

Electronic Supplementary Information (ESI)

A facile procedure to fabricate nano calcium carbonate/polymer-based superhydrophobic surfaces

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Experimental details

Materials

NPCCA-602 nano calcium carbonate with the diameter of 40-60 nm was kindly offered by Shandong Haize Nano Co., Ltd of China. *n*-Butyl methacrylate, glycidyl methacrylate, azobisisobutyronitrile (AIBN), epoxy resin, curing agent, and other reagents were used as received without further purification.

Preparation of acrylate copolymer

Following the previously reported procedure in Ref. 1. In a 100 mL three-necked round-bottomed flask was placed styrene (3.0 g), *n*-butyl methacrylate (15 g), glycidyl methacrylate (4.5 g), and toluene (40 mL). Under nitrogen stream protection, the flask was immersed in an oil bath maintained at 85 °C, and the mixture was stirred for 40 min. Azobisisobutyronitrile (AIBN, 0.2 g) in 5 mL of toluene was placed in the dropping funnel and added dropwise over 15 min to the mixture, then the mixture was stirred for another 3 h. The resulting mixture was precipitated in excess petroleum ether (b.p. 60-90 °C), and dried in a vacuum, resulting in acrylate copolymer as a colorless and transparent solid. The synthetic route was shown in Fig. S1.

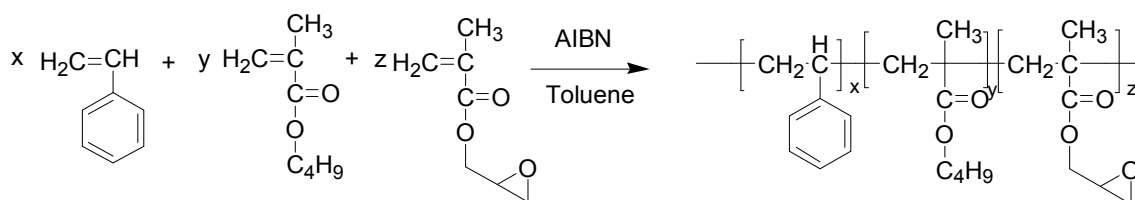


Fig. S1 Synthetic route of acrylate copolymer

Preparation of nano calcium carbonate/epoxy composites

10 mL of toluene/acetone mixture ($v/v = 2:1$), 1.0 g of calcium carbonate nanoparticle, 1.0 g of epoxy resin, and 0.5 g of curing agent, with a nano calcium carbonate/epoxy/curing agent weight ratio of 1:1:0.5 (the weight ratio of epoxy/curing agent was fixed as 2:1), were mixed by ultrasonication. Following this process, nano calcium carbonate/epoxy/curing agent mixed samples with the weight ratio of 2:1:0.5, 4:1:0.5, 6:1:0.5, and 8:1:0.5 were respectively achieved. For comparative purpose, a sample without nano calcium carbonate was also prepared.

Preparation of nano calcium carbonate/acrylate copolymer composites

A process similar to the nano calcium carbonate/epoxy composites was conducted for the preparation of the nano calcium carbonate/acrylate copolymer composites.

Brush-coating process

The obtained composite samples were coated on the glass slide by brush coating method and placed horizontally, then dried at room temperature overnight to allow solvent to evaporate from the films.

The resultant coatings appeared ivory-white, flat, and smooth, and without any obvious protrusions by macroscopic observation.

Sand abrasion test

Following the procedure reported in Ref. 2. A sand abrasion test was performed on the apparatus as shown in Fig. S2. Sand grains with diameter of $\sim 200\ \mu\text{m}$ impinged the surface from a height of 15 cm. After sand abrasion for 5 min, the wettability of the surface was recharacterized.

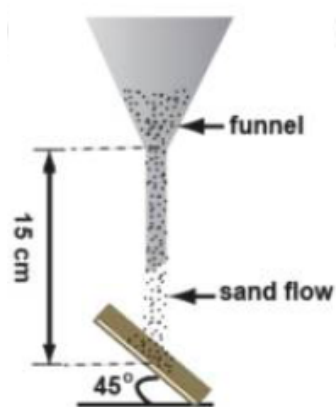


Fig. S2 The apparatus for a sand abrasion test

Characterization

The surface morphology was analyzed using a JSM-6510LV scanning electron microscope (SEM) for morphological observations. The wettability of the as-prepared surfaces were determined by measuring the surface contact angles made by droplets of deionized water. Measurements were performed using an OCA40 contact angle goniometer (Dataphysics, Germany) and the values reported were the average of three drops for each sample at different positions.

Table S1. Samples of nano calcium carbonate/acrylate copolymer composites with different weight ratio, and water contact angles of the resulting surfaces.

Sample	Weight ratio of nano calcium carbonate/acrylate copolymer	Water contact angle (degree)
1	0:1	77.1±0.9
2	1:1	87.5±0.3
3	2:1	134.7±0.5
4	4:1	152.5±2.0 (150.1±1.1 ^a)
5	6:1	147.6±1.6
6	8:1	151.5± 1.5

^a Determined after a sand abrasion test.

Table S2. Samples of nano calcium carbonate/epoxy composites with different weight ratio, and water contact angles of the resulting surfaces.

Sample	Weight ratio of nano calcium carbonate/epoxy	Water contact angle (degree)
1	0:1	84.4±0.5
2	1:1	87.4±2.1
3	2:1	108.6±0.5
4	4:1	148.5±0.5 (146.1±1.0 ^a)
5	6:1	148.0±1.2
6	8:1	150.2±1.0

^a Determined after a sand abrasion test.

References

1. L. Cao, A. K. Joes, V. K. Sikka, J. Wu and D. Gao, *Langmuir*, 2009, **25**, 12444.
2. L. P. Xu, J. Peng, Y. Liu, Y. Wen, X. Zhang, L. Jiang and S. Wang, *ACS Nano*, 2013, **7**, 5077.