flat and featureless [Fig. 1(a)], displaying the typical triangular pattern of graphite in atomic scale images. By contrast, after a 4 s exposure to the oxygen plasma, small (~1 nm wide) protrusions (bright spots) are observed to develop [Fig. 1(b)]. Furthermore, following a 6 s treatment a greater density of protrusions is noticed [Fig. 1(c)], but in this case the small spots coexist with much larger protrusions (up to 5 nm wide). Fig. 1(d) shows one of these large protrusions at the top left corner of the image. It is also noticed in Fig. 1(d) that the regions outside the bright spots retain the atomic structure of perfect graphite. The protrusions are interpreted as surface atomic vacancies created through the abstraction of C atoms by active oxygen from the plasma,[11,13] and reflect an enhancement in electronic density near the Fermi level in the atoms surrounding the vacancy.[11,14,15] Moreover, it is also known that the size of the STM protrusion increases with the number of missing atoms in the graphite vacancy.[14] Therefore the 1 nm-wide protrusions of the 4 s sample [Fig. 1(b)] are ascribed to single-atom vacancies, since they were the first and smallest features encountered in any plasma etching experiment, whereas the larger protrusions of the 6 s sample [Fig. 1(c) and (d)] arise from multiatom vacancies formed by the expansion of the former after slightly longer etching times.

Due to the very nature of the oxygen plasma etching process[13] and the fact that the HOPG samples are exposed to the ambient air after the treatment,[16] the atomic vacancies are expected to possess a considerable amount of oxygen adsorbed in the form of functional groups (*e.g.*, carboxyl). In fact, we have verified by X-ray photoelectron spectroscopy (XPS) that this is the case for severely treated HOPG samples. However, the samples considered here display oxygen concentration levels below the detection limit of XPS.

Fig. 2 demonstrates that tapping mode AFM phase images are able to detect the presence of the hydrophilic oxygen groups on the defects created by the plasma. Fig. 2(a) and (c) show height and corresponding phase images, respectively, of the 6 s sample

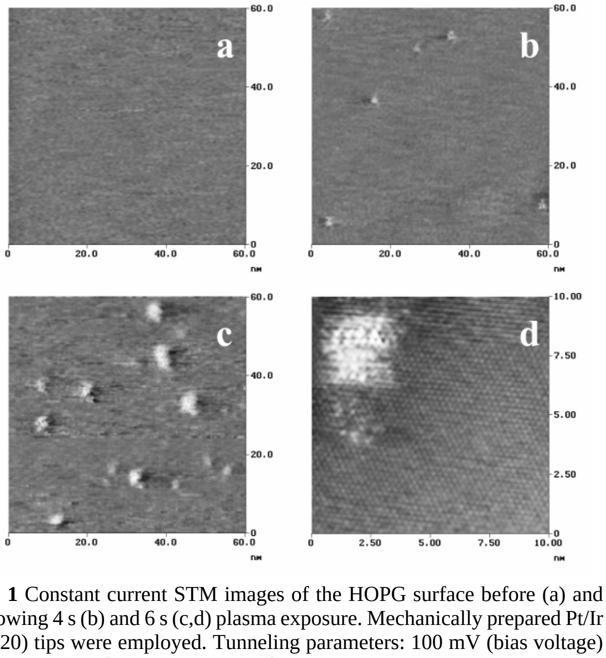

Fig. 1 Constant current STM images of the HOPG surface before (a) and following 4 s (b) and 6 s (c,d) plasma exposure. Mechanically prepared Pt/Ir (80/20) tips were employed. Tunneling parameters: 100 mV (bias voltage) and 1 nA (tunneling current). *Z* scale: 0–1 nm.

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acquired in the noncontact regime. Fig. 2(b) and (d) also present height and phase images, respectively, obtained on the same location as Fig. 2(a) and (c), but in this case in the intermittent contact regime. Small spots (4–8 nm wide and bright or dark, depending on the type of image) decorate the sample surface. They appear especially well defined in the intermittent contact height image [Fig. 2(b)], so they can be used to locate their counterparts on the phase images. One spot (marked by a black circle) is particularly noticeable in the phase images. The spots were never observed in any of the tapping mode images of untreated or 4 s plasma-treated HOPG, so their observation in the 6 s sample is attributed to the presence of the multiatom vacancies developed by this treatment. Also noticed in both height images is a shallow trench (0.1–0.2 nm deep). This type of feature was not created by the plasma (it is frequently found in pristine HOPG) and it is not a one-monolayer-deep strip of missing C atoms on the very surface, since its depth is clearly below that of a single graphene (0.335 nm). We have also verified that these trenches do not recede upon air oxidation at 650 °C, in contrast to defects exposing unsaturated sp^2 bonds.[17] Therefore, they are interpreted to be subsurface structural defects covered by a few (slightly curved) perfect graphenes.[18]

Tapping mode AFM phase images can be interpreted in terms of energy dissipated by the tip-sample interaction,[19] in such a way that more dissipative areas appear brighter (darker) in the noncontact (intermittent contact) phase images.[12] From Fig. 2(c) and (d), it is seen that the plasma-induced defects dissipate more energy than the unaltered areas of HOPG. In the specific case of noncontact situations, the origin of the energy dissipation has been shown to be the presence of a water layer on the surface.[12,20,21] Therefore, since hydrophilic regions bear thicker water layers on their surface than hydrophobic areas do, more energy will dissipate over the former in the noncontact regime. This has been previously observed on the micrometer scale on mixed CH_3- and COOH-terminated self assembled monolayers,[22] whereas this work is focused on extremely local observations. Now, for the present case, the atomic vacancies created by the plasma are expected to possess oxygen functionalities,[13,16] where water adsorption is strongly favoured,[23] particularly compared with the highly hydrophobic, unaltered areas of HOPG. It is then concluded that the bright spots in the noncontact phase images [Fig. 2(c)] are reflecting the presence of hydrophilic oxygen groups in the multiatom vacancies, and so this type of image provides a map of the spatial distribution of such groups on the surface. The fact that the trench observed in the height images appears transparent in the noncontact phase image [Fig. 2(c)] is consistent with this conclusion: as its very surface is perfect graphite, it must not possess functional groups, being as hydrophobic as the unaltered areas of the sample. However, the trench appears more dissipative than pristine areas in intermittent contact [Fig. 2(d)], implying that in this regime dissipation channels reflecting the structural (and not the chemical) heterogeneity of the sample must be active.

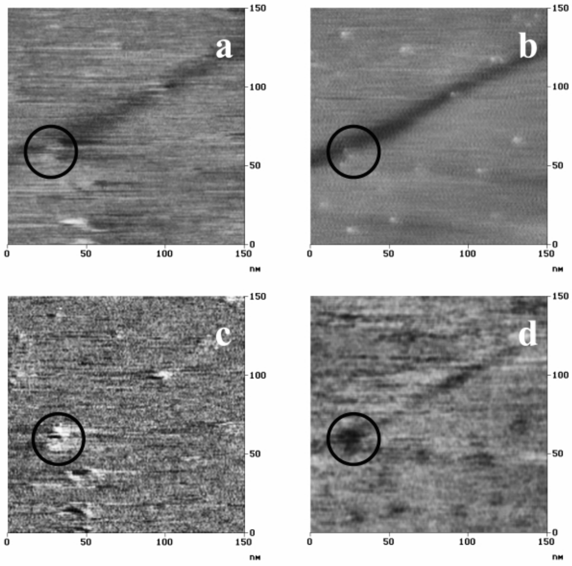

Fig. 2 Tapping mode AFM images of the HOPG surface after oxygen plasma treatment for 6 s. (a) and (c): height and phase images, respectively, obtained in the noncontact regime. (b) and (d): height and phase images, respectively, acquired in the same location as (a) and (c) but in the intermittent contact regime. *Z* scale: 0–2 nm for (a) and (b) and 0–8° for (c) and (d).

In conclusion, we have shown that very high resolution imaging of functional group distributions on carbon surfaces is possible by phase contrast in noncontact tapping mode AFM. The phase contrast in this regime can be related to local variations in hydrophilicity and, therefore, to the distribution of polar oxygen functional groups, in this case created by controlled oxygen plasma etching. Work is currently under way to apply the methodologies outlined here to the field of carbon nanotubes aiming at (i) functionalizing nondestructively the nanotube sidewalls by highly controlled plasma etching, and (ii) detecting and mapping the subsequent minute chemical changes by noncontact phase imaging.

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