

Supporting information

A Novel Damage-tolerant Superhydrophobic and Superoleophilic Material

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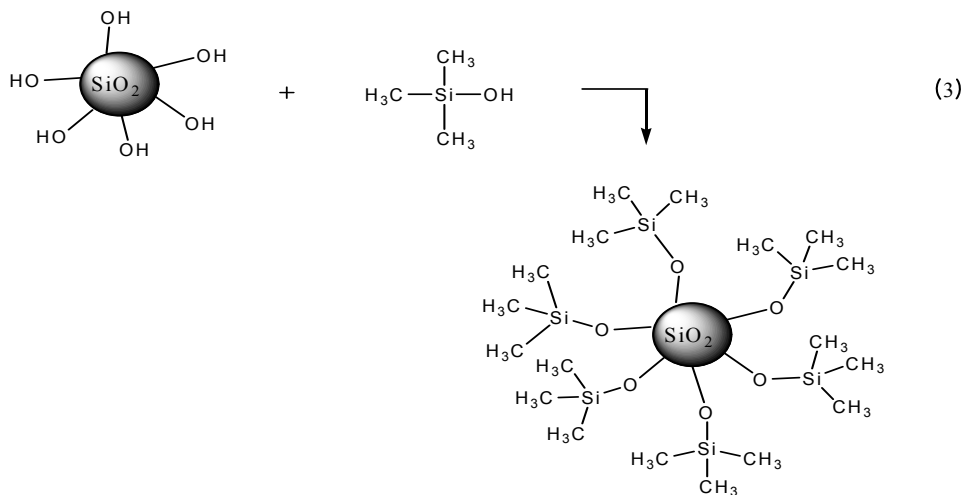
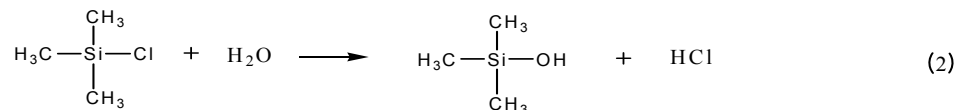
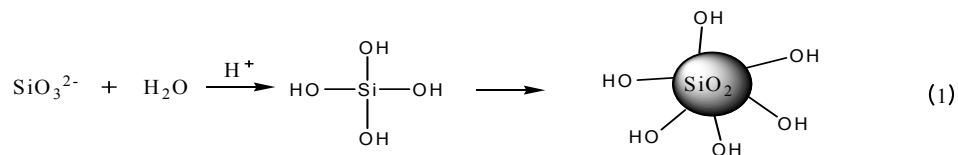
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(1) Hydrophobic SiO₂ nanoparticles and hydrophilic TiO₂ nanowires

Hydrophobic SiO₂ nanoparticles were prepared through a hydrolysis reaction. Detailed preparation and the structural characterization of hydrophobic SiO₂ nanoparticles were discussed elsewhere.^{S1-S3} Briefly, 19.4 g of NaSiO₃ · 5H₂O was dissolved in 300 ml of deionized water, followed by the addition of 100 ml of 0.24 M NH₄Cl₄ solution. The mixture solution was stirred for 3 h at 80°C. After that, the white product was filtered, washed with deionized water and alcohol until Cl⁻ could not be detected. Subsequently, the SiO₂ nanoparticles were chemically modified by using chlorotrimethylsilane (TMCS). The white product and 0.05 mol of TMCS were dissolved in 200 ml of alcohol to give a mixture solution. Then the mixture solution was heated to 80°C and stirred for 3 h. After reaction, the resulting product was filtered and dried in vacuum at room temperature for 24 h to get the TMCS-functionalized SiO₂ powder. The formation mechanism of hydrophobic SiO₂ nanoparticles is shown in scheme 1.

TiO₂ nanorods were supplied by Henan Nanomaterial Research Center of Engineering and Technology. The fabrication process is shown in reference.^{S4} Fig. S1(a) and (b) show the TEM image of SiO₂ nanoparticles and TiO₂ nanorods, respectively. From Fig. S1(a), it can be seen that the size of the nanoparticles is about 5-10 nm. Selected area electron diffraction (SAED) pattern at the center of the

sphere reveals the existence of amorphous SiO₂. Fig. S1(b) shows that the nanorods have a length of over 1 μm and a diameter of about 100 nm.



Scheme 1. Formation mechanism of the hydrophobic SiO₂ nanoparticles. [S2]

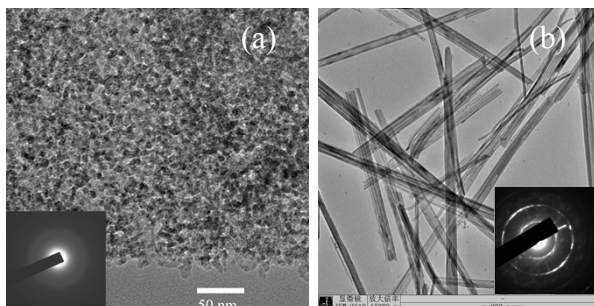


Fig. S1 TEM image of SiO₂ nanoparticles and TiO₂ nanorods (inset: the corresponding SAED pattern).

(2) Wettability evolution of the bulk material immersed in water and corrosive liquids.

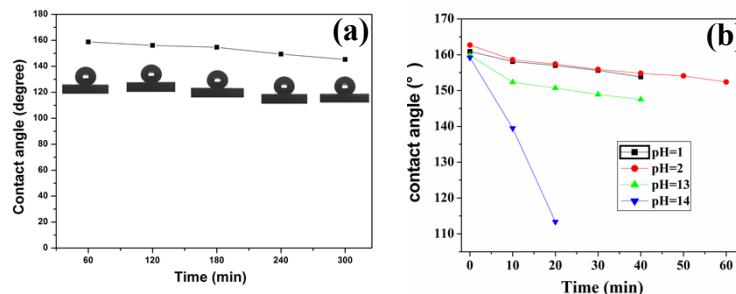


Fig. S2 Water contact angle of superhydrophobic bulk material as a function of immersion time in water (a) and corrosive liquids (b), respectively.

Figure S2(a) shows that deterioration of wetting at long-term continuous contact of water. The following mechanisms may be considered as responsible for the above behavior. The first one is a growth of adsorption/wetting films on the bulk material surface. The second one is the surface hydrophilization due to chemical interaction such as the hydrolysis end groups and hydration of all active sites tending to create hydrogen bonds, like oxygen atom in the backbone of polydimethylsiloxane.

The durability of the superhydrophobic bulk material was studied by immersion in strong acidic or alkaline solutions for different time. It was found that the bulk material demonstrates sustainable water repellency in the wide pH range of corrosive liquids, particularly under acidic conditions, as shown in Figure S2(b). The material surface sustained its superhydrophobicity for about 60 min and 30 min at continuous contact of strong acidic (pH=2) and alkaline solutions (pH=13), respectively. This result is very important for the application of the bulk material with superhydrophobicity in the wide pH range of corrosive liquids.

(3) Wear behavior of the superhydrophobic bulk material.

To thoroughly study the mechanical durability of the bulk material surface, conventional ball-on-flat tribometer experiment, which is used to comprehensively investigate the wear behavior of structured surfaces, was conducted. Fig. S3 shows the coefficient of friction as a function of number of cycles upon different loads. It was found that the coefficient of friction increased minimally as the normal loads increased from 1.0 N to 4.0 N, which indicated that the load has not obvious influence on the material wear behavior. The coefficient of friction value changed slightly during the entire experiment, which indicated that the bulk material was not being worn after 3600 friction cycles.

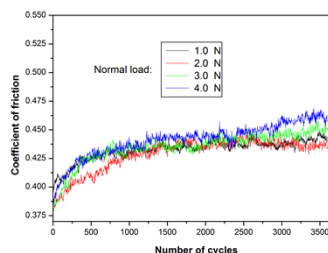


Fig. S3 Coefficient of friction as a function of number of friction cycles with the different load for 1.0N, 2.0N, 3.0N and 4.0N.

(4) The bulk material lost its superhydrophobicity after oil-fouling.



Fig. S4 A water droplet on the oil contaminated bulk material surface with water CA value about 120°.

(5) Quantitative analysis of the chemical composition of the obtained bulk material surface.

Table 1. Quantitative analysis of the chemical composition of the bulk material before and after UV irradiation.

Element	Before UV irradiation		After UV irradiation	
	Wt%	At%	Wt%	At%
O	52.49	59.94	70.96	79.56
C	17.93	27.28	7.16	10.69
Ti	24.03	9.17	16.00	5.99
Si	5.55	3.61	5.89	3.76
Total	100	100	100	100

Table 1 summarizes the obtained results for the changes of the surface chemical composition. Before UV irradiation, the ratio of O/Ti was 59.94/9.17, but it increased to 79.56/5.99 after UV irradiation. The increased values of O/Ti ratios after UV irradiation are related to an increase in the amount of hydroxyl groups. The UV irradiation can induce structural changes of TiO₂ including the generation of holes and oxygen vacancies. Such defective sites are highly reactive, and therefore react with absorbed H₂O and O₂ molecules and form Ti–O–H bonds. The Ti–O–H groups would significantly enhance the hydrophilicity of the nanocomposite material.

References

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