Nanobubbles at Hydrophilic Particle–Water Interfaces

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Supporting Information

ABSTRACT: The puzzling persistence of nanobubbles breaks Laplace's law for bubbles, which is of great interest for promising applications in surface processing, H₂ and CO₂ storage, water treatment, and drug delivery. So far, nanobubbles have mostly been reported on hydrophobic planar substrates with atomic flatness. It remains a challenge to quantify nanobubbles on rough and irregular surfaces because of the lack of a characterization technique that can detect both the nanobubble morphology and chemical composition inside individual nanobubble-like objects. Here, by using synchrotron-based scanning transmission soft X-ray microscopy (STXM) with nanometer resolution, we discern nanoscopic gas bubbles of >25 nm with direct in situ proof of O₂ inside the nanobubbles at a hydrophilic particle–water interface under ambient conditions. We find a stable cloud of O₂ nanobubbles at the diatomite particle–water interface hours after oxygen aeration and temperature variation. The in situ technique may be useful for many surface nanobubble-related studies such as material preparation and property manipulation, phase equilibrium, nucleation kinetics, and relationships with chemical composition within the confined nanoscale space. The oxygen nanobubble clouds may be important in modifying particle–water interfaces and offering breakthrough technologies for oxygen delivery in sediment and/or deep water environments.

Potential for remediation of anoxia in deep water

INTRODUCTION

Observations of nanobubbles on hydrophobic planar substrates have attracted much attention;^{1–5} however, it is not clear whether they can form and persist on rough and fully wetted (i.e., hydrophilic) surfaces under ambient conditions.^{6–9} If the remarkable stability (hours and days) of nanobubbles is universally true,^{10–12} then something is evidently missing in the existing theory because the small curvature radius implies a high Laplace pressure inside the nanobubbles that should drive bubble dissolution in the liquid instantly ($\sim 1 \mu\text{s}$).^{13,14} Studies of interfacial nanobubbles may provide new insights not only in gas–liquid–solid equilibria on the nanoscale but also in efficient and environmentally friendly nanotechnologies.¹⁵ Nanoscopic gaseous bubbles can be eventually dissolved in the bulk environment without any toxic effects commonly related to conventional solid nanomaterials.¹⁶

Atomic force microscopy (AFM) and direct optical visualization are currently the main methods for investigating interfacial nanobubbles,^{6,17–19} but they cannot detect the identity and the composition of the nanoscale objects. Elemental and chemical analysis combined with high-resolution imaging has been a key requirement for fully characterizing nanobubbles. Such an effort has been attempted using AFM followed by attenuated total reflection infrared spectroscopy

(ATR-IR), by which the existence of CO₂ nanobubbles at the hydrophobic silicon wafer–water interface was found.^{2,20} However, the image and chemical information have to be measured separately from two different samples (i.e., ex situ), which are prepared specifically for the two instruments. Moreover, homonuclear diatomic molecules such as N₂ and O₂ and inert gases are not infrared-active, so they are often undetectable by ATR-IR spectroscopy. The AFM-based characterization requires relatively flat substrates, which are inaccessible for irregular or porous particle–water interfaces that are ubiquitous in the environment. It is anticipated that studies on the physicochemical properties of nanobubbles, such as phase equilibrium and nucleation kinetics and their relationships with chemical composition, will become a challenging and exciting direction in the near future. An in situ experimental technique that can simultaneously resolve the nanoscale morphologies and the chemical composition inside nanobubble-like objects (i.e., distinguish nanobubbles from

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other objects) at various interfaces is of fundamental significance for studying these properties of nanobubbles.

Synchrotron-based scanning transmission X-ray microscopy (STXM) can simultaneously provide nanometer-resolved maps and elemental information for target objects under in situ conditions.^{21–23} STXM imaging has been used to visualize the micro- and nanobubbles of SF₆ and Ne, but the chemical information inside the bubbles has not been obtained because of the limitation of the instrument.²³

Here, we use STXM to explore the O₂ nanobubbles at a hydrophilic particle–water interface. The chemical composition of the nanobubbles is analyzed by means of near-edge X-ray absorption fine structure (NEXAFS) spectra. NEXAFS spectroscopy probes the excitation of core electron by X-rays into unoccupied molecular orbitals and provides element-specific information.^{24,25} We prepare an O₂-aerated diatomite (SiO₂·*n*H₂O, a hydrophilic siliceous material that is widespread in natural environments²⁶) suspension as the model system. Surface nanobubbles were generated using temperature variation.^{14,27} The stability of O₂ nanobubbles on the hydrophilic particles was investigated hours after oxygen aeration.

METHODS

Materials and Sample Preparation. A diatomite (analytical grade, Beijing Chemical Regents Co.)–water suspension (0.55 g/L, 100 mL glass beaker) was aerated with pure O₂ (99.99%) in an ice–water bath under ambient pressure for 1 h. The degree of gas supersaturation was more than 150% over the experiment period (Figure S1). The control sample (an unaerated diatomite suspension) was prepared by the same operation as above, but did not have O₂ aeration. The mixture was centrifugated for 15 min at a relative centrifugal force of 2240 g (5000 rpm) to remove large particles from solution, and then the supernatant was extracted and subjected to STXM measurements at an ambient temperature of 25 °C. The ice–water bath was used to enhance the dissolved O₂ level in the solution, and the temperature-increasing operation was carried out to generate oxygen bubbles at the solid–liquid interfaces.^{14,27} The small contact angle of water on the diatomite (17°, JY-PHb, Jinhe Co.) showed that the diatomite was highly hydrophilic (Figure S2). BET surface area analysis indicated a specific surface area of 7.4 m²/g (ASAP-2010, Micromeritics) for the diatomite. The particle-size distribution, measured with a Mastersizer 2000 analyzer (Malvern, U.K.), ranged from 0.4 to 5.5 μm. The volume-average particle diameter was 3.67 μm. All solutions were produced in ultrapure water (resistivity 18 MΩ·cm).

In Situ STXM Measurement and Data Treatment. The STXM experiment was carried out on beamline 11.0.2 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The STXM instrument at ALS provides images with a spatial resolution of ~25 nm and an energy resolution ($E/\Delta E$) of 2500–7500 for X-ray photons of 200–2000 eV (~0.08 eV at the O K-edge). The STXM chamber was filled with 760 Torr He prior to sample measurements. A droplet (water or suspension, ~2 μL) was placed on a 5 mm × 5 mm Si wafer with a 0.5 mm × 0.5 mm opening of a 100-nm-thick Si₃N₄ membrane and covered with another Si₃N₄ membrane. The borders of the Si₃N₄ sandwich were sealed using epoxy. Then the resulting wet cell was loaded into the sample holder in the STXM chamber after the glue solidified. The wet cell was measured on the optical microscope by counting the interference fringes. The O₂ spectrum was recorded as the partial pressure of oxygen gas (2 Torr) in the STXM chamber. For measurements of the spectrum of water vapor, the STXM chamber was opened to a flask with water until the partial pressure of water vapor inside the chamber was 2 Torr.

The monochromatic X-ray beam was focused to a spot size of 25 nm in diameter using a Fresnel zone plate, and the sample was then raster scanned at the focal point through detecting the transmitted X-

ray flux. The transmitted X-ray intensity was recorded using a scintillator and photomultiplier tube and measured as a function of photon energy and position. The recorded transmitted X-ray intensity (*I*) of the samples was normalized by the incident intensity (*I*₀) and converted to an optical density (absorbance) of $OD = -\ln(I/I_0)$. Image stacks were obtained by scanning the sample in the *x*–*y* directions of selected areas with a step increment of 0.2 eV over the energy range of 525.0–555.0 eV. After the stack was spatially aligned, principle component analysis (PCA) was used to obtain the primary components in the data set. Subsequently, cluster analysis (CA) was performed to group pixels (i.e., classify areas in the sample) according to statistical similarities in their spectra.^{21,28} The STXM data were processed using the aXis2000 software package (available from <http://unicorn.mcmaster.ca/aXis2000.html>).

RESULTS AND DISCUSSION

The O K-edge NEXAFS spectra of oxygen gas, water vapor, and liquid water are presented in Figure 1 and are in good

Figure 1. O K-edge NEXAFS spectra of oxygen gas, liquid water, and water vapor.

agreement with the literatures.^{22,24,29–31} The NEXAFS of oxygen gas is characterized by a strong resonance at 531.2 eV and a weak, broad absorption feature in the energy range of 537–545 eV. The broad absorption band is due to the 1s → σ^* transition, and the strong resonance (nearly 5-fold the intensity of the σ^* region) is attributed to the 1s → π^* transition.²⁴ By taking advantage of the distinct strong absorption feature, the π^* signature at ~531 eV can be used as a clear indicator of the presence of O₂ in a well-controlled system.^{31,32}

To explore the O₂ nanobubbles at hydrophilic particle surfaces, two diatomite suspension samples are prepared by the same procedure, except for the pure O₂ (99.99%) aeration process. The STXM image of the unaerated diatomite suspension is shown in Figure 2a. The dark- and pale-gray shades are due to the different transmitted intensities, and the particle regions (dark gray) within the suspension become visible. Absorption spectra extracted from the water medium and solid regions are compared in Figure 2b. The spectrum from the water phase shows essentially the same shape as that of pure liquid water (Figure 1), which consists of three main regions: the pre-edge (around 535 eV), the main edge (537 to 538 eV), and the postedge (540 to 541 eV).²⁹ The NEXAFS of the solid region is consistent with the characteristics of SiO₂, which is characterized by a weak π^* resonance at ~532 eV and a high σ^* resonance in the energy range of 535–545 eV.²² The difference between the spectra of the diatomite and water phase (Figure 2b inset) does not show any significant spectral features

Figure 2. STXM image and X-ray absorption spectra of an unaerated diatomite suspension. (a) STXM image recorded at 539.2 eV. (b) O K-edge NEXAFS spectra taken from the regions shown in (a). The inserted chart is the difference spectrum obtained by subtracting the blue curve from the red one.

Figure 3. Characterization of an O₂-aerated diatomite suspension. (a) STXM image recorded at 538.5 eV. (b) Cluster map of the sampling region. (c) O K-edge NEXAFS spectra corresponding to the clusters shown in (b) and the O₂ reference. The inserted chart is the difference spectrum obtained by subtracting the blue curve from the green one.

of oxygen gas. Therefore, no signal of oxygen gas is observed in the unaerated diatomite suspension sample.

The STXM image of the diatomite suspension after 1 h of O₂ aeration is presented in Figure 3a. A chemical contrast map of the sampling region (Figure 3b) is obtained by principle component analysis and cluster analysis (PCA-CA) of all NEXAFS spectra for each pixel.²¹ The PCA-CA analysis identifies four chemically distinct regions across the particle–water interfaces that exhibit different NEXAFS spectra in Figure 3c. The blue pixels represent the water phase. The spectrum extracted from the O₂-aerated water phase shows spectral features nearly identical to those of unaerated water (Figure 2b), except for a small absorption feature at around 531 eV (blue line in Figure 3c), suggesting that the O₂ saturation level in the water phase has been increased to the extent that is detectable for the STXM measurement after 1 h of O₂ aeration and temperature enhancement. The intensity ratio of the π^* resonance (at 531.2 eV) to the σ^* resonance (at around 538 eV) of the NEXAFS spectra taken from the region in and around the particle is significantly greater than those of diatomite and water (Figure 2b), which indicates the existence of O₂ at the particle–water interface. The high spatial resolution of STXM mapping allows us to discern the individual O₂-filled nanobubbles with diameters down to 25

nm (colored spots in Figure 3b, typically 25–50 nm) as well as a cloud of O₂ nanobubbles around the diatomite particles. The nanoscale density-gradient pattern of O₂ surrounding the water-dispersed particle obtained from the cluster map indicates that the O₂ content within the nanobubbles at the diatomite–water interface may vary to a large extent. The intensity of the π^* resonance increases significantly from bulk water to solid surfaces (Figure 3c), indicating the accumulation of O₂ near the particle surfaces. The weak σ^* resonance feature of oxygen gas (approximately one-fifth of the intensity of the π^* resonance) is not directly observed, which may be overwhelmed by the strong absorption band originating from dense water and solid phases. (See the difference between the green and blue spectra in the Figure 3c inset, which shows a spectral profile similar to the O₂ spectrum.)

Our findings indicate that the surfaces of water-dispersed particles can be decorated by a stable nanoscale gas phase through simple aeration and temperature variation. It is reported that nanobubbles could form in a solution supersaturated with air and that they were stable on hydrophobic surfaces.³³ Our results suggest that nanobubbles can also stably exist on hydrophilic surfaces. Gas supersaturation in solution and temperature fluctuations happen frequently in nature, and the existence of nanobubbles on the particle–water interface

may be a common phenomenon. There are many kinds of water-dispersed micro/nanoparticles in nature, such as enzymes, microorganisms, cells, and mineral particles. Many interfacial behaviors, biochemical processes, adsorption/desorption, dissolution/precipitation, dispersion/aggregation, ion exchange, interfacial electron transfer, and catalysis would be changed in the presence of a nanocloud around the particles. Although these studies are of great interest to science and technology, they have been greatly hindered by the lack of techniques to quantify nanobubbles on practical solid surfaces that are often rough and irregular. Our finding may lift the technical barriers and lead to rapid development in nanobubble-related interfacial studies.

The persistence of nanobubble clouds at the particle–water interface may open novel environmental and aquatic engineering applications. O₂-filled nanobubbles loaded on macroscopic particles of clay or soil can be purposely delivered to polluted water and especially anoxic sediment and can efficiently revive polluted natural waters.^{34–36} The hypoxia and anoxia problem in deep water is an extremely difficult issue to tackle cost-effectively by conventional technologies such as aeration and ventilation.³⁷ The O₂ nanobubble materials may lift the bottleneck problems of safety, cost, and performance of nanomaterials for the remediation of anoxia and eutrophication in aquatic environments.¹⁵ The window period created by O₂ nanobubble materials and the triggered physicochemical and microbial responses may greatly change the sediment–water processes, which will in turn affect the air–water exchange of greenhouse gases. Studies in interfacial nanobubbles may lead to breakthrough technologies for the remediation of environmental pollution.

CONCLUSIONS

We observe nanoscopic gas bubbles >25 nm with direct proof of O₂ inside the nanobubbles at a hydrophilic particle–water interface under ambient conditions by using scanning transmission X-ray microscopy. We find a stable cloud of O₂ nanobubbles at the diatomite particle–water interface hours (at least 4 h for the whole STXM experiment process) after oxygen aeration and temperature treatment. STXM is a promising technique for studying the nanobubbles' nucleation process near solid/water interfaces on irregular and rough surfaces. The persistence of nanoscopic gases on a fully wetted hydrophilic surface prompts the need for further exploration of the nature of gas–liquid–solid equilibria on the nanoscale and the extent of nanobubble applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.6b01483](https://doi.org/10.1021/acs.langmuir.6b01483).

Measurement of the degree of oxygen supersaturation and the contact angle of water on the diatomite (PDF)

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Notes

The authors declare no competing financial interest.

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