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Fabrication of superhydrophobic/superoleophilic cotton for application in the field of water/oil separation

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ABSTRACT

Cotton with superhydrophobic and superoleophilic properties had been successfully fabricated for application in the field of oil/water separation by the combination of SiO_2 nanoparticles on cotton fiber surface and subsequent octadecyltrichlorosilane modification. The as-prepared cotton could be used to selectively absorb various common oils and organic solvents up to above 50 times of its own weight while repelling water completely. The absorbed oils were easily collected by a simple vacuum filtration, and the recovered cotton could be reused for several cycles while still keeping high absorption capacity. Moreover, the as-prepared cotton was simply spun into cloth, which not only could be tailored to the water-repellent clothing but also could be used in the oil/water separation filter system. The results presented in this work might provide a simple, low-cost and environment friendly approach for application in the field of water/oil separation.

1. Introduction

With the frequently occurred water pollution caused by oil spillage and chemical leakage, the removal and collection of the organic contaminant from water has attracted great attention (Aurell & Gullett, 2010; Cheng et al., 2011; Lee & Rogers, 2013). The conventional methods of solving these problems include mechanical extraction, chemical degradation, combustion, and absorbent materials. Due to the economy and efficiency for removal and collection of oil, absorbent materials including inorganic mineral materials (Lee & Rogers, 2013; Teas et al., 2001), complex materials (Zhou & Chuai, 2010), and natural materials (Banerjee, Joshi, & Jayaram, 2006) etc., are considered a most desirable choice for the oil spill cleanup. Although these absorption materials have been widely studied and applied in practical applications for the removal and collection of spilled oil, there still exist some limitations such as environmental incompatibility, inadequate buoyancy, low oil absorption capacity, high cost, and poor reusability, and so on. Particularly, some materials absorb water and oil simultaneously, which indicates a poor hydrophobicity and reduces the oil/water separation selectivity and efficiency (Angelova, Uzunov, Uzunova, Gigova, & Minchev, 2011; Ceylan et al., 2009; Sidik et al., 2012). Therefore, the new oil-absorption materials with environmental compatibility, adequate buoyancy, high absorption capacity, low cost, good reusability, excellent selectivity and efficiency are significant for the development of the prevention and disposal of water pollution.

In recent years, some materials with the extreme wettability both superhydrophobicity (water contact angle higher than 150° and sliding angle less than 5°) and superoleophilicity (oil contact angle less than 5°) have attracted great interest for scientific community and potential applications in the area of oil/water separation because they only absorb oil while repelling water (Lee, Johnson, Drelich, & Yap, 2011; Song, Gaware, Rúnarsson, Másson, & Mano, 2010; Zhang, Wang, Wang, & Li, 2013; Zhang, Wang, Wang, Shi, & Li, 2012). As known from previous literature, the superhydrophobic property is attributed to the combination of micro/nano hierarchical structures of the substrate and the low surface energy of the surface (Li, Reinhoudt, & Crego-Calama, 2007; Zhang, Shi, Niu, Jiang, & Wang, 2008). On the basis of this principle, many different methods, such as laser/plasma etching (Song, Tang, Li, & Xiao, 2013; Yoon, Moon, Lyoo, Lee, & Park, 2009), phase separation (Zhao et al., 2005), layer-by-layer assembly (Jiang et al., 2005), lithographic patterning (Fürstner, Barthlott, Neinhuis, & Walzel, 2005), chemical vapor deposition (Ishizaki, Saito, & Takai, 2010), solution-immersion method (Li, Zhang, & Wang, 2008) and sol–gel method (Wang, Liu, et al., 2011) have been developed to design and fabricate superhydrophobic surfaces. Among these methods, the sol–gel method, generated micro/nano-structure onto the surface, has been found to be one particularly good technique for fabricating superhydrophobic coatings onto substrates because of its high efficiency and simplicity.

Cotton is a kind of favorable natural plant fiber material with various excellent characteristics such as softness, flexibility,

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environment friendly, and biodegradability. The fabrication of superhydrophobic/superoleophilic cotton-based materials could find potential applications in the field of oil/water separation. For instance, Wang et al. reported a simple drop-coating method for fabricating superhydrophobic and superoleophilic cotton textiles which can remove water in oil (Zhang et al., 2013). Zhou et al. prepared superhydrophobic and superoleophilic cotton fabrics for oil/water separation by a facile vapor phase deposition process (Zhou et al., 2013). In addition, a variety of materials, such as TPU film (Yang, Wang, Wang, Chen, & Chen, 2010), porous ceramic membrane (Su, Xu, Zhang, Liu, & Li, 2012), copper meshes (Pan, Wang, & Wang, 2008), graphene-based sponges (Nguyen, Tai, Lee, & Kuo, 2012), cotton fabric (Zhang & Wang, 2013) and polymer brushes (Tan, Hughes, Nagl, & Huck, 2012) have been prepared to separating oil from water (or water from oil). However, to the best of our knowledge, few studies have been reported regarding the fabrication of the cotton exhibiting superhydrophobicity and superoleophilicity simultaneously as a kind of oil-absorption material for the water/oil mixture separation with sol–gel method.

In this study, we presented a facile method to fabricate oil-absorption material based on superhydrophobic/superoleophilic cotton. The surface of cotton fibers was initially pretreated by NaOH aqueous solution, then coated with a film of SiO_2 nanoparticles via sol–gel process and subsequently modified with octadecyltrichlorosilane through a simple solution-immersion step. The as-prepared cotton could be used to selectively absorb various kinds of oils and organic solvents up to above 50 times of its own weight while repelling water completely. The cotton also showed good buoyancy on the water surface, and good reusability in oil/water separation cycle. The removal and the collection of the absorbed oils were easily achieved with the help of vacuum air pump. Moreover, the as-prepared cotton fibers could be simply spun into a piece of cloth, which could not only be tailored to the water-repellent clothing but also be used in the oil/water separation filter system. The results of this study provided an approach to fabricate superhydrophobic/superoleophilic cotton for application in the field of oil/water separation.

2. Experimental

2.1. Materials

Cotton was obtained locally. Tetraethoxysilane (TEOS, chemically pure), $NH_3{\cdot}H_2O$ (28%), glacial acetic acid (99.5%), anhydrous ethanol, toluene, *n*-hexane, chloroform, sodium hydroxide (analytical grade), methylene blue and Sudan III were obtained from Tianjin Kaitong Chemical Reagent Co, China. Gasoline, diesel and soybean oil came from the local market, Harbin, China. Octadecyltrichlorosilane (OTS) used for surface hydrophobic modification was purchased from New Jersey. Deionized water was self-made. All of the chemicals were used as received without further purification.

2.2. Pretreatment of the cotton

First, the cotton was ultrasonically washed with deionized water three times, and then put into a beaker containing 2% NaOH aqueous solution. Second, boiling the solution in the beaker for 10 min. Third, the cotton was washed several times with deionized water until the pH level of filtrate reached neutrality. Finally, the pretreated cotton was dried at 50 °C for 24 h.

2.3. Preparation of SiO_2 nanoparticles on the cotton fiber

The SiO_2 nanoparticles were prepared on the cotton fiber by a sol–gel process. In detail, the pretreated cotton was immersed into the mixture solution of 45 mL ethanol, 5 mL TEOS, 5 mL deionized water. Then, 5 mL $NH_3{\cdot}H_2O$ used as the catalyst was added dropwise into the mixture at room temperature under magnetic stirring (400 rpm) for 0.5 h (a homemade porous polyethylene baffle was used to separate the cotton from the magneton, for the purpose of preventing the nonuniform growth of nanoparticles aroused by the magnetic stirring).

After that, the cotton coated with SiO_2 nanoparticles was removed and washed by anhydrous ethanol for three times, blown to dry by N_2 and dried in a vacuum oven at 50 °C for 12 h eventually. SiO_2 nanoparticles synthesized on the cotton fibers by the above method are hydrophilic, with hydroxide groups on the SiO_2 nanoparticles surface.

2.4. Modification of SiO_2 nanoparticles coating on the cotton fibers

The surface modification of SiO_2 nanoparticles coating on the cotton fibers was performed by a self-assembly of OTS monolayer. First, the OTS ethanol solution was prepared by magnetic stirring the mixture of the 100 mL anhydrous ethanol, 2 mL OTS, 0.25 mL H_2O, 0.05 mL glacial acetic acid at room temperature for 4 h. Then, the cotton sample coated by SiO_2 nanoparticles was immersed into the OTS ethanol solution. The modification was maintained at 60 °C for 4 h. The resulting cotton was washed several times with anhydrous ethanol, and dried in a drying oven at 60 °C.

2.5. Characterizations

The geometric microstructures of cotton fibers were characterized by using scanning electron microscopy (SEM, FEI QUANTA200). The elemental composition of resulting cotton fiber surface was determined by Fourier transform infrared spectroscopy (FT-IR, Magna-IR 560, Nicolet) and X-ray photoelectron spectrometer (XPS, PHI Thermo Fisher Scientific Company Quantera), respectively. The water contact angles (WCAs) were measured with 5 μL deionized water droplet at room temperature using an optical contact angle meter (Hitachi, CA-A), and the final WCA was determined by averaging the measurements taken from at least five different positions on cotton fiber samples which were adhered on the glass slide by double-sided adhesive tape.

2.6. Measurements of maximal oil absorption capacity

For purpose of investigating the maximal oil absorption capacity of the superhydrophobic/superoleophilic cotton for common oils and organic solvents, the experiments of oil absorption were carried out in the pure oils and organic solvents, and the final maximal oil absorption capacity was determined by average value of 5 times experiments. Compared with the superhydrophobic/superoleophilic cotton, the oil absorption capacity of raw cotton before and after OTS treatment was measured by the same method. In typical absorption measurements, the cotton samples (1 g) were immersed in pure oil at room temperature, then left for a moment for saturated absorption, and finally weighted before draining for 15 s. The absorption capacity *Q*, defined as $Q = (M_{\text{saturated absorption}} - M_{\text{initial}})/M_{\text{initial}}$, was employed to measure how much oil was caught by the cotton samples.

2.7. Reusability

The superhydrophobic/superoleophilic cotton of absorbing oil was placed into a sand core funnel and drained under mild suction by a vacuum air pump for 5 min after weighting. Then the oil would be collected and the resultant cotton would be reused in the next absorption/collection cycle. The absorption/collection