Facile Fabrication of Superhydrophobic and Superoleophilic Bulk Materials with Excellent Durability

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Research Article

ABSTRACT

Development of superhydrophobic material is hindered by their susceptibility to mechanical abrasion and oil fouling. Here, to address these issues, we prepared robust superhydrophobic and superoleophilic SiO_2/polytetrafluoroethylene bulk material with good adaptability and easy repairability. Removing the outer layer damaged by abrasion or fouled by oil causes almost no loss of its superhydrophobicity. More importantly, this bulk material demonstrates sustainable superhydrophobicity under the condition of strong acid or alkali. In addition, the obtained bulk material is both superhydrophobic and superoleophilic, which means it can be used to selectively absorb oil from oil-water mixture. This bulk material with easy repairability is expected to satisfy the future demands in the practical applications.

INTRODUCTION

Superhydrophobic surfaces in nature, having a water contact angle (CA) larger than 150° and exhibiting almost no adhesive to water droplets, have numerous applications in corrosion protective coatings [1-3], self-cleaning surfaces [4,5], oil-water separation, [6-8] anti-icing [9,10], non-wetting fabrics [11,12], droplet transportation [13], photonic applications [14], and so on. However, those natural or artificial superhydrophobic surfaces with micro/nanostructure are easily destroyed by some low load contacts, such as finger contact, abrasive wear, and washing cycles. The poor mechanical durability is always the main barrier to their practical applications [15,16]. Additionally, unlike the living biological surfaces, the biomimetic water-repellent materials, once destroyed, can hardly self-healing [17]. In conclusion, seeking an effective way to mitigate the mechanical damage is really urgent. Not long ago, a few methods have been developed to tackle the mechanical damage problem [18-22]. By compression of the superhydrophobic metal particles, Larmour et al. prepared superhydrophobic composite material with mechanical durability and easy repairability. The high CA was still retained even after accidental damage, and hydrophobicity could be restored after fouling by abrasion [23]. Using a type of elastic polyurethane material, Su et al. [24] gained superhydrophobicity with fairly good abrasion resistance.

In this study, we demonstrated a facile method for the fabrication of superhydrophobic SiO_2/ polytetrafluoroethylene nanocomposite bulk material by compression of the mixture of hydrophobic silica nanoparticles and polytetrafluoroethylene (PTFE) particles. The chemical durability of the superhydrophobic bulk material was investigated by immersion in strong acidic or alkaline solution for different time. It was found that the sample had better corrosion resistance in strong acidic solution than alkaline solution. In addition, the as-prepared superhydrophobic surface also demonstrated superoleophilic properties and could be used to selectively absorb oil from oil/water mixture. Importantly, the non-wetting property could be restored by a simple regeneration process once the superhydrophobicity lost. The introduction of easy repairability into the superhydrophobic surface will mitigate problems caused by mechanical damage or oil fouling, which is expected to satisfy the future demands in the practical applications.

EXPERIMENTAL

Hydrophobic SiO_2 nanoparticles used in this study were prepared through a hydrolysis reaction, followed by surface

functionalized with chlorotrimethylsilane. The detailed fabrication process and structural characterization of the hydrophobic SiO_2 nanoparticles were discussed in our previous reported work [25]. PTFE powder was provided by Alfa Aesar Company. Mechanical abrasion was carried out using 800-mesh standard abrasive paper.

The SiO_2/PTFE nanocomposite material was fabricated by directly mixing PTFE powder with SiO_2 nanoparticles and cold pressing. A typical process is as follows. PTFE powder was first thoroughly mixed with SiO_2 powder by grinding for 20 min. The mass ratio of SiO_2 to PTFE is 1:4. 2.0 g of the mixture were placed into a mold and pressed at a pressure of 30 MPa for 3 min to form a dense bulk material. Then, the flattening bulk material was rubbed by an 800-mesh standard abrasive paper to get a superhydrophobic surface.

SEM images were obtained using a JSM-6701F field-emission scanning electron microscope (FESEM, JEOL, Japan). The chemical composition of the as-prepared bulk material was investigated using x-ray photoelectron spectroscopy (XPS), which was conducted on a PHI-5702 electron. The water CA and sliding angle (SA) were measured using a DSA100 CA instrument (Germany) with about 5 μL droplets of water or other corrosive liquids. The average CA and SA values were obtained by measuring the same sample in at least five different positions, and images were captured with a digital camera (Panasonic, DMC-ZS20).

RESULTS AND DISCUSSION

Figure 1a shows the photographs of water droplets placing on the bulk material surface. The surface is so hydrophobic that water droplets can exhibit approximately spherical shapes with the water CA and SA value of 157 ± 2° and 3 ± 1° respectively. Surprisingly, the interior of the bulk material also shows excellent superhydrophobicty. The cut bulk material sustains its original surface superhydrophobicity, displaying similarly a high apparent CA (156 ± 2°), as shown in **Figure 1b and 1c**. It can be seen from **Figure 1d** that when submerged in water, the bulk material surface acts like a sliver mirror when viewed at a glancing angle. This mirror-like phenomenon was due to the formed air plastron between water and the superhydrophobic surface [26].
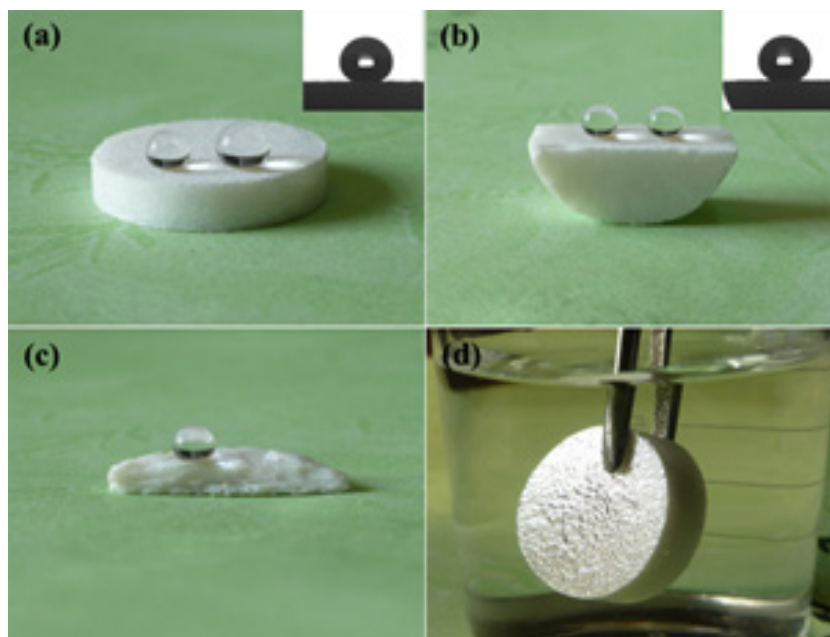

Figure 1. Photographs of water droplets (a) on a freshly prepared bulk material surface with water CA about 157 ± 2°, (b) on the cross section and (c) on the interior of the bulk material with water CA about 156.3 ± 2°. (d) Mirror-like phenomenon can be observed on the bulk material when submerged in water.

The FESEM images of the as-prepared SiO_2/PTFE bulk material are shown in **Figure 2**. It can be seen from **Figure 2a** that the surface is relatively smooth except for some irregular clusters that randomly distribute on it. **Figure 2b**, the high-magnification image, shows that numerous aggregations of nanoparticles with diameter about 100 nm are observed, showing a nanometer-scale roughness. Interestingly, we find from **Figure 2c and 2d** that the inner of the bulk material contains micrometer scale roughness features which are similar as the surface. It is believed that the aggregation of hydrophobic SiO_2 and PTFE nanoparticles results in the surface roughness, which in turn influences the wettability of the surface.

XPS analysis was carried out to determine the surface composition of the as-prepared SiO_2/PTFE sample. As shown in **Figure 3**, the XPS peaks of Si 2p, Si 2s, C 1s, O 1s and F 1s are clearly visible, indicating hydrophobic SiO_2 and PTFE coexist on the surface. The peak of F 1s is located at 689.55 eV, which is consistent with the accepted binding energy value for F from PTFE [27]. Besides, it can be also seen that the peak of Si 2p at 103.6 eV attributed to SiO_2 completely.

Apart from improving the mechanical durability, an effective alternative way should have such advantages as simple fabrication or easy repairability. However, what is interesting is that the prepared bulk material can easily renew the superhydrophobicity when
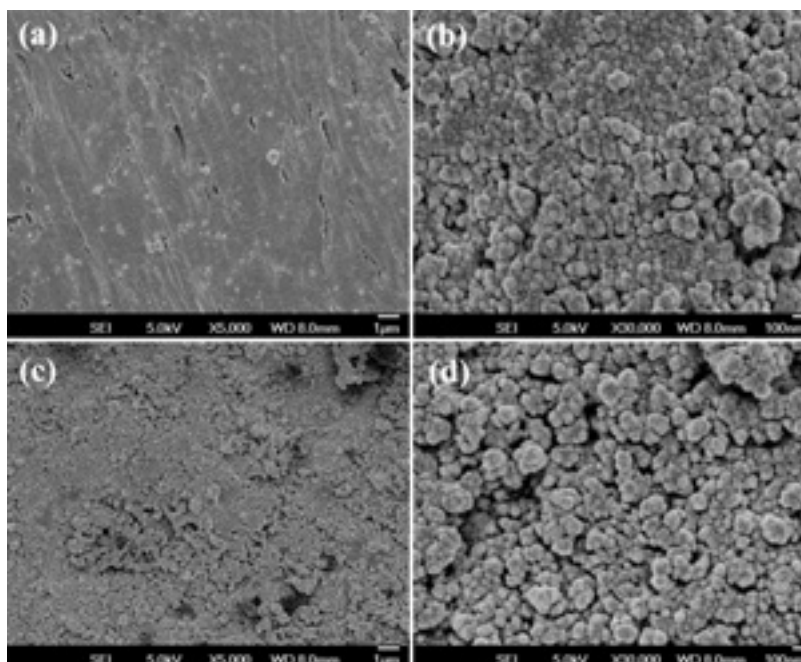
Figure 2. FESEM images of the surface (a, b) and (c, d) the interior of the as-prepared bulk material under different magnifications.
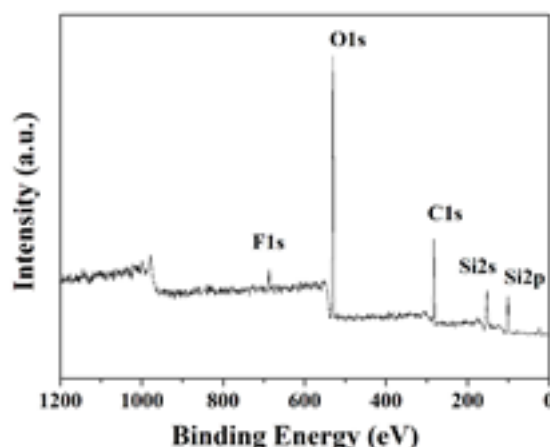

Figure 3. XPS survey spectrum of the bulk material surface.

damaged by mechanical scratch or oil contamination. **Figure 4** shows the change of the surface wettability if it is deliberately fouled by oil or damaged by a finger. When a tetradecane droplet drop on the bulk material, it spreads quickly as shown in **Figure 4a**, indicating an oil CA of almost 0°. It can be seen from **Figure 4b** that the water CA decreases dramatically after fouling by tetradecane. Another experiment was carried out by pressing gently on the middle of the sample with index finger (**Figure 4d**). The result in **Figure 4e** indicates that the compression could clearly weaken its water-repellency, making a water drop stick to the vertical surface. More interestingly, the non-wetting property can be easily restored by an easy regeneration process of removal of the damaged surface layer. As shown in **Figure 4c and 4f**, the superhydrophobicity with the CA larger than 150° recovered after exposing the interior of the bulk material. This easy regeneration is expected to satisfy the future demands in the practical application.

Note that when a drop of petroleum ether was placed on the sample surface, it quickly drawn into the interior with an oil CA about 5°, showing a superoleophilic property. Since the bulk material is superhydrophobic and superoleophilic, it can be used to remove oil from water. As illustrated in **Figure 5a-5c**, the bulk material could selectively adsorb light oil (lower density than water) floating on water surface within a few seconds. When the sample was taken out, the oil was absolutely drawn and the water became clear. Similar phenomena were also observed in the absorption of heavy oil (higher density than water) from water as shown in **Figure 5d-5f**. Almost all of chloroform sinking in the water could be removed by absorbing into the bulk material. The absorption capacity was typically used to measure the weight of oil that could be captured by the superhydrophobic material. The absorption capacity here was defined as $(m_{saturated} - m_{initial})/m_{initial}$ [28]. It was found that the absorption capacity varied from individual to individual, and mainly depended on the density of the oil or organic solvent. As shown in **Figure 6**, the absorption capabilities vary greatly with the density. That is to say, the bigger is the specific gravity, the larger is the absorption capability.

Importantly, the as-prepared SiO_2/PTFE bulk material can be used as a corrosion resistant surface, which is an extremely
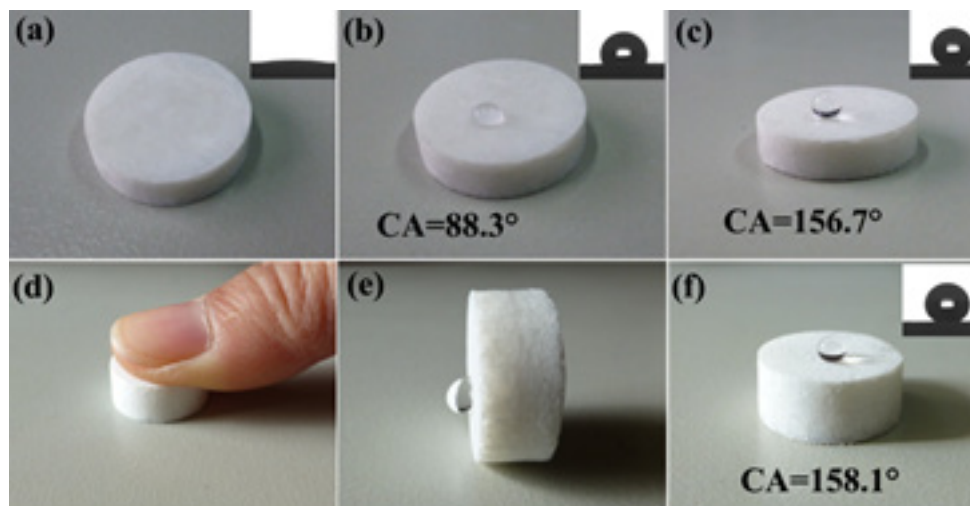
Figure 4. Loss and regeneration of the superhydrophobicity of the bulk material. (a) the spreading of a tetradecane droplet on the bulk material surface; (b) a water droplet on the oil-fouling surface with a CA about 88°; (c) regeneration of superhydrophobicity by removing the oil-fouling layer; (d) a finger pressing the bulk surface; (e) the surface lost the superhydrophobicity and a water droplet sticking to surface; (f) regeneration of superhydrophobicity by removing the destroyed layer.
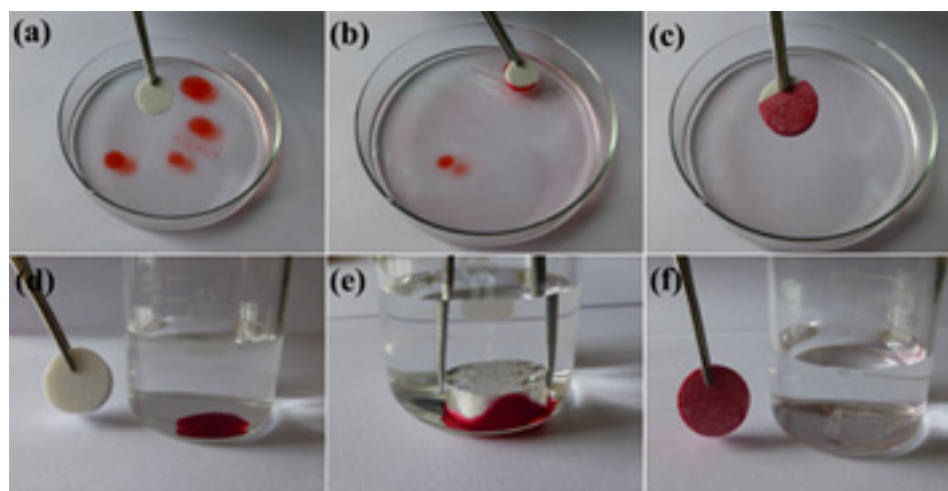
Figure 5. Optical images of the removal of petroleum ether (a-c) and chloroform (d-f) from water by the bulk material. The petroleum ether and chloroform were labeled with oil red for clear observation.
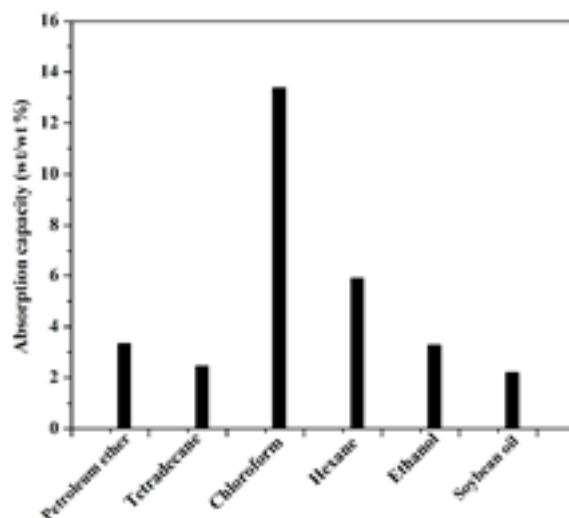

Figure 6. Bar graph showing the absorption capabilities of as-prepared sample for different types of oil or organic solvent.

useful application in our daily life. As shown in **Figure 7a**, the surface remained extreme water repellence even if the pH of the testing liquid varied from 1.0 to 14.0, indicating that the bulk material has good corrosion resistance. In order to gain a deeper understanding about the stability, we investigated the wettability evolution by immersing the bulk material into some corrosive mediums. **Figure 7b-7c** show the water CA of the bulk material as a function of immersion time in acidic and alkaline solutions,

respectively. It can be seen that the CA decreases gradually with the increase of immersion time whether in the solution of pH 2 or pH 13. When the immersion time in the acidic solution reaches to 50 min, the bulk material surface still sustains its superhydrophobicity with CA more than 150°. However, the CA significantly reduces to 145° with the further increase of the immersion time to 60 min, indicating the degradation of its water-repellence. As shown in **Figure 7c**, the CA of the bulk material is still larger than 145° even though it has been immersed in alkaline liquid for 60 min. This result is very important for the application of bulk material with sustainable hydrophobicity in corrosive liquids.
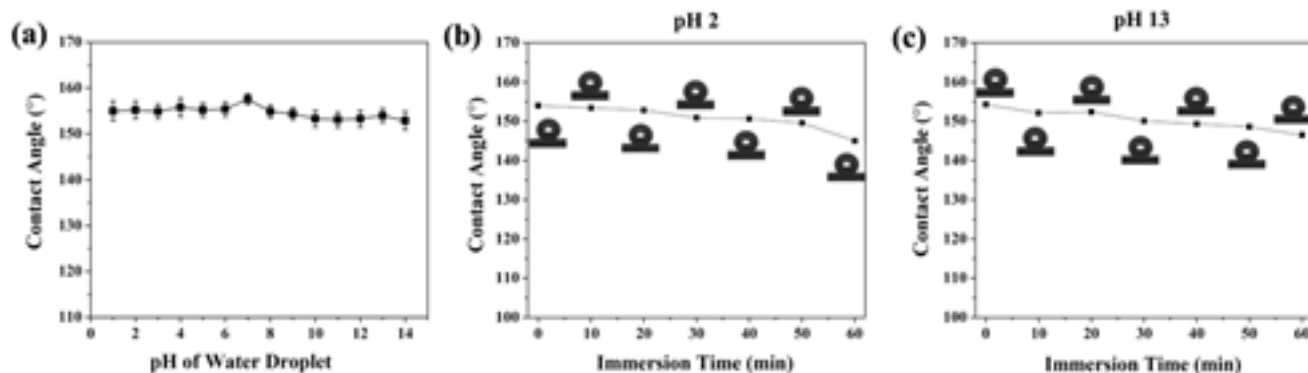
Figure 7. Relationship between pH of water droplet and CA of the bulk material surface (a). The water CA of the bulk material as a function of immersion time in acidic (b) or alkaline (c) solution.

CONCLUSIONS

We have developed a simple, inexpensive and time-saving method for the fabrication of superhydrophobic SiO_2/PTFE superhydrophobic bulk material. The obtained material can be used to remove oil from the water surface because of its superhydrophobicity as well as superoleophilicity. In addition, the material surface shows rather stable superhydrophobicity toward corrosive mediums, particularly under acidic conditions. Importantly, when fouled by oil or damaged by outside forces, its superhydrophobicity could be easily recovered by removing the destroyed layer. So, for the foreseeable future, the introduction of easy repairability will open a new avenue to extending the lifespan of superhydrophobic surfaces for practical applications.

ACKNOWLEDGMENTS

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