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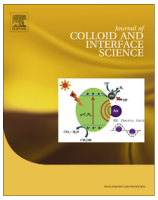

Regular Article

Bio-inspired one-pot route to prepare robust and repairable micro-nanoscale superhydrophobic coatings

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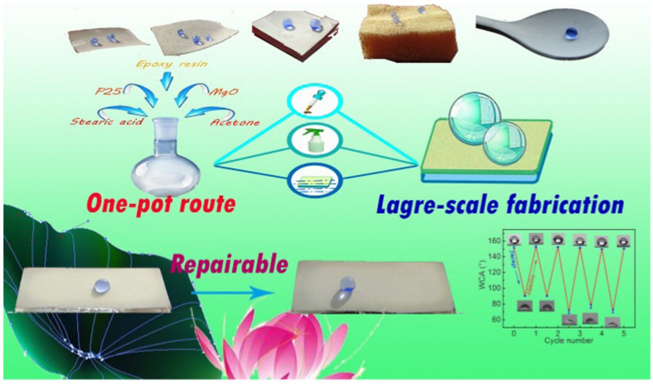
GRAPHICAL ABSTRACT

We have demonstrated one kind of micro-nanoscale superhydrophobic coating via a novel one-pot route on arbitrary substrates. This coating has avoided complex process, noxious chemicals and high cost successfully. It not only displays excellent mechanical stability but also shows unique repairable ability to recover its superhydrophobicity under various damages.



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ABSTRACT

Superhydrophobic (SHP) coatings inspired by lotus have great application prospect for our daily life. Regrettably, three formidable challenges, namely, complex fabrication, weak mechanical stability and large-scale fabrication, have already existed for a long time in this research field. Here, a robust micro-nanoscale P25 (Nano TiO_2)/MgO/epoxy resin (ER) SHP coating has been fabricated via facile one-pot route, which can be applied to arbitrary substrates through multiples methods. P25/MgO/ER SHP coating not only displays excellent mechanical stability but also shows unique repairable ability to recover its superhydrophobicity under various damages by extreme environment such as low temperature, strong acid or alkali and this repairable process can be repeated for many times. P25/MgO/ER SHP coating also is easy to large-scale fabrication with very low cost.

1. Introduction

Nature, a wise teacher of human beings, has always been the source of original innovation scientific research. Study from nature has been an important way to create new materials and devices,

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and also has been pushing the development of human society. Therefore, bionics has been one important branches of science. The classic example, inspired by the lotus leaves in nature, superhydrophobic (SHP) surfaces, characterized by a water contact angle (WCA) larger than 150° and a sliding angle (SA) lower than 10°, has been an significant research topic because its many special advantages such as self-cleaning, anti-icing, corrosion resistance, and anti-bacteria [1–3]. In 1997, with the aid of scanning electron microscope (SEM), Barthlott and Neinhuis [4] discovered that the superhydrophobicity lotus leaves were caused by micro-scaled papillae and superficial epicuticular wax. In other words, roughness surface morphology and low surface energy substance co-create SHP surface. Subsequently, Jiang et al. [5] further disclosed that branch-like nanostructures on top of the micropapillae result in the good superhydrophobicity, that is, micro- and nanoscaled hierarchical structure is conducive to superhydrophobicity. Hereafter, scientists try every means to create various artificial SHP surfaces with fine micro- and nano-scaled hierarchical structures. With deepening of the research, many innovative applications including antifouling, water collection, bio-ion channel and energy-conversion system, all of which have received a lot of attention over the past decade [6].

There is no doubt that coating will be the most direct and effective way to connect SHP technology and human life. As an indirect modification method, SHP coatings can create a new functional layer that is totally different with the original substrate, which turn surfaces into SHP to obtain great applicability and practicability [7]. However, similar to other SHP surface, the development of SHP coating has been slowed down by stability issues including chemical durability and, especially, mechanical stability. Inherently, the micro- and nano-scaled hierarchical structures of SHP coating are fragile and vulnerable. Externally, it is inevitable for coatings to be damaged by abrasion situation in life. So, poor mechanical stability has turned into the bottleneck for SHP coating. To handle this issue, many researchers have put in a lot of effort over the years.

There are two mainstream solutions in this research field today. The first one is repairable SHP materials. Briefly, superhydrophobicity of repairable materials can be recovered after damaged. For example, several years ago, Esteves et al. [8] has demonstrated a robust SHP coating via an all-in-one dispersion by a simple drop-cast method, which can recover their surface chemical composition spontaneously to re-obtain superhydrophobicity at room temperature upon damage. Very recently, Tian and coworkers [9] have reported one kind of porous SHP engineered silicone coatings after sufficient exposure to heat. The SHP coating can be generated and regenerated (repaired) fast with a propane torch, and strongly adhere to different surfaces of diverse compositions. These excellent works have drawn great inspiration for successor. However, repairable SHP materials always need special condition to trigger or need long time to achieve, which have limit its use in our life.

The second solution is "paint+adhesive" strategy, which was put forward by Lu et al. [10] for the first time in 2015. They created dual-scale TiO_2 nanoparticles ethanol based suspension coated with perfluorooctyltriethoxysilane, which can be sprayed onto commercial adhesives covered surfaces and a robust water-repellent surface generated. The combination of paint SHP layer and adhesive layer vastly enhance the mechanical stability SHP coating. Along this way, some novel functional two-layer robust SHP coatings have been reported subsequently. For example, Chen et al. [11] have fabricated similar low-cost and mono-scale perfluorooctyltriethoxysilane coated calcium carbonate nanoparticles suspension to create a SHP surface on adhesive substrates. Our group also has done much in-depth researches inspired by the above works. Recently, we have demonstrated two-layer robust superamphiphobic coating and SHP omnipotent protective coating successfully to cope with some extreme circumstances [12,13]. This two-layer "paint+adhesive" strategy, to some extent, can alleviate the mechanical stability issue, but the coating procedure need two or more steps with special installation. These difficult coating technical problems have proved extremely challenging especially in practical application situation for our daily life. To sum up, one-layer, in situ, repairable, green, and inexpensive SHP coating with high mechanical stability for arbitrary substrates will be a perfect resolution, which is the dream and pursuit of research community today.

To this end, based on outstanding previous researches, we have demonstrated one kind of near-perfect micro-nanoscale P25/MgO/ER SHP coating via a facile one-pot route on arbitrary substrates. This P25/MgO/ER SHP coating has avoided complex process, noxious chemicals and high cost successfully. It not only displays excellent mechanical stability but also shows unique repairable ability to recover its superhydrophobicity under various damages. This SHP coating possesses great applicability and practicability, which can satisfy our daily life needs well.

2. Experimental

2.1. Materials

E51 Epoxy resin and curing agent were purchased from Beijing Yuhong Waterproof Technology Co. Ltd. MgO (AR) and Stearic acid (CP) were purchased from Longxi Chemical Reagent Co. Ltd, Shantou, China. P25 (Nano TiO_2) was obtained from HeqianTrading Co, Ltd, Guangzhou, China. All other chemicals were analytical-grade reagents and used as received. Millipore water (resistivity ~18 MΩ cm) was used throughout this study.

2.2. Preparation of P25/MgO/ER dispersion

P25/MgO/ER dispersion was prepared via simple one-pot route illustrated in Fig. 1. 1.67 g MgO, 0.33 g P25, 0.2 g stearic acid (STA), and 1.2 g epoxy resin with 3:1 volume ratio to curing agent were added into 50 mL round-bottom flask together. Then, 20 mL acetone also was added into this round-bottom flask under magnetic stirring at room temperature for 15 min forming oyster white P25/MgO/ER dispersion.

2.3. Preparation of micro-nanoscale P25/MgO/ER SHP coatings on arbitrary substrates

There multiple methods can be used to form micro-nanoscale P25/MgO/ER SHP coatings on various substrates. The first one is dip-coating, the substrate was immerged into oyster white P25/MgO/ER dispersion for a few seconds, and then it was taken out slowly. Those steps were repeated over two or three times. The second one is droplet-coating using dropper. The oyster white P25/MgO/ER dispersion was drip on to substrate forming coatings. The third one is spray-coating method. Remove this dispersion into a spray. The various substrates were sprayed one or a few times. All the substrate with coating was transferred to room temperature and aging for 24 h or 70 °C for 5 h.

2.4. Characterization

X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) measurement using the Al Kα line as the excitation source. Field emission scanning electron microscope (FESEM) images were obtained on JSM-6701F, both with Au-sputtered specimens. TGA and DTA measurements were done with NETZSCH STA 449 C using a dynamic heating rate of 10 °C min^{-1}. Fourier