Full Length Article

Imaging initial formation processes of nanobubbles at the graphite–water interface through high-speed atomic force microscopy

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ABSTRACT

The initial formation process of nanobubbles at solid–water interfaces remains unclear because of the limitations of current imaging techniques. To directly observe the formation process, an astigmatic high-speed atomic force microscope (AFM) was modified to enable imaging in the liquid environment. By using a customized cantilever holder, the resonance of small cantilevers was effectively enhanced in water. The proposed high-speed imaging technique yielded highly dynamic quasi-two-dimensional (2D) gas structures (thickness: 20–30 nm) initially at the graphite–water interface. The 2D structures were laterally mobile mainly within certain areas, but occasionally a gas structure might extensively migrate and settle in a new area. The 2D structures were often confined by substrate step edges in one lateral dimension. Eventually, all quasi-2D gas structures were transformed into cap-shaped nanobubbles of higher heights and reduced lateral dimensions. These nanobubbles were immobile and remained stable under continuous AFM imaging. This study demonstrated that nanobubbles could be stably imaged at a scan rate of 100 lines per second (640 μm/s).

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1. Introduction

Surface nanobubbles are gas-filled structures generated at solid–liquid interfaces and have a spherical cap shape, reaching a height off the surface of less than approximately 100 nm [1–3]. Surface nanobubbles can significantly affect diverse applications, such as the boundary conditions in microfluidics, surface cleaning, and mineral flotation; however, numerous properties of surface nanobubbles remain unclear [4–6]. The unexpected long lifetimes and unusually high contact angles (measured from the water side) of surface nanobubbles have been widely discussed [7–9]. However, the formation process of surface nanobubbles is rarely addressed and remains unclear because a direct observation of this dynamic process is difficult considering current imaging limitations [10].

Optical methods, such as total internal reflection microscopy, confocal fluorescence microscopy, and optical interference-enhanced reflection microscopy, can perform dynamic imaging [11–13]. However, the resolution of these methods is more than several hundred nanometers because of the optical diffraction limitation. Liquid cell electron microscopy has both high spatial and temporal resolution and has been previously used to image the dynamic growth of nanobubbles [10,14,15]. Nevertheless, the electron beam used in this technique can induce nanobubble formation, and interactions between the electron beam and the nanobubbles and water are unavoidable [14–16]. Furthermore, contrast images obtained using this technique cannot be used to simultaneously measure the height and surface radius of surface nanobubbles, which causes some difficulties in contact angle calculations. As a powerful topography measurement tool, atomic force microscope (AFM) has become the principal instrument for visualizing surface nanobubbles [17,18]. High-resolution AFM has revealed that dissolved gas molecules can form various nanostructures at solid–liquid interfaces, including two-dimensional (2D) ordered domains of striped patterns, 2D micropancakes, and 3D surface nanobubbles [19–23]. Observing dynamic nanobubble formation process and structural changes through AFM is difficult because the imaging speed of common AFM is low. Recently, the process of surface nanobubble formation was observed through dynamic-mode AFM at a typically low scan speed, and a nucleation mechanism was proposed according to the AFM measurement [24]. However,

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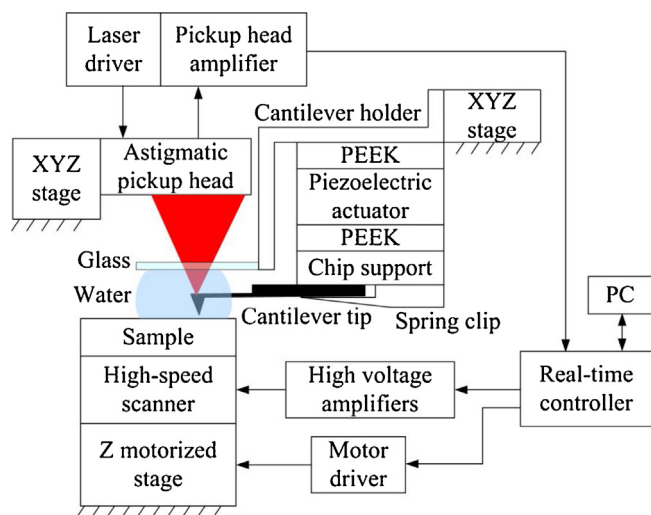**Fig. 1.** Configuration of the HS-AFM system for imaging in the liquid environment.

Fig. 2. Optical images of (a) small cantilever and (b) detection laser spot focused on back side of small cantilever. (c) Excitation spectrum of the small cantilever (USC-F2-k3, Nanoworld) in water.

numerous unknown changes occur during nucleation, and a much higher imaging speed is needed to more comprehensively understand the dynamic changes in gas-filled surface nanostructures. Fortunately, previous developments in high-speed (HS) AFM have achieved notable improvements for imaging soft matter [25–28]. Herein, we report the first HS-AFM imaging of the initial formation process of surface nanobubbles.

2. Material and methods

2.1. Astigmatic atomic force microscope

Astigmatic detection systems have the advantages of having small laser spots, compact size, and low cost [29]. We previously developed astigmatic HS-AFM for use in the air environment [30]. In this study, we further modified the astigmatic HS-AFM to enable imaging in a liquid environment. Fig. 1 shows the configuration of the HS-AFM system. An astigmatic pickup head (TOP1100Sc, TopRay Technologies) was used for detecting cantilever resonances. The laser spot of the pickup head and cantilever can be imaged using an optical imaging module [31]. Fig. 2a displays an optical image of a small cantilever (width × length: 5 μm × 10 μm; USC-F5-k30, Nanoworld). The detection laser spot can be successfully focused on the back side of the small cantilever (Fig. 2b). To enable imaging in the liquid environment, we adopted a cantilever holder design with a glass cover for containing the liquid [32]. When performing dynamic-mode AFM in the liquid environment, piezoelectric excitation may generate undesirable resonance peaks [33]. Therefore, to enhance the excitation quality, the piezoelectric actuator was placed between two polyetheretherketone (PEEK) plates to diminish these spurious resonance peaks. The cantilever chip was clamped using a spring clip that was directly screwed onto a chip support. This design isolates the cantilever from the vibration of other mechanical parts. Fig. 2c presents a typical excitation spectrum of the small cantilever (USC-F2-k3, Nanoworld) in water. The intensity at the cantilever's true resonance frequency (1.05 MHz) was much higher than that at the other spurious resonance peaks. The quality factor evaluated from the excitation spectrum was 32. The typical spring constant of the cantilever USC-F2-k3 is approximately 3 N/m. To achieve HS scanning, we used a flexure-guided scanner with resonance frequencies of 44, 13, and 6 kHz in the z, x, and y directions, respectively [30]. Movement in the fast-scan direction was driven by a sinusoidal waveform to avoid resonances. The
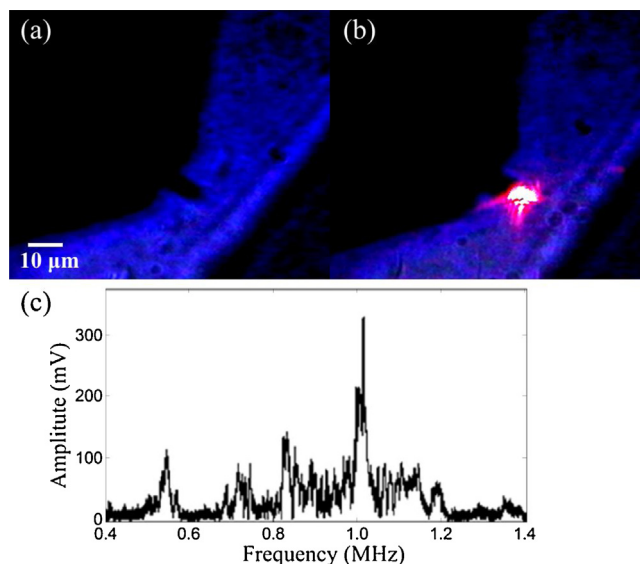
scanning function was programmed in a real-time controller (PXIe System, National Instrument).

2.2. Nanobubbles preparation

The solvent exchange method was used to generate nanobubbles on a freshly cleaved highly oriented pyrolytic graphite (HOPG) substrate, and the nanobubble formation process was imaged through the HS-AFM system [34]. The HOPG substrate was first exposed to deionized water (approximately 20 mL), following which ethanol (99.9%; approximately 20 mL; J T Baker) was injected into the water and mixed. Subsequently, approximately 10 mL of the mixed solution was drawn and removed using a pipette, after which deionized water (approximately 10 mL) was injected into the mixed solution. This process was repeated several times until the ethanol was almost completely replaced with deionized water. Because of the design of our HS-AFM system, the solvent exchange process was performed in an open environment and not a closed-fluid-cell holder, as is typical [19,35,36].

3. Results

3.1. Initial formation process

Ten minutes after the buffer exchange, continuous images were captured under the tapping mode by using the small cantilever (USC-F2-k3, Nanoworld). The free amplitude and the set-point amplitude of the cantilever were 18 and 13 nm, respectively. A scan rate of 10 lines per second (10 l/s; 25 s/frame) was used, and the image size was set to 256 × 256 pixels. We initially observed highly dynamic quasi-2D structures at the interface, which eventually formed stable and immobile cap-shaped nanostructures (interfacial nanobubbles). Fig. 3a–g displays the height and phase images obtained at different time points, and Fig. 3h plots the cross-sections measured along cutting lines A–A′ to D–D′ (Fig. 3d–g). At 0 s, an unstable bright structure was observed in the height image near the position indicated by a red arrow (Fig. 3a). In the corresponding phase image, the gas structures also appeared brighter than the pure HOPG surface, corresponding to higher tip–sample dissipation of the structures. Gas structures appeared on only several scan lines along the fast-scan direction. Similar bright lines