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Facile preparation of superhydrophobic thin films using non-aligned carbon nanotubes

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Abstract. A simple preparation method on creating superhydrophobic surface using non-aligned carbon nanotubes (CNTs) was demonstrated. Superhydrophobic CNT thin films were prepared by doping a sonicated mixture of CNTs and chloroform onto a glass slide. Water contact angles of the CNT thin films were measured using a contact angle goniometer. The thin films were characterized using laser microscope and scanning electron microscope. Experimental results revealed that the highest average contact angle of 162±2° was achieved when the films' thickness was 1.628 μm. The superhydrophobic surface was stable as the contact angle only receded from 162±2 to 157±2° after 10 min under normal atmospheric condition.

Keywords: carbon nanotubes; non-aligned, superhydrophobic; thin film; characterization

1. Introduction

The size, shape and extraordinary physical properties of CNTs, such as high strength, extraordinary flexibility and resilience, make them a subject of unabated scientific research and development in recent years (Iijima 1991, Salvetat *et al.* 1999). CNTs are one of the most common types of materials which have the potential in fabricating superhydrophobic surfaces. In nature, superhydrophobicity can be observed from many plant leaves, most commonly on lotus leaves. For example, water droplets which fall onto the top of the lotus leaf would roll or bounce off. At the same time, dust particles or surface contaminants which usually appear on the leaf can be removed simultaneously. This effect is caused by the hierarchical roughness of the leaf surface from micrometer-sized papillae having nanometer-sized branch like protrusions and the intrinsic material hydrophobicity of a surface layer of epicuticular wax covering these papillae (Ma *et al.* 2008, Shakerzadeh *et al.* 2009).

Self-cleaning is the most common application of superhydrophobic surfaces (Bhushan and Jung 2011, Lau and Gleason 2007, Song *et al.* 2009). This application can be seen in our daily lives such as window panels, roof tiles, bathroom surfaces and house walls. By implementing the

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superhydrophobicity effect on the surface, the surface contaminants can be removed easily (Ma and Hill 2006). In addition, superhydrophobic transparent conductive films have attracted much attention in different industrial areas due to their potential applications in optoelectronic devices, structural coatings, satellite dishes, solar energy panels, transparent superhydrophobic films heaters, automobile glass, smart windows, photoelectric elements, etc. (Ma and Hill 2006, Meng and Park 2010). Recently, medical devices have also implemented superhydrophobic surfaces (Sun *et al.* 2003, Berg *et al.* 2007).

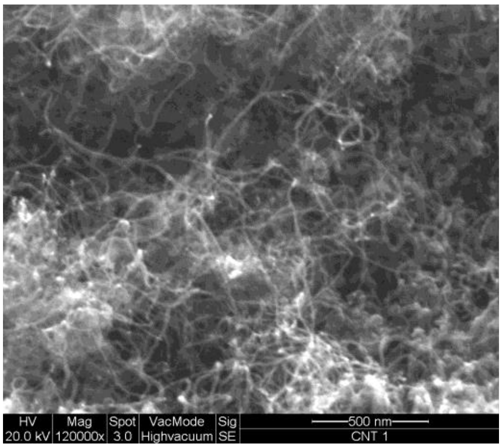
Aligned and non-aligned CNTs are commonly used for creating superhydrophobic surfaces. Based on Sun *et al.* water contact angle larger than 150° could be achieved on anisotropic aligned CNT films by adjusting its structural parameters without coating any additional chemicals or altering the chemical composition of the surface. The water contact angle obtained by using non-aligned CNTs was 136.5° (Sun *et al.* 2003). According to Wang *et al.* both aligned and non-aligned CNTs would result in a similar effect on the water contact angle. It was reported by Li *et al*. that CNT alignment is an important factor to the superhydrophobic property (Li *et al.* 2001). According to Huang *et al.* the superhydrophobic stability of raw CNTs was relatively low as the water contact angle decreased from 146 to 0° within 15 min. Hence, zinc oxide was coated onto the CNTs to increase its stability and the result was significantly improved where the water contact angles were recorded at 150° and above (Huang *et al.* 2005). It was also reported by Zhu et al. that the water contact angle of the CNT coating decreased with time, from an initial value of 128 to 0° within 25-30 min (Zhu *et al*. 2010).

Studies on the superhydrophobicity of raw CNTs have not been widely conducted. The cost of preparing superhydrophobic surfaces is relatively high due to complicated procedures and the utilization of uncommon chemical materials. The stability of the coated CNT surface was reported to be relatively low which allowed water to seep into the nanotube layer, hence resulting in lower contact angle. The main objective of the present work is to prepare superhydrophobic thin films using non-aligned CNTs where the thin films could display an equilibrium water contact angle of more than 150°. As-prepared non-aligned CNTs were used in this study without any pretreatment. The stability of the thin films was also investigated.

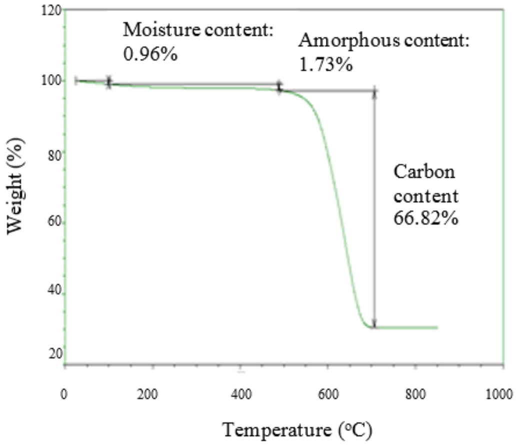
2. Experimental section

Non-aligned CNTs (multi-walled CNTs) used in this experiment were produced via methane decomposition over Co-Mo/MgO catalyst in a horizontal rotary reactor. The raw CNTs were characterized using field emission scanning electron microscopy (FESEM) (FEI Quanta 200) to obtain the morphological information of the nanotubes. Thermogravimetric analysis (TGA) was employed to determine the nanotube purity. The TGA ramping rate was set at 10℃/min from room temperature to 850 ^{o}C under 100 ml/min of purified air. Statistical analysis was performed using the TGA data to estimate the CNT content.

Chloroform was used as a solvent and mixed with CNT powder in test tubes. The volume of chloroform used and the quantity of CNT powder were controlled at 10 ml and 20 mg, respectively. The mixture was then subjected to 15 min of ultrasonication (40 kHz / 160 W) to obtain a homogenous suspension. A single thin layer of CNT coating was obtained by evaporating 100 μl of the suspension on top of a glass slide. Multiple coating layers were obtained by stacking new carbon layers on top of the existing coating. The number of CNT coating was varied from 10 to 18 to investigate the effect of film thickness on the superhydrophobic property.



(a) SEM image of raw CNTs



(b) TG curve of raw CNTs

Fig. 1 SEM image and TG curves of raw CNTs

The hydrophobicity of the CNT thin films was investigated using a Goniometer (Rame-Hart 250). 5 μl of the water droplet was collected using a Transferpitte and dropped onto the prepared surface. Water contact angle was measured using the DROP image Advanced software. The morphological structure of the coated surface was examined by FESEM (FEI Quanta 200). Laser microscope LEXT OLS 400 with 405nm was used to determine the average thickness of the CNT thin films.

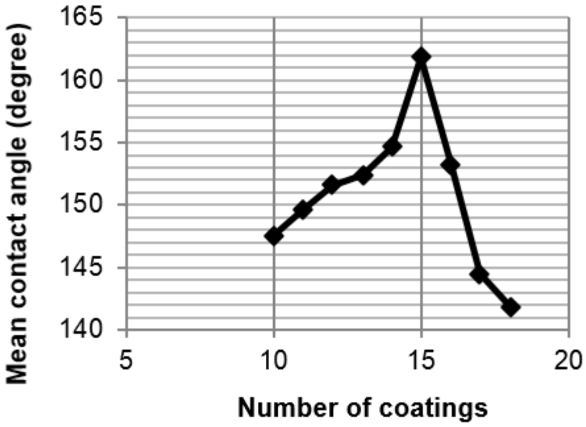
3. Results and discussion

3.1 Characterization of raw CNTs

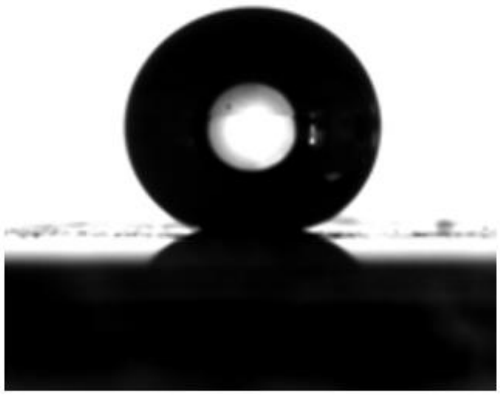
Fig. 1(a) shows the SEM image of the as-synthesized CNTs. The nanotubes were randomly distributed without any ordered alignment. Fig. 1(b) shows the TG curve of the as-synthesized CNTs. The weight loss observed at *ca.* 100℃ is attributed to the inherent moisture content of the sample, which was at 0.96%. As the temperature increased to approximately 500℃, a weight loss of 1.73% was observed, which corresponds to the amorphous carbon content. To determine the CNT content in the sample, the temperature was gradually increased to 850℃. The TG curve showed a maximum weight loss of 66.82% after 850℃, which is attributed to the nanotube content. The remaining solids with a weight percentage of 30.49% were the Co-Mo/MgO catalyst used to synthesize the CNTs.

3.2 Effect of the number of CNT coatings

The mean water contact angle against the number of coatings was plotted in Fig. 2(a). The average water contact angle on the clean glass surface was 27°. It was observed that the water contact angle increased with the number of coatings. The contact angle reached a maximum value of 162±2° after the glass slide was coated for 15 times. Further increase in the number of coating



(a) Water contact angles on CNT thin films as a function of the number of coatings



(b) Image showing the shape of a 6 μL water droplet on the CNT films after 15 times of coating

Fig. 2 Water contact angles on CNT thin films as a function of number of coatings and an image displaying the shape of a 6 μL water droplet on the CNT films after 15 times of coating

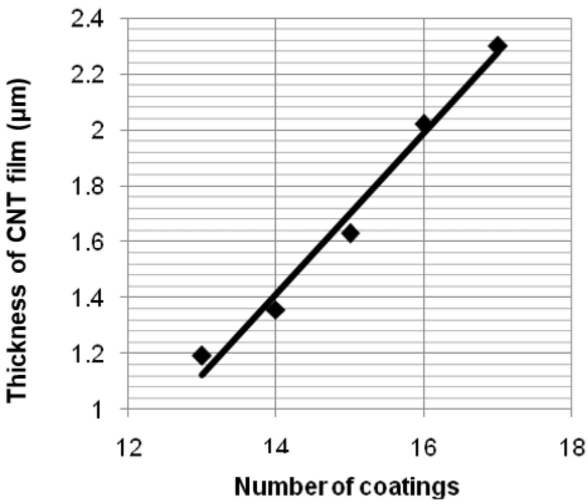
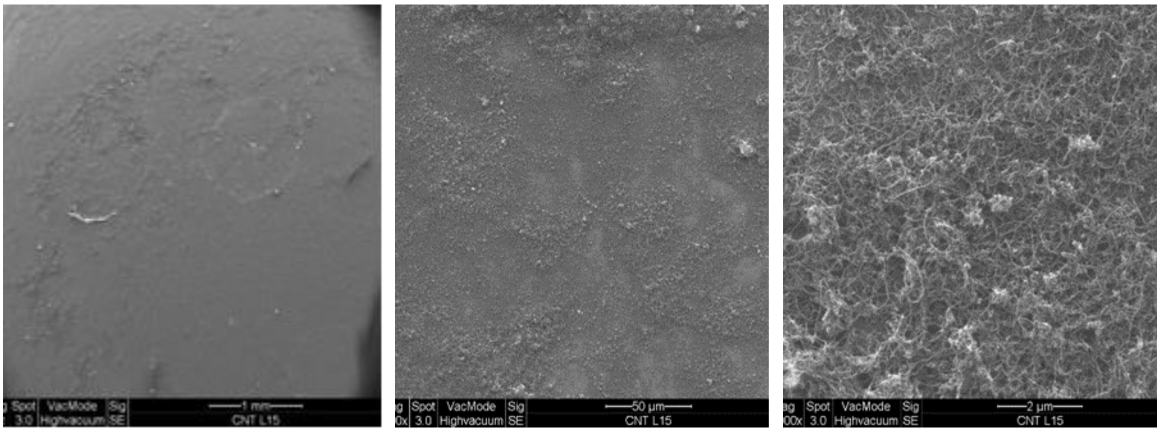


Fig. 3 Thickness of CNT films as a function of the number of coatings

decreased the contact angle. This showed that the non-aligned CNTs used in this study demonstrated the superhydrophobic property. Fig. 2(b) shows the shape of 6 μL water droplet on the CNT films after 15 times of coating.

As the number of coating increased, sufficient air was trapped in the coated surface, preventing water from intruding into the voids between the CNT network, hence decreasing the contact area between the coated surface and the water droplet (Xu *et al.* 2009).When the contact area was reduced, the apparent contact angle increased. However, the contact angle began to decrease when the number of coatings increased above 15 (see Fig. 2(a)). This might be due to the distortion of fibrous CNT network by the weight of water droplet because a thick CNT layer is easier to be



(a) Low (b) Medium (c) High

Fig. 4 SEM images of CNT films at different magnifications

deformed as compared to a thin layer. This caused the surface CNT to slowly dense into the voids within the network, thereby reducing the porosity of the CNT network and the surface air gaps (Meng and Park 2010), and leading to a decrease in water contact angle.

The average thickness of the thin film for different coating numbers was measured using a laser microscope LEXT OLS 400. Although the preparation of the multi-coated surface was done by dropping an approximately constant volume of suspension at the same spot on top of the glass surface followed by vaporization, the thickness of the coated surface was relatively proportional to the number of coatings (see Fig. 3). It can be observed that the thickness of the CNT films increased proportionally with the number of coatings. The thickness of 1.191, 1.357, 1.628, 2.020 and 2.301 μm were obtained for the surface coated at 13, 14, 15, 16 and 17 times, respectively. The results showed that 1.628 μm was the most appropriate thickness as it yielded the highest contact angle of 162±2°. It was also found that the water droplet placed on the CNT films rolled away when the platform was slightly tilted at *ca.* 3^{o}.

3.3 Stability of CNT films

Contact angles of water on CNT films at 15 times of coating at different time intervals were measured. The results showed that the stability of the CNT films was excellent within 10 s with a standard deviation of 0.03^{o}. A slight fluctuation in reading was observed. This was most likely caused by the vibration created from the experimental surrounding which would affect the measurement and unsettlement of the water droplet on the coated surface. A slight decrease in water contact angle in the time interval of approximately 10 min was observed. The contact angle receded from 162±2 to 157 ± 2^{o} after 10 min under normal atmospheric condition, indicating that the water droplet had slightly penetrated into the voids of the CNT network. Insufficient small voids might cause the weight of water droplet to overcome the surface tension of the air-water void interface. Penetration of water droplet into the CNT network was hindered once the water reached the more closely packed sections at the lower CNT layer. This effect led to the stability of the CNT films.

3.4 Characterization of CNT films

Fig. 4 shows the SEM images of the CNT films after being coated for 15 times on the glass substrate. An even surface was observed under SEM at low magnification level (Fig. 4(a)). As shown in Fig. 4(b), the higher magnified image revealed that the surface was considerably rough. It is understood that the roughness would further increase the superhydrophobic property of any hydrophobic surfaces (Zhang and Resasco 2009). In Fig. 4(c), CNT network could be clearly observed at high magnification. By comparing the images shown in Fig. 1(a) and Fig. 4(c), it can concluded that sonication of raw CNTs with chloroform would not cause any significant change to the nanotube morphology and the prepared CNT films were denser as compared to the as-received CNTs. This property provides a more stable surface for water. This is one of the contributory factors to the superhydrophobicity of the CNT films as prepared in this study.

4. Conclusions

A simple preparation method of superhydrophobic surface using non-aligned CNTs was demonstrated. The experimental findings showed that the prepared CNT films exhibited a superhydrophobic property with a highest average contact angle of 162±2°. The stability of the coated surface was considerably good as a slight decrease in the contact angle of *ca.* 5° was observed in a time interval of 10 min. The superhydrophobic stability of the prepared surface is much better than that reported elsewhere. The SEM observation of the CNT thin films also revealed that the surface possessed multiscale roughness which might be the reason for having a stable superhydrophobic surface.

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