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Multifunctional hollow superhydrophobic SiO_2 microspheres with robust and self-cleaning and separation of oil/water emulsions properties

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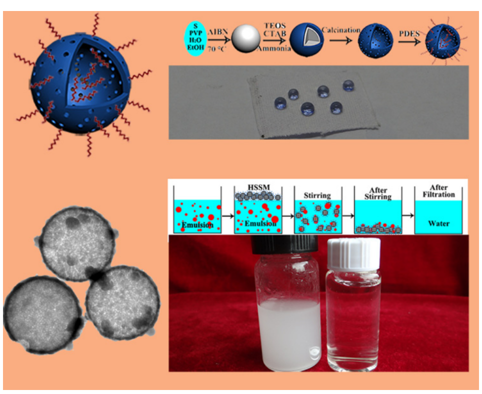
GRAPHICAL ABSTRACT

Multifunctional hollow superhydrophobic SiO_2 microspheres created by template method and self-assembly functionalization can be used in stable superhydrophobic coating and removal of oil from water.



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ABSTRACT

Superhydrophobic materials have drawn great attention due to its' remarkable non-wetting properties and applications in many fields. In this paper, we synthesize a hollow superhydrophobic SiO_2 powder by typical template method and self-assembly functionalization. Robustness of many superhydrophobic surfaces has become the development bottleneck for industrial applications. Aiming at this problem, the adhesive epoxy resin is specially taken to use as the binding layer between superhydrophobic SiO_2 powder and substrates to create robust superhydrophobic coating. The mechanical durability of the obtained superhydrophobic coating is evaluated by a cyclic sandpaper abrasion. Also, the chemical stability of this superhydrophobic coating is assessed by exposuring it to different pH conditions and UV irradiation, respectively. Significantly, because of the special structure and superhydrophobicity/superoleophilicity of the hollow microspheres, these hollow superhydrophobic SiO_2 powders manifest great oil-adsorbing capacity, which thus can be used to separate oil/water mixtures and remove oil from oil-in-water emulsions.

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1. Introduction

Superhydrophobic surface, identified as one kind of surface with high water contact angle greater than 150°and low sliding angle lower than 10°, has attracted tremendous attention in the past decades for its remarkable water-proofing property and potential applications [1–4]. Inspired by the superhydrophobic phenomenon of lotus leaves, water strider, and other organisms in nature, researchers found that there are two key points to construct superhydrophobic surface, that is, creating micro/nano hierarchical structures and then modified with low-surface-free-energy materials [5–7]. In other words, micro-nano roughness and low surface energy are the two key configurations of fabricating superhydrophobic surfaces through forming an air sublayer. At the same time, with the rapid development of materials science and biomimetic studies, various approaches have been applied to create superhydrophobic materials, such as chemical vapor deposition (CVD) [8], electrodeposition [9], hydrothermal technique [10], electrospinning method [11], and etching [12]. Therein, as one efficient method to construct superhydrophobic materials, physical coating has been the hottest surface treatment method. Coating process cannot be affected by many factors such as composition, size, roughness, and shape of the substrates. Based on this, outstanding work has been made to explore the superhydrophobic coating. Yoon's group demonstrated a coating with high transparence in visible range and excellent superhydrophobicity through the electrospraying method [13]. Yang and co-workers fabricated robust superhydrophobic coatings which can tolerate organic solvents and high water flushing speed through using strawberry-like hemispherical Janus particles [14]. A superhydrophobic gel nanocoating with good transparency, stability, and rapid self-healing superhydrophobicity was reported by Guo' group [15]. However, poor robustness of many superhydrophobic surfaces has become the development bottleneck for industrial applications of the superhydrophobic surfaces. Until recently, Lu et al. proposed a view that assigns the robustness to adhesive field [16]. Utilizing adhesives to improve the robustness of surface structures based on superhydrophobic powders becomes a significant research topic.

Owing to the extreme wettability, superhydrophobic materials have many applications such as self-cleaning [17], corrosion resistance [18,19], anti-icing [20], and so on. Meanwhile, with the development of related research fields, a series of innovative applications including drag reduction [21], energy conversation [22,23], droplet manipulation [24], and water collection [25,26], have emerged, especially for oil/water separation application. It is necessary to mention that worldwide oil-contaminated water caused by industrial wastewater and oil spill accidents makes it highly imperative to separate and remove the oil or organic pollutants from water [27,28]. Different from the traditional high-energy-consumptive separation methods such as distillation, centrifugation, electrophoresis and pressure filtration, superhydrophobic materials open a new approach for oil–water separation with highly efficient and low energy consumption processes. Since Jiang et al. firstly created a superhydrophobic and superoleophilic mesh for oil/water separation from a mixture based on its extreme wettability towards oil and water [29], oil/water separation taking advantage of the special wettability of various materials has drawn considerable attention from researchers [30–32]. For example, Jiang and co-workers fabricated a stable superhydrophobic and superoleophilic ZnO-coated stainless steel mesh film that can be applied into effective separation of oil and water mixture [33]. Guo et al. created stable superhydrophobic and superoleophilic soft porous materials, which can be used in oil/water separation [34]. Li and co-workers reported fabrics with double sides showed both superhydrophobic and superoleophilic properties for oil separation and capture from water [35].

It is no doubt that the above-mentioned materials have excellent performance in the separation of free oil/water mixtures. However, it is notable to point out that these materials only play a good role in the separation of dispersed phase with diameter more than 150 μm while some oil/water dispersions and emulsions are composed of the dispersed phase with diameter from 20 μm to 150 μm and less than 20 μm, respectively [36]. Compared with immiscible oil/water mixtures, the emulsion is more difficult to separate. Aiming at this problem, many materials with extreme wettability have been successfully prepared for separating various emulsions [37–41]. Meng et al. prepared a superhydrophilic and underwater superoleophobic PVDF membrane by surface-coating a hydrogel onto the membrane surface, which showed superior performance for oil-in-water emulsion separation [42].

Jiang and co-workers demonstrated a Co_3O_4 nano-needle steel mesh with superhydrophilicity in air and low-adhesion superoleophobicity under water, which can be used in the separation of oil-in-water emulsions with high efficiency and high flux [43]. Jin' group reported a SWCNT/TiO_2 nanocomposite ultrathin film with superhydrophilic and underwater superoleophobic properties after UV-light irradiation for separation of oil-in-water emulsions [44]. However, most materials applied in the separation of oil-in-water emulsion are superhydrophilic and underwater superoleophobic, while many superhydrophobic materials have no effect on oil-in-water emulsions separation. Some superhydrophobic materials have been reported in the separation of oil/water emulsions. For examples, Xu et al. exhibited superhydrophobic/supero leophilic iron particles which can be adopted to remove oil from oil/water emulsions under a magnetic field [45]. In this work, hierarchically structured magnetic superhydrophobic/superoleophili city particles with ability to separate oil phases in surfactant-free oil-in-water emulsions were got through coating core microsized iron with copper nanoflakes shells and subsequently modified by mercaptan. Lai' group has developed intelligent robust fluorine-free superhydrophobic PDMS–ormosil@fabrics, which can separate oil/water emulsion [46]. However, there are still little work concern on the oil-in-water emulsions through superhydrophobic materials.

In this paper, adopting PS microspheres as hard template, we prepared PS@SiO_2 microspheres through a template method. Then, after removal of PS and modified by 1H,1H,2H,2H-Perfluorodecyl triethoxysilane (PDES), the superhydrophilic SiO_2 powders have been converted into multifunctional hollow superhydrophobic SiO_2 microspheres. Taking advantage of the excellent superhydrophobicity and stability of these powders, it can be applied into superhydrophobic coating with excellent mechanical and chemical stability. In addition, based on the adsorption capacity and superhy drophobicity/superoleophilicity of porous hollow superhydrophobic SiO_2 microspheres, these powders also can be used in the separation of oil-in-water emulsions.

2. Experimental section

2.1. Materials

Styrene (S) (AR) was obtained from Tianjin DAMAO Chemical Reagent Co. Inc., China. Polyvinylpyrrolidone (PVP) (AR) (Mr ≈ 10,000) was purchased from Shanghai SITONG Chemical Reagent Co. Inc., China. N,N-Azodiisobutyronitrile (AIBN) (AR) was obtained from Tianjing YUEFENG Chemical Reagent Co. Inc., China. Tetraethoxysilane (TEOS) (AR) was purchased from Shantou