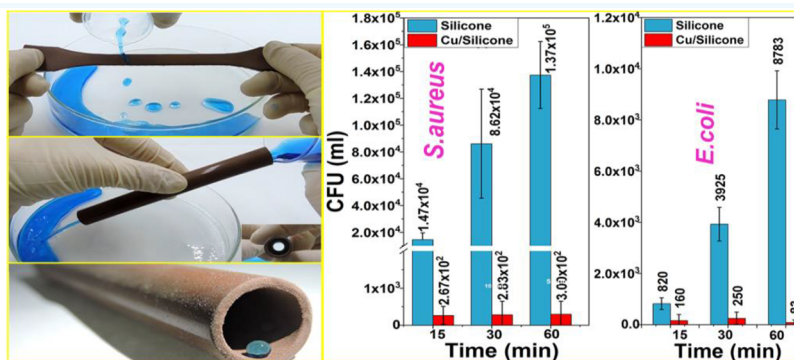


Flexible and Strong Robust Superhydrophobic Monoliths with Antibacterial Property

Huanhuan Wang,[#] Keli Wang,[#] Haitao Lu, Ivan P. Parkin, and Xia Zhang*



ABSTRACT: The self-cleaning properties of water-repellent superhydrophobic surfaces hinder bacterial adhesion. However, one of the most critical issues for superhydrophobic surfaces is the durability or stability of the water-repellent property, since the micro- or nanoscale structures on superhydrophobic surfaces are fragile and can be easily destroyed. Once the superhydrophobicity is lost, the surface anti-adhesion and antibacterial properties will decline. In this work, we present a large-scale fabrication of free-standing silicone-based composite monoliths with strong robust superhydrophobic properties under abrasion, stretching, bending, twisting, knife-scratch, high external pressure and low temperature. The water-repellent property prevents bacteria adhesion, and the addition of antimicrobial particles will further kill any surface-attached bacteria. The general fabrication can be extended to other elastic silicone-based antibacterial materials on a large scale, which are potentially advantageous in practical applications.

KEYWORDS: superhydrophobic, silicone rubber, antibacterial adhesion, robust, flexible

1. INTRODUCTION

The surface of an object exposed to the environment is prone to breeding various harmful bacteria, which has brought great risk to human life and production.¹ Antibacterial surfaces can prevent bacterial adhesion or inactivate bacteria attached to the surface.² Although many remarkable methods have been developed over recent years, there is still an urgent need to design and generate antimicrobial surfaces.³⁻⁷

The adhesion of bacteria to the substrate is the first stage of bacterial colonization and subsequent biofilm formation; hence, the preparation of surfaces preventing the initial adhesion of bacteria to the substrate becomes one strategy to solve the problem.¹ At present, the concept of using superhydrophobicity to prevent bacterial growth is a direction for designing antibacterial surfaces.^{8,9} Superhydrophobicity can reduce the adhesion of bacteria to the solid surface, allowing bacteria to be easily removed before a biofilm forms on the surface.¹⁰ Many researchers have shown that superhydrophobic surfaces display excellent antibacterial adhesion properties.¹⁰⁻¹² El-Safty et al. prepared a series of superhydrophobic surface coatings for marine antifouling.¹³⁻¹⁸ Zhang et al. prepared a superhydrophobic surface containing a bimetallic

composition (Cu/Ag) that exhibited certain antibacterial activity using a galvanic replacement approach followed by a thermal oxidation process.¹⁹

Adding bactericidal properties to superhydrophobic materials and getting composite antibacterial materials possess two merits: one is to prevent the adhesion of bacteria on the surface of the material, and the other is to kill any attached bacteria. At present, many attempts have been made to develop composite antibacterial materials by combining superhydrophobicity with antibacterial metals (such as Ag, Cu, Zn, Co, etc.) or with photocatalytic materials (such as TiO₂, ZnO, etc.) to improve their antibacterial properties.²⁰⁻²⁶ Berendjchi et al. prepared a superhydrophobic antibacterial surface on cotton fabric by doping the antibacterial metal Cu nanoparticles with

silica-based sol, which showed perfect antibacterial activity against Gram-negative bacteria and Gram-positive bacteria.²⁷ Chung et al. fabricated a perfluoroantimonythiol silver composite with superhydrophobic and antifouling properties by reacting silver nitrate with perfluorodecanethiol, and the silver nanoparticles that were generated on the wires exhibited antibacterial properties after UV irradiation.²⁸

There are many natural and manmade superhydrophobic surfaces which are easily damaged by mechanical shock or deformation, thereby limiting their outdoor and indoor applications.^{29–31} The loss of superhydrophobicity will reduce the antibacterial property. Hence, it is still challenging to develop a long-term superhydrophobic material that is tolerant against mechanical deformation such as bending, twisting, abrasion, and scratching.^{32–39} To improve the durability of the superhydrophobicity, an elastic surface is regarded as a good candidate, since the elastic microstructures will be compressed and deformed to avoid being broken under external pressure and abrasion cycles, and the elastic material can usually return to its original state after removal of external pressure.⁴⁰ Silicone is a common elastic polymer with good flexibility, chemical stability, and biocompatibility, and so it is widely used in microfluidic devices and biomedical applications.⁴¹ In this work, we employed a universal method for the fabrication of different superhydrophobic composite monolithic materials that combines flexible silicone rubber with antimicrobial particles (Cu, Co, TiO₂, ZnO) to provide anti-adhesion properties and bactericidal properties against both *Staphylococcus aureus* and *Escherichia coli*. This work possess the following three merits: (1) the obtained flexible surface can maintain its durable superhydrophobicity during stretching and shrinking; (2) different from superhydrophobic coatings, the obtained monoliths possess a permanent water-repellent property not only on the upper surface but also on the interior surface; and (3) the monolith contains antimicrobial particles, which can further kill any surface-attached bacteria once superhydrophobicity is lost (something that is difficult to achieve). In addition, the method employed is simple and universal and can be used to fabricate other different antibacterial materials on a large scale.

2. EXPERIMENTAL DETAILS

2.1. Materials and Chemicals. Poly(dimethylsiloxane) (PDMS, vinyl terminated; Sylgard 184 kit) and curing agent were purchased from Dow Corning Corp. (USA). Dimethicone ((CH₃)₃SiO-[(CH₃)₂SiO]_nSi(CH₃)₃, 5000 cs) was obtained from Huazhirun Chemical Co. Ltd. (Shanghai, China). Copper microparticles (Cu) and cobalt microparticles (Co) were purchased from Damao Chemical Reagent Factory (Tianjin, China). Titanium dioxide (TiO₂) was provided by Billions Chemical Co. Ltd. (Henan, China). Zinc oxide (ZnO) was purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Nutrient agar and broth as biochemical reagents were purchased from Oboxing Biotechnology Co. Ltd. (Beijing, China). The experimental strains were Gram-positive bacteria *S. aureus* (ATCC 35696) and Gram-negative bacteria *E. coli* (ATCC 232832), which were purchased from China General Microbiological Culture Collection Center (CGMCC). All the chemicals were analytical grade and used as received.

2.2. Preparation of Elastic Superhydrophobic Cu/Silicone Composite Monoliths. In a typical synthesis, PDMS (10 g) was mixed with Cu microparticles, dimethicone, and a curing agent in a weight ratio of 10:16:1:1 and stirred to get a uniform precursor. The precursor was poured into a Teflon mold, pumped to get rid of the bubbles, and cured at 60 °C for 4 h. After curing, the sample's uppermost layer was removed to get the superhydrophobic composite

monoliths. Cu/silicone with different shapes could be easily prepared by using different molds. Herein, the addition of dimethicone is to improve the elasticity of the obtained Cu/silicone.⁴²

2.3. Preparation of Elastic Co/Silicone, TiO₂/Silicone, and ZnO/Silicone Superhydrophobic Monoliths. The employed curing method can also be used to fabricate other silicone-based monoliths. In a typical synthesis, 10 g of PDMS was mixed with Co microparticles, dimethicone, and a curing agent at a weight ratio of 10:8:1:1 and stirred to get a uniform precursor. The precursor was poured into a Teflon mold, pumped to get rid of the bubbles, and cured at 60 °C for 4 h. After curing, the uppermost layer was removed to get the superhydrophobic Co/silicone composite monoliths. The fabrication of ZnO/silicone monolith was the same as that of Co/silicone monoliths. For the preparation of TiO₂/silicone monoliths, the weight ratio of PDMS, TiO₂ microparticles, dimethicone, and a curing agent was 10:12:1:1, and the fabrication process was the same as that of Co/silicone monoliths.

2.4. Characterization. The surface morphology of the superhydrophobic monoliths was examined by field emission scanning electron microscopy (FESEM, Carl Zeiss, UK). Thermogravimetric (TG) measurements were obtained on a Netzsch STA 449 C thermogravimetric analyzer from 25 to 1000 °C at a dynamic heating rate of 10 °C min⁻¹ under a N₂ atmosphere. X-ray photoelectron spectrometry (XPS, AXIS Ultra) was used to confirm the surface chemical composition of the superhydrophobic silicone. The contact angle (CA), sliding angle (SA), and contact angle hysteresis were measured on a DSA-100S optical contact angle instrument (KRÜSS, Germany) with a 10 μL water droplet at room temperature. The ellipse (tangent) method is used to fit the advancing contact angle and the receding contact angle of the liquid, and the difference between the two is the contact angle hysteresis. The average CA value was determined by measuring the same sample at five different positions. All optical photos and videos were taken with a digital camera (Nikon, P600), and the blue droplets were distilled water droplets dyed with methylene blue to aid visualization. The samples were prepared as dumbbell-shaped test specimens (ASTM D412) for tensile tests, which were carried out at 500 mm/min tensile rate on a microcomputer-controlled electronic universal testing machine (Gotech TCS-2000, Taiwan, China). The hardness (Shore A) and rebound resilience of the sample were measured according to ASTM D2240 and ASTM D7121 with an LX-A Shore hardness tester and an MZ-4065 rubber resilience testing machine, respectively (both were purchased from Jiangdu Pearl Rubber and Plastic Machinery Factory Co. Ltd., China). An UV-accelerated weathering tester (UV-II, Shanghai Pushen Chemical Machinery, Shanghai, China) was used to evaluate the UV resistance of the prepared superhydrophobic silicone under 30 °C and 45% humidity.

2.5. Antibacterial Adhesion Test. Gram-positive bacteria *S. aureus* and Gram-negative bacteria *E. coli* were selected as experimental strains to evaluate the bacterial adherence of the samples. Before experiment, the glassware, phosphate-buffered saline (PBS, 0.1 mol/L, pH = 7.3), broth medium, and agar were placed in an autoclave for 20 min (0.1 MPa, 120 °C). The silicone and Cu/silicone were made into cylindrical specimens (diameter: 1 cm, thickness: 1.5 mm) and washed three times with absolute ethanol. The experimental table and the tested samples were pre-ultraviolet sterilized for 2 h.

Colony-counting was used to calculate the number of bacteria adhering to the surface of the sample after contact with bacteria at different times. The specific experimental steps are as follows: Onto the sample surface was dripped 10 μL of 10⁸ colony-forming units (CFU/mL) bacterial suspension, which was kept in contact at room temperature for periods of 15 min, 30 min, and 1 h. The samples were gently dipped twice in 5 mL of PBS to remove the unattached bacteria from the surface. Afterward, the samples were transferred to test tubes containing 2 mL of broth medium and eluted for 5 min on a micro-eddy mixer (WH-2). The obtained bacterial suspension was diluted with broth by a 10-fold serial dilution. Under sterile conditions, 20 μL portions of different concentrations of the bacterial suspension were coated onto the sterilized agar medium uniformly and incubated in a

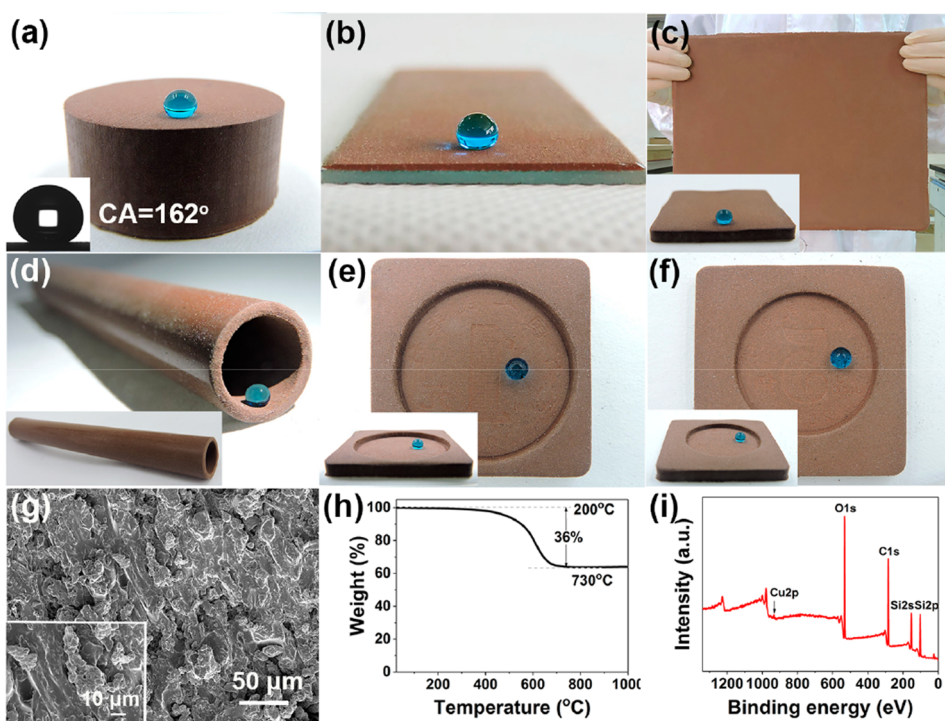


Figure 1. (a–f) Water droplet sitting on Cu/silicone surfaces with different shapes (monolith, sheet, and tube). (g) SEM image, (h) TG image, and (i) XPS full spectrum of the obtained Cu/silicone monoliths.

DHP-9082 constant-temperature incubator (37 °C, 56% RH, Zhengzhou Nanbei Instrument & Equipment Co., Ltd., China) for 20–24 h. The number of viable bacteria was calculated by colony-counting (Sup G6R, Hangzhou Shineso Technology Co., Ltd., China). The operation was performed in parallel three times to reduce the experimental error.

Similarly, the numbers of bacteria adhering to Co/silicone, TiO₂/silicone, and ZnO/silicone were obtained by immersing the samples in 10⁸ CFU/mL of the bacterial suspension. The monoliths were taken out after 1 min and eluted by 2 mL of PBS. Then the bacterial suspension was serially diluted and enumerated on the agar plates.

2.6. Bactericidal Test. In the bactericidal test, the growth curve of the bacteria was studied by the optical density (OD) method, and the bactericidal rate was determined by colony-counting.^{20,25,26} The 10⁶ CFU/mL bacterial suspension was obtained by diluting the 10⁸ CFU/mL bacterial suspension.

The experimental groups (diameter: 1 cm, thickness: 1.5 mm) of pure silicone, Cu/silicone, Co/silicone, TiO₂/silicone, and ZnO/silicone were separately added to test tubes containing 5 mL of broth medium. Then 50 μL portions of the 10⁶ CFU/mL bacterial suspension were separately added into the test tubes and incubated (37 °C, 130 r/min) in an ATS-03M2R shaking bath for periods of 0, 6, 12, 18, and 24 h. Five mL of sterilized broth medium was used as a reference group for the spectrophotometric test, and 5 mL of broth medium containing only 50 μL of the bacterial suspension was used as a control group. After reaching a certain incubation time, the corresponding test tubes were taken out and measured at a wavelength of 600 nm by an UV–vis spectrophotometer (SOPTOP, UV2400, Shanghai Sunny Hengping Scientific Instrument Co., Ltd., China), and the growth curve of the bacteria was plotted according to OD values as a function of time. The OD values were calculated by using the following equation:

$$OD_{600} = \log 1/T$$

where OD₆₀₀ and *T* are the optical density and transmittance values of the bacterial culture solution at 600 nm, respectively.

The bacterial suspension in contact with the monoliths for 24 h was serially diluted with broth and enumerated on the agar plates. The

experiment was reproduced three times, and the average value was calculated to report the bacteriostatic rate:²⁰

$$\beta = \frac{C - A}{C} \times 100\%$$

where *C* (CFU/mL) is the average number of viable colonies in the control tubes incubated for 24 h, and *A* (CFU/mL) is the average number of the surviving bacteria in the test tube after contact with the monoliths for 24 h.

3. RESULT AND DISCUSSION

Superhydrophobic Cu/silicone elastic monoliths were fabricated by curing the mixture of copper microparticles and polydimethylsiloxane (PDMS, commonly called silicone). Figure 1a shows a water droplet sitting on the monolith surface with spherical shape, with the water contact angle about 162° ± 1° and sliding angle about 9° ± 1° (Figure S1). The superhydrophobic Cu/silicone composite can be prepared in thin films on a large scale as shown in Figure 1b,c. Figure 1d–f shows that the elastic Cu/silicone composite can also be prepared in different shapes. Interestingly, the interior of the elastic tubes can also be adjusted to be superhydrophobic, which will benefit the lossless transport of microfluids. SEM observations were carried out to investigate the surface morphology, and it was found that the surface contains micro- and nanoscale roughness features from micrometer-sized copper powder and the bulk of silicone, which are the key factors for forming a superhydrophobic surface. In order to study the thermal stability of the superhydrophobic surface, TG analysis (Figure 1h) was carried out. Cu/silicone superhydrophobic elastomer did not show an obvious weight loss before 200 °C, which indicated that the sample had good thermal stability before 200 °C. A strong weight loss of about 36% was observed from 200 to 730 °C, which can be attributed to the fracture and decomposition of silicone. The XPS full

spectrum (Figure 1i) shows that the surface of the Cu/silicone elastomer mainly contains Si, Cu, C, and O and does not contain any fluorine-containing substances, indicating the obtained silicone composite is environmentally friendly.

The elastic Cu/silicone can be readily made into superhydrophobic sheets, which can be easily folded and twisted many times and returns to their original shape without cracks or loss of integrity (Figure 2a,b and Video S1). The elastic

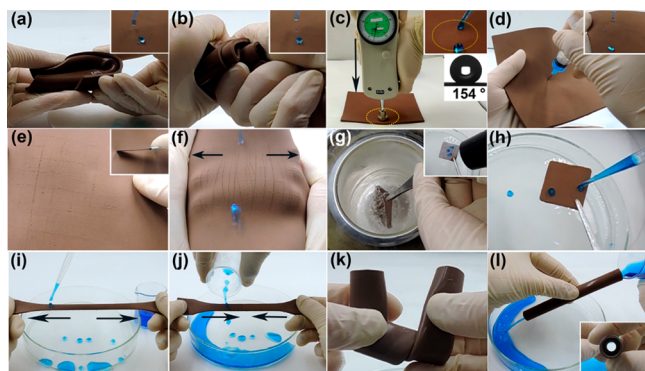


Figure 2. Obtained Cu/silicone and demonstrations of how the surface can maintain superhydrophobicity under different damage conditions: (a, b) folded and kneaded; (c) compressed under a load of 270 N; (d) penetrated by a needle; (e, f) scratched by a knife and stretched by hand; and (g, h) immersed in liquid nitrogen. (i, j) Water droplet bouncing on the stretched surface. (k) The surface was twisted by hand. (l) The interior surface of the Cu/silicone tube shows superhydrophobicity.

items also can withstand external pressure of 270 N. After the pressure is released, the silicone will restore to the original structure and retains the superhydrophobicity with a water CA of $154 \pm 1^\circ$ (Figure 2c and Video S2). Importantly, the surface of the sample was also subjected to a needle penetration test (Figure 2d and Video S3). The sample surface does not have particularly large pores and remains superhydrophobic after being penetrated for many cycles. Similarly, the elastic superhydrophobic surface can withstand knife-scratch, as shown in Figure 2e,f and Video S4. After being deeply cut by a knife, the monolith surfaces maintain the water-repellent property. After being stretched, a crack on the destroyed surface is obvious, and the water droplets can easily slide away without wetting the scratched areas. After the external force is released, the crack recovers immediately because of the elasticity. The Cu/silicone monolith can withstand extremely low temperature, as shown in Figure 2g,h and Video S5. The monolith was placed in liquid nitrogen for about 10 s, and a white layer of ice was seen to be formed on the surface after it was taken out. A water droplet can easily freeze on the monolith surface, but after the being heated by a hair dryer, the monolith recovers the superhydrophobicity immediately and water droplets cannot wet the surface; instead they slip away easily.

It is very important that the obtained flexible water-repellent surfaces can maintain the superhydrophobicity with low sliding angle, and the water droplet can bounce on the stretched surfaces, as shown in Figure 2i,j and Video S6. If a water droplet is dropped on the stretched surface, it can keep its spherical shape. As shown in Figure S1c, the superhydrophobicity was maintained when the strain on the sample increased to 40%. Moreover, superhydrophobic materials can

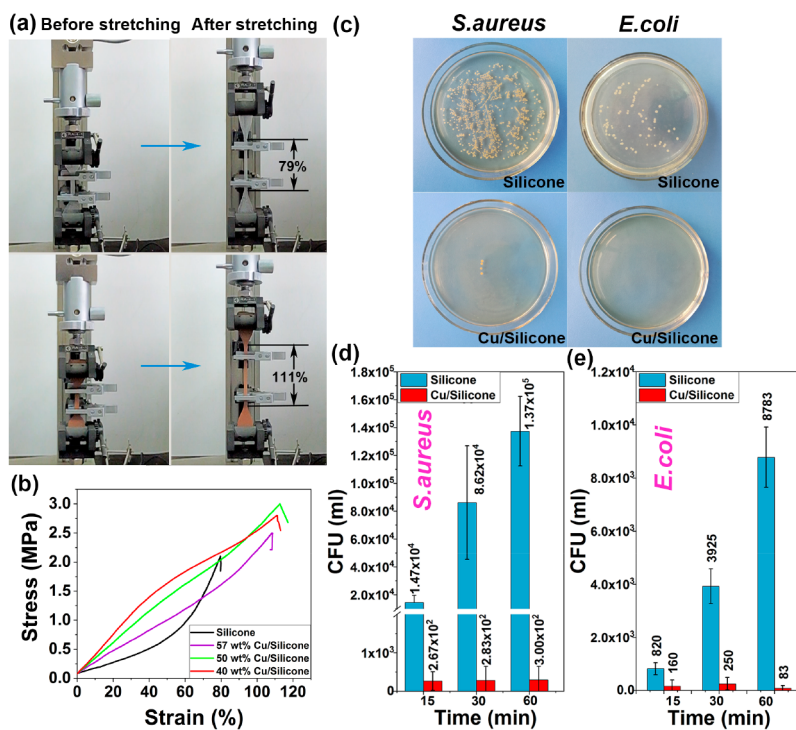


Figure 3. Optical image of the superhydrophobic Cu/silicone elastomer before and after stretching. (b) Strain–stress curves of Cu/silicone. (c) Antibacterial adhesion against the test bacteria *S. aureus* and *E. coli* after 1 h of contact time with the sample surface of the control silicone and Cu/silicone. (d) Number of bacterial colonies adhering to the surface of the sample after contact with *S. aureus* and *E. coli* for 15 min, 30 min, and 1 h at room temperature.

also be used to transfer water, as shown in the [Figure 2k,l](#) and [Video S7](#). The superhydrophobic tube can be quickly restored to its original state after being twisted. After the water passes through the superhydrophobic tube, there is no pollution or adhesion in the tube, which will prove useful for microfluid transportation, medical treatment, and other applications.

The mechanical properties of elastic superhydrophobic materials are also a very important feature in real-life applications. Herein, the stretchability of the pure silicone and Cu/silicone was also investigated, as shown in [Figure 3a](#). It can be seen that the elongation of pure silicone is 79% before break, while the elongation of Cu/silicone is 111%, which indicates that Cu/silicone has a greater elongation than pure silicone. [Figure 3b](#) and [Table 1](#) show the tensile stress–strain

Table 1. Mechanical Properties of the Obtained Superhydrophobic Cu/Silicone Monoliths

Cu/ silicone	mechanical properties				
	tensile strength (MPa)	elongation at break (%)	modulus at 100% elongation (MPa)	hardness (shore A)	rebound resilience (%)
0 wt%	2.1	79.6	—	37	48
40 wt%	2.5	108.4	2.2	49	40
50 wt %	3.0	112.7	2.6	50	40
57 wt%	2.8	111.1	2.6	52	38

curves and mechanical properties of the obtained Cu/silicone composite with different amounts of copper addition; it is found that both the tensile strength and elongation at break increase with the addition of Cu microparticles, and when the addition of Cu microparticles reaches 50 wt%, the maximal

tensile strength and elongation at break are about 3.0 MPa and 112.7%, respectively. Upon further increasing the addition of Cu microparticles, the tensile strength and elongation at break will decrease. It is believed that the addition of excessive Cu particles will destroy the internal network structure of the silicone, thereby reducing the mechanical properties of the Cu/silicone composite materials.

Due to the presence of the surface air layer, the superhydrophobic material greatly reduces the actual contact area between the surface of the material and the bacteria, thus exhibiting low adsorption and easy desorption of the protein,⁴³ which allowed bacteria to be easily removed before they formed a biofilm on the surface.¹⁰ Herein, the anti-adhesion property of the obtained Cu/silicone was also studied, as shown in [Figure 3c](#). Superhydrophobic Cu/silicone has better antibacterial adhesion properties than pure silicone. In order to further study the relationship between the number of superhydrophobic surface-adhering bacteria and the contact time, specific quantitative tests were carried out on the number of adherent colonies on the surface of samples at different contact times ([Figure 3d,e](#)). It is clear that the adhesion of the two bacteria on the pure silicone surface increases sharply as the contact time goes on. Meanwhile, the adhesion numbers of *S. aureus* and *E. coli* on the Cu/silicone surface are reduced by about 450 times and 100 times compared to those on the pure silicone, which indicates that the superhydrophobic Cu/silicone has excellent antibacterial adhesion properties. In addition, it is noticed that the antibacterial effect of Cu/silicone against *E. coli* is superior to that against *S. aureus*.

It is well known that many metal and metal oxides such as Co, ZnO, and TiO₂ have antibacterial properties.²⁴ In this work, the employed general method can be used to fabricate other silicone composite monoliths that bear both superhydro-

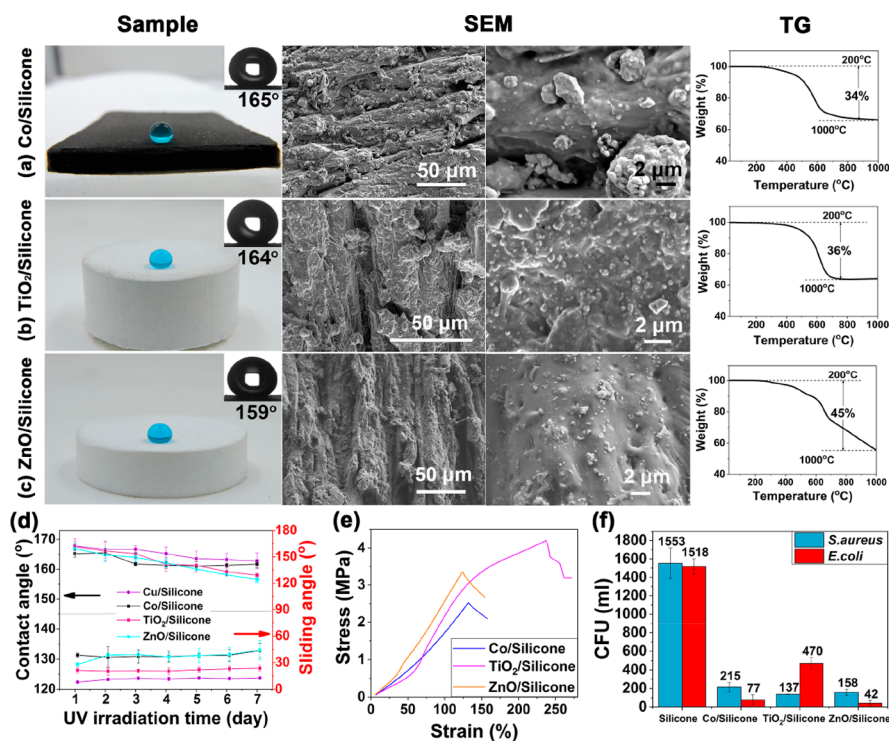


Figure 4. (a–c) Optical and SEM images, and TG analysis of the Co/silicone, TiO₂/silicone and ZnO/silicone blocks. (d) Relationship between contact angle, sliding angle, and UV irradiation. (e) Strain–stress curve. (f) Anti-adhesion properties of the obtained different monoliths to *S. aureus* and *E. coli*.

phobicity and antibacterial properties. As shown in Figure 4a–c, the Co/silicone, TiO₂/silicone, and ZnO/silicone can be prepared with different shapes with water contact angles about 165°, 164°, and 159°, respectively. From SEM observation, it is clear that many micro- or nanoparticle aggregations contribute to the surface roughness, which will benefit the superhydrophobicity. The elemental mapping and EDS image (Figures S2 and S3) reflect that the elements were uniformly distributed on the obtained monolith surfaces.

Before 200 °C, there is almost no weight loss, indicating the stability of the obtained samples. However, the weight of all the samples started to decrease at 200 °C, followed by a sharp decrease above 200 °C due to the decomposition of the silicone. Another important concern is the UV resistance of superhydrophobic surfaces in consideration of outdoor applications (Figure 4d). Superhydrophobic composite coatings are usually subjected to UV-light exposure, and the presence of large quantities of organic components leads to the oxidation and formation of hydrophilic groups.⁴⁴ Herein, we also investigated the UV resistance of the obtained monoliths, as shown in Figure 4d and Figure S4. It is clear that under 7 days of UV irradiation, the Cu/silicone maintains a lower sliding angle and the contact angle hysteresis, which indicates the UV irradiation stability of the obtained Cu/silicone, while the contact angle hysteresis of the other three types of composite monoliths was slightly different, increasing with the increase of UV irradiation time.

Herein, the stretchable property of the three types monoliths was also investigated. As shown in Figure 4e and Table S1, the tensile strengths of all the samples are larger than that of the pure silicone. It is noticed that the TiO₂/silicone composite has better elongation at break than the other samples. It is expected that TiO₂ nanoparticles have large specific surface areas and high surface activities, and there are many oxygen vacancies on a TiO₂ nanoparticle surface, which makes the TiO₂ nanoparticles have a chemical relationship with oxygen from silicone, thereby improving the compatibility between TiO₂ nanoparticles and silicone. The mechanical durability was investigated, and it was found that the monolith surface could retain superhydrophobicity after a 4200 cm sandpaper abrasion under an external load of 100 g, as shown in Figure S5. All of the obtained samples still retained superhydrophobicity, and the weight loss was less than 2%, indicating the extremely excellent robustness. The obtained composite monoliths had excellent self-cleaning properties, as shown in Figure S6 and Video S8. The monoliths showed no adhesion when dipped and then removed from mud. The composite monoliths also showed anti-adhesion to *S. aureus* and *E. coli* (Figure 4f), and it was found that the antibacterial adhesion of the obtained monoliths is much better than that of the pure silicone monoliths, indicating that the low surface energy of the superhydrophobic monoliths surface does reduce bacterial adhesion. The numbers of bacterial adhesion to the sample can also be found by the colony-counting method, as shown in Figure S7. Visible differences could be observed in the colony numbers, and the number of bacteria attached to the prepared superhydrophobic monoliths is much lower than that on the pure silicone surface.

Although superhydrophobic surfaces can reduce bacterial adhesion, many studies have reported that the antibacterial adhesion of superhydrophobic surfaces is only effective in a short period of time, generally no more than 4 h.⁹ Superhydrophobic surface will adhere bacteria once the

superhydrophobicity is lost, and the bacteria will colonize the surface and multiply. However, if the superhydrophobic monoliths are composed of bactericidal particles, the bactericidal particles will inhibit the growth of the bacteria or even kill the bacteria when the superhydrophobicity is destroyed. In this study, the antibacterial properties of the monoliths were investigated by measurement of optical density (OD₆₀₀) and broth dilution. When the light passes through the bacterial suspension, the light transmittance would be reduced due to the absorption or scattering. The microbial cell concentration is inversely proportional to the transmittance and is proportional to the OD value. Figure 5a,b shows the

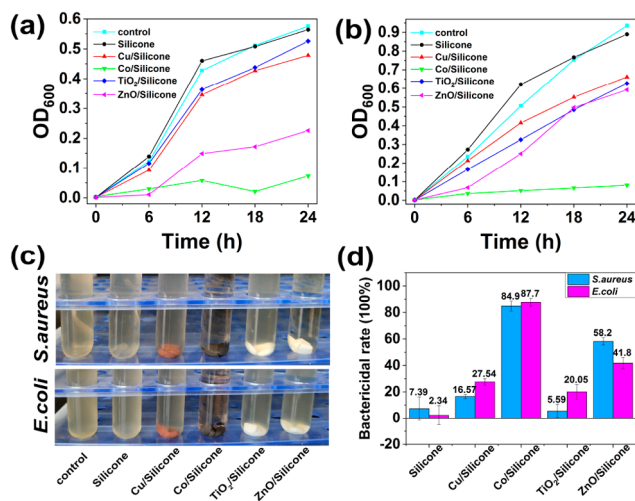


Figure 5. Growth curves of (a) *S. aureus* and (b) *E. coli* after contact with different monoliths. (c) Optical photograph of the bacterial suspension of *S. aureus* and *E. coli* in contact with the test monoliths for 24 h. (d) Antibacterial rate of different monoliths in contact with (c) *S. aureus* and (d) *E. coli* for 24 h.

bacterial growth curves of typical *S. aureus* and *E. coli* in contact with different monoliths in liquid broth culture medium. Compared with the blank group, pure silicone shows almost no inhibition for the bacterial growth. However, the as-prepared monoliths show bacterial growth retardation at different levels, and compared with other composite monoliths, the Co/silicone surface shows the best the bacterial growth inhibition.

Figure 5c shows an optical image of the obtained different composite materials after continuous contact with bacterial suspensions of *S. aureus* and *E. coli* for about 24 h. It is obvious that the bacterial suspensions in most of the test tubes are cloudy, except for the bacterial suspension that contains Co/silicone composite items. This observation indicates that the Co/silicone has a better antibacterial property since the turbidity of the bacterial suspension increases with the increase of bacterial concentration. To further verify the antibacterial rate of the superhydrophobic monoliths, a broth dilution technique was employed. The bacterial suspension, after contact with different monoliths for about 24 h, was subjected to 10-fold serial dilution, and bacterial counts were performed by plate colony-counting to determine the antibacterial rate. As shown in Figure 5d, Co/silicone composite monoliths exhibit the highest antibacterial rate; the Cu/silicone monolith has certain antibacterial effects, and the antibacterial effect against

E. coli is superior to that of *S. aureus*, which is consistent with the results from Figure 3e.

4. CONCLUSION

We have developed a general and simple method to fabricate robust superhydrophobic composite monoliths, and the presence of metal or metal oxide composition endows an enhanced antibacterial activity. The elastic surface can maintain the robust and durable superhydrophobicity under various harsh conditions such as extremely low temperature, high pressure, UV irradiation, wear, knife-scratch, and needle penetration. Importantly, after 4000 cm sandpaper abrasion, the composite shows a high retention ratio with robust superhydrophobicity. Under a stretched state, the monolith surface remains durable with water-repellent property, and the water droplet can bounce from the surface quickly, which shows that the silicone composite has good elastic and mechanical durability. The non-adhesion to mud as well as high adhesion inhibition effects to *E. coli* and *S. aureus* reflect the surface anti-fouling property, and this is expected to provide unique advantages for self-cleaning and antibacterial applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at

Table S1, mechanical properties of superhydrophobic elastomer; Figure S1, relationship between the water-repellency and Cu addition and plot of water contact angle, sliding angle, contact angle hysteresis, and retention ratio as functions of the abrasion distance; Figure S2, SEM image and element distribution mapping of the Co/silicone, TiO₂/silicone, and ZnO/silicone; Figure S3, EDS images and the atom percent of elements in the four types composite monoliths; Figure S4, water contact angle hysteresis of the obtained monoliths as a function of UV irradiation time; Figure S5, durability of the superhydrophobic monoliths; Figure S6, self-cleaning properties of the obtained composite monoliths; Figure S7, antibacterial adhesion test of silicone, Co/silicone, TiO₂/silicone, and ZnO/silicone (PDF)

Video S1, Cu/silicone maintains superhydrophobicity after being folded and twisted and returns to its original shape (MP4)

Video S2, Cu/silicone monolith is pressed by a Newton meter at ~270 N, and the monolith surface sustains the water-repellent property after the pressure (MP4)

Video S3, Cu/silicone monolith maintains the water-repellent property after being penetrated by a needle for many times (MP4)

Video S4, durable superhydrophobicity test (MP4)

Video S5, extremely low temperature test (MP4)

Video S6, water droplet bouncing on the stretched surface (MP4)

Video S7, water flows out of the superhydrophobic tube after it is folded (MP4)

Video S8, the obtained monoliths are dipped and then removed from the mud to test their self-cleaning properties (MP4)

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Notes

The authors declare no competing financial interest.

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