Unidirectional Transport and Effective Collection of Underwater CO$_2$ Bubbles Utilizing Ultrafast-Laser-Ablated Janus Foam

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ABSTRACT: Manipulating gas bubbles in aqueous ambient is of great importance for applications in water treatment, gas collection, and matter transport. Here, a kind of Janus foam is designed and fabricated by one-step ultrafast laser ablation of one side of the copper film, which is treated to be superhydrophobic. Janus foam exhibits not only the capability of unidirectional transport of underwater bubbles but also gas collection with favorable efficiency up to $\sim 15$ mL cm$^{-2}$ min$^{-1}$. The underlying physical mechanism is attributed to the cooperation of the buoyancy, adhesion, and wetting gradient forces imposed on the bubbles. 1. INTRODUCTION Bubbles are ubiquitous in nature and organisms but remain challenging to understand and manipulate. The effective manipulation regarding collection, transport, and the chemical reaction for underwater gas bubbles plays a crucial role in both scientific research and industrial applications such as water treatment, mineral flotation, and microreactions in aqueous ambient.1–4 For instance, by virtue of an agitation way that creates small bubbles, more surfaces are produced to capture the contaminants by the floating froth and clarify wastewaters. For living creatures, the humpback whales hunt fishes by producing numerous tiny gas bubbles around them.5 In industrial settings, quick detachment of gas bubbles on a heated surface can significantly boost the efficiency of boiling heat transfer.6–9 Moreover, capturing and collecting gas bubbles can elevate the gas diffusivity in aqueous ambient, followed by accelerating the mass exchange efficiency in the ocean.10 Consequently, the realization of directional transport and effective collection of gas bubbles are of vital importance for various potential applications.

In order to manipulate underwater gas bubbles, a variety of microstructures have been developed such as metallic meshes, organic sheets or microcones, and so forth.11–15 Hu et al. realized a channel-controlled Janus membrane for underwater unidirectional bubble penetration by a femtosecond laser-assisted ablation and nanoparticles deposition approach.16 Lu et al. developed a superaerophilic carbon-nanotube-array electrode using a solvothermal method, which would boost the oxygen-bubble adhesion and the diffusion process.17 Jiang and coworkers reported a reliable bubble manipulation sheets via regulating a series of interfaces with well-ordered microstructures and controllable chemical compositions on silicon surfaces.18 Generally, most of these substrates can be divided into superhydrophobic/superhydrophilic surfaces12,19–21 and lubricant-infused surfaces.22–26 Among these, three driving forces can be considered to be the sources of bubble transport: buoyancy,5,22,23,27 wetting gradient, and Laplace gradient forces arising from substrate’s properties.19,22,23 For buoyancy-based cases, an upward motion of gas bubbles can be realized via dynamically rotating and tilting the substrate.19,22,23 For wetting gradient and Laplace gradient forces, effective bubble transport can be achieved via surface energy modification and specially designed morphology.

As a kind of typical wetting gradient device, Janus membrane, featuring superhydrophobicity and superhydrophilicity on two opposite surfaces, has exhibited excellent capability of unidirectional bubble penetration and demonstrated the potential applications in underwater bubble manipulation.11,29,30 Nevertheless, current studies on “bubble Janus” mainly focus onto realizing the unidirectional bubble passage/blockage capability (i.e., “bubble diode”). The relevant bubble collection efficiency is rarely mentioned. In a practical scenario, the collection
efficiency of bubble Janus is undoubtedly crucial and, therefore, should be further concerned. Metallic foams (e.g., copper and nickel), featuring the advantages of low density, high porosity, and mechanical flexibility, are capable of transporting and collecting water droplets unidirectionally. Nevertheless, there are few reports available on underwater bubble manipulation with the use of metallic foams.

Herein, we fabricate a kind of Janus copper foam for unidirectional transport and effective collection of underwater gas bubbles. Janus foam is constructed via one-step laser ablation on a single side of the superhydrophobicity-treated copper foam. This Janus foam exhibits not only the capability of unidirectional penetration of underwater gas bubbles from the laser-treated side to the opposite side but also effective gas collection performance by reaching up to \(~15\) mL cm\(^{-2}\) min\(^{-1}\) at a 1 m s\(^{-1}\) laser scanning speed. As a demonstration for underwater carbon capture, Janus foam allows the CO\(_2\) gas flow to penetrate the “bubble diode” and react with the alkaline phenolphthalein solution. This bubble Janus with facile fabrication and favorable collection performance will find broad applications in bubble transport, carbon capture, and controllable gaseous reactions.

2. RESULT AND DISCUSSION

We choose copper foam to fabricate the bubble Janus because it has a relatively larger specific surface than that of traditional membrane-shaped Janus. Commercially available copper foam sheets (thickness \(~1\) mm) were cleaned ultrasonically in acetone. The foam PPI (defined as the pore amount per linear inch) was chosen to be 90, 130, and 160, respectively. The cleaned samples were then treated with chemical coating to exhibit superhydrophobicity. Therefore, the superhydrophobic copper foams were ablated by line-by-line ultrafast laser scanning on one side to form Janus foams (Figure 1a). The laser fabrication system and optical path can be found in our previous work. After the single-side laser ablation, the laser-treated side of copper foam turned dark, showing hydrophilicity with a water contact angle (WCA) of 59° and super-aerophobicity with a bubble contact angle (BCA) of 151°, respectively. Whereas the untreated side (i.e., the super-hydrophobic side) maintained pristine purple-red, on which WCA and BCA were measured to be 154 and 28°, respectively (Figure 1b). It is observed that Janus foam allows gas bubble to penetrate from laser-treated side to the other side but not in the opposite direction (Figure 1c, Movie S1). Our Janus foam exhibits an excellent unidirectional bubble transport property.

The surface morphology and chemical element analysis of pristine, superhydrophobic, and laser-treated copper foams are further characterized. As shown in Figure 2a (top row), a cellular-like structure was observed on the surface of pristine foam. Judging from the magnified scanning electron microscopy (SEM) image (middle row), the surface of a single copper branch was relatively smooth. Energy-dispersive X-ray spectroscopy (EDS, bottom row) revealed that the proportions (atom %) of elements Cu, O, and Si were 99.54, 0.44, and 0.02%, respectively, which illustrates that the primary element was pristine copper. For the superhydrophobic copper foam (Figure 2b), the magnified SEM image shows that the roughness of the copper branch was elevated because of the existence of superficial Glaco coating which contained superhydrophobic silica nanoparticles. As a consequence, the proportions of elements O and Si were significantly increased by up to 21.56 and 8.89%, respectively, while the proportion of Cu correspondingly decreased to 69.55%. It should be noted that the laser-treated superhydrophobic foam exhibited micro/nanoscale composite structures (Figure 2c). During the laser ablation process, the initial frame of copper foam remained unchanged, but the smooth surface of each branch was induced by a femtosecond laser to generate hollow porous microstructures under the combined effect of laser shock compression and debris deposition. The average size of the hollow pore was estimated to be 4 \(\mu\)m, as shown in Figure 2c. More details can be found in the magnified SEM image in which the flat branch surface was interspersed with sporadic micro- and nano-mastoids because of high energy laser ablation. In essence, the formation of nano-mastoids was attributed to the resultant of plasma expansion, local burst, and recrystallization of the irradiated matter. As compared with that of the superhydrophobic foam, O and Si components of the laser-ablated sample had diminished (2.81 and 0.19%, respectively), which were still slightly greater than that of the pristine one.

Realizing effective gas/bubble collection is important for bubble Janus designs in an aqueous environment. Till date, existing studies on bubble Janus mainly focus onto realizing the passage/blockage capability with regard to bubbles, whereas the related collection efficiency is rarely mentioned. To investigate bubble collection efficiency of our Janus foam, we setup a purpose-built apparatus consisting of an iron support, accessory containers, and an electric gas bubble generator (Figure 3a). The gas bubbles were produced at a stable air flux from the bubble generator and gathered beneath underwater Janus foam. The Janus foam is immersed beneath the water–air interface at a fixed depth of about 2 cm to ensure the flux consistency of the bubble flow. The dynamic process of bubble collection by underwater Janus foam is shown in Figure 3b (also see Movie S2). Zero time was defined as the moment when bubbles initially passed through Janus foam and adhered on the upper surface. Because of the continuous generation of the gas flow from the bottom, the tiny bubble kept growing larger on the upper surface. When the buoyancy force exceeded the adhesion force from the substrate, the gas bubble would detach from the Janus foam and finally be collected. Figure 3c shows the variation of gas/bubble output volume over time (red curve). The blue curve represents the corresponding linear fit result. According to the experimental data, the bubble generator could produce a stable airflow at \(~32\) mL cm\(^{-2}\) min\(^{-1}\). The gas collection rate

![Figure 1](image-url)
(GCR) of Janus foam (90, 130, and 160 PPI) with diverse laser scanning speeds is shown in Figure 3d, from which one can observe that Janus foam exhibited a GCR of approximately 7 mL cm\(^{-2}\) min\(^{-1}\) at a scanning speed of 3 m s\(^{-1}\). Moreover, the GCR of Janus foam exhibited a maximum value of 15 mL cm\(^{-2}\) min\(^{-1}\) at a scanning speed of 1 m s\(^{-1}\). In addition, Janus foam showed inconspicuous distinction in GCR among these three PPI values. Interestingly, it was noticed that when the scanning speed was set to be less than 1 m s\(^{-1}\), Janus foam could hardly collect gas bubbles. This phenomenon is considered to be the fact that a slower laser scanning speed will result in excessive laser ablation, followed by elevated penetration resistance for bubble Janus because of the enlarged thickness of the superhydrophilic (superaerophobic) layer. On the contrary, the GCR of Janus foam gradually decreased with the increase in a laser scanning speed (>1 m s\(^{-1}\)), which could be attributed to the reduction of wetting gradient forces between superaerophobic and aerophilic sides. In other words, the superaerophobic surface tends to be aerophobic or even aerophilic as the scanning speed decreases. Noting that the gas collection failure is not equivalent to the gas blockage. As a matter of fact, a membrane with a double-faced fluid affinity (e.g., a double-faced hydrophilic membrane for water droplet) could still transport target fluid slowly in an arbitrary direction. This issue has been studied extensively and goes beyond the scope of this paper. In addition, the GCR exhibited inconspicuous distinction among different samples with 90, 130, and 160 PPI, which demonstrated that the GCR parameter was insensitive to PPI values.

The mechanism of unidirectional bubble penetration through Janus foam was briefly discussed. For Janus foam, the gas bubble only penetrates the foam if the resultant force imposing on the bubble exceeds the resistance from the water film adsorbed in the hydrophilic side of the foam. There are four kinds of forces acting on the water film: the capillary force \(F_C\), gravity force \(F_G\), hysteresis resistance force \(F_H\), and pressure difference \(F_P\) between the gas film and the gas bubble (Figure 4a). The capillary force \(F_C\) and gravity force \(F_G\) are expressed by

\[
F_C = 2\pi r \gamma \cos \theta_w
\]

(1)

\[
F_G = \pi r^2 \rho g h
\]

(2)

where \(r\) is the pore radius, \(\gamma\) is the surface tension of water, \(\theta_w\) is the WCA in air, \(\rho\) is the water density, and \(h\) is the thickness of the water film. The pressure difference \(F_P\) is equal to the gravity force \(F_G\) and the capillary forces \(F_C\) from the opposite directions cancel out under a static condition. Generally, the increase in water wettability (as well as WCA \(\theta_w\)) in the hydrophilic side of the foam would lead to the decline of the \(F_G\) along the downward direction. Consequently, the resultant force of two capillary forces would tend to push the bubble upward. It can be deduced that the sole elevation in water wettability is beneficial for the
unidirectional transport and collection performance without modifying the hydrophilic layer thickness. Unfortunately, during the Janus foam fabrication process, the enhancement of laser ablation would also increase the thickness of the hydrophilic layer $h$, followed by the increase in the gravity force $F_G$ according to eq 2, which is otherwise harmful to bubble penetration. From the Discussion section, it can be found that the construction of both appropriate wettability and thickness of the hydrophilic layer is crucial for spontaneous bubble penetration. However, it is usually difficult in theoretical prediction of the optimum values of water wettability and thickness for the laser-ablated layer. Our exploration suggested that a WCA of $\sim 60^\circ$ in air, and a laser-ablated-layer thickness of $\sim 100 \mu m$ were preferred, and this parametric condition was employed throughout the experiments.

When the gas bubble is attached to the superaerophobic surface (Figure 4b), there are three external forces exerted on the bubble along the penetration direction (upward): the buoyancy force $F_B$, the wetting gradient force $F_W$, and the adhesion force $F_A$. In this case, the resultant force $F_R$ will reach the maximum value

$$F_R = F_B + F_W + F_A$$  (3)

With the assistance of the driving force $F_D$, the enlarged bubble could eventually exceed the external drag forces and thus penetrates Janus foam. Whereas in the contrary direction, the component of the dominant force $F_W$ along the penetrating direction is neutralized. As a consequence, the resultant force $F_R \approx F_B + F_A$ is insufficient to drive the directional movement of gas bubbles. The bubble will horizontally spread on the aerophilic side, resulting in the blockage. The gas collection process includes the initial contact, bubble grow, and final penetration, as shown in Figure 4c. As numerous tiny bubbles contact with the superaerophobic side of Janus foam, the bubbles adhere to the surface and subsequently coalesce into larger bubbles. The enlarged gas bubbles keep growing and penetrating vertically to the aerophilic side when the driving force $F_D$ is large enough. In addition, the internal gas among the foam pores will bridge the gap from the superaerophobic side to the aerophilic side, eventually leading to the spontaneous and continuous transport of gas bubbles in the vertical direction.

Carbon capture and storage are considered to be important and urgently needed in controlling greenhouse gas emissions and their effects on climate change.\textsuperscript{11a,b} Based on the excellent capability of bubble transport, a demonstrative application of underwater carbon capture utilizing Janus foam was performed.

The proof-of-concept experiments were conducted using a commercial CO$_2$ generator consisting of a compressed carbon dioxide cylinder and a reducing valve and then passed through the pipe into a water-containing beaker. In order to visualize the chemical reaction process between acidic bubbles and the alkaline solution, a certain amount of the phenolphthalein reagent was added. The reaction between carbon dioxide and sodium hydroxide is described as

$$NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

As the acidic bubbles were continuously injected into the alkaline solution, the PH value gradually decreased, leading to the decolorization of phenolphthalein. Finally, the color of alkaline phenolphthalein solution was converted from purple-red to transparent after 8 min of the entire reaction (Figure 5b,c and Movie S3). The effective CO$_2$ capture and transport of this Janus foam could be used in facilitating the sustained harvest of organic gases from the seafloor. It should be emphasized that the gas collection capability of Janus foam is also generic for universal bubble harvest in different gases, which could further broaden its application scenarios.

3. CONCLUSIONS

In conclusion, a kind of Janus copper foam is proposed for unidirectional transport and effective collection of underwater gas bubbles. This Janus foam is fabricated by utilizing a facile and effective ultrafast laser ablation strategy. Janus foam can enable the underwater bubbles to transport spontaneously and unidirectionally from laser-treated side to the untreated side. The underlying physical mechanism of unidirectional penetration is attributed to the cooperation of the buoyancy, adhesion, and wetting gradient forces imposed on the bubble. The gas collection performance of Janus foam prepared with diverse parameters, including the laser scanning speed, and the PPI value is also systematically explored. Our Janus foam exhibits not only the capability of unidirectional penetration of underwater gas bubbles but also the effective gas collection performance with a maximum value of $\sim 15 \text{ mL cm}^{-2} \text{ min}^{-1}$ at a laser scanning speed of 1 m s$^{-1}$. The proof-of-concept demonstration for underwater carbon capture is shown in which Janus foam could effectively capture underwater CO$_2$ gas bubbles and facilitate neutralization with the alkaline solution.
We anticipate that the bubble Janus will further extend the applications of bubble transport, carbon capture, and controllable gaseous reactions under aqueous conditions.

4. EXPERIMENTAL SECTION

4.1. Materials and Fabrication. Commercially available copper foam sheets (PPi 90, 130, and 160, thickness ~1 mm) were cut into appropriate sizes and cleaned ultrasonically in acetone and deionized water. The cleaned samples were treated with a commercial coating reagent (Glaco Mirror Coat “Zero”, Soft 99 Co.) containing superhydrophobic silica nanoparticles and organic reagents. Thereafter, the superhydrophobic copper foams were mounted on a x-y-z mobile platform and ablated via line-by-line ultrafast laser scanning at different speeds from 0.5 to 3 m/s. The scanning spacing between two adjacent lines was 10 µm in both the x and y coordinates’ direction. The laser pulses (a central wavelength of 1064 nm, 150 kHz train of 10 ns) from a nanosecond laser system (JPT, YDFLIP-60, Singapore) were focused onto the sample surface and scanned in accordance with the preset pattern through a galvanometric scanning system (SG7110, Sino-Galvo) with a focal length of 63 mm. The mean power of the laser beam was fixed at ~10 W.

4.2. Characterization. The water/BCAs on Janus foam were measured with a contact-angle system (Innovo CA100C, China) using a sessile drop method. The water/bubble volume was set as 5 µL. Surface morphologies of samples were observed by a secondary electron scanning electron microscope (Zeiss EVO18) with an accelerating voltage at 20 kV. Chemical component analysis was measured through EDS (Bruker XFlash 6130).

4.3. Gas Bubble Collection. The bubble-collecting experiments were carried out on a purpose-built apparatus which consisted of an iron support, accessory containers, and an electric gas bubble generator. The gas bubbles were produced at a stable air flow from the bubble generator and gathered beneath Janus foam which was tightly adhered to the larger end of a plastic syringe. The gas collocation rate of Janus foam was calculated according to the collected volume of gas bubbles versus corresponding elapsed time. Each average value was obtained through five independent experiments at 20 °C temperature and normal atmospheric pressure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c00464.

Unidirectional penetration of gas bubbles on Janus foam (AVI)

Bubble penetration process (AVI)

Reaction between CO2 bubbles and alkaline phenolphthalein (AVI)

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Notes

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