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UV/mask irradiation and heat induced switching on–off water transportation on superhydrophobic carbon nanotube surfaces

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ABSTRACT

We used a simple spray-coating process to prepare superhydrophobic carbon nanotube (CNT) surfaces with a water contact angle (CA) of 160° and a sliding angle (SA) of 3° on desired substrates without any chemical modification. After being irradiated by UV light through a photomask, the as-prepared low adhesive superhydrophobic CNT surface changes to high water adhesion. However, further heating the irradiated CNT surface, the irradiated CNT surface becomes its original low water adhesion again. Reversibly switchable transition between the low water adhesion and high water adhesion can be realized simply by UV/mask illumination and heat treatment alternately. Simultaneously, the adhesive force of the superhydrophobic CNT surfaces changes from low (~8.9 μN) to very high (~133.6 μN). Based on the reversible water adhesion transition on the superhydrophobic CNT surfaces through UV illumination and heat treatment alternately, switching on–off water transportation was achieved. This switchable water adhesion on the superhydrophobic CNT surfaces could have potential applications in areas requiring multifunctional CNT-based surfaces.

1. Introduction

Superhydrophobic surfaces with special adhesion have received considerable attention in both fundamental research and practical application [1–10]. Different requirements need the superhydrophobic surfaces with different adhesions, because it is the adhesive property that ultimately determines the dynamic action of the water on the surface [11–13]. According to the different water adhesions on the surfaces, superhydrophobic surfaces can be divided into two classes: low adhesion to water and high adhesion to water. Low adhesive superhydrophobic surfaces were initially inspired by the lotus leaf, with droplets rolling off spontaneously; while the high adhesive superhydrophobic surfaces were originated from gecko's feet and rose petals, with droplet pinning on the surface vertically or even turn upside down [14–17]. However, all these superhydrophobic surfaces keep their adhesion to water invariable. Therefore, it is important to fabricate superhydrophobic surfaces with reversibly switchable water adhesion between low adhesion and high adhesion to broaden the applications of the superhydrophobic surfaces.

The wettability of CNT surfaces has recently attracted a great deal of attention because of its potential applications [18–22]. Due to the special nanostructure and surface properties of CNTs, further surface functionalization or textured arrangement could facilitate easy control of their wetting properties. Accordingly, there are also some reports on superhydrophobic CNT surfaces recently, and much of the work is attempted to create self-cleaning surfaces [23–27]. However, to the best of our knowledge, there are few papers reporting the switchable adhesion transition on the superhydrophobic CNT surface. In our work, superhydrophobic CNT surfaces were prepared by a one-step spray-coating method without any chemical modification, on which the water adhesion can be reversibly switched between low adhesive superhydrophobicity and high adhesive superhydrophobicity. After being exposed to UV illumination through a photomask, the as-prepared superhydrophobic low adhesive CNT surface becomes high adhesion to water. Further heating the irradiated superhydrophobic surface, it recovers the original low adhesive state. So the low adhesive state and high adhesive state on the superhydrophobic CNT surface can be reversibly switched by UV/mask irradiation and heat treatment alternately without sacrificing superhydrophobicity. Accordingly, the adhesive force of the superhydrophobic CNT surfaces changes from ~8.9 μN to ~133.6 μN. Based on the reversible water adhesion transition on the superhydrophobic CNT surfaces through UV illumination and heat treatment alternately, switching on–off water transportation was achieved.

2. Experimental

Pristine multiwalled CNTs were purchased from Chengdu Organic Chemicals Co., Ltd., China (synthesized by a CVD process; purity > 99.9%)

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with a diameter of 30–50 nm and a length of 10–20 μm. The preparation process of CNT surfaces is as follows: 20 mg of multiwalled CNTs was dispersed in 10 mL of ethanol using an ultrasonic bath for 30 min to get a homogeneous dispersion, and the resulting suspension was sprayed onto stainless steel substrates with 0.2 MPa nitrogen gas using a spray gun. The resulting CNT surfaces were dried at room temperature for overnight. When the as-prepared low adhesive superhydrophobic CNT surfaces were exposed to UV light (185 nm, 2 μW/cm^2) through a photomask (320 mesh) for about 90 min, the wettability of the CNT surfaces was still superhydrophobicity; however, water droplets were firmly pinned on the irradiated superhydrophobic CNT surfaces. After the irradiated CNT surfaces were heated at 120 °C for 90 min, the adhesive property of the surfaces can be recovered their original low adhesion to water. The low and high adhesive superhydrophobicity was realized by the alternation of UV/mask and heat treatment.

The morphological structures of the as-prepared surfaces were examined by field emission scanning electron microscopy (FE-SEM, Zeiss). The distilled water contact angle (CA) and sliding angle (SA) were measured with a SL200KB apparatus at ambient temperature. The volume of the individual water droplet in all measurements was 5 μL. The average water CA and SA values were obtained by measuring the same sample at least in five different positions. The adhesive forces of the superhydrophobic CNT surfaces were measured using a high sensitivity micro-electromechanical balance system (Dataphysics DCAT 11, Germany). Firstly, a 5 μL of droplet was suspended on a metal ring and the superhydrophobic surface was put on the plate of the balance system, the surface started to move upward at a constant speed of 0.02 mms^{-1}. Subsequently, the surface was moved downward once in contact with the droplet. Simultaneously, the balance force gradually increased up to the maximum value, which was defined as the adhesive force of the superhydrophobic surface. The surface chemical composition of the as-prepared samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5702) using Mg Kα radiation as the excitation source and the binding energies were referenced to the C 1s at 284.80 eV.

3. Results and discussion

Low adhesive superhydrophobic CNT surfaces were created by the subsequent introduction of roughness and low energy surface via a spray-coating deposition of CNTs. The typical FE-SEM images of the as-prepared CNT surface at low and high magnifications are shown in Fig. 1. As shown in Fig. 1a, the surface exhibits hierarchical nanotextured surface morphology that is self-similar throughout the surface area. Some protrusions and pores with different sizes are clearly seen on the CNT surface. The high-magnification FE-SEM image (Fig. 1b) shows that this rough structure is formed by entangled CNTs, which is due to quick evaporation of the solvent during the flight of the atomized slurry toward the substrate. Without any chemical modification, the CNT surface shows superhydrophobic properties with a high CA of 160 ± 1° (Fig. 1a inset) and a low SA of about 3° (Fig. 1b inset).

Arranged hydrophilic/superhydrophobic CNT areas were successfully prepared by UV illumination through a photomask. After being irradiated by UV light through the photomask for a certain time, the light transmission regions of the CNT surface became hydrophilic domains and were surrounded by the non-irradiated areas which remain superhydrophobicity. Consequently, the alternatively arranged hydrophilic/superhydrophobic CNT areas were obtained. Owing to the occurrence of hydrophilic domains, the water adhesion on the superhydrophobic CNT surface changes dramatically from low to high adhesive property after 90 min irradiation without sacrificing superhydrophobicity (Fig. 2a). When the UV-irradiated surfaces were heated at 120 °C for 90 min, the irradiated CNT surface returns to its original low water adhesion again (Fig. 2a). The transition was repeated several times, and a good reproducibility of surface water switchable adhesion was observed (Fig. 2b).

By using the high-sensitivity micro-electromechanical balance system, the adhesive forces of the superhydrophobic CNT surfaces were assessed accurately. Fig. 3 shows the force–distance curves for the low adhesive and high adhesive superhydrophobic CNT surfaces respectively. When the UV-irradiated surfaces were heated at 120 °C for 90 min, the low adhesive rolling state can be recovered and the adhesive force of the low adhesive superhydrophobic CNT surface was about 8.9 μN (Fig. 3a). After being irradiated with UV light through a mask for 90 min, the high adhesive superhydrophobic CNT surface was obtained again and the adhesive force of the high adhesive superhydrophobic CNT surface was about 133.6 μN (Fig. 3b).

It is reported that whether a water droplet is pinned on or rolls off the superhydrophobic surface is ascribed to the distinct contact modes (the Cassie state or the Wenzel state) [11,28]. In addition, the superhydrophobic states may be tuned between the Cassie state with low adhesion and the Wenzel state with high adhesion through changing the chemical composition of a surface or its microstructure. Using FE-SEM, we found that the surface morphologies of the CNT surfaces are nearly the same before and after UV or heat treatment, which indicates that the reversible switching between the low and high state is mainly caused by the surface chemical composition. A possible model exhibiting the transition between low adhesive to high adhesive superhydrophobicity on the CNT surface is shown in Fig. 4. To confirm the change of surface chemical composition, the CNT surfaces were analyzed by carrying out XPS before and after UV irradiation. Fig. 5 shows the survey and O 1s XPS spectrum of the superhydrophobic CNT surfaces before and after UV treatment. It can be seen that the C 1s and O 1s peaks are detected for both the surfaces. The amount of relative of oxygen increases after UV treatment, whereas, decreases after heat treatment (Fig. 5a). To get more information on the changes of the

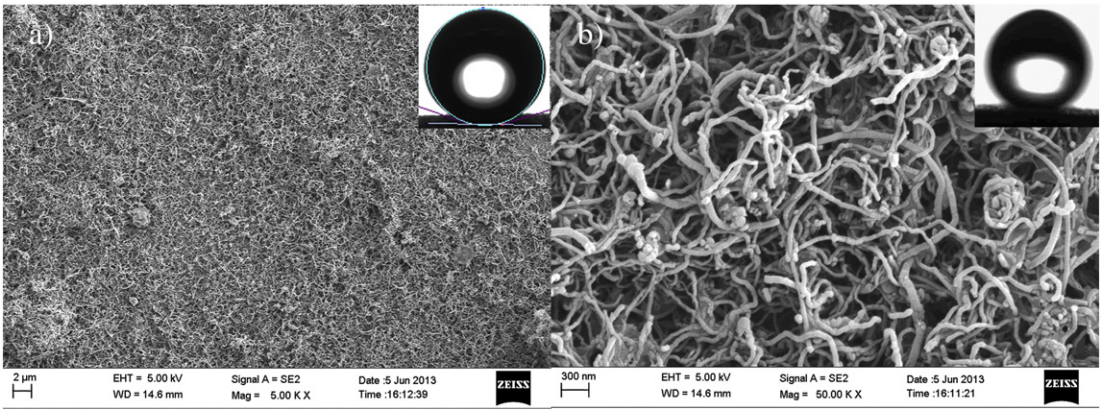

Fig. 1. (a, b) FE-SEM images of the as-prepared CNT surfaces at low and high magnifications. The insets show the water droplet on the surfaces with (a) a CA of 160 ± 1° and (b) a SA of 3°.