Supporting Information

Facile Preparation of Durable and Robust Superhydrophobic Textiles by Dip Coating in Nanocomposite Solution of Organosilanes

Junping Zhang,* Bucheng Li, Lei Wu, and Aiqin Wang

Experimental section

Materials: Tetraethoxysilane (TEOS, 99.9%) and *n*-hexadecyltriethoxysilane (HDTES, 95%), were purchased from Gelest. Anhydrous ethanol, ammonium hydroxide solution ($NH_3 \cdot H_2O$, 25% by weight), toluene and triethylamine (Et_3N) were purchased from China National Medicines Corporation Ltd. The wool textiles were kindly supplied by EMPA Testmaterials AG, Switzerland. All chemicals were used as received without further purification. Deionized water was used for all the experiments and tests.

Preparation of HD-oligomer/HD-silica nanocomposite: The nanocomposite was prepared by a modified Stöber method. [1] The ammonia saturated ethanol solution was prepared by passing $NH_3 \cdot H_2O$ through a drying column, and then bubbling it through anhydrous ethanol. The ammonia concentration in ethanol was about 3 M. In a typical synthesis, 0.62 mL of TEOS and 1.24 mL of HDTES were charged into the mixture of ammonia saturated ethanol solution and anhydrous ethanol (1:1) at 50 ℃. The solution was ultrasonicated for 10 min, and then a predetermined amount of water was injected quickly into the solution under ultrasonication. After reacting for 48 hours, the nanocomposite was washed with 20mL of ethanol for 3 times and dried in an oven at 60 ℃.

Fabric*ation of superhydrophobic textiles:* A dip coating solution was prepared by adding a proper amount of the HD-oligomer/HD-silica nanocomposite into a solvent composed of 4 mL of toluene and 0.2 mL of Et_3N. Then, a piece of the cleaned wool fabric (3 × 3 cm, cleaned with anhydrous ethanol) was immersed in the as-prepared coating solution and ultrasonicated for 30min at 30 ℃. Finally, the coated sample was annealed at 60 ℃ in an oven for 50min.

Measurement of water shedding angle (WSA): Owing to the fact that the surfaces of some substrates such as textile are macroscopically rough, it is very difficult to detect the full drop profile for contact angle (CA) measurement (Fig. S1). Consequently, the classical CA measurement, highly dependent on the method of drop shape analysis, is unsuited to reliably evaluate the wetting properties of the surfaces. Thus, WSA is used instead of CA and sliding angle according to a previous reported method (Fig. S2a). [2, 3]

Typically, the samples were fixed onto a sample holder (Fig. S2b) and placed on the tilting table of the Contact Angle System OCA 20 (Dataphysics, Germany). The syringe was positioned with the needle tip 10 mm above the tilted sample and in a way that a drop falling from the needle would contact the substrate 20 mm from the bottom end of the sample. The needle with an inner diameter of 110 μm was used to produce liquid droplets with a volume of 10 ± 0.3 μL. To determine the WSA, measurements were started at an inclination angle of 50 °. Droplets of liquid were released onto the sample at a minimum of three different positions. If all drops completely bounced or rolled down the sample, the inclination angle was reduced by 2 ° and the procedure repeated until one or more of the droplets would not completely roll down the surface. The lowest inclination angle at which all the drops completely rolled down or bounced off the surface was noted as the WSA.

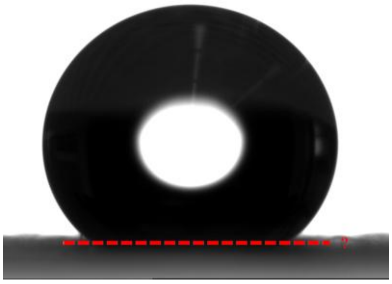

Fig. S1. Typical image of a water droplet on the superhydrophobic textile.

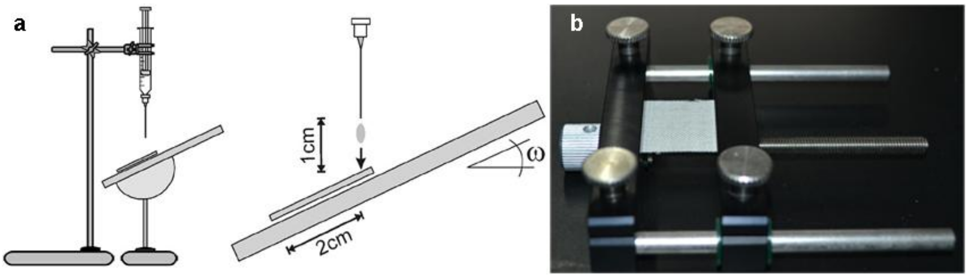

Fig. S2. (a) Principle setup employed for measuring SHA (ω) (3) and (b) the sample holder.

Abrasion test: The abrasion test was performed according to a previously reported method (Fig. S3). [4] The sample was fixed onto the stainless steel column and moved repeatedly (40 cm for one cycle) on the abrasion partner under certain pressure. In order to simulate the authentic utilization, the abrasion tests were performed by using A4 paper or sandpaper (2000 meshes) as the abrasion partner. The WSA after 10, 50, 100 and 200 cycles of abrasion was recorded. To test repairability, the sample obtained after 200 cycles of abrasion at 5.0kPa was dip coated again according to the same procedure and the WSA was measured.

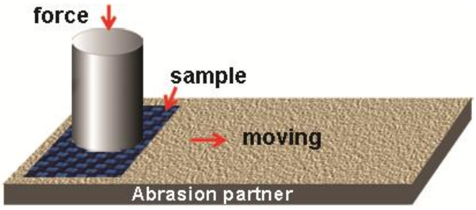

Fig. S3. Schematic illustration of the abrasion test employed to evaluate the mechanical durability of the samples.

Laundering test: The samples were washed in a washing machine with 10 pieces of cotton textiles (20 × 20 cm) for 10 cycles (30 min each) at room temperature. After each washing cycle, the fabric was washed in turn with deionized water and absolute ethanol for three times, and then dried in an oven at 60 ℃ before WSA measurement.

Characterization: The micrographs of the samples were taken using a field emission scanning electron microscope (SEM, JSM-6701F, JEOL) and a field emission transmission electron microscope (TEM, TECNAI-G2-F30, FEI). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold (~ 7 nm). For TEM observation, the samples were prepared as follows. A drop of the nanocomposite dispersion in toluene was put on a copper grid and dried in the open atmosphere. The energy dispersive X-ray analysis (EDX) was done on an attachment to SEM or TEM. Infrared (IR) spectra of samples as KBr pellets were taken using a Thermo Nicolet NEXUS TM spectrophotometer. The mechanical properties of pristine and coated wool fabrics were measured using a universal testing machine (CMT4304, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) equipped with a 200 N load cell at room temperature with gauge length of 3 mm and crosshead speed of 2 mm/min. All the tests were carried out in triplicate.

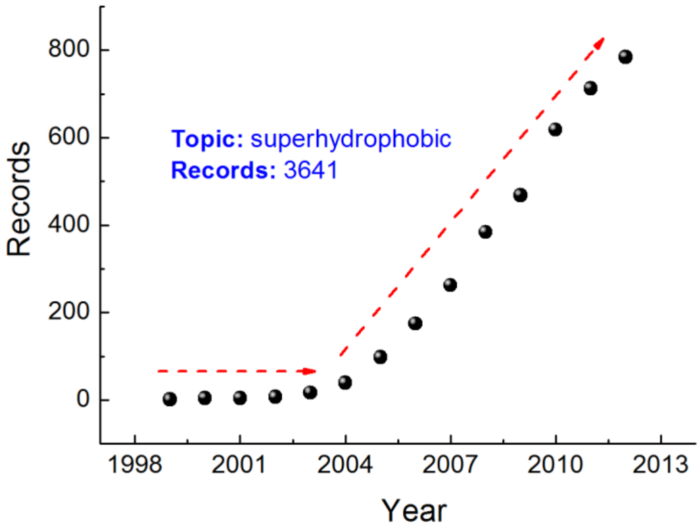

Fig. S4. Records of superhydrophobic coatings in the ISI Web of Knowledge using "superhydrophobic" as the topic word.

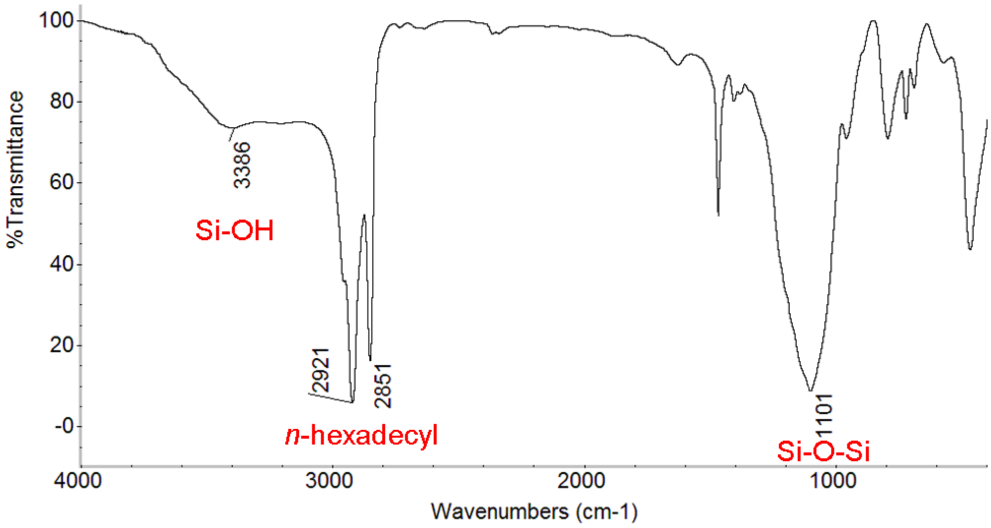

Fig. S5. IR spectrum of the HD-oligomer/HD-silica nanocomposite.

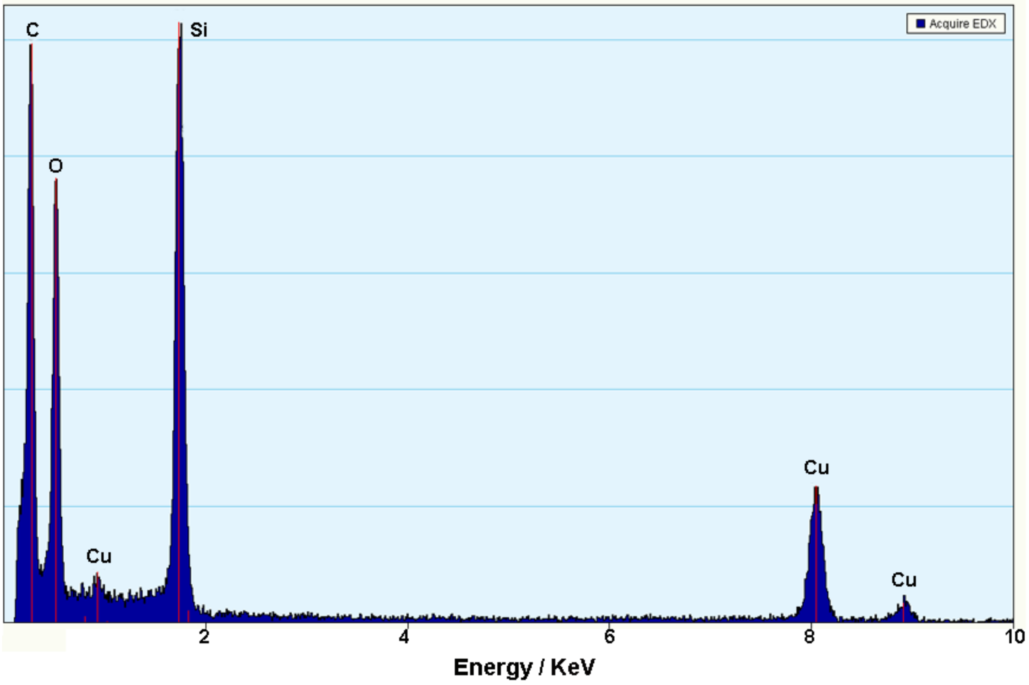

Fig. S6. EDX spectrum of the HD-oligomer/HD-silica nanocomposite.

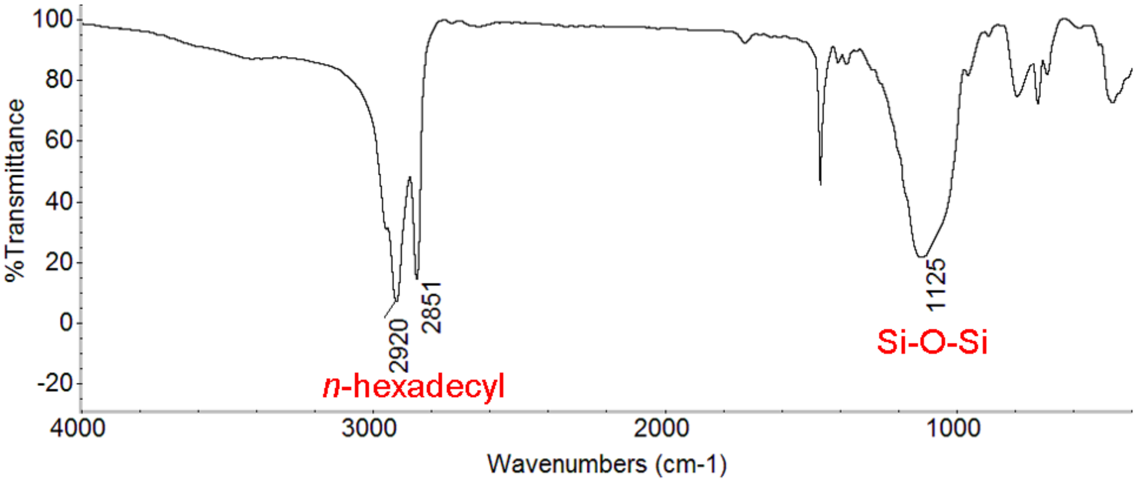

Fig. S7. IR spectrum of the residue after dip coating of a fabric in the HD-oligomer/HD-silica nanocomposite dispersion.

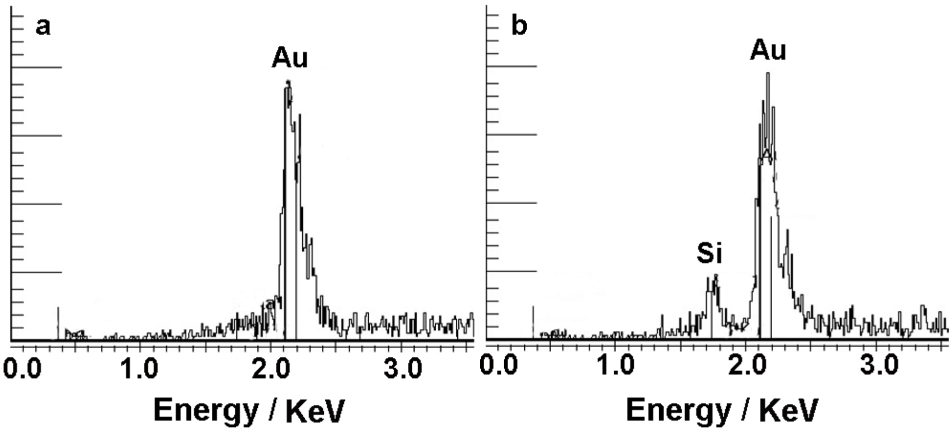

Fig. S8. EDX spectra of the (a) pristine and (b) coated wool fabrics.

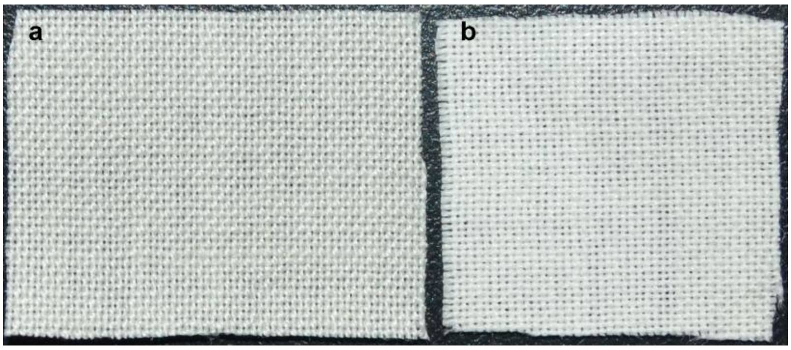

Fig. S9. Images of the (a) pristine and (b) coated wool fabrics.

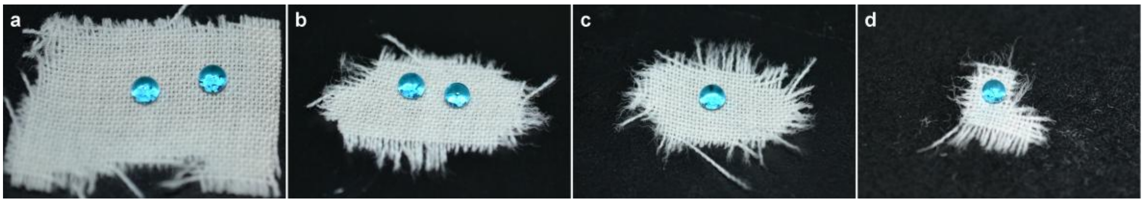

Fig. S10. Images of the coated wool fabrics after (a) 10, (b) 30, (c) 50 and (d) 100 cycles of abrasion at 5.0 kPa using sandpaper as the abrasion partner.

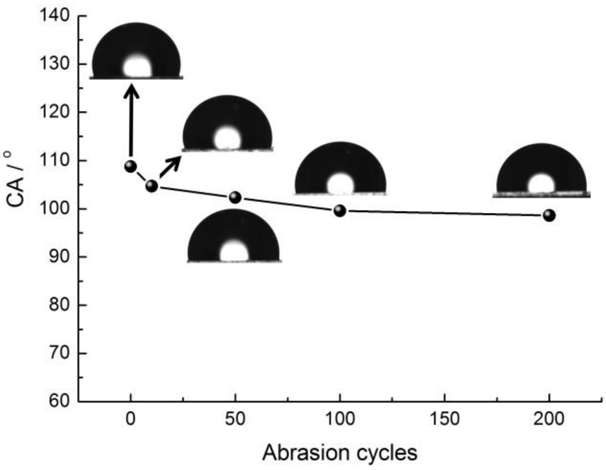

Fig. S11. CA changes depending on abrasion cycles (40cm each) at 5.0 kPa by using the glass slide as the substrate.

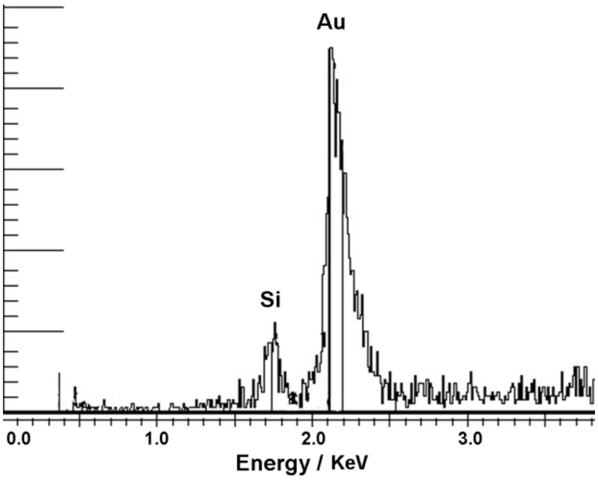

Fig. S12. EDX spectrum of the coated wool fabric after 200 cycles of abrasion at 5 kPa.

Table S1. WSA of water drops (10 μL) on the superhydrophobic textile after treated under various conditions.

Treatments	WSA / °
After preparation	3.0
In 0.1M HCl (1h)	3.0
In toluene (7 days)	8.0

In acetone (7 days)	8.0
In chloroform (7 days)	10.0
Outdoor (7 days) [a]	4.0
UV irradiation (365nm, 24h, distance to sample: 10mm)	4.0

[a]. In December in Lanzhou, China. The outdoor temperature is in the range of -15 to -3 ℃.

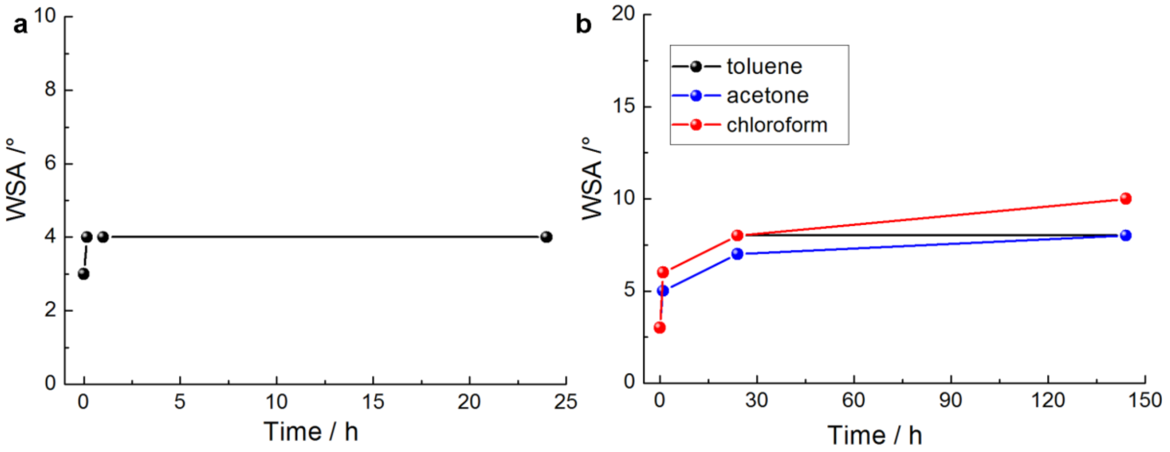

Fig. S13. Variation of WSA of water drops (10μL) on the superhydrophobic textile with (a) UV irradiation time and (b) immersion time in organic solvents.

Table S2. Mechanical properties of the pristine and coated wool fabrics.

Parameters	Pristine	Coated
Sample thickness / mm	0.29	0.32
Tensile strength / MPa	161.4 ±8.9	175.7 ±2.3
Elongation at break / %	29.9 ±8.7	38.3 ±5.8

M**ovie S1.** Water drops bounce off the superhydrophobic wool fabrics after 200 cycles of abrasion at 5 kPa (part 1) and 10 cycles of machine wash (part 2). This video highlights the excellent superhydrophobicity after abrasion and laundering.

Movie S2. Water drops bounce off the superhydrophobic wool fabrics after scratching with a scalpel (part 1), adhesion of double side tape (part 2), finger press (part 3) and twisting by hands (part 4). This video highlights the excellent superhydrophobicity after these qualitative tests of the mechanical stability.

REFERENCES

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4. X. T. Zhu, Z. Z. Zhang, J. Yang, X. H. Xu, X. H. Men and X. Y. Zhou, *J. Colloid Interf. Sci.*, 2012, **380**, 182-186.