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Adjustable Underwater Gas Transportation Using Bioinspired Superhydrophobic Elastic String

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Abstract: Dynamic and precise manipulation of the gas flow in a liquid environment through a facile and reliable approach is of great importance for directional gas transportation and multi-phase chemical reactions. In this research, elastic superhydrophobic strings were prepared by a one-step, non-fluorinated dip-coating strategy. The surface-treatment string demonstrated a good superaerophilicity underwater. By simply elongating or shortening superaerophilic strings, the gas flux underwater was precisely manipulated in a gas-siphon underwater experiment. The result reveals that a large strain of the treated string induces a low gas flow, and a rope woven with more strings results in a larger range of gas flow regulation. The elastic superhydrophobic/superaerophilic string was utilized to adjust the reaction time of carbon dioxide and sodium hydroxide aqueous solution successfully. Furthermore, in a wet oxidation experiment for treating simulated flue gas composed of nitric oxide (NO), nitrogen and oxygen, superhydrophobic and stretched strings with a strain of 200% demonstrated a 7.9% higher NO removal efficiency than that of untreated strings. Interestingly, NO removal efficiency can be regulated by mechanical stretching of gas-conducting strings. We believe that this facile and low-cost approach provides a valid method of on-demand manipulation of the gas flow for underwater gas transportation.

Keywords: superhydrophobic; superaerophilic; gas transportation; elastic string



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1. Introduction

The continuous and directional transportation of gas bubbles with low-energy-consuming properties in an aqueous environment is of vital importance in modern science and technology, such as gas evolution reaction [1], CO₂ capture/reduction [2,3], mineral flotation [4], harmful gas treatment [5,6], and so on. Unfortunately, due to the ultralight property, the behaviors of gas bubbles in aqueous media are mainly dominated by the buoyancy, which is always directed vertically upward and drives gas bubbles out of the water, resulting in their difficult manipulation [7]. Regulating the bubble's behavior in a controlled manner is meaningful in the optimization of gas-involved processes [8]. Recently, functional surfaces possessing special gas superwettability (i.e., superaerophilicity and superaerophobicity) have emerged as a useful pedestal for manipulating the bubble's behavior [9]. Conventionally, for a superhydrophobic surface, the water contact angle (WCA) with the solid surface exceeds 150°, and for a superaerophilic surface, the bubble contact angle (BCA) with the solid surface is less than 10°. The superhydrophobic surface usually reveals superaerophilicity underwater. Li et al. prepared superhydrophobic porous copper wires with rectangle, wave, and helix shapes and realized spontaneous and directional bubble transportation on copper wires in aqueous media [10]. Zhang et al. reported a bioinspired pressure-tolerant asymmetric slippery surface for continuous self-transport of gas bubbles in an aqueous environment, which was constructed by CO₂ laser cutting,

superhydrophobic modification, and fluorinert infusion [8]. Zhu et al. fabricated a kind of Janus copper foam for unidirectional transport and effective collection of underwater CO₂ bubbles. Janus foam was constructed via one-step laser ablation on a single side of the superhydrophobicity-treated copper foam [11]. Generally, the superhydrophobic surface has outstanding interaction with bubbles in an aqueous environment, which is commonly known as the underwater superaerophilic interface [12,13].

Up to now, two difficulties have hindered the development of the underwater transportation of gas bubbles using a superwetting surface: (i) Aside from gas bubbles, can high-flux gas be transported on the superhydrophobic surface underwater? (ii) Can the flux of gas transportation on the superhydrophobic surface be adjusted by a simple method [9]? Recently, Zhang et al. reported a superhydrophobic/superaerophilic yarn with fiber network structures, and they realized the directional transport of bubbles and a gas-siphon underwater with high flux. This research proves the feasibility that continuous, directional, and high-flux gas transportation underwater can be achieved by a porous superhydrophobic rope [9]. Nevertheless, dynamic and precise manipulation of the gas flow in a liquid environment still faces great challenges. Recently, Zhang et al. constructed a bio-inspired elastic liquid-infused material by infiltrating porous silicone with a low-surface-energy perfluoro lubricant as lining liquid [14]. Under mechanical stretching, on-demand control on the bubble contact angle, merging and splitting underwater can be reversibly regulated. This study demonstrated that elastic material could be utilized for the regulation of the superwetting behavior of bubbles. In this study, elastic superhydrophobic/superaerophilic strings were prepared for the flux modulation of underwater gas transportation. By simply elongating or shortening superaerophilic strings, the gas flux underwater was precisely manipulated, and thus the speed of the gas–liquid chemical reaction was adjusted.

2. Materials and Methods

2.1. Materials

The elastic string, knitted of 74.9% nylon fiber and 25.1% spandex fiber, was purchased from Wenzhou Yishui Textile Co., Ltd. (Wenzhou, China). Hexadecyltrimethoxysilane (HDTMS, 95%) was purchased from Bide Pharmatech Ltd. (Shanghai, China). Hydrochloric (HCl) acid, phenolphthalein, anhydrous alcohol, and trisodium citrate dihydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Marble was purchased from Shanghai Hutai Jinghua Technology Research Institute (Shanghai, China). Oxone (2KHSO₅·KHSO₄·K₂SO₄) was bought from Shaoxing Shangyu Jiehua Chemical Co., Ltd. (Shaoxing, China). N₂ (99.99%), O₂ (99.99%), and NO (99.9%) were supplied by Qingdao Ludong Gas Co. Ltd. (Qingdao, China). All chemicals were used without further purification.

2.2. Surface Treatment

Before surface treatment, a string (length: 25 cm; diameter: 3 mm) was ultrasonically cleaned in ethanol for 1 h and then dried at 50 °C. For the following surface treatment, an alcosol was prepared by adding 7.5 mL of 0.36 wt% aqueous HCl solution into 30.0 mL of 3 wt% HDTMS/ethanol solution at 60 °C with stirring for 5 min. Then, the string was immersed in the HDTMS alcosol at 60 °C for 6 h. After the string was taken out, washed with hot ethanol (60 °C), and dried at room temperature for 20 h, a superhydrophobic string was obtained.

2.3. Stability Test and Regeneration

The stability of surface-treated strings in water was tested with various immersion times. To avoid floating, two ends of the strings were fixed underwater. Water contact angles (WCAs) of the strings as a function of immersion time were measured. In the washing durability test, the surface-treated strings were laundered in water containing 0.37 wt% soap powder under mechanical stirring with a stirring speed of 400 rpm at 40 °C for 45 min. Then, after drying, the WCA of the string was measured to evaluate surface

damage. The surface-damaged strings were regenerated by one-step dip-coating in HDTMS alcosol according to the method in Section 2.2.

2.4. Gas Transportation

Flow regulation of the gas siphon underwater: In order to realize flux-adjustable gas-self siphon underwater, an experimental device was built, which consists of a gas storage tank, a strand of surface-modified rope (length: 24~25 cm) with a varying number of strings, and a homemade mechanical stretching device of strings for gas flow regulation. The gas storage tank with 100 mL of air was inverted and immersed in water. One end of the surface-modified string was fixed in the top of the air storage tank, whose depth is 1 cm. The middle part of the string with a length of 4 cm was fixed between the two movable ends of the mechanical stretching device. The other end of the string was placed out of the water.

Flow regulation of CO₂ transportation underwater: The experimental device for the adjustment of CO₂ flux consists of three parts, a CO₂ generating device, a homemade mechanical stretching device of string for gas flow regulation, and a CO₂ reaction device. CO₂ was produced by adding 100 mL of 2 M aqueous HCl solution into 15 g of marble blocks. Then, CO₂ was introduced into the mechanical stretching device 12 cm underwater with a strand of surface-modified rope. The rope (length: 24 cm) was woven with two elastic strings together, and its middle part with a length of 4 cm was fixed between the two ends of the stretching device. Rope strain was adjusted by elongating or shortening the rope underwater. Finally, CO₂ was introduced into a magnetically stirred aqueous NaOH solution (3.3 mM, 30 mL) using phenolphthalein as an indicator. The stirring speed was 100 rpm. The color change of the mixed solution reveals the reaction process between CO₂ and NaOH solution. The gas transportation process was recorded by a camera (iPhone XS Max).

2.5. Removal of NO

The self-designed experimental apparatus mainly comprises a simulated flue gas system, a gas–liquid reactor, an analytical system, and a tail gas treatment system. NO, N₂ and O₂ were used to make the simulated flue gas. NO was first diluted with N₂ to a concentration of 200 ± 20 ppm using a compressor, and the flow of the mixed gases was 900 mL/min. O₂ was supplied from a compressed gas steel cylinder with a flow of 100 mL/min. Three gases passed through a gas-mixing chamber and flowed to the gas–liquid reactor. The rotameter and the valve were used to monitor the gas flow through the reactor. The gas–liquid reactor was a heated gas-washing bottle (250 mL) with six gas-holes at the bottom of the bottle body. A total of 220 mL of oxone aqueous solution (2KHSO₅·KHSO₄·K₂SO₄, concentration: 1 g/L) as NO oxidant was added into the bottle. Elastic strings were woven on the surface of the gas guide pipe of the bottle cap manually. A stretched string brings a large strain and a close arrangement on the gas guide pipe. The mixed gases passed through the gas–liquid reactor, and the inlet and outlet concentrations of NO were measured using a flue gas analyzer. Tail gas was treated by potassium permanganate solution (16.7 g/L, 300 mL) before being discharged. The removal efficiency (%) of NO was calculated by the following Equation (1) [15]:

$$\text{Removal efficiency (\%)} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% \quad (1)$$

where C_{in} is the inlet concentration of NO and C_{out} is the outlet concentration.

2.6. Characterization

The water/bubble contact angles (W/BCAs) on elastic strings were measured with a Theta machine (Biolin Scientific, Gothenburg, Sweden) at an ambient temperature. The water/bubble volume was set as 3 µL. The surface morphologies of samples were observed using field emission scanning electron microscopy (SEM, Quanta FEG, FEI, Hillsboro, ORUSA). Before SEM observation, the samples were sprayed with Au. The chemical

component analysis was measured through an energy-dispersive spectrometer (EDS, Noran System 7, Thermo Fisher Scientific, Waltham, MA, USA). The Fourier-transform infrared (FTIR) spectrum was analyzed on the Thermo Scientific Nicolet iS10 D3 system (Thermo Fisher Scientific, Waltham, MA, USA) using the KBr pellet method. NO concentration was measured using a flue gas comprehensive analyzer (Laoying3022, Qingdao Lonying Environmental Technology Co., Ltd., Qingdao, China).

3. Results and Discussion

Herein, a one-step, non-fluorinated dip-coating strategy was utilized for the surface treatment of elastic strings (Figure 1a). To achieve this goal, an HDTMS alcisol was prepared. By simply immersing strings in the HDTMS alcisol and then drying at room temperature, a superhydrophobic elastic string was fabricated successfully. The FTIR spectra of pristine and surface-treated strings are shown in Figure 1b. For pristine strings, the characteristic peaks located at 1632, 1536, 1259, and 1104 cm^{-1} are assigned to the C=O, N-H, and C-N, C-O-C stretching vibrations, respectively [16–20]. The strong C-H asymmetrical and symmetrical stretching vibrations of $-\text{CH}_2-$ groups appear at 2919 and 2857 cm^{-1} , respectively [21]. All these absorption peaks of the sample indicated the existence of nylon 6 and spandex fibers. For treated strings, the absorption peak at 1030 cm^{-1} corresponds to the Si-O-Si stretching vibration, and the absorption peaks at 2919 and 2857 cm^{-1} assigned to $-\text{CH}_2-$ asymmetrical and symmetrical stretching vibrations originating from alkyl chains ($-\text{C}_{16}\text{H}_{33}$) of HDTMS strengthen obviously, proving that the hydrolysis–condensation products of low-surface-energy HDTMS are grafted onto the fiber surface [22,23].

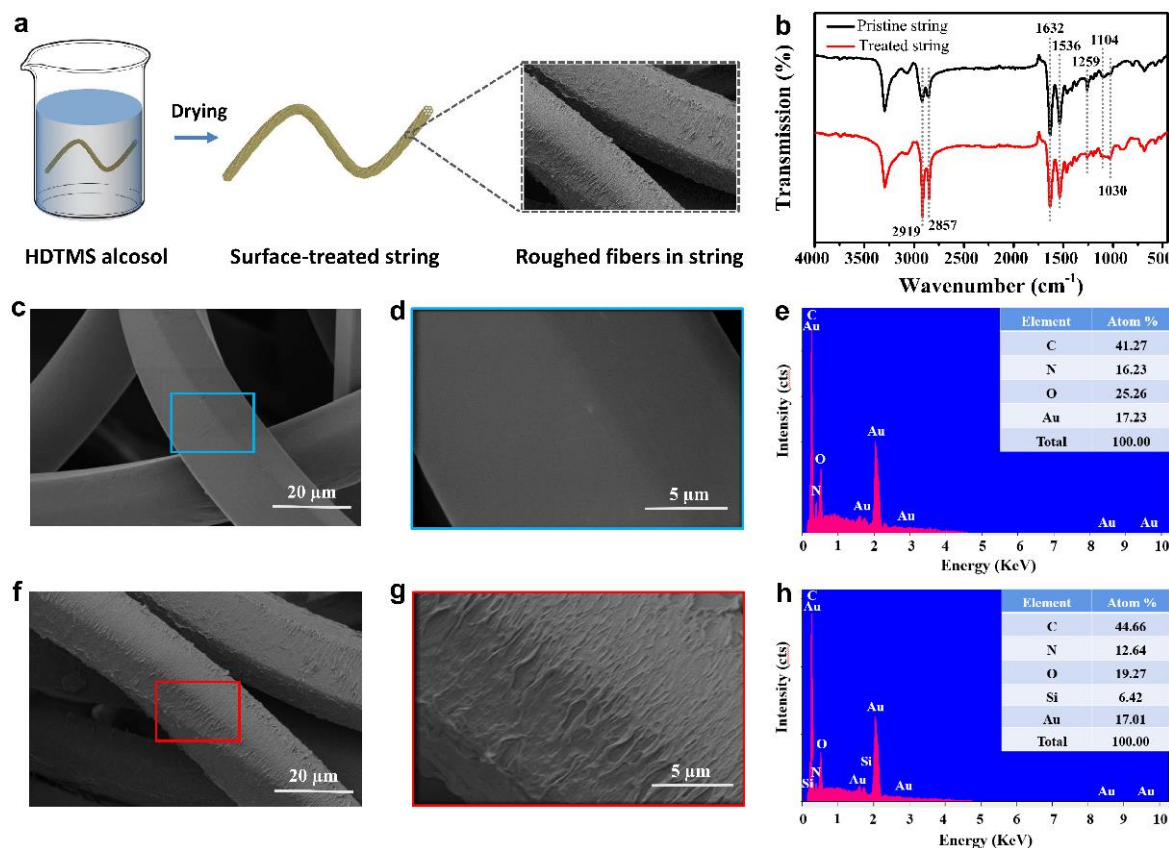


Figure 1. (a) Schematic diagram of the surface treatment for the elastic string. (b) FTIR spectra of pristine and treated strings. (c) Low-magnification and (d) high-magnification SEM images of the pristine string. (f) Low-magnification and (g) high-magnification SEM images of the treated string. (e,h) are EDS spectra of the pristine and treated strings.

The microscopic morphologies of pristine and treated strings were observed using SEM (Figure 1c,d,f,g). Pristine strings reveal a feature of smooth fibers (Figure 1c,d), whereas the surface of treated strings wrinkles (Figure 1f,g). The average fiber diameter of pristine strings was approximately 20 μm . The distance of the wrinkles ranged from ~200 to ~600 nm. EDS was used to analyze the chemical composition of pristine and treated strings (Figure 1e,h). Si element was detected on the surface of treated strings (Figure 1h), confirming that the hydrolyzed and condensed HDTMS products coated on the fiber surface. Additionally, the surface C/O ratio increased from 1.61 of the pristine string to 2.32 of the treated string, which was attributed to long alkyl chains of grafted HDTMS. For treated strings, low-surface-energy alkyl chains combining with micro/nanoroughness on fiber surfaces benefit the improvement of fiber hydrophobicity [24,25].

After surface modification, elastic strings obtain a good superhydrophobicity in the air. Figure 2a reveals that two colored water drops of 3 μL of cannot stay on the surface of the pristine string and permeate into it rapidly. By using the video shooting and analyzing the function of the contact angle meter, it was found that the absorption process of the water droplet happened within 1.95 s and the final WCA of the original string was 0° (Figure 2b), showing a hydrophilic feature [26]. For the treated string, 3 μL water microdroplets remained spherical on the surface with a WCA of 161.0° , which stayed stable for a long time (60 s or more). The improvement of hydrophobicity confirms the effect of one-step dip-coating of HDTMS alcisol. The superhydrophobic surface treatment brings a superaerophilic property for the elastic string in water media [27]. As shown in Figure 2c, when immersing the pristine string in water, the air stored between the string fibers was exhausted and became completely wetted, inducing the pristine string to sink down (inset of Figure 2c). For the treated string submerged in water, it was observed that there was a layer of air enclosing it. After being unclapsed, the treated string floated up onto the water (inset of Figure 2c). The measurement of BCAs underwater demonstrates diverse gas–solid behaviors of pristine and treated strings. Figure 2d shows that a 3 μL gas bubble stayed stably on an untreated string with a BCA of 116.4° , indicating an aerophobic characteristic, while a 3 μL gas bubble was absorbed entirely in an extremely short time of 0.06 s with a BCA of 0° , demonstrating a superaerophilic property underwater [28].

The long-term stability of surface-treated strings in water was tested for 7 days (Figure S1). The WCA of the original string was 161.0° , and after 7 days it decreased to 155.7° . The WCA of the string with the immersion time of 4 to 7 days declined slightly from 155.8° to 155.7° , indicating good stability in water [29]. The good stability of the superhydrophobic strings is attributed to the Cassie state of the surface, in which an air layer exists between strings and water (Figure 2c), which delays the interaction between water and HDTMS coating. Unfortunately, the washing durability of surface-treated strings is not good. After being laundered, the WCA of the strings decreased from 161.0° to 128.3° , indicating the loss of superhydrophobicity. Further, the surface-damaged strings can be regenerated by one-step dip-coating in HDTMS alcisol. After regeneration, the WCA of the strings recovered to 161.1° , revealing a good regenerating property.

The elastic property of strings provides the possibility to adjust the superhydrophobicity and superaerophilicity. A minute CuSO_4 droplet (3 μL) stayed in an almost spherical shape with a WCA of 161.0° in the air (Figure 3a). With the strain increasing, WCA decreased. When the string strain was regulated to 100% and 150%, the WCA of the elongated string turned to 151.2° and 143.7° , respectively (Figure 3b). Stretched strings remained superaerophobic in water with BCAs of 0° (Figure 3c,d). Interestingly, when being elongated, a bubble emerged at the left end (a high position in water) of the string and the bubble volume increased with increasing strain. By recovering the string to the original state ($\varepsilon = 0$), the bubble turned small and disappeared finally, which indicated that gas capacity per unit string length could be manipulated reversely by simply stretching or shortening the string. Utilizing this, the gas flow of the gas siphon could be manipulated simply by adjusting the string strain. To achieve this, a homemade experimental setup for a gas-self siphon underwater was built and a mechanical stretching device was used to

adjust the string strain (Figure 3e). Figure 3g shows the gas flow as a function of strains for the ropes woven with a various number of strings (Figure 3h). With the rope strain increasing, the gas flow declined. On the other hand, it is found that the gas flow will increase as the number of string strands increases. Furthermore, for a rope, a large number of strings leads to a large difference in the gas flow under the same change in strains. For example, the gas flow of one string decreased from 0.032 to 0.015 mL/s when the string strain was adjusted from 0 to 150%, while for the rope fabricated with five strings, the gas flow declined from 0.230 to 0.060 mL/s under the same strain change. It can be explained that a large number of strings increases the diameter of gas-trapped rope and thus affects the gas flow of self-siphon underwater notably.

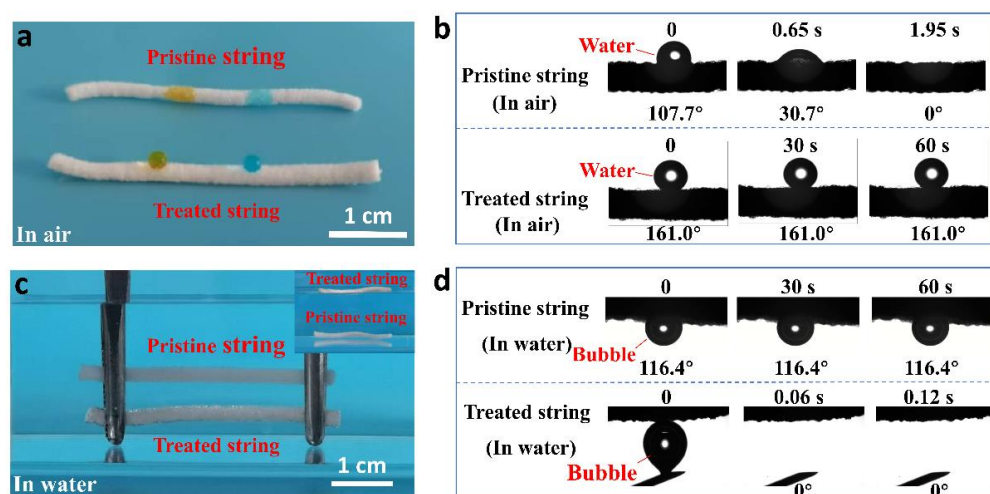


Figure 2. Wetting behaviors of pristine strings and surface-treated strings in air and water. (a) Digital images of the wetting behavior of the pristine and treated strings in the air. A CuSO₄ droplet (blue) and a FeCl₃ droplet (yellow) with the same volume of 3 μL were placed on the pristine and treated strings. (b) WCA images of the pristine and treated strings in the air for various time periods. The volume of the water droplet is 3 μL. (c) Digital images of the pristine and treated strings soaked in water. Inset of (c): when being released, the pristine string sank to the bottom and treated string floated on water. (d) BCA images of the pristine and treated strings in water for various time periods. The volume of the bubble is 3 μL.

The mechanism for the adjustable gas flow using stretchable supraaerophilic string is explained as follows (Figure 3f). The string is woven with a large number of thin nylon and spandex fibers and every fiber is supraaerophilic after one-step dip-coating surface-treatment. We define d_0 as the string diameter, d_1 as the average distance between fibers, and $d_{\text{gas}0}$ and $d_{\text{gas}1}$ as the gas thickness captured by the string surface and fiber surface, respectively. Under a stretching condition ($\epsilon > 0$), the superhydrophobicity/supraaerophilicity of fibers is weakened, which is proved by the WCA change in Figure 3c, inducing $d_{\text{gas}0}$ and $d_{\text{gas}1}$ decreases. On the other hand, stretching leads to a decrease in the distance between fibers (d_1) in the string, which compresses the space for gas storage within the string. Therefore, the change in surface wetting behaviors of fibers and the string combining with the change in fiber arrangement in the string results in a change in the gas flow of the supraaerophilic string. It is worth mentioning that since the strain can be precisely regulated by mechanical stretching, dynamic and precise manipulation of the gas flow for a superhydrophobic/supraaerophilic elastic string in a liquid environment is successfully accomplished.

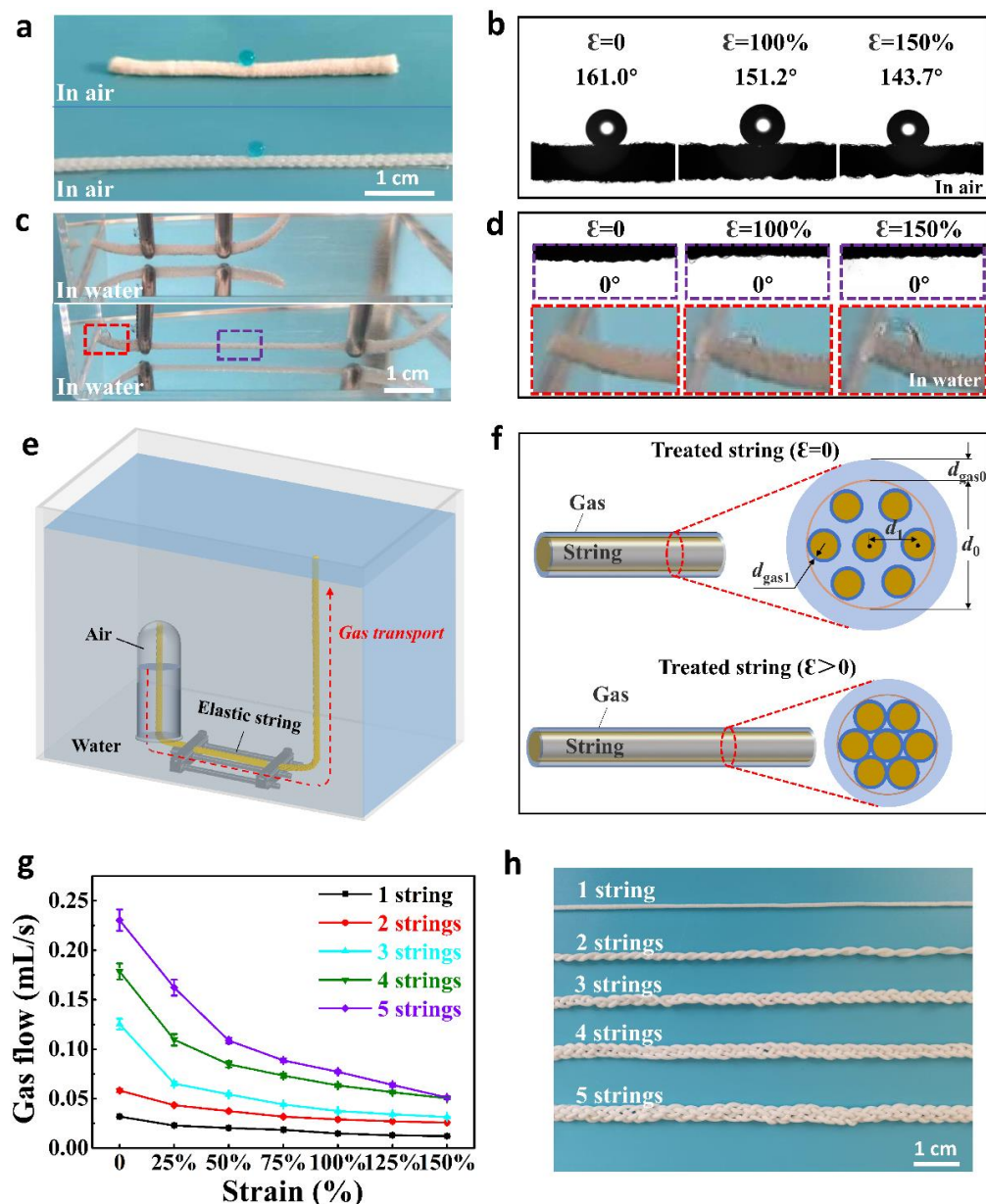


Figure 3. (a) Digital images of the wetting behaviors of the surface-treated elastic strings in the air. CuSO_4 droplets (3 μL) were placed on the treated strings with a strain of 0 and 150%, respectively. (b) WCA images of the treated strings in the air with various strains. The volume of the water droplet is 3 μL . (c) Digital images of the treated strings with a strain of 0 and 150% soaked in water, respectively. Red dashed box: A bubble appeared on the left of the string. (d) BCA images of the treated strings underwater with various strains. A bubble grew larger with the strain increasing at the left end of the string. (e) Schematic illustration of the experimental setup for gas-self siphon underwater. (f) A model diagram for explaining the adjustable gas transportation. (g) Gas flow of gas siphon underwater using different numbers of treated strings woven together with various strains. (h) Plaiting strands of strings together manually to obtain ropes with different diameters.

By adjusting the strain of the gas-conducting elastic string, the gas flow underwater and the speed of the gas-liquid chemical reaction can be effectively manipulated. A typical chemical reaction of CO_2 and NaOH was utilized as a demonstrative experiment of gas flow regulation. CO_2 was produced by adding aqueous HCl solution into marble blocks (Figure 4a). CO_2 flow was regulated by changing the strain of the rope underwater using a mechanical stretching device (Figure 4b), and then it was introduced into a stirred aqueous

NaOH solution containing phenolphthalein as an indicator. Figure 4c–g shows the color change of the NaOH solution over time under various rope strains. For an unstretched rope, it took 4 min 32 s to turn colorless, which implied a pH value of the solution near 8 and NaOH was close to complete reaction. With the strain increasing, the time of the reaction extended. For a rope with a strain of 150%, 15 min 27 s was needed to finish the neutralization reaction. In brief, a small strain will induce a high flow of CO₂ transportation underwater, otherwise the opposite.

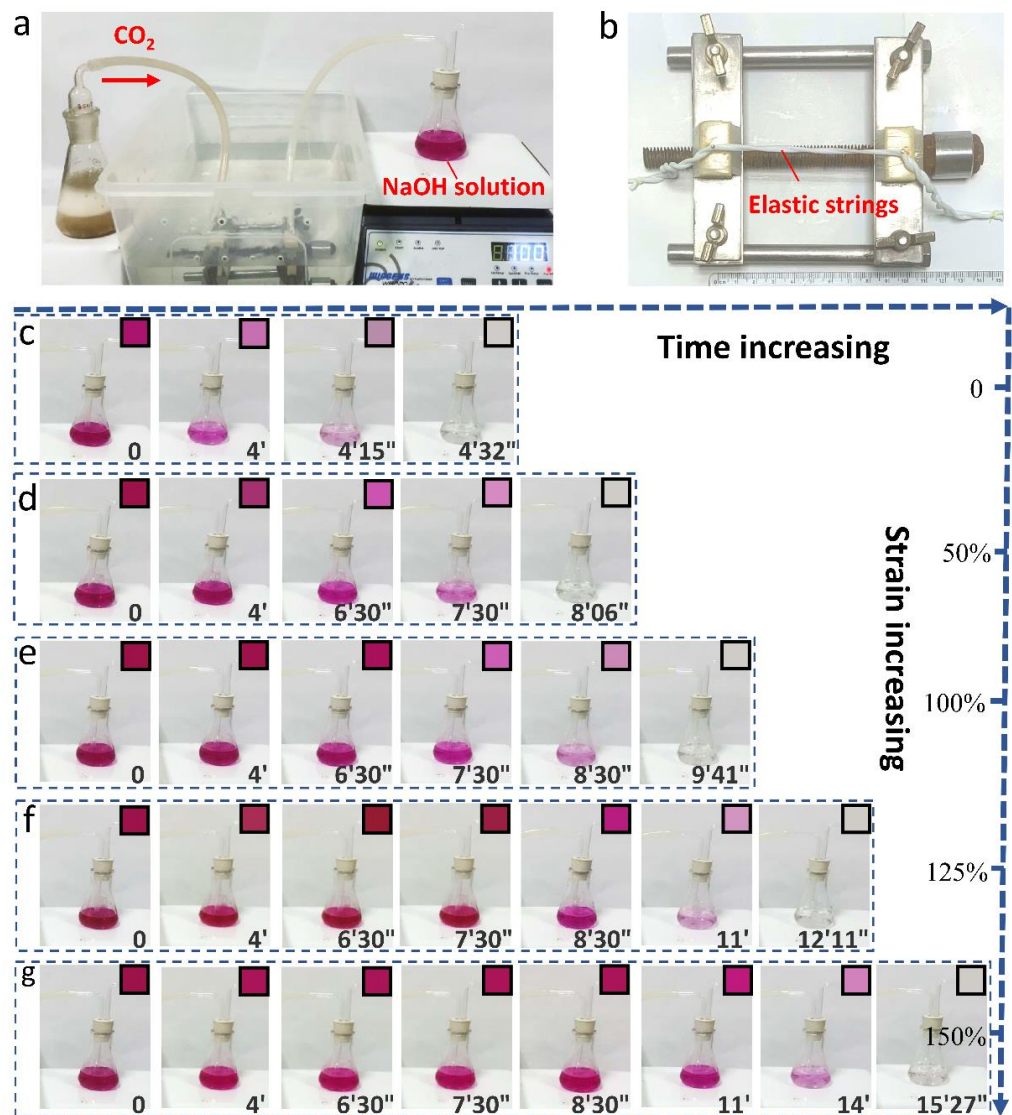


Figure 4. (a) The CO₂-conducting experimental setup with a strain-adjustable surface-treated rope (two strings) underwater. (b) The homemade mechanical stretching device for the strain adjustment of the rope. (c–g) Color change of aqueous NaOH solution with time under various strains of surface-treated rope.

NO_x, as a noxious gas, is commonly derived from anthropogenic sources such as power plants, incinerators, and boilers during coal combustion, which is one of the major air pollutants [30,31]. A possible approach to remove NO_x is wet oxidation using oxone solution (2KHSO₅·KHSO₄·K₂SO₄) [32]. The mechanism of NO removal by wet oxidation includes oxidation removal of oxone and oxidation removal of SO₄[−]· free radicals and ·OH free radicals. Generally, the oxidation removal of ·OH free radicals plays a leading role [33]. NO, as the main composition of NO_x, has very low solubility in water [33], which results in

the traditional wet removal device having difficulty in removing NO efficiently. Herein, our design concept is based on the following considerations. First, the superaerophilic property of the surface-treated string raises the gas–liquid contact area, which is beneficial to gas–liquid reaction efficiency. Second, the elastic characteristic can be utilized to adjust the gas–liquid contact area and further adjust gas–liquid reaction efficiency. Figure 5a shows the schematic diagram of the experimental setup for NO removal [34]. Six elastic strings were woven on the surface of the bottle cap of a gas-washing bottle with various strains (Figure 5b,c), which acted as a gas–liquid reactor. Stretched strings bring a large strain and a close arrangement on the bottle cap. A mixed gas of NO, N₂ and O₂ was induced from the gas inlet of bottle gap and then entered the aqueous oxone solution through two ways. One way was to enter the reaction liquid through bubbles produced by the gap between the glass gas-hole at the bottom of the bottle cap and elastic string, and the other was to transport into oxone solution through the surface of treated strings.

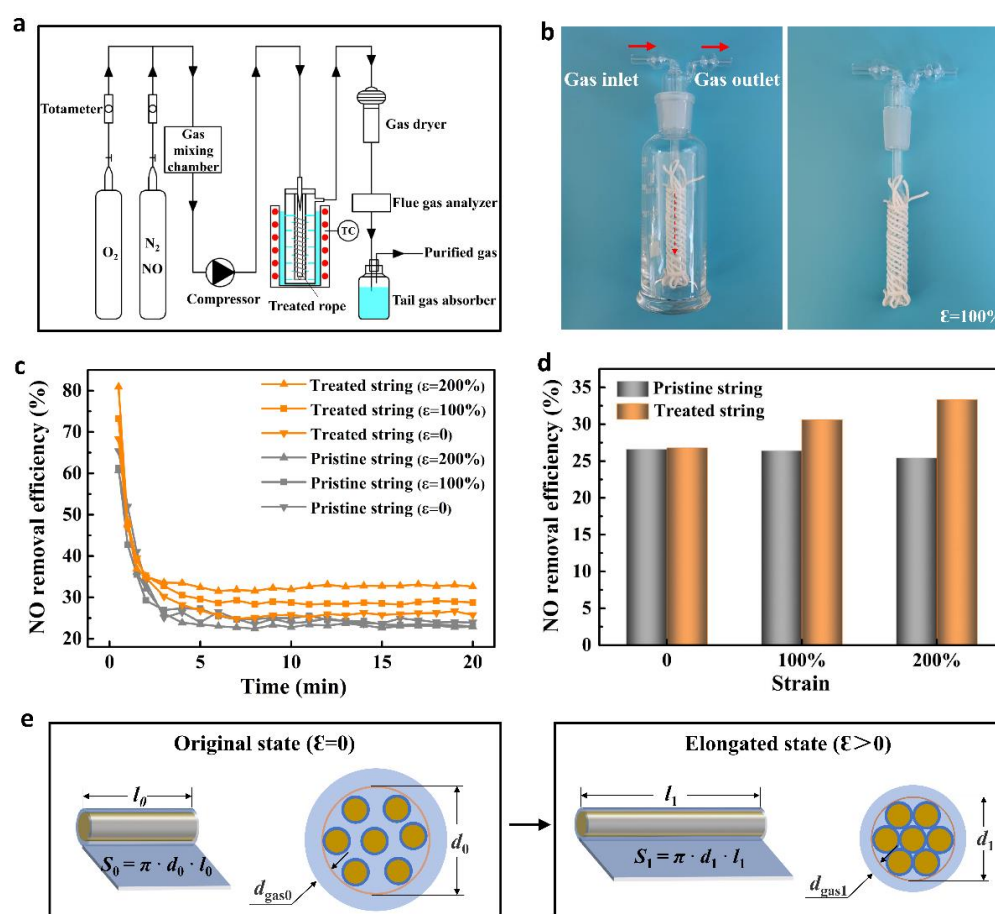


Figure 5. (a) Schematic diagram of the experimental setup for NO removal. (b) A gas-washing bottle as the gas–liquid reactor with six elastic strings woven on the surface of the bottle cap with various strains. (c) NO removal efficiency of treated and pristine strings as a function of the string strain in the aqueous oxone solution. (d) NO removal efficiency of treated and pristine strings with various strains as a function of time. (e) Schematic illustration of gas–liquid reaction area (S) and gas membrane thickness (d_{gas}) under original and stretched conditions.

Figure 5c shows that NO removal efficiency declined sharply in the first five minutes and maintained a relatively stable state in the following 15 min. Generally, in this study, a low NO concentration brings a high NO removal efficiency. In the first five minutes, NO was just introduced into the reactor and the reaction was just started. The initial NO concentration was low, and the removal rate of NO was high. With the increase in gas treatment time, the NO concentration in the reactor increased and gradually reached an

equilibrium, inducing the reaction between NO and oxone aqueous solution to gradually turn stable after five minutes. Therefore, NO removal efficiency declined sharply in the first five minutes and then turned stable in the following 15 min. In addition to reaction time and NO concentration, the factors affecting the NO removal rate through wet oxidation include reaction temperature, pressure, gas–liquid contacting area, etc. In this study, the effect of gas–liquid contact area on NO removal efficiency was investigated in detail. Figure 5d reveals that the total NO removal efficiency in 20 min by using treated strings with various strains of 0, 100%, and 200% is 26.79%, 30.62%, and 33.33%, respectively, while that by using pristine strings with the same strain is 26.61%, 26.43%, and 25.43%, respectively. This result proves that surface-treated superaerophilic strings have a higher NO removal efficiency than pristine strings under the same strain, and simultaneously, a high strain of superaerophilic strings bring high removal efficiency. It is well known that a gas layer exists on the superaerophilic/superhydrophobic string surface, and the gas–liquid reaction area (S_0) under the original conditions ($\varepsilon = 0$) can be calculated by the following Equation (2):

$$S_0 = \pi \times d_0 \times l_0 \quad (2)$$

where d_0 and l_0 are the initial diameter and length of a string, respectively. Similarly, at a stretched state, the gas–liquid reaction area is calculated by

$$S_1 = \pi \times d_1 \times l_1 \quad (3)$$

where d_1 and l_1 are the diameter and length of the elongated string, respectively. According to the definition of strain (ε), $l_1 = l_0 (1 + \varepsilon)$ [35]. Supposing that the volume of the string is unchanged during the elongation, S_1 can be obtained by

$$S_1 = \pi \times d_0 \times l_0 \sqrt{1 + \varepsilon} \quad (4)$$

when $\varepsilon > 0$, $S_1 > S_0$. Generally, the increase in the gas–liquid reaction area is beneficial for the increase in NO removal efficiency. On the other hand, under the stretched conditions, gas membrane thickness (d_{gas}) decreases compared with that ($d_{\text{gas}0}$) at the original state, which reduces the diffusion distance of gas molecules to an aqueous solution, which is beneficial for the rise in NO removal efficiency [36]. In contrast, the elongated untreated string even has a slight decrease in NO removal efficiency. It can be explained by the fact that the bubble volume entering the reaction solution through the gap between the glass vent and the untreated string increases after stretching, resulting in a decrease in the contacting area between bubbles and solution and thus a reduction in NO removal rate.

In comparison with previous research, the novelty of this study is summarized as follows: (i) Elastic superhydrophobic strings were prepared with adjustable superaerophilicity underwater; (ii) three typical applications of the superaerophilic elastic string were demonstrated, including the regulation of the gas flow in gas siphon underwater, the adjustment of reaction time of CO_2 and NaOH aqueous solution, and the wet oxidation of NO with extremely low solubility in water; and (iii) the utilization of the elastic superhydrophobic string provides a facile and reliable strategy for the dynamic and precise manipulation of the gas flow underwater.

4. Conclusions

In summary, elastic strings knitted of nylon and spandex fibers were surface-treated by a one-step dip-coating of hexadecyltrimethoxysilane (HDTMS) alcosol. The treated string obtained a water contact angle of 161.0° in air and a bubble contact angle of 0° in water, featuring good superhydrophobicity and superaerophilicity, which was attributed to the low-surface-energy alkyl chains of HDTMS and micro/nanowrinkle. The superwettability of the treated string can be adjusted by simply elongating or shortening with a mechanical stretching device. Three typical application experiments were demonstrated, including the regulation of the gas flow in gas siphon underwater, the adjustment of the reaction time of

carbon dioxide and sodium hydroxide aqueous solution, and the wet oxidation of nitric oxide (NO) with extremely low solubility in water. The experimental results reveal that a large strain of treated string induces a low gas flow in water. Significantly, in the treatment of simulated flue gas composed of NO, nitrogen and oxygen, stretched surface-treated strings with a strain of 200% demonstrated 7.9% higher of NO removal efficiency than that of untreated strings. Utilizing the elastic superhydrophobic string provides a facile and reliable strategy for the dynamic and precise manipulation of the gas flow underwater, which can find applications in directional gas transportation, gas–liquid chemical reaction, and hazardous gas treatment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12050638/s1>, Figure S1: Water contact angles of surface-treated strings as a function of immersion time in water.

Author Contributions: Y.S. and M.L. carried out the experiment, collected the data, performed the data analyses, and wrote the manuscript. X.L. carried out the experiment of NO removal. D.S. revised the manuscript and provided theoretical guidance. Y.X. offered some valuable suggestions on the content of the manuscript. Z.X. designed and conducted the project. All authors have read and agreed to the published version of the manuscript.

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