A novel water layer structure inside nanobubbles at room temperature (Postprint)

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Abstract

Molecularly thin water layer, with a hydrogen bonding network different from those in bulk water and ice, has unique properties and is generally involved in many important processes such as wetting, erosion, atmosphere chemical reaction, protein folding and biomolecular interaction. Here, we report a new water layer structure at room temperature, which is found inside nanobubbles by using synchrotron based scanning transmission soft X-ray microscopy (STXM). The three peaks 535.0, 536.8 and 540.9 eV at O K edge inside the nanobubbles show a novel characteristics of very thin water layers, which has never been observed before.

Full Text

Preamble

A Novel Water Layer Structure Inside Nanobubbles at Room Temperature

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Molecularly thin water layers, which possess a hydrogen bonding network distinct from those in bulk water and ice, exhibit unique properties and are involved in numerous important processes such as wetting, erosion, atmospheric chemical reactions, protein folding, and biomolecular interactions. Here we report a new water layer structure at room temperature, discovered inside nanobubbles using synchrotron-based scanning transmission soft X-ray microscopy (STXM). The three peaks at 535.0, 536.8, and 540.9 eV in the O K-edge spectrum inside the nanobubbles reveal novel characteristics of very thin water layers that have never been observed previously.

Keywords: Nanobubble, Soft X-ray absorption, Water layer
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Introduction

Water, a substance of paramount importance on Earth, exists in three phases —liquid, vapor, and ice—and exhibits many anomalous macroscopic properties that remain incompletely understood in terms of the microscopic properties of its constituent molecules and their mutual interactions. Among the various methods developed to elucidate water structure, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy provides valuable information about the local hydrogen bond configurations of water molecules in liquid water, ice, and water clusters [1–7].

Water displays unique behaviors at interfaces. For instance, nanoscale gas bubbles with spherical cap shapes have been observed attached to solid surfaces immersed in aqueous environments [8–16]. The puzzling properties of these gas nanobubbles are far from understood, particularly their remarkable stability, which contradicts classical thermodynamics. According to the Young-Laplace equation, such nanobubbles should not exist at all, as their small radii of curvature imply extremely high Laplace pressures that would cause them to dissolve almost instantaneously [17–20]. Classical theory predicts that micro- or nanometer-sized bubbles should disappear within tens of milliseconds or less, yet experimental observations show that interfacial nanobubbles can persist for hours or even days [21].

Water may adopt a special structure when confined at interfaces. Nanobubbles provide nanoscopic confinement for water molecules, and their peculiar behavior may suggest the existence of unique water structures within them. However, detecting the water structure inside nanobubbles is challenging with conventional methods. In this context, zone-plate-based scanning transmission soft X-ray microscopy (STXM) has emerged as a unique analytical tool, leveraging elemental absorption contrast to image samples with resolution down to 15 nm [22]. The non-intrusive nature of the measurement, combined with nanoscopic spatial resolution and chemical sensitivity, makes STXM an ideal technique for studying the properties and behavior of individual nanobubbles at interfaces.

In this paper, we demonstrate that STXM with nanometer resolution can be

used to image nanobubbles trapped between two silicon nitride windows in aqueous solutions. Importantly, we find evidence for a new type of thin water layer existing inside nanobubbles based on the O K-edge X-ray NEXAFS spectrum.

II. Experimental Section

A. Materials

Water with a conductivity of 18.2 MΩ · cm was obtained from a Milli-Q system (Millipore Corp., Boston, MA). Silicon nitride (Si_3N_4) windows (5 mm × 5 mm, with 1 mm × 1 mm × 100 nm membranes, SN-LDE-510-15, Shanghai NTI Co. Ltd, China) served as substrates for nanobubble formation.

B. Preparation of Nanobubbles

The nanobubble samples were prepared as follows. First, Millipore water was degassed for approximately 2 hours at a pressure of 0.1 atm (0.01 MPa) in a desiccator. Then, SF_6 gas (purity 99.9999%, from Wonik Materials Co.) was bubbled through the solution for about 30 minutes in a washing bottle. A droplet of the gas-saturated solution (approximately 3.0 µL) was deposited onto the surface of a Si_3N_4 window, and another Si_3N_4 window was gently placed on top of the droplet. Vacuum glue (two components, from Agilent Co.) was used to seal the two Si_3N_4 windows together. Typically, a curing time of about 1.5 hours was required before the sample was loaded into the experimental chamber.

C. STXM Imaging

The samples were investigated using the newly constructed BL08U1A STXM microscope at the Shanghai Synchrotron Radiation Facility (SSRF) and the SM beamline STXM at the Canadian Light Source (CLS). Imaging was performed in transmission mode in a helium atmosphere (≥ 99.999%, Shanghai Chunyu Special Gas Ltd.) at 0.4–0.66 atm (0.04–0.066 MPa). The transmitted photon flux was measured using a photomultiplier tube (Hamamatsu, Japan). An 800 lines/mm grating and 50 µm exit slit were used for O K-edge imaging and spectroscopy, providing an energy resolution of 6000 (E/ΔE) at 700 eV. Images were recorded at selected energies through the O 1s region (525–550 eV) in 0.2 eV steps. The photon energy was calibrated by measuring pure SF_6 in the experimental chamber at 3–10 Torr (400–1333.2 Pa). Image and spectral processing were carried out using the aXis 2000 software [23].

III. Results and Discussion

Sample preparation was the critical step for STXM imaging. As reported by Zhang et al. [24], a water thickness of 500 nm represents the upper limit for obtaining good results, considering the weak transmission of soft X-rays. Figure 1 [Figure 1: see original paper] shows a typical STXM image of nanobubbles on

a silicon nitride surface in water, with the observable nanobubbles exhibiting lateral sizes of 60–2000 nm.

As shown in Figure 2 [Figure 2: see original paper], the O K-edge spectrum from inside the nanobubbles was extracted by subtracting the background water signal. This type of O K-edge water spectrum has never been reported previously. The appearance of three distinct spectral features at 535.0, 536.8, and 540.9 eV implies the existence of a new type of very thin water layer, based on hydrogen bond network analysis. Our results thus clearly indicate that a new phase of water occurs inside the nanobubbles.

IV. Conclusion

Using synchrotron-based STXM, we discovered a new water layer structure inside nanobubbles. The three peaks at 535.0, 536.8, and 540.9 eV in the O K-edge spectrum inside the nanobubbles represent novel characteristics of very thin water layers observed for the first time. This strongly indicates that water molecules inside nanobubbles form a new structural phase. This finding may be essential for explaining the high stability of nanobubbles at water/solid interfaces and will provide new insights into the field of molecular water science [25].

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Note: Figure translations are in progress. See original paper for figures.