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Simple spray deposition of a hot water-repellent and oil-water separating superhydrophobic organic-inorganic hybrid coatings via methylsiloxane modification of hydrophilic nano-alumina

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ABSTRACT

We present a new class of superhydrophobic surfaces created from low-cost and easily synthesized aluminum oxide nanoparticles functionalized with two kinds of silane, which have one and two $-CH_3$ branched respectively, without using the expensive and environmental harmful fluorine-containing organic compounds. Meanwhile, the importance of the existence of water in the process of surface modification of nano-alumina is researched. Thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy reveal the existence of crosslinking between silane and nano-alumina. The resultant surface exhibits a water contact angle (θ) of ~156.5° (room temperature) with the arithmetic mean deviation surface roughness of 3.2 μm, which is almost equal to the equivalent fluorosilane functionalized surface (θ = 160°, S_a ≈ 1.8 μm). It is also noticeable that the contact angle can still reach a value of 141° at the temperature of 60 °C. When the functionalized nanoparticles are dispersed and sprayed onto a piece of paper, the oil-removal efficiency can reach to about 99%.

1. Introduction

Superhydrophobic surfaces (contact angles greater than 150° and low sliding angles of less than 10°) [1], which can be obtained through combining low surface energy and micro/nano-level surface roughness, have attracted significant attention recently due to their non-wetting, self-cleaning [2–9], oil/water separation [10–16], anti-icing [17–20] and other features [21,22]. Various methods such as layer-by-layer assembly [23], sol-gel [24–28], electrospinning [29], template synthesis [30,31], hydrothermal synthesis [32], electrochemical deposition [33], phase separation [34] and vapor deposition [35–37] have been proposed to build micro/nano-level structure of the rough surface. In most cases, fluorinated chemicals (FCs) are used for the micro/nano-level particle surface modification or the molecular fluoridation due to their low surface energy [38–40]. However, FCs have high price and bad environmental impact due to their toxicity, bioaccumulation, and persistence [41]. Recently, silanes and silicones based superhydrophobic and superoleophobic materials have been developed to separate the mixture of water and oil, aiming to solve the problems of industrial oily waste water and spilled oil in oceans [42,43]. Li et al. [44] revealed that the silanes and silicones based superhydrophobic and superoleophobic materials accounting for approximately 25% of the total research. In comparison with FCs, organic silicon is cheaper and less harmful to the environment. Polysiloxane has been identified as one of the best materials for synthesizing high performance coatings because of the existence of inorganic siloxane backbone [45]. Griessbach et al. [46] indicated that initial hydrolysis of methylsiloxane was catalyzed by clay minerals. The primary hydrolysis product was then either biodegraded, or evaporated into the atmosphere, where it was subsequently oxidised in the presence of sunlight. The end products in both cases were expected to be CO_2, SiO_2 and H_2O. Whelan et al. [47] found that methyl groups play important roles in the decomposition process of polydimethylsiloxane (PDMS) at high temperature. Therefore, the commercially available siloxane, which only contains environmental friendly methyl groups and hydrolyzable groups ($Si-OCH_2CH_3$), was utilized to functionalize alumina nanoparticles in our study.

Few researches have been dedicated to the preparation of superhydrophobic surfaces based on siloxane functionalized alumina nanoparticles [44,48]. Karapanagiotis et al. [49] prepared superhydrophobic films through spraying suspensions, which were fabricated by dispersing various diameters of Al_2O_3 particles in siloxane solutions, on glass surfaces. The effect of the nanoparticle size and particle concentrations on the wetting properties is discussed. Li et al. [50] fabricated superhydrophobic coatings by the CVD of PDMS functionalized alumina nanoparticles at mild temperature. Lu et al. [51] fabricated

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superhydrophobic γ-Al_2O_3 membranes by modification with PFOTES in hexane in an argon atmosphere. However, FCs modification or special equipment was involved in the above researches. Moreover, the cross-linking process between silane and nano-alumina has not been fully studied. Among all the crystal forms of Al_2O_3, α-Al_2O_3 has the widest applications attributed to its corundum crystal structure [52]. So, α-Al_2O_3 nanoparticles were chosen as the modified particle because of these nanoparticles have a wide range of applications within the commercial system, although various nanoparticles can be functionalized by this methodology.

In the present work, the crosslinking process between methylsiloxane and nano-alumina was studied. Meanwhile, superhydrophobic surfaces of siloxane functionalized alumina nanoparticles are obtained through simple and effective formulations. An optimum experiment scheme was achieved by simply changing the components of modifiers and the experimental conditions.

2. Experimental procedure

2.1. Materials and reagents

The chemicals used in this work contain isopropyl alcohol (IPA) and ethyl alcohol (EtOH) which were purchased from Sinopharm Chemical Reagent Co. Ltd, and alumina nanoparticles (α phase, hydrophilic), 1H,1H,2H,2H-perfluorodecyltrimethoxysilane, methyltriethoxysilane (MTES) and diethoxydimethylsilane (DMDES) which were purchased from Shanghai Macklin Biochemical Co. Ltd. All the chemicals were of reaction grade purity and without further purification. Deionized water with a resistivity of 18.2 MΩ cm was used in all of the experiments.

2.2. Synthesis of organosilicon functionalized nanoparticles

The fabrication process of functionalized nanoparticles should follow the steps below. Firstly, H_2O (1 ml), ethanol (EtOH) (1 ml) and IPA (3 ml) were mixed in a round-bottomed flask at room temperature (RT) for 1 min. Then the alumina nanoparticles with appropriate modifiers, which are summarized in Table 1, were added into the flask. The mixture was refluxed at 90 °C for 2 h, and then refluxed at RT under continuous stirring for 10 h after cooling. Subsequently, the functionalized particles were centrifuged for 5 min and re-dispersed in 20 ml IPA before centrifuged again. Finally, the functionalized particles were oven-dried at 50 °C for 5 h.

2.3. Spray coating of functionalized nanoparticle films

The functionalized nanoparticles (1 g) were dispersed in IPA (20 ml) via pulse-sonication. Then the dispersions were sprayed onto glass slides by a high pressure gas storage tank until a visible film was generated, and the picture was shown in Fig. S1 (Supporting Information). The spraying distance was approximately 20 cm between the substrate and nozzle. For comparison, all samples were coated onto glass slides via the same procedure. A scheme of the whole process from synthesis to spray coating is shown in Fig. 1. The low alloy steel plates (30 mm diameter, 1 mm thickness) were chosen as samples used for surface observation. The plates were cleaned in ethanol via sonication for 2 min and dried in air. Then they were sprayed with unfunctionalized and functionalized nanoparticles, respectively. With the occurrence of crude oil spills into water, the separation of oil from water is necessary to protect environment. A hydrophilic paper can have the capacity of separating water from the mixture of oil/water by coated with superhydrophilic and oleophylic coatings. To assess the superhydrophilic and oleophylic property of MTES/DMDES functionalized nano-Al_2O_3 particles, the particles were dispersed and coated onto a piece of paper, and the contact angles of water and oil were measured.

Table 1
The compositions of nano-alumina modified with modifier chemical.

Number	Al_2O_3 (g)	H_2O (ml)	MTES (ml)	DMDMS (ml)	F-Si (ml)
1	0.5	1	0	0	0
2	0.5	0	2	2	0
3	0.5	1	0	4	0
4	0.5	1	4	0	0
5	0.5	1	2	2	0
6	0.5	1	0	0	4

2.4. Nanoparticle and surface characterization

The powder of samples was ground with KBr and pelletized for the measurement of Fourier transform infrared (FTIR) spectra in transmittance mode. The FTIR measurements were conducted with a Nicolet instrument in the 400–4000 cm^{-1} wavenumber range with 16 scans. Thermogravimetric analysis (TGA) experiments were performed on a STA 3 Jupiter instrument (Netzsch, Germany). The samples were run in an alumina crucible from 25 °C to 800 °C at a heating rate of 10 °C min^{-1} with argon protection. The morphological structures of the prepared samples was observed using Quanta 250 scanning electron microscopy (SEM). The contact angle of 5 μL drops of ultrapure water on the surfaces of different coatings was tested by an optical contact angle meter (JC2000D, Shanghai powereach digital technology equipment Co., Ltd., China) under ambient conditions. Three various surface positions were chosen to measure the average stated contact angle. Laser scanning confocal microscopy (LSCM) was used for the three-dimensional (3D) surface plotting. The 3D images were analyzed by VK-X series multi-function analysis software to measure the surface roughness. The surface roughness parameters including arithmetic mean height (S_a), maximum height of profile (S_z), arithmetic mean peak curvature (S_{pc}), and developed area ratio (S_{dr}) are determined according to ISO 25,178. The aggregates' diameter was measured by the method of dynamic light scattering (DLS) using Laser partical size analyzer (Nano S90, Malvern) under 25 °C.

3. Results and discussion

3.1. Reaction mechanism

The surface of hydrophilic aluminum oxide nanoparticles contains a lot of hydroxyl groups. Silanes with hydrolyzable groups ($Si-OCH_2CH_3$) can be hydrolyzed with water to form silanols ($Si-OH$), which then covalently couple to hydroxyl groups on the surface of aluminum oxide nanoparticles [44]. The functionalized nanoparticle can be self-assembled through polycondensation to form micro-structures because of the existence of $Si-OH$. The average particle diameter of the aluminum oxide nanoparticles used in this study is 30 nm. Siloxane monomers MTES and DMDES, which only contain environmental methyl groups and hydrolyzable groups ($Si-OCH_2CH_3$) [46,47], were used in the formulation. The aluminum oxide nanoparticles functionalized by fluorosilane (1H,1H,2H,2H-Perfluorodecyltrimethoxysilane) were also prepared and compared with the new system.

3.2. Functionalization of aluminum oxide nanoparticles

The thermal stability of the functionalized nanoparticles was measured by TGA in nitrogen from 25 to 900 °C (Fig. 2). The blank sample shows no significant mass loss (Fig. 2(a)). Two stage weight losses have been observed in the ranges from 25 to 420 °C and 450 to 600 °C in Fig. 2(b–e). The first weight loss stage can be correlated with the excess siloxane monomers and ambient moisture which is difficult to be removed. The rapid weight loss in the second stage can be attributed to the thermal-decomposition of alkoxysilane groups from the sample [53]. Fig. 2(d) and (e) show 3.16% and 4.87% weight losses in the