

Detection of Nanobubbles at the Interface of TiO₂ Coated Mica in Water

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Abstract

Nanobubbles formed at a solid-liquid interface have attracted a lot of attention because of their unique physical and chemical properties, and their foundational interests in life science, physics and other science areas. We found that the nanobubbles could be created on TiO₂ coating surface in pure water by the “solvent exchange” method. By using a temperature-controller accessory and a single-probe thermocouple to control the temperature in atomic force microscopy (AFM) liquid cell, we studied the influence of temperature and degassing on the aggregation of nanobubbles on the TiO₂ coatings surface.

Keywords: Nanobubbles; TiO₂ coatings; Solvent exchange method

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1. Introduction

Nanobubbles are ubiquitous and play an important role in the formation such as long-range attractive forces at hydrophobic interfaces, fluid boundary slip, adsorption of biomolecules at surfaces, and stabilization of colloidal system [1-4]. However, it is difficult to detect directly the interfacial nanobubbles (i.e., discrete compartments of gas) from a continuous layer of water. The results reported from different research groups were still contradictory somehow [5, 6]. In last few years, we have established a general approach, deliberately inducing nanobubbles on the solid substrate surface by the so called “solvent exchange” method, under a controllable manner [7, 8]. This not only enables us to generate nanobubbles on the surface in a highly reproducibly, but also provides a platform for studying fundamental properties of as-generated nanobubbles.

Due to good chemical stability, photocatalytic property, corrosion resistance, and toxicity, nano-scale TiO₂ has been extensively employed in areas such as solar cells, hydrogen production, and environmental protection [9]. It has been demonstrated, theoretically and experimentally, that the photocatalytic efficiency

of TiO₂ depends critically on photogenic carrier density and the rate of carrier mobility [10]. Additionally, similar to other heterogeneous catalytic systems, the photocatalysts also meet deactivation [11]. So we can speculate that if nanobubbles generated at the photocatalytic process and absorbed at the interface of the TiO₂ photocatalysts, as a result, the effective surface of the photocatalyst would be reduce. In previous works, we have already reported that during the photocatalytic reaction process there are many nanobubbles can be generated and absorbed on the TiO₂ coatings surface [12]. However, the origin of the gas in the nanobubbles and the life time of the nanobubbles have not been clarified yet. In this report, we further confirmed the nanobubbles on the surface TiO₂ coatings can be generated by using the so-called “solvent exchange” method and degassing process.

2. Materials and Methods

2.1 Materials and instruments

Water used in the experiments, with a conductivity of 18.2 MΩ•cm, was purified through a milli-Q system

(Millipore Corp, Boston, MA). Chemical reagents, such as tetraisopropyl orthotitanate (TIPT, $\text{Ti}(\text{C}_3\text{H}_7\text{O})_4$), ethyl acetoacetic (EAcAc), and ethanol are analytic reagents and were purchased from Chinese Chemical Reagent Co.. Mica was from Sichuan Ya'an Industry Co. Ltd.

Atomic force microscopy (AFM) imaging was performed with Multimode Nanoscope V SPM (Veeco Metrology Group, NY) in tapping mode. A triangle cantilever (NP-s, Veeco Metrology Group, NY) with a nominal force constant of $\sim 0.58 \text{ N/m}$ was used. The driving frequency, driving amplitude and scanning rate for the cantilever in water were set at 5.0-9.5 kHz, 250-600 mV, and 1-2 Hz, respectively. Before imaging, cantilevers, O-ring and the liquid cell were cleaned carefully with ethanol and Milli-Q water, in sequence and were dried with nitrogen gas. A temperature-controller accessory (Veeco Metrology Group, NY) was utilized to control the temperature in the liquid cell and a single-probe thermocouple was used to measure the temperature of liquids in the cell. The environmental temperature was controlled at $25 \pm 2^\circ\text{C}$.

2.2 Fabrication of TiO_2 coatings

The details for preparation of TiO_2 thin films have been reported previously [13, 14]. Briefly, to facilitate the observation of nanobubbles, freshly cleaved mica was used as the substrate, and the TiO_2 sol was prepared from TIPT as the following. Ethanol, 20 ml, and EAcAc, 1 ml, were mixed at room temperature, then, 2 ml of TIPT were added and the solution was stirred continuously for one hour. Within 30 min, $\sim 0.2 \text{ ml}$ distilled water was carefully added to the solution for hydrolysis and the mixture was stirred for ten hours. The as-obtained yellow transparent solution was aged for two days before coated on Mica surface.

The sol was coated onto the freshly cleaved mica by spin coating. In a typical experiment, 20 μl of sol was dropped on the mica surface at a spinning rate of 5000 rpm for 20s at room temperature. The samples were further annealed in a vacuum oven for 20 min at 150°C , and then in a Muffle furnace for 30 min at 450°C .

2.3 Generation of nanobubbles on the TiO_2 coatings.

In this work, we select ethanol and ultrapure water as solvents to create nanobubbles on the TiO_2 surface by solvent exchange method. First, a TiO_2 coated mica slide was mounted on a magnetic plate of AFM, upon which there was a fluid cell aligned with an O-ring. The pure water was introduced into the fluid cell using a syringe. Then, the water in the liquid cell was replaced with ethanol. Finally, the ethanol was replaced with water. During the solvent replacement, the AFM height and phase images were acquired under tapping mode to detect the formation of nanobubbles at different stage. At the same time, a control experiment was

also carried out on the bare mica as that we have previously reported [15-18].

By using a temperature-controller accessory and a single-probe thermocouple to control the temperature of water in the liquid cell, we investigated influence of temperature on the formation of nanobubbles at the interface of TiO_2 thin films and water using TM-AFM. In a typical experiment, 120 μL of cold water ($\sim 4^\circ\text{C}$) were injected into the liquid cell and the interface was imaged by AFM and record in both height and phase. The temperature of the water was increased with a interval of 10°C .

2.4 Degassing process

After the nanobubbles were generated at the surface of the TiO_2 coatings, the samples were carefully moved a desiccator and were degassed under a vacuum of 0.1atm for at least 2.5 h. Then the interface of TiO_2 thin films was imaged by TM-AFM.

3. Results and discussion

3.1 Characterization of TiO_2 thin films surface in air

Figure 1a, b show the AFM images of TiO_2 coated on mica. The TiO_2 nanoparticles, with sizes of 5 to 15 nm in diameters (Figure 1c), were packed densely to form uniform thin film. The TiO_2 films were flat with a root-mean-square (rms) roughness of 1 nm (Figure 1b) as confirmed previously [12, 13, 19]. The as-prepared TiO_2 nanoparticles should presume anatase crystalline structure. The thickness of the TiO_2 thin films was $\sim 89 \text{ nm}$ measured from the AFM height image.

3.2 Formation of nanobubbles at the interface between water and TiO_2 using solvent exchange method

The "Solvent exchange" method has widely been used as a simple and reproducible method to generate the nanobubbles at solid/liquid interfaces. This method provides us an easy way to study the properties of nanobubbles at the solid/liquid interfaces using AFM imaging, too. Usually, the nanobubbles can be formed when a solid surface is exposed to an aqueous medium supersaturated with gases. In solvent exchange process, the supersaturation of a gas, such as air, can be achieved by replacing the ethanol with pure water. Before replacing water with ethanol, the high-resolution AFM images of the interface of mica and TiO_2 coatings (Figure 2a, b and 2e, f) showed that no nanobubbles or other forms of the gaseous state absorb on the solid surface. Similar to that we observed in air, the two substrates interface were smooth and uniform. Meanwhile, there is no contrast in the phase, too, which means that the surfaces are homogeneous. However, after the water was replaced with ethanol,

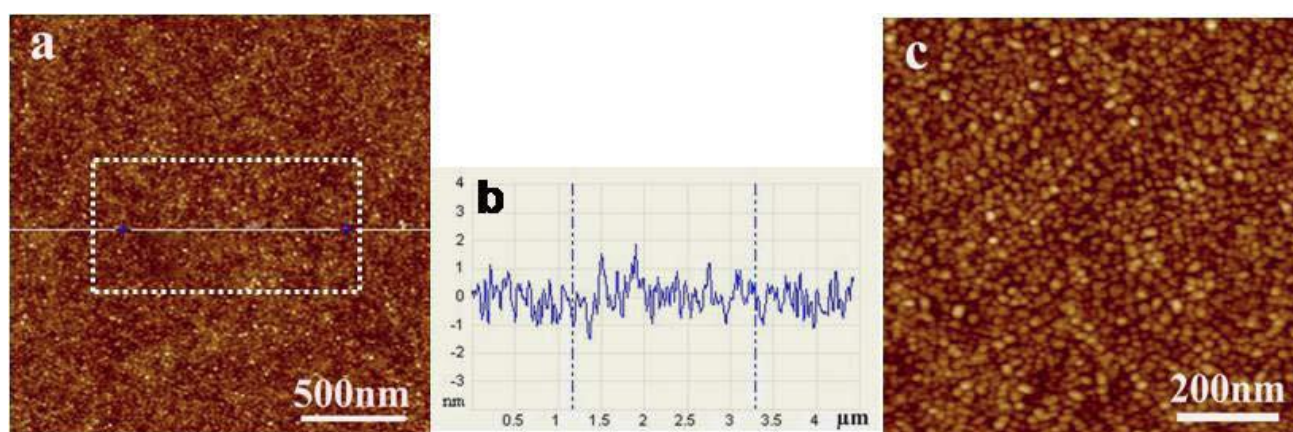


Figure 1. Typical TM-AFM images and section analysis of the TiO_2 coated on mica surface in air. a) height image; b) section analysis of the marked region in Figure 1a and c) the high-resolution image of the Figure 1a.

manynanoscale spherical features (Figure 2c, 2d, 2g and 2h) were observed on the surfaces of the mica and TiO_2 coatings. The phase images of the same areas show the distinctive contrast between these features and the substrates. It is well known that the phase image is very sensitive to variations of material properties such as elasticity, adhesion, and viscoelasticity, the contrast in Figure 2d and 2h indicate that those features are different in nature from the substrate shown in Figure 2b and 2f. This is similar to the result we observed on bare mica surfaces that leads us to believe the bright features at the TiO_2 surface are nanobubbles. In addition,

by comparing the number of nanobubbles absorbed on the mica and TiO_2 surface, it is not difficult to recognize that the density of nanobubbles on the TiO_2 surface is higher than that on the mica. The results may be explained by the formation mechanism of nanobubbles. Generally, two conditions, high surface roughness and appropriate hydrophobic properties, are essential for the formation of nanobubbles on the surface of substrates. From high-resolution image of the TiO_2 thin films (Figure 1c), we knew that the TiO_2 thin films are composed of nanoparticles, which may provide nucleation sites for gas absorption at the interface.

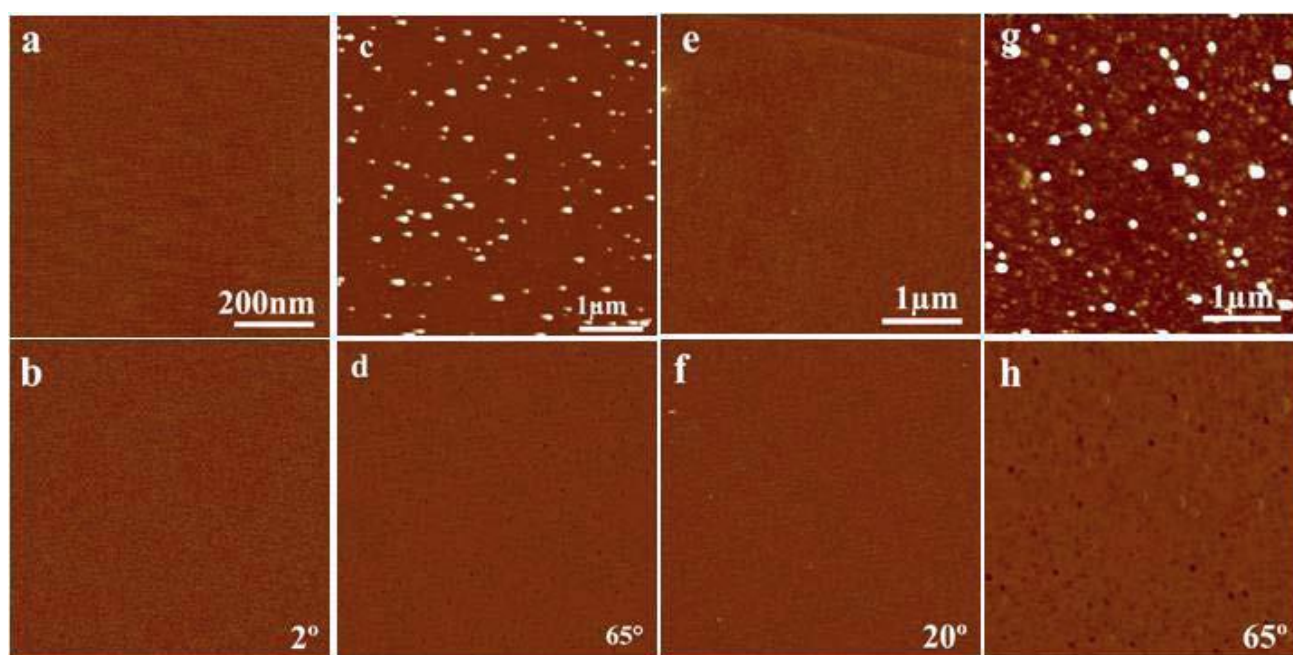


Figure 2. a,b) TM-AFM height and phase images of mica in pure water. c,d) TM-AFM images of the same area but the water was replaced with ethanol by water. e,h) TM-AFM height and phase images of the TiO_2 -coating surface in pure water. e, f) before displacing ethanol by water and d) after displacing ethanol by water.

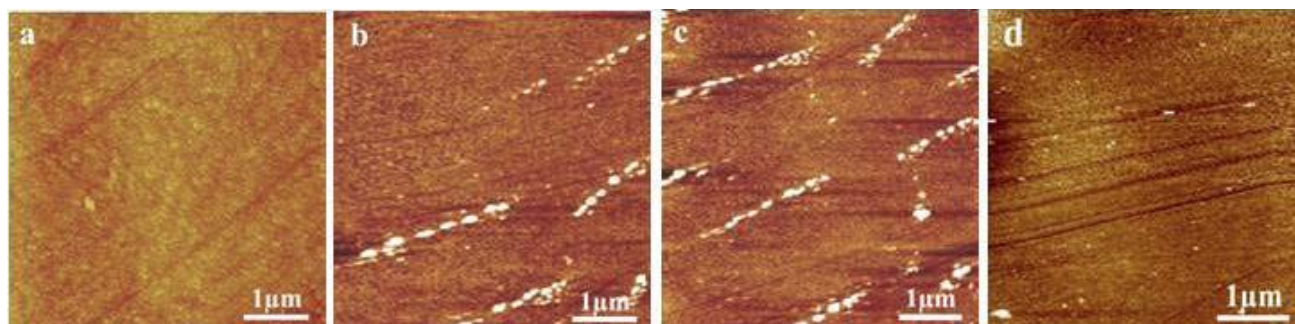


Figure 3. TM-AFM height images showing the effects of temperature and degassing on the formation of nanobubbles at the TiO_2 coated mica interface in pure water. (a) 4 °C; (b) 10 °C; (c) 20 °C; (d) degassing for two and half hours.

3.3 Evolution of the nanobubbles

It is well known that chemical reactions may result in the the heat energy and accordingly temperature change that are one of the important physical and chemical factors that have been linked to the nucleation process of nanobubbles at the solid/water interface. Figure 3a-c illustrates that the evolution of nanobubbles with the water temperature in a dark condition. When the cold water was introduced into the liquid cell, no nanobubbles were observed at the interface (Figure 3a). After the temperature of water increasing to $\sim 10^\circ\text{C}$, the nanobubbles begin to form at the interface (Figure 3b). The volume and number of the nanobubbles significantly increases with the rising of water temperature (shown in the Figure 3c). In addition, it is worthy to point out that the nanobubbles easily absorbed at the step of the TiO_2 thin films.

To further confirm the formation of nanobubbles, a degassing process was carried out. Figure 3d shows an AFM image of the TiO_2 surface after partial degassing. It showed that the nanobubbles disappeared after the degassing. The result illustrates that the gases concentration.

4. Conclusion

We have demonstrated that the nanobubbles can generate at the interface between the TiO_2 thin films and water using the solvent exchange method. At the same time, we also investigate the evolution process of nanobubbles at the TiO_2 interface with the temperature of water. Degassing experiment further demonstrates the existence of nanobubbles on the TiO_2 thin films.

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