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Fabrication of superhydrophobic fibre and its application to selective oil spill removal

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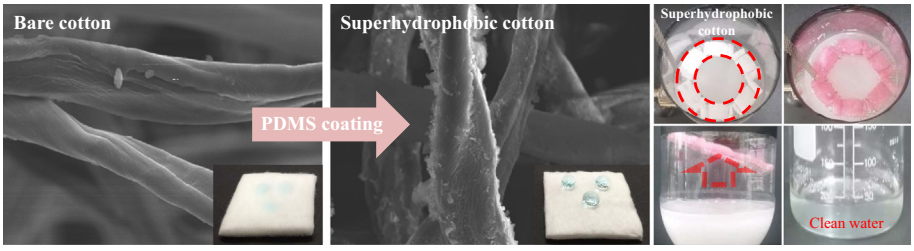
HIGHLIGHTS

- The cotton-based absorbents were fabricated using simple dip-coated method.
- The superhydrophobic absorbents can selectively absorb oil from oil/water mixture.
- The superhydrophobic oil-absorbents show an outstanding recyclability.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrophobic SiO_2 nanoparticles were prepared by depositing polydimethylsiloxane (PDMS) on SiO_2. By dip-coating a solution of PDMS-coated SiO_2 and adhesives dissolved in hexane, cotton and kapok surfaces were modified. The dip-coated cotton and kapok showed high repellency towards water with a water contact angle exceeding 150°. High selectivity towards oil sorption from oil/water mixture was also achieved. The dip-coated cotton and kapok were shown to be able to absorb a quantity of oil ~20–60 times their own weight, depending on the type of oil. It was also demonstrated that the absorbed oil can be mechanically extracted from the absorbent and the absorbent can be reused.

1. Introduction

Spill oil treatment has drawn much attention in the field of environmental science and technology, as ecosystem contamination from spilled oil released into seas and rivers has been a great concern for the last several decades [1]. Various techniques are currently available for selectively removing oil from water [2–4], and it is well established that among the various oil removal techniques, highly efficient absorbents can be beneficial for treating spilled oil [5–8].

An oil absorbent should show a very high oil absorption capacity. Such a property is roughly correlated to porosity [9–11] and thus, highly porous materials have been considered as potential oil absorbent candidates. At present, most commercially available oil absorbents consist of fibrous materials with high porosity originating from vacancies between individual fibres. In addition, many meso/macroporous materials have been synthesized and used for the absorption of oil [12,13]. Another important requirement of high-performance oil absorbents is high selectivity towards oil from oil/water mixture. As such, absorbents should be highly hydrophobic [5,6,14,15], otherwise the absorbent wet

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by water becomes much less efficient for oil absorption when compared to that of the dry absorbent, or the pre-absorbed oil can be replaced by water, resulting in the release of oil into the environment. Either the fibre of hydrophobic materials (e.g., polypropylene) can be used as an absorbent [16,17], or one can provide hydrophobicity to a non-hydrophobic porous material by using thin layers of hydrophobic molecules [18]. Oil absorbents should also be inexpensive, as a large quantity of absorbent is generally needed for removing spilled oil released into the ecosystem after an accident. It is also worth mentioning that most commercial absorbents can rarely be recycled. Therefore, the development of recyclable absorbents would be beneficial in the treatment of spilled oil.

By providing superhydrophobicity to highly porous absorbents, the efficient removal of oil from oil/water mixtures can be realised. Superhydrophobicity refers to the phenomenon whereby water droplets show a contact angle exceeding 150° on a surface. Water droplets do not wet but rather roll down superhydrophobic surfaces. Superhydrophobicity stems from a combination of two different factors, namely the hydrophobic chemical functionality of a surface and the dual surface roughness, the latter of which consists of nanometre-scale structures superimposed on micrometre-scale assemblies. Such a surface configuration results in water-repellent behaviour since water droplets can be repelled by air pockets that exist at the interface between dual-roughness solid surfaces and water [19–21]. Superhydrophobic surfaces with alkyl surface termination generally show significant resistance towards wetting by water and a high affinity for non-polar hydrocarbon molecules. Consequently, superhydrophobic surfaces are appropriate for the selective removal of oil from oil/water interfaces [9,22].

Recently, it was demonstrated that the thermal evaporation of polydimethylsiloxane (PDMS) on various solid surfaces can result in a thin homogeneous coating of PDMS with a thickness of less than 5 nm [23,24]. PDMS-coated surfaces have been shown to be hydrophobic and, in combination with dual surface roughness, PDMS-terminated surfaces can become superhydrophobic. The advantage of using PDMS coatings prepared by thermal vapour deposition is that thin PDMS layers can be deposited independent of the chemical composition of the substrate. Note that the use of a silane coupling agent is limited to surfaces terminated by hydroxyl groups. It has also been demonstrated that PDMS coatings are highly stable under acidic and basic conditions or when subjected to UV irradiation [25,26]. In addition, PDMS is inexpensive and thus, can be utilized in real applications beyond laboratory scale experiments.

In the present work, the new method for the fabrication of stable superhydrophobic cotton and kapok is suggested. PDMS-coated SiO_2 nanoparticles were prepared using simple thermal vapour deposition method and subsequently adhered to commercial cotton and kapok fibre surfaces using a devised dip-coating method. It is worth emphasising that the hydrophobic coating method on SiO_2 does not require chemicals other than PDMS (such as solvent). The water-repellent properties, oil absorption capacity, and selectivity of the dip-coated fibres were studied, and the potential application of these materials in remedying contaminated water is discussed. Also, recyclability of the used superhydrophobic absorbent is demonstrated.

2. Experimental

2.1. Preparation of the samples

A schematic description of the experimental set-up for coating PDMS on SiO_2 nanoparticles is displayed in Fig. 1(a). Fluidic PDMS

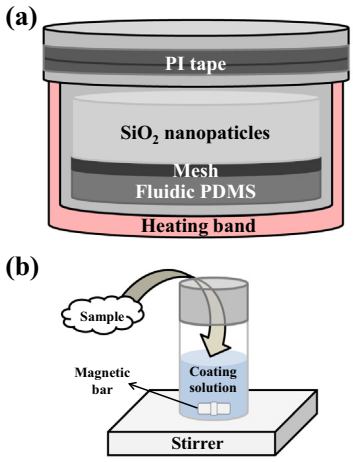

Fig. 1. Schematic diagrams of the experimental set-up for (a) the preparation of hydrophobic coating on silica nanoparticles, and (b) the preparation of dip-coating solution.

(Dow Corning, Sylgard 184) and SiO_2 nanoparticles (Degussa, Aerosil 200, mean particle size = 24 μm) were placed in a steel use stainless (SUS) chamber in a 1:1 weight ratio. In order to physically separate the fluidic PDMS and SiO_2 nanoparticles, an SUS mesh was placed between them. The SUS chamber was sealed with polyimide (PI) tape and then heated with a temperature controlling system consisting of a heating band, a K-type thermocouple, a temperature controller, and a power supply. During thermal vapour deposition of the PDMS, the temperature of the SUS chamber was maintained at 300 °C for 16 h.

After thermal vapour deposition, the PDMS-coated SiO_2 (P-SiO_2) nanoparticles were deposited on fibres, namely absorbent cotton (Hanil Corporation, Hanil cotton) or kapok (Alex animal farms, kapok cotton), using a dip-coating method (Fig. 1(b)). The fibres were dipped in a coating solution consisting of P-SiO_2, a PDMS adhesives mixture (PDMS:curing agent = 10:1, weight ratio) and hexane (DAEJUNG, purity = 95%) with a constant stirring speed of 1200 rpm for 5 min. The curing agent (Dow Corning, Sylgard 184 curing agent) is known to be a mixture of various siloxanes. After the dipping process, the coated fibres were placed on a mesh above a hot plate at 200 °C for 20 min under atmospheric conditions. For each sample, the dipping and drying processes were repeated 3 times.

2.2. Sample characterisation

The water contact angle of the fibres was measured before and after dip-coating. Here, 3 μL of distilled water was dropped on the fibre surface, and the contact angle of the water droplet was measured with a Theta Optical tensiometre (KSV Instruments, Ltd.) and a digital camera connected to a computer. KSV bundle software (Attention Theta) was employed, and Young–Laplace curves were utilized for data fitting. The average of three water contact angles was obtained by taking measurements at 3 different positions for each sample. In addition, the fibres were attached to a glass substrate with double-sided adhesive tape and then, tilted with an inclination from 30° to 5° for the measurement of water shedding (sliding) angle. A syringe was fixed over the samples with a distance of 10 mm between the end of a needle and sample surface. Then, 5 μL of distilled water was dropped onto 3 different positions for each sample surfaces. The minimum inclination angle that all water droplets bounce off and roll down the sample surfaces was determined as water shedding angle [27]. In order to identify the surface functional groups present on the specimens, Fourier