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Fabrication of high performance superhydrophobic coatings by spray-coating of polysiloxane modified halloysite nanotubes

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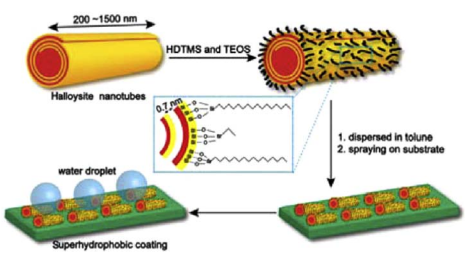
GRAPHICAL ABSTRACT

Schematic illustration for the synthesis of the POS@HNTs and the superhydrophobic POS@HNTs surfaces fabricated by spray-coating (the blue-colored globule represents water droplet on the surfaces).



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ABSTRACT

Superhydrophobic coatings with high water contact angles, ultralow sliding angles, excellent stability, oil/water separation, and self-cleaning functions were fabricated by spray-coating the suspensions of polysiloxane modified halloysite nanotubes (POS@HNTs) onto various substrates. The hydrophobic treatment of HNTs was performed by hydrolytic co-condensation of *n*-hexadecyltriethoxylsilane and tetraethoxysilane on the surfaces of the HNTs. A thick POS layer is located on the surfaces of the HNTs, which makes HNTs hydrophobic. The POS@HNTs were characterized using scanning electron microscopy, transmission electron microscope, Fourier transform infrared spectroscopy, X-ray diffraction analysis, X-ray photoelectron spectroscopy and thermogravimetric analysis. The effects of the ratio of silane and HNTs on the transparency, morphology, and wettability of the coatings were investigated. The transparency of the coating decreases with the increase in the silane loading. The water contact angles of the POS@HNTs coating increase with the increase in the silane loading, but the water sliding angles of the coatings are nearly independent on their ratio. The stability, oil/water separation, and self-healing capability of the coatings were also studied. The coatings on different substrates show high contact angle towards different liquid, e.g. 1 M HCl, 1 M NaOH, tea, and milk. Also, the POS@HNTs coated meshes can efficiently separate oils from water with high separation efficiency. In addition, the POS@HNTs coated gloves show a self-cleaning effect. All these results suggest that the POS@HNTs exhibit great potential for their application in waterproof materials, self-cleaning coating, and oil/water separation devices.

1. Introduction

Superhydrophobic coating is a surface that is extremely difficult to wet. The contact angle of a water droplet on these surfaces exceeds 150° and the sliding angle of water is less than 10° [1]. The superhydrophobic effect is also referred to as the lotus effect, and a droplet

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impacting on these surfaces can fully rebound like an elastic ball. There are a lot of animals and plants in the nature that have the characteristics of superhydrophobicity, such as the surface of the lotus leaf, butterfly wings, and the leg of water strider [2]. The fabrication of the superhydrophobic surfaces has caused extensive attentions all over the world, which has become one of research hotspots in nanotechnology area [3]. The typical applications of the superhydrophobic surface include waterproof function, self-cleaning, anti-icing, corrosion resistance, and oil/water separation [1,4]. The superhydrophobic function is related to both chemical composition and structural characteristics of the surfaces which help trap a thin air layer that reduces attractive interactions between the solid surface and the liquid. For example, the lotus leaf surface possesses special micro/nanoscale binary structure and epicuticular wax crystalloids covered on its surface.

In order to prepare the superhydrophobic surfaces, many approaches have been employed to create appropriate roughness on a hydrophobic surface or modify a rough surface by low-surface-energy materials [5]. Phase separation, template printing method, electro/chemical deposition, electrospinning, laser and plasma etching, in situ growth, and so on can be classed into the first type. Xu et al. prepared a superhydrophobic surface with a CA of 163.0 ± 1.0° and SA of 7.0 ± 1.0° by casting the micellar solution of poly-(styrene)-*b*-poly (dimethylsiloxane) by vapor-induced phase separation [6]. An electrodeposition method for controllable fabrication of a superhydrophobic surface with a water CA of 162 ± 1° and a SA of 3 ± 0.5° was developed by deposition of nickel on copper substrate in the presence of (heptadecafluoro-1,1,2,2-tetradecyl)triethoxysilane [7]. On the other hand, superhydrophobic surfaces can be prepared by modifying a rough surface with low-surface-energy materials, i.e., solution immersion, thermal spraying, heat treatment, chemical vapor deposition, assembly and polymerization on the substrates. In order to introduction of low-surface-energy materials, a facile and rapid candle-soot deposition strategy to fabricate superhydrophobic coatings on porous materials of copper foam and various textile fabrics was recently studied [8]. Thermal spraying represents a simple, fast, and effective scale-up manufacturing methods for coating with large area. For example, spray-coating metal alkylcarboxylates of $Cu[CH_3(CH_2)_{10}COO]_2$ onto glass, aluminum, or other substrates can lead to a superhydrophobic surface with a static water CA of ~160° and a SA of 5° [9]. Superhydrophobic and transparent coatings onto paper can also be prepared by spraying alcohol suspensions of SiO_2 nanoparticles [10]. The development trend of the fabrication of superhydrophobic coating includes adopting facile method, improving mechanical durability, utilization of low cost raw materials, and realization of multifunction such as self-repairing [11].

Halloysite nanotubes (HNTs) are natural clay nanoparticles, with chemical formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ [12,13]. HNTs exhibit a tube diameter of 15–50 nm and tube length of 300–1500 nm with aspect ratio of 6–100. HNTs have aluminum innermost and silicate outermost surfaces, which are positively and negatively charged respectively. The raw HNTs are hydrophilic and can be readily dispersed in water by mechanical stirring or ultrasonic treatment. The silanol and aluminols located in the inner side and edges of the HNTs are expected to react with silanes to change the surface into hydrophobicity [14,15]. For example, Yuan et al. modified and characterized the surfaces of HNTs with hydrophobic γ-aminopropyltriethoxysilane towards the application in polymer nanocomposites, enzyme immobilization and controlled release [16]. Lvov et al. modified HNTs inner and outer surfaces via sequential treatment using octadecylphosphonic acid and organosilane coupling agents. The octadecylphosphonic acid immobilized in HNTs lumen significantly increased the adsorption capacity of hydrophobic ferrocene molecules [17]. In 2013, Takahara et al. prepared low-energy HNTs surfaces by grafting with a long-chain alkylsilane, *n*-octadecyltrimethoxysilane (ODTMS). The surface-modified HNTs formed pincushion agglomerates on the surface of the liquid droplets, which create superhydrophobic surface similar to that of the plant gall surfaces [18]. Very recently, a durable underwater superoleophobic mesh was prepared by layer-by-layer (LBL) assembly of poly (diallyldimethylammonium chloride) (PDDA) and HNTs on a stainless steel mesh, which shows promising application in oil-water separation due to its stable oil-water performance, remarkable chemical and mechanical durability and the facile and eco-friendly preparation process [19]. However, there is no report on preparing HNTs superhydrophobic coating over large areas by a facile spraying method up to now.

In the present work, we first modified the HNTs surfaces by hydrolytic condensation of *n*-hexadecyltrimethoxysilane (HDTMS) and tetraethoxysilane (TEOS) to obtain polysiloxane modified HNTs (POS@HNTs). Then the superhydrophobic coatings were prepared by spray-coating the homogeneous POS@HNTs toluene suspension onto different substrates. The surface properties and morphology of HNTs before and after POS modification are characterized. The effects of the ratio of silane and HNTs on the transparency, morphology, and superhydrophobicity of the HNTs coatings were investigated. The stability, oil/water separation, and self-healing capability of the HNTs coatings were also studied. All the results suggest that the sprayed coated POS@HNTs exhibit superhydrophobic properties with oil/water separation and self-cleaning properties, which makes them good candidates in separation of oil from harsh water conditions and contamination prevention area.

2. Experimental

2.1. Raw materials

Halloysite nanotubes (HNTs) were purchased from Guangzhou Runwo Materials Technology Co., Ltd., China. Hexadecyltrimethoxysilane (HDTMS, ≥85%, Aladdin) and tetraethoxysilane (TEOS, Tianjin Damao Chemical Reagent Factory, China) were used and the chemical formulas of the silane and HNTs were shown in Fig. 1. Aqueous ammonia (25–28%, Tianjin Damao Chemical Reagent Factory, China), anhydrous ethanol (≥99.7%, Tianjian Fuyu Fine Chemical Co., Ltd., China) and toluene (≥99.5%, Tianjin HongDa Chemical Reagent Factory, China) were all of analytical grade. Glass slides (width × length × thickness: 25.4 × 76.2 × 1 mm, Sail Brand, China) were used as the main substrates for spray-coating. All of the other chemicals were used as received without further purification. Ultrapure water from Milli-Q water system was used to prepare the aqueous solutions.

2.2. Preparation of POS@HNTs

The POS@HNTs were prepared by triggering the hydrolytic condensation of silanes on the surface of HNTs [20]. Typically, 0.50 g of the HNTs, 0.25 g of the TEOS and 0.25 g of the HDTMS were dispersed in the mixture of 10 mL of anhydrous ethanol and 2 mL of aqueous ammonia. Then the solution was ultrasonicated for 30 min at room temperature. The hydrolytic condensation was first conducted at 60 °C for 30 min then at room temperature for 24 h under magnetic stirring. The resulting slurry is treated by centrifugation at 6000 rpm for 5 min and washing with ethanol for three times. After drying the products at 65 °C for 24 h, the POS@HNTs powder was finally obtained. The code of the POS@HNTs represents the percent of total weight of silanes to the weight of HNTs. For example, the 20% represented the weight of TEOS, HDTMS, and HNTs was 0.05, 0.05, and 0.5*g*. And the 60% represented the weight of TEOS, HDTMS, and HNTs was 0.15, 0.15, and 0.5*g*. The weight ratio of the TEOS:HDTMS was set as 1:1 (mole ratio of TEOS:HDTMS is 1.67:1) according to the reference [21]. TEOS acted as coupling agent which was beneficial to the hydrolytic condensation of HDTMS on the surface of HNTs.

2.3. Preparation of POS@HNTs coatings

The superhydrophobic coatings were fabricated by spray-coating

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