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Fabrication of a superhydrophobic carbon nanotube coating with good reusability and easy repairability

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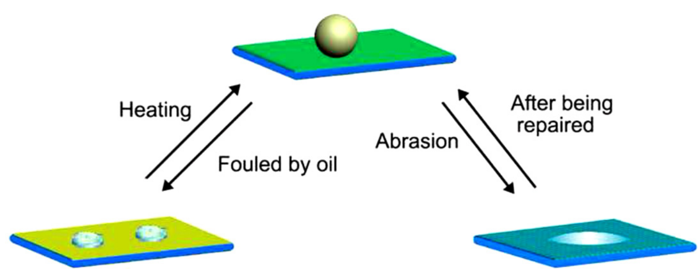
HIGHLIGHTS

- The coating can keep superhydrophobicity after thermal treatment at 400 °C.
- The oil-contaminated coating can regenerate superhydrophobicity after heating.
- The obtained superhydrophobic coating possessed easy repairability.

GRAPHICAL ABSTRACT

A superhydrophobic coating with good reusability and easy reparability was fabricated by a facile method.



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ABSTRACT

Development of superhydrophobic surfaces is severely hindered by their susceptibility to oil fouling and mechanical damage. Herein, to address this challenge, we fabricated a superhydrophobic coating with good reusability and easy repairability by spraying multiwalled carbon nanotubes (CNTs) onto substrates followed by surface fluoration. Water droplets exhibit spherical shape on the obtained coating and could roll off the coating at a small tilt angle. Due to its thermal stability, the oil-fouled CNTs coating can regenerate its superhydrophobic property for repeated use by thermally removing the oil contaminants in air. Moreover, when the CNTs coating loses the superhydrophobicity owing to mechanical abrasion, it can be easily rendered with superhydrophobicity once more by a simple regeneration process.

1. Introduction

There has recently been a significant amount of research directed toward achieving superhydrophobic textured surfaces due to their wide applicability in the fields of self-cleaning, antifogging, anticorrosion, and water-oil separation [1–6]. Until now, various artificial superhydrophobic surfaces have been produced by mimicking the natural non-wetting surfaces, such as lotus leaf, in different ways [7–11]. However, the susceptibility to oil fouling severely hinders the use of superhydrophobic surfaces in practical applications [1,12–15]. Due to their high surface energy, man-made superhydrophobic surfaces are easily fouled by oils and other organic matters, which are difficult to remove and negate the superhydrophobic behavior of the affected surface. To overcome the oil fouling problem, many research groups have paid much attention to designing superamphiphobic surfaces [12,16–19]. Although the obtained superamphiphobic surfaces resist oil fouling, they usually require some special surface textures such as the re-entrant geometry or overhang architecture to provide the needed surface roughness, which poses a tough fabrication challenge. Thus, seeking

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an effective way to solve the oil contamination problem has become an urgent demand.

In addition to oil fouling problem, mechanical damage is another obstacle that must be overcome before textured superhydrophobic surfaces gain widespread use in practical applications [1,12,13]. Mechanical wear on the superhydrophobic surfaces could destroy the microscopic roughness and hydrophobic layer that are essential to establish superhydrophobicity [20–22], which caused a decline in their non-wetting property. Till now, great progress has been made to develop mechanically robust superhydrophobic surfaces [12,23–25]. On the other hand, developing superhydrophobic surfaces with easy repairability has also been proven to be an effective way to migrate the mechanical damage problem [26–29]. For these surfaces, the superhydrophobic property can be restored just by deposition of new materials when loss of superhydrophobicity occurred, allowing local repair the damaged surfaces at anytime and almost anywhere.

Spray coating is a simple way to produce superhydrophobic surfaces with the advantage of compatibility with almost any substrate type, and spraying carbon nanotube based materials to form superhydrophobic surfaces with desired tunable surface wettability, controllable surface adhesion, or optical transparency has been described previously by our lab and others [30–33]. However, little work has been reported on solving the mechanical abrasion and oil fouling problems of superhydrophobic surfaces by spraying carbon nanotube. In this study, to solve the problems caused by oil fouling and mechanical damage, we fabricated a superhydrophobic carbon nanotube coating with good reusability and easy repairability by spray coating. The obtained coating can retain its superhydrophobicity after thermal treatment at 400 °C, and this thermal durability allowed the oil-fouled coating to restore its original superhydrophobicity just by thermally removing the oil contamination in air. Moreover, the mechanically damaged coating can restore its superhydrophobic property for repeated use after a simple regeneration process. This study provides a new avenue to extending the life span of superhydrophobic surfaces for practical applications.

2. Experiment

2.1. Materials

Multiwalled carbon nanotubes (CNTs) were purchased from Chengdu Organic Chemicals Co. Ltd., China (purity 99.9%, with a diameter and length of 30–50 nm and about 30 μm, respectively), and used as received. Formic acid and acetone were of analytical grade and used as received. Trichloro(1H,1H,2H,2H-perfluorooctyl)silane was purchased from Sigma–Aldrich.

2.2. Fabrication of superhydrophobic CNTs coating

0.2 g CNTs was ultrasonically dispersed in 30 mL formic acid for 10 min. Subsequently, an equal volume of acetone was added to the CNTs dispersions, and sonication was continued for another 10 min. The resulting suspension was sprayed onto glass, metal, or other substrates to form coatings (see Fig. S1a) with 0.2 MPa nitrogen gas using a spray gun. The coatings were dried in an oven at 120 °C for 1 h allowing the formic and acetone to evaporate completely.

To realize superhydrophobic property, the obtained coatings and an open glass vessel containing about 0.1 mL of fluorosilane were put in a sealed desiccator with high vacuum for 2 min at room temperature. Afterwards, the coatings were placed in a vacuum oven at 80 °C for 1 h to remove untreated fluorosilane residues.

2.3. Characterization

Contact angle (CA) and sliding angle (SA) measurements were performed using a Krüss DSA 100 (Krüss Company, Ltd., Germany) apparatus at ambient temperature. The volume of water droplet in each measurement was approximately 5 μL. Scanning electron microscopy measurements were carried out using a JSM-6701F field-emission scanning electron microscopy (FESEM, JEOL, Japan). X-ray photoelectron spectroscopy (XPS) characterization was performed on a PHI-5702 electron spectrometer using an Al Kα line excitation source with the reference of C 1s at 285.0 eV.

3. Results and discussion

Fig. 1a and b shows FESEM images of the sprayed CNTs coating at low and high magnifications. As shown in Fig. 1a, the sprayed coating surface is not flat, with large numbers of microscale protrusions distributing on it. Randomly orientated and entangled CNTs are exposed outside the protrusions surface and thus form a hierarchical textured surface texture (Fig. 1b). Moreover, a mass of pores are distributed on the coating surface, which can dramatically increase the trapped air within the grooves. The structured CNTs coating could provide the needed texture to enable the formation of a superhydrophobic surface, based on recent investigations [2,3].

The surface details of the textured CNTs coating are preserved after modification with fluorinated silane by CVD. After surface fluorination, the peak for F 1s is detected at 689.0 eV (see Fig. 1c), and XPS analysis demonstrates that the content of F is up to 39%. This high concentration of fluorine, when combined with the rough textures, results in the CNTs coating with superhydrophobicity.

The water repellency of the CNTs coating is highlighted in Fig. 1d, which shows that water droplets exhibit typical spherical shapes on the fluorinated CNTs surface. The bright and reflective surface visible underneath the water droplets is a signature of trapped air and the establishment of composite solid–liquid–air interfaces [34]. The formation of this composite state allows the CNTs coating surface to display a high CA (163°) and a low SA (3°) with water droplets placed on it, as shown in Fig. 1e and f. When submerged in water, the superhydrophobic CNTs coating surface acts like a sliver mirror when viewed at a glancing angle (see Fig. 1g), due to the total reflectance of light at the air layer trapped on the surface [35]. This trapped air can effectively prevent a wetting on the CNTs surface underwater. After one day of full immersion, the CNTs surface is completely dry to the touch and still displays a large CA with water droplets.

We developed the method reported by Cao et al. to assess the adhesion between superhydrophobic CNTs coating and a water droplet [36]. It can be seen that a water droplet suspending on a syringe is difficult to be pulled down to the surface in also case, even though it is deformed severely (see Fig. 2a), which indicates that the adhesive force between water and the CNTs coating is low. When a water droplet is dropped under gravity from a height of 3 mm, it can bounce away from the coating surface, leaving the surface dry. With continuous bouncing on this superhydrophobic coating, the water droplet moves from left to right rapidly (for less than 3 s). This bouncing and rolling process is clearly shown in Fig. 2b, and this result indicates that the fluorinated silane coated CNTs coating possesses robust superhydrophobicity under dynamic wetting. Additionally, the fluorinated CNTs coating can keep its superhydrophobicity at least two months at atmosphere conditions, indicating its long-term stability.

We next investigated the thermal stability of the superhydrophobic CNTs coating. As shown in Fig. 3, thermal treatment at 400 °C for 2 h does not weaken the superhydrophobicity of the CNTs