



Mechanical- and oil-durable superhydrophobic polyester materials for selective oil absorption and oil/water separation



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ABSTRACT

The low stability and complicated fabrication procedures seriously hindered practical applications of superhydrophobic materials. Here we present a facile approach for preparing durable superhydrophobic polyester materials by dip-coating in a nanocomposite solution of polymerized tetraethoxysilane and *n*-hexadecyltriethoxysilane. The coated samples exhibit excellent superhydrophobicity, superoleophilicity, mechanical and chemical stabilities. This is attributed to the tight binding of the nanocomposite on the polyester fibers and the inherent stability of silicone. The coated samples can quickly absorb petrol, diesel and crude oil, and show very high selectivity in oil/water separation. In addition, the coated samples could maintain their superhydrophobicity, oil absorption capacity and oil/water selectivity after harsh mechanical damage, 90 days of immersion in oils and ten cycles of absorption–desorption. Moreover, this approach is simple and can be easily scaled up for producing samples on a large size, which makes it very promising for practical oil absorption.

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1. Introduction

Owing to the increased amount of oily wastewater accompanying the development of industry and society as well as the frequent oil spill accidents (e.g.), there is a growing demand for functional oil absorbing and oil/water separation materials [1–6]. Various approaches, e.g., self-assembly, electro-spinning and lithography, have been used for preparing such functional materials [7,8]. Many materials were used for preparing oil-absorbing materials, such as mesh/membrane [5,9–12], sponge [6,13–16], activated carbon [17–19], microporous polymers [20], macroporous gels [21], and crosslinked polymer gels [22–25]. However, there still remain a lot of limitations for large scale fabrication of such functional materials and for practical applications because of costly and complicated fabrication procedures, harsh practical conditions, low stability and flexibility as well as poor selectivity and recyclability, etc. Therefore, it is necessary to find simple methods for preparing excellent materials to overcome the aforementioned limitations.

The wettability of materials is one of the most important parameters influencing their performance. Traditional materials for oil absorption are hydrophobic and oleophilic. It is promising to design novel oil absorbing materials with high oil/water selectivity by enhancing the hydrophobicity and oleophilicity. As is well known, both the surface chemical composition and the geometrical

structure control wettability of a surface [26–29]. Thus, there is a chance to prepare excellent materials for oil/water separation by introducing materials of low surface energy and proper surface topography, which will make them superhydrophobic and superoleophilic.

Superhydrophobic surfaces, characterized by high water contact angle (CA > 150°) and low CA hysteresis, have many potential applications [30–32], including microfluidics, textiles and oil/water separation. Various materials [28,33–35], including textiles, silicon, metals and plastics, have been used as substrates for the preparation of superhydrophobic surfaces. Until now, there have been a handful of studies using superhydrophobic materials for oil/water separation, such as manganese oxide nanowire [7], metal meshes [36,37], filter paper [38], sponge [6,16,23] and carbon foam [24]. The pioneering work about using superhydrophobic materials for oil/water separation is encouraging but still has some problems, which seriously hinder their practical applications. On one hand, most of the reported superhydrophobic materials have poor mechanical and chemical stability, and depend on sophisticated procedures and expensive materials. On the other hand, poor mechanical stability of the substrates (e.g., filter paper and polymer film), potential toxicity of manganese oxide nanowires and low flexibility of metal meshes also restrict their applications for oil/water separation.

Porous materials such as sponges are good candidates for oil/water separation owing to their large pore volume, flexibility as well as low price and high mechanical stability under harsh

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practical conditions. However, these materials will absorb water and oil simultaneously. We prepared silicone nanofilaments coated superhydrophobic polyester textiles, which showed nice selective oil absorption and oil/water separation [5]. However, mechanical stability of the silicone nanofilaments coating remains to be improved.

Here, we report a simple, versatile and low-cost approach for the fabrication of durable superhydrophobic polyester materials by dip coating in a nanocomposite solution prepared using tetraethoxysilane (TEOS) and *n*-hexadecyltriethoxysilane (HDTES). The superhydrophobic polyester materials show excellent superhydrophobicity, superoleophilicity, mechanical (e.g., abrasion and scratching) and chemical (e.g., long time immersion in oils) stabilities. Meanwhile, the superhydrophobic materials exhibit high oil/water selectivity in the cleanup of oil from water. The as-prepared materials can quickly absorb petrol, diesel and crude oil. In addition, the dip coated material could maintain its superhydrophobicity and oil absorption capacity even after harsh mechanical damage, 90d of immersion in oils and ten cycles of absorption-desorption. Moreover, the facile approach can be easily scaled up for producing samples in large size. Owing to simplicity of the method, excellent superhydrophobicity, outstanding durability and reusability, the as-prepared environmental friendly superhydrophobic polyester materials are very promising for practical selective oil absorption and oil/water separation.

2. Experimental section

2.1. Materials

TEOS (99.9%) and HDTES (95%) were purchased from Gelest. Anhydrous ethanol, toluene, *n*-hexane, ammonium hydroxide solution (NH₃·H₂O, 25% by weight), acetic acid, methylene blue and oil red O were purchased from China National Medicines Corporation Ltd. Commercial polyester materials I and II were supplied by HM Group (China). The only difference between polyester I and II is their thickness. Commercial petrol, diesel and crude oil were purchased from Sinopec, Lanzhou, China. All chemicals were used as received without further purification. Deionized water was used for all the experiments and tests.

2.2. Preparation of organosilane-based nanocomposites

The nanocomposites which we termed HD-polymer/HD-silica were prepared by a modified Stöber method [39]. The ammonia saturated ethanol solution was prepared by passing the NH₃·H₂O solution through a drying column and then bubbling it through anhydrous ethanol. The ammonia concentration in ethanol was about 3 M. In a typical synthesis, 1.40 mmol of TEOS and 1.40 mmol of HDTES were charged into the mixture of 5 mL of ammonia saturated ethanol and 5 mL of anhydrous ethanol at 50 °C. The solution was ultrasonicated for 10 min, and then 1.44 g water was injected quickly into the solution under ultrasonication. After reacting at 70 °C for 48 h, the nanocomposite was washed with 20 mL of ethanol for 3 times and dried in an oven at 60 °C.

2.3. Fabrication of superhydrophobic polyester materials

Firstly, a piece of polyester material I (1 × 1 × 0.5 cm) or II (3 × 3 × 0.1 cm) was washed in turn with deionized water and ethanol for several times, and then dried in an oven at 60 °C. The dip coating solution was prepared by adding 40 mg of the HD-polymer/HD-silica nanocomposite into 4 mL of toluene containing 0.2 mL of acetic acid. Then, a piece of the cleaned polyester

material was immersed in the as-prepared coating solution and ultrasonicated for 30 min at 50 °C. Finally, the coated sample was annealed at 60 °C in an oven for 50 min.

2.4. Measurement of water shedding angle (WSA)

Owing to the fact that the surfaces of some substrates such as textile, sponge and material are macroscopically rough, it is very difficult to detect the full drop profile for CA measurement (Fig. S1). Consequently, the classical CA measurement, highly dependent on the method of drop shape analysis, is unsuited to reliably evaluate the wetting properties of the surfaces. Thus, WSA is used instead of CA and sliding angle according to a previous reported method (Fig. S2) [31,40]. Typically, the samples were fixed onto glass slide and placed on the tilting table of the Contact Angle System OCA 20 (Dataphysics, Germany). A syringe was mounted above the tilting table with a fixed needle to a substrate distance of 10 mm. The syringe was positioned in a way that a drop falling from the needle would contact the substrate 8 mm from the bottom end of the sample. The needle with an inner diameter of 110 μm was used to produce liquid droplets with a volume of 7 ± 0.3 μL. To determine the WSA, measurements were started at an inclination angle of 50°. Droplets of liquid were released onto the sample at a minimum of three different positions. If all drops completely bounced or rolled down the sample, the inclination angle was reduced by 2° and the procedure repeated until one or more of the droplets would not completely roll down the surface. The lowest inclination angle at which all the drops completely rolled down or bounced off the surface was noted as the WSA.

2.5. Mechanical abrasion test

The abrasion test was performed according to a previously reported method (Fig. S3) [41]. The sample was fixed onto the stainless steel column and moved repeatedly (40 cm for one cycle) on the abrasion partner at 5 kPa. In order to simulate the authentic utilization, the abrasion tests were performed by using sandpaper (2000 meshes) as the abrasion partner. The WSA after 10, 50, 100 and 200 cycles of abrasion were recorded. Before WSA measurement, the samples were firstly washed with ethanol, and then dried at 60 °C because a lot of sands penetrated into the samples during the test. Mechanical stability of the samples was also qualitative tested by scratching with a scalpel.

2.6. Stability in oil

A piece of the sample was immersed in petrol and diesel for 1, 7 and 90 days. Afterwards, the sample was washed with hexane and dried in an oven at 60 °C before WSA measurement.

2.7. Selective oil absorption

A piece of sample was immersed in oil at room temperature. The sample was taken out from the oil after 1 min, drained for several seconds and wiped with filter paper to remove excess oil. The oil absorption capacity *k* of the sample was determined by weighing the sample before and after oil absorption and calculated according to the following equation:

$$k = (M_t - M_i) \times 100\% / M_i \quad (1)$$

where *M_t* is the weight of the wet sample with oil (g) and *M_i* is the weight of dry sample (g).

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