Supporting Information

A simple preparation of F-TiO_2-HNT superamphiphobic surface with tube-point-like micro/nano hierarchical structure for self-cleaning and anti-fouling

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Experimental section

1.1 Materials.

Tetrabutyl titanate (TBT) (98.5%), isopropanol, hydrochloric acid, ammonia water, sodium hydroxide, and sodium chloride were purchased from China National Medicines Corporation Ltd. Tetraethyl orthosilicate (TEOS), methylene blue, glycol**,** rapeseed oil, 1H,1H,2H,2H-perfluorodecyltriethoxysilane（PFDTES） were provided by Aladdin Reagent Co. Ltd, China. Carbon black was purchased from Anhui Zesheng Technology Co., LTD. Halloysite nanotube (HNT) was purchased from Xi 'an Minchuangda Biotechnology Co., LTD. Glycerol (98.5%), 85% phosphoric acid, and aluminium hydroxide were obtained from Alfa Aesar. All chemicals were of analytical grade without further purification.

1.2 Preparation of F-TiO_2-HNT superamphiphobic powder.

2 ml of tetrabutyl titanate was dispersed in isopropanol with 0.4 g, 0.7 g and 1 g of HNTs, respectively. The solution pH was adjusted to about 4 with 1 M HCl solution, and the

hydrothermal reaction was carried out at 160 °C for 24 h followed by centrifugation. Three TiO_2-HNTs (TH) hybridized powders (TH-0.4, TH-0.7, and TH-1) were obtained after drying. Then, the TH powder was dispersed into ethanol, ammonia, and deionized water, and tetraethyl orthosilicate (TEOS) and 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDTES) were added to the suspension in appropriate amounts for six hours (see Table S1 for the formulation) and then centrifuged and separated. After vacuum drying, FTH superamphiphobic powder was obtained.

1.3 Preparation of the aluminum phosphate (AP) binder.

The aluminum phosphate (AP) binder was prepared through the conventional synthesis of an inorganic binder. The orthophosphoric acid with 85wt.% in water was diluted to 60 wt.% by adding deionized water. Then, aluminum hydroxide was added into dilute orthophosphoric acid in a molar ratio of 3:1, followed by stirring at 100 °C for 3 hours

1.4 Preparation of F-TiO_2-HNT superamphiphobic surface

The prepared AP binder dispersion (2 g) was mixed with 5 ml deionized water, stirred for 5 min and sonicated for 10 min at room temperature to form solution A. Meanwhile, FTH superamphiphobic powders (1 g) were dissolved in anhydrous ethanol (15 ml) under stirring and sonicated for 10 min to form solution B. Solution A and solution B are mixed and stirred for 10 min to obtain solution C for a subsequent experiment. Finally, the suspension containing superamphiphobic particles was sprayed onto the original copper foam for several times by a spray gun until the surface was completely and evenly covered by F-TiO_2-HNT particles. The sprayed copper foam was put into an oven at 80℃ for 2h to obtain the superamphiphobic copper foam surface.

The surface of superamphiphobic slides was prepared by sieving deposition. It is suitable for vials containing FTH powder. The bottle has a perforated cap with a stainless-steel mesh so that the powder can be easily deposited on a binder-treated surface such as spray or double-sided glue through a sifting action.

Table S1 Six groups of fluorinated formulations

	TH (g)	Et2O (ml)	NH3·H2O (ml)	DI (ml)	TEOS (μl)	PFDTES (μl)
FTH-1	0.3	80	6	6	500	50
FTH-2	0.3	80	6	6	300	50
FTH-3	0.3	80	6	6	100	50
FTH-4	0.3	80	6	6	100	90
FTH-5	0.3	80	6	6	100	70
FTH-6	0.3	80	6	6	100	30

Table S2 The superamphiphobic surfaces based on nanotubes or nanowires

Nanotube	Reentrant structure	Preparation method	CA/°	Characteristic	Ref.
SiO_2 nanotube	Crosslinked nanotubes	Stencil Removal	WCA=162.2±1.0 n-decane=154.8±1.0	Transparent Heat-resistant liquid	[1]
HNT	Crosslinked nanotubes	Surface Modification	WCA=172 n-hexadecane=160°	chemical durability	[2]
SiO_2 nanotube	Crosslinked nanotubes	Stencil Removal	WCA=166.8 n-octane=155.6	transparent	[3]
MWCNTs	Crosslinked nanotubes	Surface Modification	WCA=172.2±4.2 n-octane=157.9±2.7	repelling both cool and hot liquids	[4]
ZnO@HNTs	rod-dot micro/nano hierarchical structures	Sol-gel	WCA=165.2±1.0 rapeseed oil=154±0.9	Superhydrophobic even after 1h UV irradiation	[5]
SiO_2@HNTs	rod-dot micro/nano hierarchical structures	Hydrolytic condensation	WCA≥150 n-heptaned≥150	UV resistant, chemically durable	[6]
MWCNTs	Crosslinked nanotubes	Fluoridation treatment	WCA=172 n-cetane=163	chemically durable	[7]
AgNPs@ACN	Crosslinked nanotubes	Electrostatic spinning	WCA≥165 n-Dodecane≥165	Sensing properties	[8]
PANI/fCNTs	Core-shell structure	in situ polymerization, Acid corrosion, hydrothermal method	WCA=167 glycerin>150	High temperature and corrosion resistance	[9]

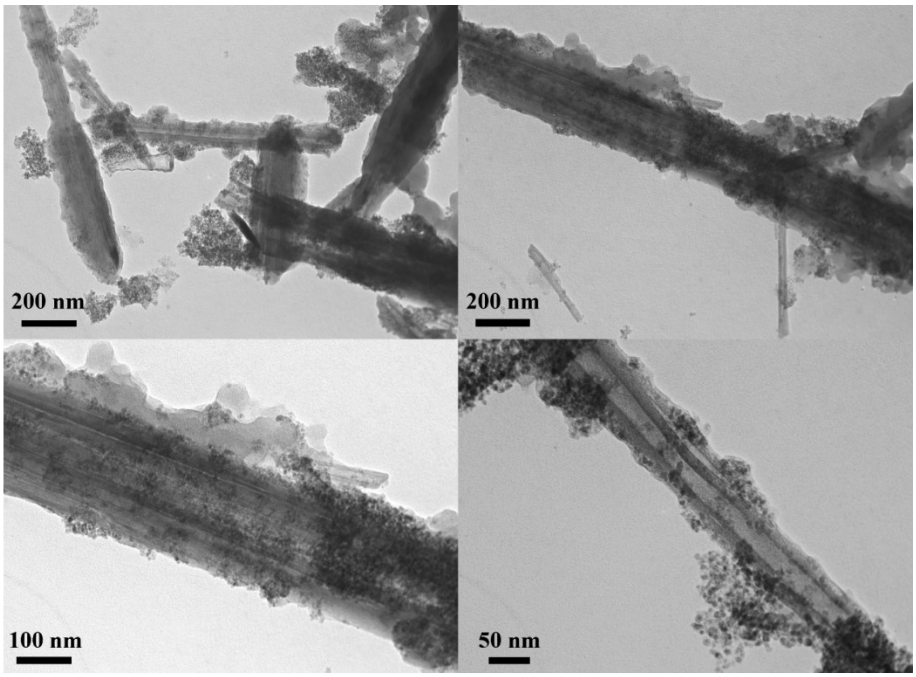

Figure S1. Transmission Electron Microscopy (TEM) image of FTH-4 powder

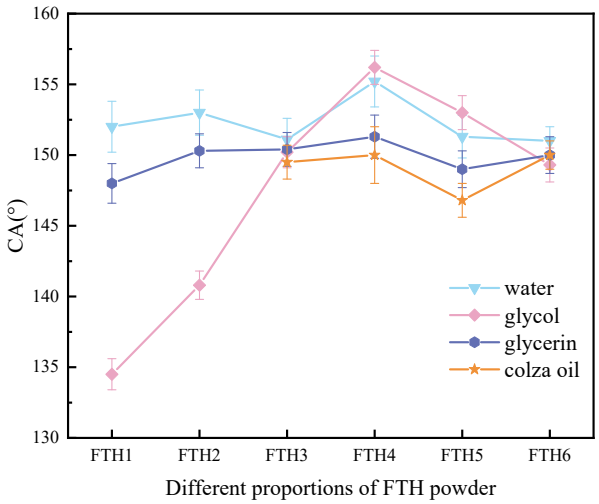

Figure S2. The contact angle of FTH1~6 for water and three oils

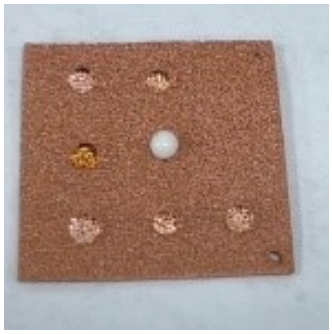

Figure S3. Optical photograph of seven types of water/oil droplets on a surface of superamphiphobic foam copper

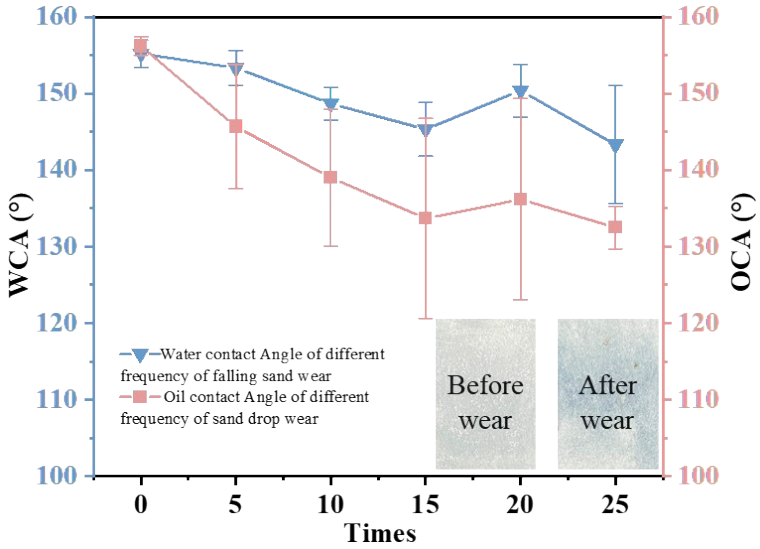

Figure.S4 Water contact Angle and oil contact Angle after falling sand wear, the lower right corner is the optical photos before and after wear.

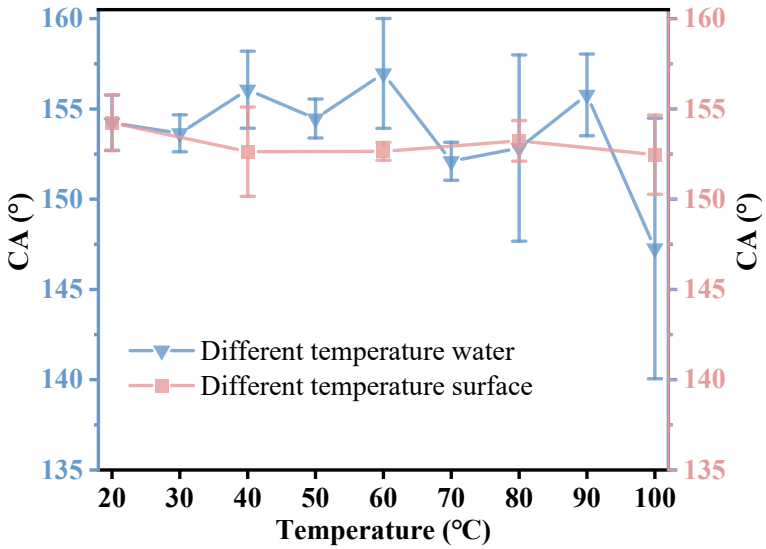

Figure.S5 Contact angles of water at different temperatures and water contact angles of superamphiphobic surfaces at different temperatures

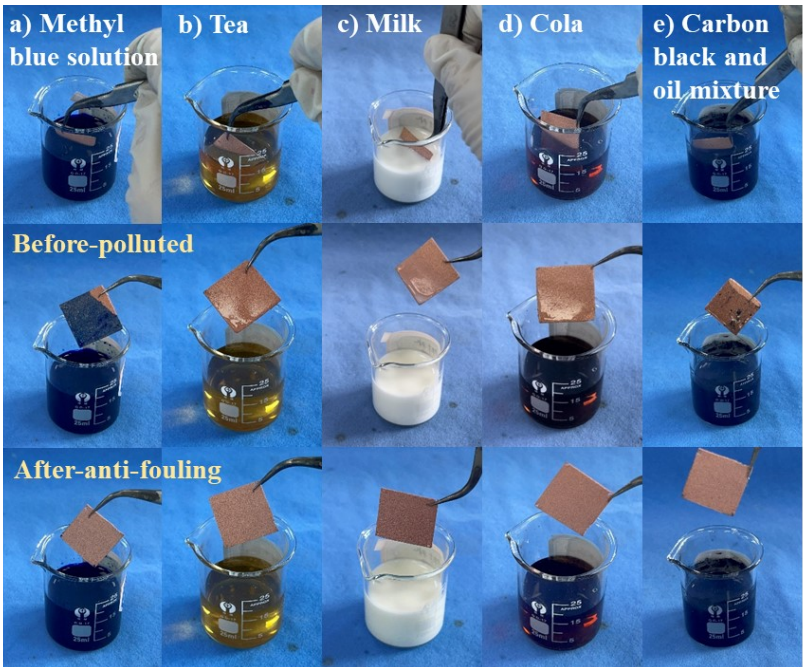

Figure S6. Antifouling test of superamphiphobic foam copper immersed in five kinds of sewage. (a) methyl blue aqueous solution; (b) Tea; (c) Milk; (d) Cola; (e) Carbon black mixed with rapeseed oil solution.

Movie S1-S3. FTH superamphiphobic surface is self-cleaning. (S1) Methyl blue; (S2) Carbon black; (S3) Sand.

Movie S4-S8 FTH superamphiphobic surface anti-fouling. (S4) Methyl blue; (S5) Cola; (S6) Tea; (S7) Milk; (S8) Carbon black mixed with rapeseed oil solution.

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