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Bio-inspired spontaneous splitting of underwater bubbles along a superhydrophobic open pathway without perturbation

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Abstract

Bubbles are pervasive in aqueous media, and on account of numerous advantages of tiny bubbles, efficient bubble splitting is favorable in a wide range of applications. However, underwater bubble splitting faces a lot of challenges because bubbles tend to coalesce during the rising due to the action of buoyancy and surface energy, and the consumption of considerable external energy is needed. Inspired by the bubble bursting phenomenon on the feathers of high-speed swimming penguins, we proposed a new bubble splitting strategy based on the energy conversion of bubble transportation on superhydrophobic open pathways. A porous superhydrophobic coating was first developed via a bubble-template assisted fabrication method, which provides hierarchical micro/nanostructures and robust air plastron. Gas bubbles can transport along the superhydrophobic open pathways without perturbation, and split into smaller ones by taking advantage of the potential energy contributed by buoyancy. By controlling the superhydrophobic pathway, the size of the split bubbles can be controlled precisely. We also demonstrated that a bubble splitting device could be applied in underwater reactions where an enhanced gas–liquid mass transfer is desired. This bubble splitting strategy may offer new prospects for underwater bubble manipulation and unfold a potential in many bubble-involved fields.

INTRODUCTION

In various application sceneries, such as environmental, agricultural, chemical, and biological engineering, bubbles are ubiquitous in aqueous media.1 Substantial efforts have been made to investigate the manipulation of underwater bubbles in the past decades.2–4 In comparison with larger bubbles, tiny bubbles possess numerous advantages, such as large special surface area, additional Laplace pressure,4 small rising velocities, and high mass transfer efficiency.5 Therefore, dispersing tiny bubbles with high efficiency is valuable in many bubble-involved processes,6 for example, improvement of heat transfer7 and enhancement of gas–liquid mass transfer.8 Due to the actuation of the surface tension, underwater bubbles which are brought together by the surrounding liquid flow tend to coalesce to minimize the interface area. Bubble splitting, as the reverse process of coalescence, needs to overcome the surface energy. Moreover, the behaviors of gas bubbles are mainly dominated by buoyancy, moving the bubbles upward in an aqueous environment. Conventionally,
bubble shearing by high-speed stirring or mechanical agitation and bubble splitting by squeezing through porous membranes are the commonly used methods to divide bubbles into smaller ones.9 Besides this, splitting bubbles by electrowetting on a dielectric surface has also been developed.10 Nevertheless, all bubble splitting methods require considerable external energy input and complex devices and bring significant disturbance to the fluid medium.

In nature, many terrestrial plants and animals, such as leaves of Loropetalum chinense, diving fly Ephydra hians, water spider Argyroneta aquatic,11,12 can maintain a persistent plastron of air, which is created by the superhydrophobicity of micro/nanostructures on their surface, for serving as oxygen (O2) reservoir or drag reduction layer.13 Inspired by these phenomena of air plastron, superhydrophobic surfaces have been applied to transport gas underwater through the air plastron.14,15 These superhydrophobic surfaces can provide a stable gas layer for gas spreading, however, they have not been specifically optimized for gas transport. They are usually prepared with compact and dense micro/nanostructures with a high solid ratio,16,17 which make it difficult to trap large volumes of gas, hindering the application of the gas transport strategy using air plastron. Most recently, bioinspired surfaces with superwettability show advantages in the manipulation and transportation of underwater bubbles,18–23 but they cannot fully address the issues of high energy consumption.

Emperor penguins can trap large amounts of gas in their plumage through their superhydrophobic fur. When they dive and swim in water at high speeds, numerous air bubbles are continuously generated from the plumage and form a bubble trail behind them, which can significantly reduce the drag (Scheme 1a).24 Inspired by the phenomenon that the air plastron is stored in penguins’ plumage and the accompanied gas transportation and bubble generation, we proposed a new bubble splitting strategy by using a well-tailored superhydrophobic open pathway. Thanks to buoyancy, an object such as a gas bubble submerged in a liquid stores a certain amount of potential energy, which is essentially the incremental gravitational potential energy of the liquid.25 Therefore, we hypothesize that bubble potential energy can serve as an efficient source to offset the surface energy of bubbles in the rising process, and eventually facilitate the bubble splitting process (Scheme 1b). To realize high-efficient gas transport, we first designed and prepared a robust superhydrophobic coating with hierarchical micro/nanostructures via a gas-bubble template-assisted fabrication method. Then, by applying the superhydrophobic coating on the disk and rods, a superhydrophobic open pathway was developed, through which gas bubbles can transport in the fluid medium without causing perturbation and be split into smaller ones with precisely controllable size. Finally, we demonstrated the bubble splitting device can be applied in scenarios requiring enhanced gas–liquid mass transfer. Our strategy offers new insight into underwater gas transportation and holds potential in submerged applications and bio/chemical reactors.26

RESULTS AND DISCUSSION

The hierarchical superhydrophobic coating is fabricated via a gas-bubble template-assisted strategy (Figure 1a).27,28 A fluoropolymer solution, traditionally as a hydrophobic penetrating sealer, is blended with hydrophobic fumed silica nanoparticles and stirred to generate foam, which serves as the final precursor for creating porous coating.

SCHEME 1 Design of the bubble splitting strategy. (a) Schematic illustrating the phenomenon that the air plastron trapped in emperor penguin’s plumage is expelled into fine bubbles and generates bubbly wakes (bubble trail) behind the penguin. (b) The spontaneous bubble splitting device utilizes the bubble potential energy to realize controllable bubble splitting as the bubble rises.
Compared with the traditional sacrificial template method, the bubble-template-assisted method does not need the removal of the template substances, and more importantly, it can produce large-scale continuous micron cavities and channels. Hydrophobic fumed SiO$_2$ nanoparticles are used to provide mechanical strength to the coating and additional nanostructures. In that SiO$_2$ nanoparticles make the solution viscous, alcohol is added as a solvent to dilute the solution, which also contributes to foam formation. When the volume ratio of alcohol and fluorochemical is fixed, the viscosity of the coating solution increases dramatically with the increase of nanoparticle mass ratio (Supporting Information: Table S1). Too much viscosity is not conducive to the coating process, and too little viscosity goes against the foam formation which plays an important role in the preparation of the coating. When the mass ratio of SiO$_2$ nanoparticles is less than 2%, the foam disappears quickly and nanoparticles settle after 15 min (Supporting Information: Figure S1). In contrast, the solution with a SiO$_2$ mass ratio of 4% remains stable for a long time. After stirring and vortex, the solutions are coated on glass slides. As a control group, the coating surface with a SiO$_2$ mass ratio of 0.4% just becomes dry and rough during solvent evaporation, with few bubbles and cavities (Supporting Information: Figure S2a). On the contrary, a large number of bubbles with an average diameter of ~50 μm, are evenly distributed in the coating of 4% SiO$_2$. As the solvent evaporates, all the bubbles burst under the interfacial capillary force and cavities gradually form in situ (Supporting Information: Figure S2b). As a result, micron-scale morphology with evident crater-like structures, which are connected by grooves and channels, is obtained using this bubble-template method (Figure 1b). After drying, the coatings with different SiO$_2$ mass ratio presents distinct micrometer morphology,
which indicates that SiO₂ nanoparticles can serve as a skeleton of the coating to maintain its shape when their concentration reaches a critical value. Meanwhile, SiO₂ nanoparticles provide nanometer structures for the coatings, which explains why the coatings exhibit similar nanoscale morphology. When the mass ratio of SiO₂ increases to 6%, the crater structures disappear and the morphology is island structures (Supporting Information: Figure S3). Therefore, for the porous hierarchical microstructures, the optimal mass ratio of SiO₂ is 4%.

The wettability of the coatings was characterized. Water contact angles (WCA) of the coatings are greater than 150° when the mass ratio of SiO₂ is over 1.2%, namely showing superhydrophobicity (Figure 1c). The coating with a SiO₂ mass ratio of 4% performs excellent superhydrophobicity, which is further demonstrated that a droplet can bounce off the coating surface many times without visible residue (Figure 1d and Supporting Information: Movie S1). The difference in WCA of the coatings with various mass ratios demonstrates that the superhydrophobicity is mainly derived from the hierarchical microstructures of the coating, which suspend the water droplet to a Cassis-Baxter state.²⁹⁻³¹ It is well-known both theoretically and experimentally that superhydrophobic surfaces in air are superaerophilic when immersed in water.³²⁻³⁵ Accordingly, bubble contact angles (BCA) of the coatings submerged underwater are 0° when the SiO₂ mass ratio is over 1.2% (Figure 1c and Supporting Information: Figure S4). When the coating with a SiO₂ mass ratio of 4% is submerged, a small bubble spreads immediately after contacting the surface underwater (the BCA is 0°) (Figure 1e), which indicated the existence of a gas layer in the microstructures at the solid–liquid interface. The thickness of the hierarchical coating is approximately 100 μm and these micron-scale craters on the surface are interconnected (Supporting Information: Figure S5). Therefore, the gas layer trapped in the microstructures is continuous, which is similar to the air plastron on creature surfaces. In addition, the coating has good thermal stability at temperatures below 150 °C (Supporting Information: Figure S6).

When superhydrophobic surfaces with adapted morphology are dipped into water, it is possible to observe a silvery mirror-like sheen at their submerged surfaces because of the reflection of light from an air layer retained at the surfaces (Figure 1f), which is the signature of a Cassis-Baxter state.³⁶⁻³⁷ A silvery sheen is observed at the surface of the coating with a SiO₂ mass ratio of 4% when it is inserted into water, and the sheen can last for at least 24 h (Supporting Information: Figure S7a), which reveals the stable water-repellency of the coating. In contrast, on the surface of the coating with 0.4% SiO₂, the sheen cannot maintain due to the infiltration of water in the surface’s microstructures. The submerged surfaces of the coatings are observed in detail, and it is found that the hierarchical micro/nanostructures favor the stability of the air plastron. The coating with SiO₂ 0.4% does not possess sufficient space among the microstructures to hold the air plastron, which is eventually invaded by surrounding water (Supporting Information: Figure S7b). However, the coating with SiO₂ 4% preserves the gas plastron with the hierarchical structures and the gas plastron does not completely dissolve into water within 24 h. In addition, owing to the connectivity of the structures, gas can flow throughout the air layers. As a consequence, when a coating surface with SiO₂ 4% is immersed in water, the solid–liquid interface is replaced by two interfaces: solid–gas and gas–liquid (Figure 1g).

Now that the coating with SiO₂ 4% can introduce a robust and connected gas film (gas plastron), it can be used for bubble manipulation. If there are two bubbles of different sizes on the coating surface, they will spontaneously merge, driven by the unequal Laplace pressure arising from their different curvatures (Figure 2a). The gas in the small bubble, which has a smaller radius of curvature, is transported to the big bubble through the air film, so the small bubble (Bubble 2) shrinks gradually until disappears, and the big one (Bubble 1) gradually grows up until they complete merge (Figure 2b). Even on a complex patterned path, such long-distance bubble transport and merging can occur (Supporting Information: Figure S8, Movie S2). Nevertheless, bubbles are subjected to hydrostatic pressure underwater, so if the hydrostatic pressure difference arising from the height difference is greater than the Laplace pressure difference between two bubbles, the gas will be transported from the big bubble to the small one through the air film (Figure 2c). Therefore, when the coating surface is tilted to the point where the hydrostatic pressure difference is sufficient to overcome the Laplace pressure difference, the bubble at the lower edge of the surface (Bubble 1) gradually shrinks, and a new bubble (Bubble 2) forms at the upper edge (Figure 2d). Bubble 2 appears on the top edge of the inclined plane because the height difference between this site and Bubble 1 is the largest, which suggests that the gas transport through air film takes the pathway with the greatest driving force. Moreover, Bubble 2 cannot eventually detach from the upper edge because of the adhesion caused by the excellent aerophilicity of the surface underwater (Figure 2d). Therefore, it is confirmed that, taking advantage of the gas plastron introduced by the superhydrophobic coating, the long-distance bubble transport and merging in a two-dimensional (2D) surface can be realized. In such 2D gas transport, the pressure difference between two bubbles on the coating surface is the driving force, and the main drag arises from the air film pathway. The hierarchical porosity of the coating not only affects its superhydrophobicity by the Cassis-Baxter state, but also impacts the formation of gas film and gas transport (Supporting Information: Figure S9), which further confirms that in addition to nanoscale porosity, the micrometer structures produced by the bubble template-assisted method are of significance. In addition, although the thickness of the coating has no effect on its superhydrophocity, excessively thin coating fails to gas transport because of too thin air film path. A larger driving force, namely the pressure difference, is required to transport air (Supporting Information: Figure S10).

Analogous to that the field of droplet manipulation is progressing toward smaller size,³⁸⁻³⁹ bubble splitting has attracted increasingly wide attention due to its significance in many fields, such as fermentation, heat transfer, water treatment, and energy harvesting. It is well known that millimeter-free bubbles in water rise at a velocity of 10⁻⁵⁻⁻⁵ cm/s under buoyancy.⁴⁰ The ascending of a bubble inevitably causes the flow of surrounding water, and the external flow induces an internal circulation within the bubble (Figure 2e). Since underwater resistance to bubble movement is large, only a tiny fraction of bubble potential energy is
converted into the kinetic energy of the bubble, while a majority of bubble potential energy is converted into the kinetic energy of the surrounding water and eventually dissipated, which causes bubble potential energy to always be ignored. Therefore, it is of great benefit to use bubble potential to overcome interface energy to achieve self-powered bubble splitting. Inspired by penguin feather splitting the air plastron, a spontaneous bubble splitting device (SBSD) was designed on the basis of the excellent performance of the prepared coating. On the 2D superhydrophobic surface with the coating, bubbles can be trapped and transported over a long distance, but cannot escape. To achieve self-powered bubble splitting, it is necessary to design the path and the destination site of bubble transport properly. The path can be fixed by introducing the gas plastron to a one-dimensional (1D) surface, and the bubble detachment can be controlled by limiting the boundary of the destination site. So SBSD consists of a disk serving as a bubble collecting reservoir and an antenna-like pole acting as the pathway to transport gas, which is completely coated by the superhydrophobic coating. A bubble in contact with SBSD can be captured by the disk and slowly transported to the top of the pole, where the height difference is greatest, and then released in the form of small bubbles from the top, which is equivalent to the bubble being split into several small bubbles (Figure 2e). When SBSD is immersed in water, a silvery mirror-like sheen is observed on the surface of both the disk and the pole, indicating the formation of the gas plastron (Supporting Information: Figure S11). After being collected on the disk, a bubble of 70 μL (Bubble 0) cannot be split by an SBSD with a height of 1.5 cm but can be divided into three small bubbles (Bubble 1, Bubble 2, and Bubble 3) by an SBSD with a height of 4 cm (Figure 2f). This result indicates that there is a height threshold for bubble splitting when the diameter of the pole is fixed.

To investigate the effect of key parameters of SBSD on bubble splitting, the height and radius of the pole are defined as $H$ and $r$, respectively. The experimental results show that for a fixed $r$, $H$ has a critical value, and the corresponding critical value of $H$ decreases with the increase of $r$. And when $H$ is greater than the corresponding critical value, the number of splitting bubbles is independent of $H$ (Figure 3a). Studying the size of the small bubbles released, it is found that the radius of small bubbles $r_a$ increases gradually with the increase of $r$, and is independent of $H$ (Figure 3b).
FIGURE 3  The characteristics and mechanism of bubble splitting with the as-fabricated device. (a) The threshold height of the devices with various tip radii for releasing small bubbles. (The initial bubble volume is 70 μL. Only the bubbles released from the tips count), (b) The radius of the bubbles released as a function of the tip radius. H is 40 mm. Error bars represent the standard deviation of five bubbles. (c) Dynamic mechanism of bubble growth. The red dotted lines represent the critical state of the gas–water interfaces. (d) Force analysis of bubble detachment from the pole tip. (e) Correlation between the number of small bubbles produced by splitting and the volume of the initial bubble. (f) Volume distribution of minute bubbles released from the different devices.
To elaborate on the mechanism of bubble splitting, a simplified theoretical model was established, as illustrated in Figure 3c,d. First, the excellent superaerophilicity underwater of the coating enables the disk easily to capture underwater bubbles (Figure 1e). And the superaerophilic pole is located in the center of the disk, so the trapped bubbles tend to stick to the middle of the disk in the shape of a spherical cap. Second, as for gas transport, the formation of the 1D gas plastron on the pole is pivotal, which provides the pathway for bubble transport. The water-repellency and the hierarchical micro/nanostructures of the coating contribute to inducing the stable and connected gas plastron (Supporting Information: Figure S12). Virtually, this bubble transport strategy is essentially making full use of the water-repellency of the superhydrophobic surface with hierarchical structures to create an open channel underwater, of which one wall is the rod surface and the other wall is the gas–water interface (Supporting Information: Figure S13).

Therefore, the solid rod is equivalent to a half-wall open capillary, in which conveying the gas brings about little perturbation to the water. Furthermore, the gas transport is driven by pressure difference. The internal pressure of the collected bubble is composed of hydrostatic pressure \( P_0 + \rho g H_1 \) and Laplace pressure \( 2y/R_i \), where \( P_0, \rho, g, H_1, \) and \( y \) are atmospheric pressure, water density, gravitational constant, depth of the underwater, and surface tension of the gas–water interface, respectively. As shown in Figure 3c, the radius of the gas–water interface \( R_i \) increases as the gas is transported. The minimum of \( R_i \) equals the disk radius \( R \), when the Laplace pressure reaches the maximum. Particularly, the minimum of the Laplace pressure is 0, when the gas–water interface is flat in an ideal state (\( R_i = \infty \)). Under the action of hydrostatic pressure, the gas in the collected bubble tends to transport upward. Therefore, when the total pressure at the top of the pole is lower than the pressure inside the collected bubble, the bottom gas will flow to the top and form a gas spherical cap at the top. The internal pressure of the gas cap is also composed by hydrostatic pressure \( P_0 + \rho g H_2 \) and Laplace pressure \( 2y/R_i \). With the gas transport, the radius of the top gas cap \( r_i \) decreases and then increases, of which the minimum is equal to the radius of the pole \( r \). So the maximum Laplace pressure for the cap is \( 2y/r \). In summary, the preconditions for spontaneous gas transport can be expressed as:

\[
P_0 + \rho g H_1 + 2y/R_i \geq P_0 + \rho g H_2 + 2y/r_i.
\]

(1)

Therefore, it is found that the hydrostatic pressure difference must be greater than the Laplace pressure difference. Namely,

\[
\rho g H \geq 2y/n - 2y/r_i.
\]

(2)

where \( H \) is the height of SBSD. To achieve bubble splitting completely, this equation must hold true even when the difference of Laplace pressure is maximum:

\[
H \geq \frac{2y}{\rho g r_i} \cdot \max \left( \frac{1}{R_i}, \frac{1}{R} \right).
\]

(3)

Consequently, the theoretical threshold of the height \( H \) is obtained, that is, \( H \geq \frac{2y}{\rho g r_i} \), which is in good agreement with the experimental results (Figure 3a). At the final step, the tiny bubbles at the top of the rod must be able to detach. The force analysis at the moment of separation from the top is illustrated in Figure 3d. By assuming that the bubble shape is a spherical cap, the force driving the bubble up can be expressed as:

\[
F_{\text{lift}} = F_0 + F_N = \rho g V_i + \frac{2\pi y r_i^2}{r_i}
\]

(4)

where \( F_0 \) and \( F_N \) represent the buoyancy force and the reaction force on the bubble; \( V_i, r, r \) are the volume of the bubble cap, the curvature radius of the bubble cap, and the radius of the rod (Supporting Information: Analysis in S1). By balancing the lift force of the bubble cap and the surface tension at the top boundary, the radius of the released bubbles \( r_i \) is calculated as:

\[
r_i = \frac{3}{2\pi} \left( \frac{3}{2} f \right)^{1/3} \left( r - \frac{r_i^2}{r} \right)
\]

(5)

where \( f \) is the Harkins correction factor (Supporting Information: Analysis in S1) (Figure S14). Eventually, substituting the empirical value leads to a semi-analytical model:

\[
r_i = \frac{3}{2\pi} \left( \frac{27}{40} \pi r \right) = \frac{3}{2\pi} \left( \frac{27}{40} \lambda^2 r \right)
\]

(6)

where \( \lambda = \left( \frac{3}{2\pi} \right)^{1/3} \) is the capillary length of water, which is in perfect agreement with the experiment (Figure 3b). The consistency of the theoretical model and experiment indicates that the size of the released bubbles is controllable by parameters of SBSD, such as \( H \) and \( r \).

In addition, the number of bubbles produced by splitting is linearly related to the volume of the collected bubbles (Figure 3e), which promises that the bubble splitting process is stable and has scale-up feasibility. The volume distribution of split bubbles shows that the size of the released bubbles is very uniform by this strategy (Figure 3f), which further confirms the controllability of the bubble splitting. In the process of bubble splitting with SBSD, the collected bubble is divided into small bubbles and rises to the height of \( H \) without perturbation, so the bubble potential energy transforms into interface energy of gas–liquid, essentially the gravitational potential energy of the aqueous medium into its surface energy (Figure 2e). Therefore, the energy-conversion efficiency can be defined as the ratio of interface energy increment to bubble potential energy reduction:

\[
\eta = \frac{\Delta S \cdot \gamma}{\Delta E_b}.
\]

(7)

where \( \Delta S \) stands for the change of the surface area of bubbles, and \( \Delta E_b \) represents the reduction of bubble potential energy. When a large bubble with a volume of \( V_i \) is completely split into \( N \) equal bubbles with a volume of \( V_a \), the energy-conversion efficiency is expressed as:

\[
\eta = \frac{3 \left( 1 - N^{1/3} \right) \gamma}{\rho g r_i H}.
\]

(8)
(Supporting Information: Analysis in SI (Figure S15). Therefore, SBSD is also considered as an energy storage device, which efficiently converts bubble potential energy usually neglected into surface energy of the aqueous medium without causing a disturbance of the medium. This is a huge optimization and improvement of the system for the negative effects of buoyancy and is expected to have applications in energy harvesting.

To improve the efficiency of bubble splitting, the bubble splitting on double-rod SBSD is verified (Figure 4a). When the heights of the two poles are the same, the pressure differences between the disk and the tops of the two poles are the same, resulting in identical numbers of released bubbles from the two poles (Figure 4b). And when the heights of the two rods are different, bubbles are more likely to be released from the top of the higher rod.

O₂ is a vital substrate relevant to plenty of biological and biogeochemical processes in nature and human life. In a wide range of fields, such as aquaculture, fermentation, and sewage treatment, O₂ is required to be continuously bubbled due to the low solubility of O₂ in aqueous solutions. However, the behavior of gas bubbles is mainly dominated by the buoyancy moving gas bubbles upward, resulting in a short retention time in an aqueous environment, which leads to a significant waste of O₂ and energy. Compared with large bubbles, many features of small bubbles, such as large special surface area, increasing internal pressure, and long retention time resulting from slow rising, contribute to improving the gas–liquid mass transfer efficiency. Here, we installed SBSD into a 1 L bioreactor, which is one of the most prominent biochemical devices. The installation is compositely of a pump, gauge, detector, and computer, in which the concentration of the dissolved oxygen (DO) is recorded in real-time (Figure 4c). The DO concentration slowly increases with pumping bubble into the water, but the DO does not reach the dynamic saturation value within 200 min (Figure 4d), which indicates the low mass transfer efficiency of O₂ for the traditional stirrer. In contrast, when a superhydrophobic (SHP) disk serves as a stirrer, the mass transfer efficiency of O₂ is improved a little bit. Then, it is found that the O₂ mass transfer efficiency is significantly improved using SBSD with two rods, nearly doubling the traditional efficiency (Figure 4d). SBSD cannot only enhance mass transfer by splitting bubbles but also utilize buoyancy without disturbance, eliminating the adverse effects of buoyancy. Besides, it does not require additional energy input. So SBSD is an efficient strategy to enhance gas–liquid mass transfer, which is promising to be applied in other fields such as artificial fishery.

The combination of high-efficiency agitation and mass transfer is the pivotal technology of large-scale ventilation fermentation.

**FIGURE 4** Application of the bubble splitting device to enhance mass transfer. (a) The optical images of the double-rod device with different heights. (b) The dispersion of discharged bubbles from two rods of different heights. (c) Installation diagram of the measuring system for dissolved oxygen (DO) in water. (d) The concentration evolution of DO with time. The three stirrers are a traditional disk-shaped stirrer, a superhydrophobic disk-shaped stirrer, and an as-fabricated device with two rods (H = 4 cm, r = 0.6 mm), respectively.
engineering, which is a significant factor affecting microbial respiration and metabolism and energy-saving efficiency. To improve the utilization efficiency of oxygen-rich gas in the fermentation system, the traditional methods include changing the gas path, designing the geometry of the stirrer, and increasing the stirring rate. Airlift reactor improves mixing by the gas−liquid turbulent produced by gas lifting. Although a longer gas−liquid contact time is obtained, the bubbles are large and the gas−liquid transfer efficiency is low. Stirred-tank fermentor breaks bubbles and obtains a large number of tiny bubbles through high-speed stirring shear. However, the disorderly rise of free bubbles makes the retention time of bubbles short. Meanwhile, high shear may destroy cell membrane, causing cell death and fermentation efficiency reduction. SBSD can prolong the retention time and enhance gas−liquid mass transfer by capturing bubbles and splitting them into tiny bubbles. Therefore, SBSD has great prospects to be applied to promoting bacterial proliferation (Figure 5a). As a proof of concept, the bacterial reproduction rate by this strategy was compared with that of the traditional stirring method. After cultivation at room temperature for 24 h, the concentration of Escherichia coli (E. coli) in the set containing SBSD was significantly higher than that of stirring set (Figure 5b−e), indicating SBSD can improve bacterial proliferation rate without stirring. So this strategy of bubble splitting is promising to be applied in fermentation engineering and bioreactor.

**CONCLUSION**

In summary, a superhydrophobic coating with micro/nano-hierarchical structures was fabricated via the gas-bubble template-assisted strategy, for which the gas-bubble templates provide cavities for gas retention and transport. When the superhydrophobic coating is submerged, a stable and uninterrupted sheathing layer of air is introduced at the solid−liquid interface by virtue of its excellent superaerophilicity underwater. The air plastron provides a gas pathway on the coating surface to enable long-distance bubble transport. Furthermore, inspired by the bubble trail phenomenon in penguins' plumage, a spontaneous bubble splitting strategy was proposed based on transforming bubble potential energy into surface energy. And a SBSD consisting of a disk and a pole was designed to create a duct-like 1D air plastron as an open pathway, along which perturbation of the gas transport to the aqueous medium is minimized, therefore reducing the viscous dissipation. Both experimentally and theoretically, the highly controllable bubble splitting can be achieved by controlling the height and radius of SBSD to some extent, and bubble potential energy is utilized efficiently to split bubbles without any external energy consumption. In addition, it was demonstrated that the device provided a new way to enhance the mass transfer efficiency of underwater bubbles and promote the
proliferation rate of underwater microbes. This strategy of spontaneous bubble splitting along the open pathway offers new insights into bubble transport and manipulation, and it is promising to be applied in many fields including gas-involved reactions, energy harvesting, bio/chemical reactors, and microfluidics.

METHODS

Ethanol and fluorochemical Capstone ST-110 (Sigma-Aldrich) were mixed in a centrifuge tube with a volume ratio of 9:1 and stirred until the clear flaxen solution was obtained. Hydrophobic fumed silica AEROSIL R202 (the average particle size of SiO2 NPs is 14 nm; Sigma-Aldrich) was added into the solution with different mass ratios. After whisking by vortex machine for 5 min, the milky cloudy solution was obtained, which was filled with evenly dispersed foam. The coatings could be applied directly to various substrates, and hydrophobicity was achieved after drying for a few minutes at room temperature, as shown in Figure 1a. For instance, it was spin-coated on a clean glass slide using a spin-coater (KW-4A, Institute of Microelectronics of Chinese Academy of Sciences).

Commercial copper wires of different diameters and lengths are welded to circular aluminum sheets with a radius of 1 cm to obtain the homemade disks and poles. Then the disk and pole are polished with sandpaper. SBSD was fabricated after rinsed thoroughly and dip-coated with the coating of 4 wt% SiO2. Since the coating is at least 50 μm thick, the surface roughness of the copper wire is not exposed. Therefore, the micro/nanostructures of SBSD are just the coating surface structure.

The hierarchical micro/nanostructures of the superhydrophobic coating were investigated by a field emission scanning electron microscope (SEM; Philips XL30CP) at 10.0 kV. Contact angle measuring was conducted with OCA20 equipment (Data Physics). The volumes of droplets used for measuring static contact angle were 10 μL. The bubble contact angle was measured at about 5 cm underwater at a temperature of 20 °C. The viscosity measurements were performed on a rotational rheometer (Malvern Kinexus Lab®). Optical images were taken with a camera (Nikon D5500) and the spreading details of the bubble were recorded with a high-speed CCD (i-speed 3; Olympus). The air plastron on the coating was observed by an optical microscope (Nikon Eclipse Ni-E upright fluorescence microscope). After the coating was dyed with Rhodamine 6 G (Sigma-Aldrich), confocal images were captured by Zeiss Laser Scanning Microscope LSM 880 NLO with an Airy scan. The thermal property of samples was measured by thermogravimetric analysis (TGA, TA Q600 differential thermal analyzer) at a heating rate of 10°C/min.

The measurement system was installed as Figure 4c. The installation is composed of a pump, gauge, detector (Leici JPSJ-605F), and computer. Air is blown in the reactor at the rate of 1.2 standard cubic foot per hour (SCFH) (33.96 L/h). The water in the reactor is stirred at 300 rpm and the three stirers are a traditional disk-shaped stirrer (4 cm diameter), a superhydrophobic disk-shaped stirrer (4 cm diameter), and two SBSDs (the disk is 2 cm diameter, and the pole H = 4 cm, r = 0.6 mm), respectively. The concentration of DO is recorded in real-time.

Green fluorescent protein labeled E. coli was firstly cultivated on standard LB agar for 24 h in a biological incubator at 37 °C. The colony was obtained and dissolved into the nutrient broth (a single colony in 100 mL) to prepare the preculture medium. The culture medium was fully homogenized by high-speed shaking. Afterward, the medium was divided equally and poured into three reactors for different experimental sets separately. Each reactor was closed with a lid. Then the cultivation was performed for 24 h at room temperature. Bacterial in the first set grew naturally, as a control. Air was blown in both the second and third sets at the rate of 0.5 SCFH (14.2 L/h). The second set was stirred at 300 rpm by Teflon magnetic stirrer; two SBSDs (the disk was 2 cm diameter and the pole H = 4 cm, r = 0.6 mm) were fixed in the third set without stirring. Fluorescence images were captured by using the ECLIPSE Ni-E (Nikon) microscope. Colony counts were obtained by plate counting.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ETHICS STATEMENT

The authors declare that none of the work contained in the manuscript is published or currently under consideration elsewhere. All authors have contributed to, read and approved the submitted manuscript. The authors declare no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.