Atomic-Resolution Imaging of Graphite–Water Interface by Frequency Modulation Atomic Force Microscopy

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Received November 1, 2011; accepted November 6, 2011; published online November 24, 2011

Graphite has a layered structure, with neighboring layers being bound by weak van der Waals force, while carbon atoms in a layer are strongly connected to each other by sp² covalent bonds. The graphite surface has a hydrophobic nature and the graphite–water interface has been of great interest to researchers, especially in recent years.¹⁻⁵ A molecular dynamics simulation indicates that there is a uniform water layer at the graphite/water interface.⁶⁻⁸ Although much attention has been paid to the difference between structured water layers on hydrophilic surfaces and those on hydrophobic surfaces, there have been few sufficient experimental studies on atomic/molecular-scale solid–water interface structures.

Recently, we have developed a high-resolution frequency modulation atomic force microscope (FM-AFM) working in liquid environments and successfully obtained atomic-resolution images of mica and calcite using stiff cantilevers with a small oscillation amplitude.⁹⁻¹⁰ In addition to its noninvasive, high-resolution imaging capability, the FM-AFM allows us to visualize solvation structures at solid/liquid interfaces through quantitative measurements of the interaction forces between the tip and sample surfaces.⁹⁻¹⁰ Furthermore, the jump-to-contact, which usually perturbs force-distance measurements near the surface in static-mode AFM, can be avoided using FM-AFM. However, atomic-resolution imaging of the graphite surface in liquids using FM-AFM, to the best of our knowledge, has never been reported. In contrast to the fact that the lattice periodicity of the graphite surface has been routinely detected by static-mode AFM in various environments,¹₀⁻¹² true atomic-resolution imaging of the graphite by FM-AFM has been successfully conducted only under some limited conditions, i.e., by imaging in ultrahigh vacuum (UHV) at low temperatures or by imaging in UHV with an extremely small amplitude using effectively stiff cantilevers.¹³⁻¹⁶ These imaging conditions, which can provide a large Q-factor, a low thermal noise in the cantilever oscillation, and a large force signal,¹³⁻¹⁵ significantly improve the signal-to-noise ratio in FM-AFM. The difficulty in atomic-resolution AFM imaging of the graphite surface probably lies in the relatively weak interaction force between the tip and the surface and also in the small lattice constant. The distance between the nearest neighbor carbon atoms in a graphite layer is 0.142 nm, and the lattice constant, corresponding to the distance between the nearest neighbor hexagons, is 0.246 nm, which is about half of that in a muscovite mica surface. In addition, although a small oscillation amplitude mode can be used in liquid, basically the liquid environment is remarkably unfavorable for high-resolution FM-AFM imaging mainly due to an extremely low Q-factor of the cantilever.

In this study, atomic-resolution imaging of graphite in water was successfully conducted using FM-AFM at room temperature. In addition, we investigated a graphite–water interface by two-dimensional (2D) frequency shift mapping. Structured-water layers on the hydrophobic graphite surface were visualized. The results were compared with a molecular-scale hydration structure on a hydrophilic muscovite mica surface.

We used a newly developed AFM based on a commercial instrument (Shimadzu SPM-9600), where the optics and electronics were considerably modified to significantly reduce the displacement sensor noise in the optical beam deflection sensor, as described in ref.¹⁷ The AFM was controlled using a home-built controller with a field-programmable gate array module programmed with LabVIEW (National Instruments). The instrument was placed in a temperature-regulated enclosure such that the thermal drift in lateral directions during the experiments was kept less than about 0.1 nm/s. The obtained images were processed using the software WSXM (Nanotec Electronica).¹⁸

A clean graphite (0001) surface was prepared by cleavage with an adhesive tape in air and then immediately immersed in ultrapure water. A Si cantilever (Nanosensors PPP-NCH) was also immersed in water after the calibration of its spring constant by Sader’s method,¹⁹ which was 26 N/m in this experiment. The thermal noise spectrum was measured and fitted to a simple harmonic oscillator model so that the resonance frequency of 139 kHz and quality factor of 8.3 were obtained. The fitting also allowed us to estimate the displacement sensor and to evaluate the displacement sensor noise density, which was about 40 fm/√Hz.

Figure 1(a) is an FM-AFM image of a graphite (0001) surface in water obtained in the constant height (variable frequency shift) mode. The average frequency shift was about +167 Hz. The oscillation amplitude of the cantilever was kept constant at 0.21 nm peak-to-peak, which was even smaller than that used in atomic-resolution FM-AFM.
imaging of graphite in UHV with a higher flexural resonance mode in ref. 16. The upper curve in Fig. 1(b) is a cross-sectional profile of the frequency shift measured along line A–B in Fig. 1(a). The period of the corrugated profile is about 0.25 nm, which corresponds to the lattice constant of graphite. The lower curve in Fig. 1(b) shows a corresponding force profile, which was converted by a method described later, indicating the average repulsive force of about 60 pN and a corrugation amplitude of about 15 pN. The FM-AFM imaging with such a small amplitude is considered to be effective for enhancing the sensitivity to the short-range chemical interaction force between the tip and surface, which plays an essential role in atomic-scale AFM imaging.16,20 It is worth mentioning that the high dielectric constant of water might also contribute to the high-resolution imaging because it reduces the long-range van der Waals interaction between the tip and surface, which hinders the detection of the short-range force.21 The van der Waals force (FvdW) between a tip (sphere) and a plane surface is given by

\[ F_{vdW} = -\frac{A}{R^6}z^2, \]

where \( A \), \( R \), and \( z \) are a Hamaker constant, tip radius, and sphere-plane distance, respectively. Because of the lack of the experimental Hamaker constant data on SiO\(_2\) (tip material)–graphite combination, we calculated the Hamaker constants for SiO\(_2\)–vacuum–graphite and SiO\(_2\)–water–graphite, using combining laws of the Hamaker constants,22,23 or the Lifshitz theory.22 The former calculation gave 12 × 10\(^{-20}\) J in vacuum and 1.7 × 10\(^{-20}\) J in water, while the latter showed 12 × 10\(^{-20}\) J in vacuum and 5.6 × 10\(^{-20}\) J in water.22,24 Both calculations indicate that the long-range van der Waals force is considerably decreased with a reduction factor of 7.1 or 2.1.

There have been several related studies on the contrast of graphite surface imaged using UHV FM-AFM.14 It was pointed out that a large repulsive force was detected above \( \alpha \) atom sites, under which another carbon atom is located as a neighboring atom in the c-axis. Thus, the bright spots in Fig. 1(a) are possibly assigned to the \( \alpha \) sites.

A molecular-scale structure at the graphite–water interface was investigated by 2D frequency shift mapping in the following procedure. The resonance frequency shift of the cantilever was recorded while the tip was brought close to the sample. When the frequency shift exceeded a preset value, the tip was retracted to the original position. This process was repeated at the next X-position until we obtained a 2D frequency shift map in an X–Z plane, which is perpendicular to the graphite surface, as shown in Fig. 2(a). The scanned area was 5.4 nm (X) × 2.7 nm (Z). In the figure, we can clearly see one bright band (white arrow) and two adjacent dark bands (black arrows) parallel to the surface (horizontal axis), which reflects the structured-water layer at the graphite/water interface. The details are described later. The above band structure means that the frequency shift maximum and minima are located at almost the same Z-distance in all the frequency shift curves.

A solid curve in Fig. 2(b) is the average curve of all the frequency shift curves composing the map in Fig. 2(a). One maximum and two minima around a Z-distance of 0.5 nm in the curve correspond to the above-mentioned bright and dark bands in Fig. 2(a). This curve was converted into the average force versus distance curve using the formula in ref. 25, which is shown as a red curve in Fig. 2(b). The

![Fig. 1](image_url)

(a) FM-AFM image of the cleaved graphite (0001) surface in water. The image was recorded in the constant height (variable frequency shift) mode. The average frequency shift was +167 Hz. (b) Cross-sectional profile (upper curve) measured on A–B line in Fig. 1(a) and force profile (lower curve).

![Fig. 2](image_url)

(a) 2D frequency shift map at the graphite/water interface. The bright band at the Z-distance of 0.5 nm suggests the existence of the structured water layer. (b) Average frequency shift versus distance curve (blue curve) of all the frequency shift curves in (a). Average force curve obtained using Sader’s formula is also shown as the red curve.20 The large black dots indicate that the average frequency shift in the FM-AFM image in Fig. 1(a) (+167 Hz) corresponds to the average force of about 56 pN.
average frequency shift of 167 Hz during the taking of the FM-AFM image shown in Fig. 1(a) and the corresponding average force of 56 pN are indicated by the black circles on the curves in the figure. The cross-sectional force profile as shown in Fig. 1(b) was also obtained by the same conversion based on the relationship between the frequency shift and force in Fig. 2. We also compared the molecular-scale hydration structure on the hydrophobic graphite surface, described before, with that on a hydrophilic mica surface. Figure 3(a) shows an atomic-resolution topographic image of a cleaved muscovite mica surface in a 1 M KCl aqueous solution with a Si cantilever (Nanosensors PPP-NCHAuD). The honeycomb structure of the alumina silicate layer of mica was clearly resolved. It should be noted that the scanned area in Fig. 3(a) was the same as that in Fig. 1(a) to compare the graphite lattice site with the honeycomb size of the mica.

Figure 3(b) is a 2D frequency shift map obtained on a muscovite mica, which shows a complicated pattern reflecting the site-specific structured-water layers, as reported earlier. This is in remarkable contrast to the 2D frequency shift map on the graphite surface as shown in Fig. 2(a), which exhibits a simpler layered structure without site-specific features. Figure 3(c) shows a comparison between the averaged frequency shift curve measured at the mica–water interface (upper curve) and that measured at the graphite–water interface (lower curve). The distance between the two minima in the mica–water curve is 0.22 nm, while that in the graphite–water curve is 0.32 nm. Since the average distance between water molecules in the bulk phase is 0.28 nm, the difference between the above-mentioned distances is probably related to the hydrophobic/hydrophilic properties of the two surfaces. It should be noted that we have never observed site-specific frequency/force curves on the graphite so far as those in Fig. 3(b). This is, in fact, consistent with the molecular dynamics simulation showing that a uniform (not site-specific) structured-water layer is formed on the graphite surface while the existence of the site-specific structured-water layers at the mica–water interface was theoretically indicated. This non-site-specific feature at the graphite/water interface can be related to either the graphite lattice constant being smaller than the size of the water molecule and/or its hydrophobicity.

In summary, atomic-resolution images of the graphite (0001) surface in water using FM-AFM with a stiff cantilever having a small oscillation amplitude of 0.21 nm peak-to-peak were successfully obtained for all that the interaction between the tip and graphite surface is weak and that the lattice constant (0.246 nm) of the graphite surface is relatively small. Furthermore, we succeeded in obtaining a 2D frequency shift map, which shows the existence of a uniform structured-water layer at the graphite/water interface.

Acknowledgments This work was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, SENTAN Program of the Japan Science and Technology Agency, and Global COE Program of the Japan Society for the Promotion of Science.

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