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LETTER

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

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Xinde Tang,^{*a} Faqi Yu,^b Wenjuan Guo,^b Tieshi Wang,^b Qun Zhang,^b Qiangqiang Zhu,^a Xiao Zhang^a and Meishan Pei^{*b}

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A facile procedure to fabricate superhydrophobic surfaces based on nano calcium carbonate/polymer composites was described. The hydrophobicity of the resulting surfaces can be tuned by varying the weight ratio of nano calcium carbonate/polymer. The simple and robust strategy can facilitate the fabrication of superhydrophobic surfaces on general substrates.

Superhydrophobic surfaces have attracted considerable attention from fundamental research as well as practical applications.¹ Owing to their water-repellent property, superhydrophobic surfaces have emerging applications in several fields such as anti-corrosion,² self-cleaning and antifouling,³ oil-water separation,⁴ and so on. Previous research demonstrates that the combination of a hierarchical micro/nano-structure and a low surface energy material is required for the preparation of superhydrophobic surfaces, and superhydrophobic surfaces have been achieved through the control of both chemical composition and morphological structures of the surfaces.⁵

Superhydrophobic surfaces have been created by various techniques, including chemical etching, chemical bath deposition, phase separation, layer-by-layer deposition, electrode-deposition, photolithography, template technique, and plasma processes.⁶⁻¹² However, most of these structures are difficult to produce in a large-scale due to the severe conditions, complex process control and special equipment needed, and their poor durability.^{13,14} Moreover, the most significant barrier can be the difficulty of fabricating large-scale depositions in a cost-effective way. Superhydrophobic polymer surfaces,

typically fabricated by combining hierarchical micro-nanostructures, have a great technological potential because of their special water-repellent and self-cleaning properties. Whereas, polymer materials can be easily decomposed at high temperature, and the poor mechanical robustness of such surfaces has severely limited their practical applications.¹⁵⁻¹⁸

Inorganic nanoparticle/polymer composites have been used to fabricate superhydrophobic surfaces. Wong et al. prepared robust superhydrophobic surfaces using epoxy resin and silica nanoparticles, in which the epoxy resin serves as an adhesion and stress relief layer.¹⁹ Superhydrophobic films based on conventional silica particles and epoxy polymers were developed to mimic the micro/nano-scale structure of lotus leaves by Ming et al., in which well-defined silica-based raspberry-like particles are covalently bonded to an epoxy-based polymer matrix.²⁰ Superhydrophobic thermoplastic polyurethane (TPU) films based on octadecanamide (ODAA)-directed assembly of nanosilica/TPU/ODAA hybrid with a well-defined sheetlike microstructure was achieved by Yang et al.²¹ Although the above mentioned superhydrophobic surfaces showed improved mechanical robustness, most of the preparation procedures are expensive, complicated, and hard to realize in a large scale, and the resulting surfaces can be easily destroyed. Therefore, to explore a facile method for manufacturing superhydrophobic surfaces based on inorganic nanoparticle/polymer composites is still promising and challenging.

In this communication, two polymer resins, epoxy and acrylate copolymer combined with nano calcium carbonate (nano-CaCO₃) were applied for fabricating superhydrophobic surfaces, respectively. Take nano-CaCO₃/acrylate copolymer

composite for example. A certain amount of toluene/acetone mixture (v/v = 2:1) was mixed with nano- CaCO_3 , acrylate copolymer, and curing agent (the weight ratio of 1:1 for nano- CaCO_3 /acrylate copolymer and the weight ratio of acrylate copolymer/curing agent fixed as 2:1) by ultrasonication. Followed such process, nano- CaCO_3 /acrylate copolymer samples with weight ratio of 2:1, 4:1, 6:1, and 8:1 were obtained, respectively. For comparative purpose, a sample without nano- CaCO_3 was also prepared. The obtained samples were coated on the glass slide by brush coating method, and dried at room temperature overnight. Further details are presented in the ESI.†

The relationship between water contact angle and weight ratio of nano- CaCO_3 /acrylate copolymer is shown in Fig. 1. The acrylate copolymer surface showed a water contact angle of 77.1° . The surface hydrophobicity increased with an increase of nano- CaCO_3 . When the weight ratio of nano- CaCO_3 /acrylate copolymer approached to 4:1, the surface wettability kept relatively constant with a water contact angle from 147° to 152° . The water contact angle exhibits a maximum value of 152.5° at the ratio of 4:1. The changes in the surface wettability are attributed to the formed hydrophobic microstructures. Furthermore, with an increase of nano- CaCO_3 content, the composite interfaces of the formed honeycomb-like structures became clearer and clearer (Fig. 2). On the other hand, these results indicate that the optimization of nano- CaCO_3 /acrylate copolymer ratio is a crucial factor for the fabrication of such superhydrophobic surfaces.

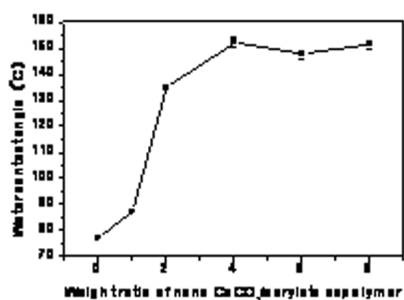


Fig. 1 Dependence of water contact angle on the weight ratio of nano- CaCO_3 /acrylate copolymer.

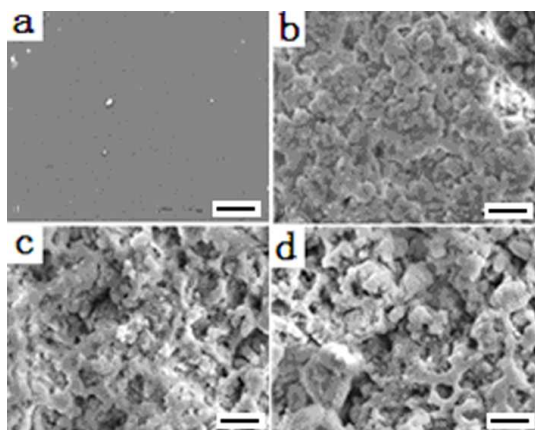


Fig. 2 SEM images of varied weight ratios of nano- CaCO_3 /acrylate copolymer: (a) 0:1; (b) 4:1; (c) 6:1; (d) 8:1. Scale bar = 10 μm .

For nano- CaCO_3 /epoxy surfaces, the relationship between water contact angle and weight ratio of nano- CaCO_3 /epoxy is shown in Fig. 3. Without nano- CaCO_3 , the epoxy surface exhibited a water contact angle of 84.4° . Increasing the content of nano- CaCO_3 , the surface hydrophobicity increased at the weight ratio of less than 4, then the water contact angles kept stable and exhibited a maximum value of 150° at the ratio of 8:1. Similar to nano- CaCO_3 /acrylate copolymer surface, with an increase of nano- CaCO_3 content, the formed honeycomb-like microstructures appeared with clear interface.

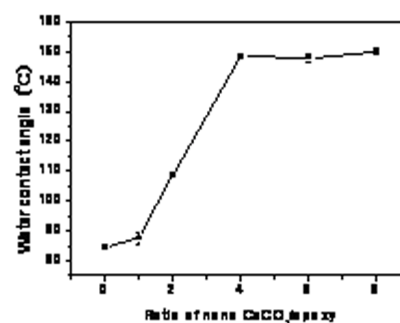


Fig. 3 Dependence of water contact angle on the weight ratio of nano- CaCO_3 /epoxy.

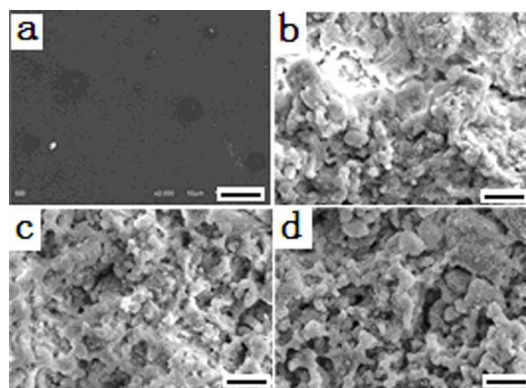


Fig. 4 SEM images of varied weight ratios of nano- CaCO_3 /epoxy: (a) 0:1; (b) 4:1; (c) 6:1; (d) 8:1. Scale bar = 10 μm .

The surface wettability is not usually governed by the chemical compositions of materials but is more likely related to the surface topographic structure.²² In general, the combination of roughness and low surface energy materials on the deposited coatings can give rise to higher water contact angles and hence superhydrophobicity.^{23–25} The low surface energy materials containing fluorine or silicon element, such as fluorinated polymers and polydimethylsiloxane (PDMS) have been used for the fabrication of superhydrophobic surfaces.^{26,27} On the contrary, Chen et al. reported superhydrophobic surfaces based on a relatively hydrophilic material, poly(hydroxybutyrate-co-valerate) (PHBV), which exhibits a contact angle of 75.9° when fabricated with a smooth surface. Superhydrophobic films with contact angles up to 158° and a sliding angle of 7° have been obtained by electrospinning of PHBV.²⁸ In our case, epoxy resin exhibited more hydrophobic than acrylate copolymer, theoretically, the hydrophobicity of nano- CaCO_3 /epoxy composite surface should be higher than that of nano-

CaCO₃/acrylate copolymer composite surface under identical conditions. Actually, the wettability of nano-CaCO₃/epoxy surface was superior to that of nano-CaCO₃/acrylate copolymer surface at an identical ratio. This indicates that the surface roughness plays a crucial role for the fabrication of superhydrophobic surfaces. When a rough surface comes into contact with water, air trapping in the trough area may occur, which would be attributed greatly to the increasing hydrophobicity.²⁹ In this case, the different interactions of nano-CaCO₃ with acrylate copolymer or epoxy may give rise to diverse surface morphologies, further result in varied wettability.

The optimization of the nanoparticle size was usually focused on fabrication of superhydrophobic surfaces in the previous reports. The water contact angles of the surfaces prepared with the fluorinated silica nanoparticles increased by increasing the nanoparticle size, which can be attributed to a large amount of air entrapment between the particles forming a composite microstructure of the solid particles and the air that reduces the effective contact area of water from the surfaces. Further increasing the size might not further influence the water contact angle.²³ For the thin polymer films using organosilane-modified silica particles of varied diameters from 50 to 100 nm, the contact angle increased to 158° and remained similar in both cases, with a further increase in size to more than 100 nm, a decrease in contact angle occurred.²⁷ To avoid this defect, in our case, monodisperse CaCO₃ nanoparticle with the size of 40–60 nm was employed to combine with polymer resin for fabricating the superhydrophobic surfaces, and the interaction between nano-CaCO₃ and polymer can impact the surface morphology, further influence the surface hydrophobicity.

Epoxy resins with a wide range of applications arises from their desirable properties, such as easy processability, high tensile strength and modulus, good chemical and corrosion resistance, dimensional and thermal stability, good creep resistance, excellent fatigue properties, low shrinkage on curing, good adhesion to various substrates, long pot life period, and easy curing.³⁰ Epoxy resin nanocomposites reinforced with silica nanoparticles have been prepared using a surface wetting method, by which silica nanoparticles were first embedded in epoxy resin.³¹ The cross-linked network structures formed through the efficient chemical reactions between amino and epoxy groups,³² resulting in core-shell structures with silica nanoparticle as core and cured epoxy resin as shell. The curing agent not only led to the cross-linking of epoxy resin, but also added covalent bonding between epoxy resin and silica, which reinforced the interfacial force of the hybrid materials. The enhancement is governed by the method of nano-reinforcement, the nano-interface, the microstructural effects, and the interaction between epoxy and inorganic nanoparticles.³³ The inorganic nanoparticle/epoxy hybrid materials have many advantages, such as fast thermal curing under moderate temperature, good adhesion on various substrates, good thermal properties, good etching resistability, reduced shrinkage, improved dimensional stability, etc.³⁴ The improved thermal stability and the enhanced mechanical property of the cured epoxy resin nanocomposites filled with silica nanoparticles were observed compared with those of the cured pure epoxy resin.³⁵

It should be noted that the hydrophobicity of toluene/acetone solvent does not directly affect the hydrophobicity of the resultant coatings due to the removal of solvent by evaporation. However, the interactions between nano-CaCO₃, polymer, and solvent can generate varied surface morphologies. In general,

the hydrophobic surfaces with hierarchical roughness tend to exhibit superhydrophobicity.^{36,37} In this case, the interaction between nano-CaCO₃ and polymer resin, and the aggregation of CaCO₃ nanoparticles can form microstructures. Nanoscale roughness can also be present on the surface because of the presence of nano-CaCO₃. The superhydrophobicity can be produced by combination of micro- and nano-scale roughness.

Mechanical wear on superhydrophobic surfaces usually shows as increased sticking of water, leading to loss of non-wettability.²⁷ In this case, the cross-linked systems with nano-CaCO₃ and polymer for enhancing abrasion resistance gave rise to the formation of robust multimaterial hierarchical micro/nano-structure surfaces. The abrasion resistance of these surfaces were verified by a sand abrasion test as a measure of harsh conditions (ESI†). At the weight ratio of 4:1, the hydrophobicity retained with water contact angle of 150° for the nano-CaCO₃/acrylate copolymer surface and 146° for the nano-CaCO₃/epoxy surface, respectively, after sand impingement. Only a slight decrease of water contact angles demonstrates that the surfaces are not vulnerable to falling sand and keep their superhydrophobicity after sand abrasion.

In conclusion, superhydrophobic surfaces were easily fabricated by brush coating process using nano-CaCO₃/polymer composite materials. The surface hydrophobicity can be tuned by the weight ratio of nano-CaCO₃/polymer. The simple and robust method, without multi-step procedure, expensive instruments, complicated experimental conditions, or special reagents facilitates the preparation of superhydrophobic surfaces in large-scale on general substrates, and endows the obtained coatings with excellent mechanical property and great abrasion-resistance. The superhydrophobic surfaces are promising in many potential application areas.

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Experimental

Materials. NPCCA-602 nano calcium carbonate with the diameter of 40–60 nm was kindly offered by Shandong Haize Nano Co., Ltd. of China. Epoxy resin and T31(A) epoxy resin curing agent were commercially available. *n*-Butyl methacrylate, glycidyl methacrylate, azobisisobutyronitrile (AIBN), and all other reagents were used as received without further purification.

Preparation of acrylate copolymer. Following the previously reported procedure.²⁶ 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.

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.

Sand abrasion test. Following the procedure reported previously,³⁸ A sand abrasion test was performed on the apparatus as shown in Fig. S2. Sand grains with diameter of ~200 μm impinged the surface from a height of 15 cm. After sand abrasion for 5 min, the wettability of the surface was recharacterized.

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.

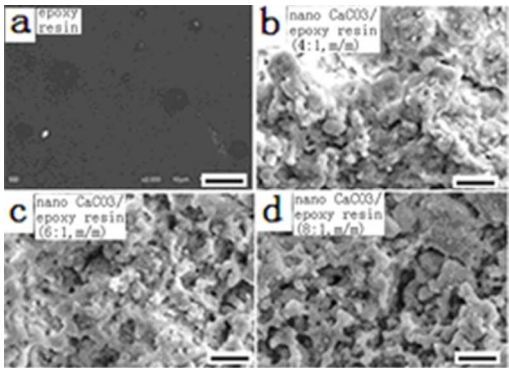
Notes and references

^a School of Material Science and Engineering, Shandong Jiaotong University, Jinan 250023, China. E-mail: xdtang8033@163.com.

^b School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China. E-mail: chm_peims@ujn.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental details and water contact angle data. See DOI: 10.1039/b0000000x/

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