Super-Hydrophobicity of Large-Area Honeycomb-Like Aligned Carbon Nanotubes

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Honeycomb-like aligned carbon nanotube films were grown by pyrolysis of iron phthalocyanine. The patterned structure was characterized by a scanning electron micrograph (SEM) and an atomic force micrograph (AFM). Wettability studies revealed the film surface showed a super-hydrophobic property with much higher contact angle (163.4 ± 1.4°) and lower sliding angle (less than 5°)—a water droplet moved easily on the surface. In contrast to a densely packed aligned carbon nanotube, the sliding feature was strongly affected by microstructure of surface.

Introduction

The wettability, which is an important property of the solid surface in practical applications, is governed by the chemical composition and the geometrical structure of the surfaces.[1] Since the chemical composition is an intrinsic property of materials, wettability is usually enhanced by the increase of surface roughness (three-dimensional microgeometry), especially by fractal structures.[2] Hydrophobicity is one of wettability, because of small contact area between surface and water, various phenomena (e.g., snow sticking, oxidation, contamination etc.) are expected to be inhibited on hydrophobic surface.[3] Recently, wettability of carbon nanotubes (CNTs) is of great interest, thus, research on carbon nanotubes would be extended to more scopes.[4] L. Dai's group reported using wettability to determine whether aligned carbon nanotube (ACNT) film was chemical modified.[5] In our previous work, super-"amphiphobic" densely packed ACNT films were mentioned.[6] However, contact angle hysteresis of untreated densely packed ACNT film was severe in the above literature. The wettability of micro-pattern aligned carbon nanotubes (ACNTs) is significant, since micro-pattern ACNTs, which are especially useful to be incorporated effectively into devices,[7] have been attracting much interest.[8] In this paper large-area honeycomb-like ACNTs were prepared by pyrolysis of iron(II) phthalocyanine (FePc). The wettability of the obtained honeycomb-like ACNT films was investigated. The honeycomb-like ACNT film surface showed special wettability features for its spectacular geometrical structure, the as-synthesized ACNT film was super-hydrophobic. The contact angle (CA) for water was higher than that of densely packed ACNT film ever reported,[5,6] more importantly, the sliding angle was much lower, namely, the water droplet moved easily even when there was little tilt of the surface. To the best of our knowledge, little attention has been paid to hydrophobic ACNT surface with low hysteresis.

Experimental Section

The substrates used in our experiment were quartz-glass plates (2 cm × 1 cm × 0.1 cm), which were ultrasonically cleaned successively in alcohol and deionized water baths prior to processing. In a typical experiment,[9] a cleaned quartz-glass plate and a quartz boat with 0.3 g FePc were placed in different region of a flow reactor consisting of a quartz-glass tube and a tube furnace fitted with a temperature controller. The pyrolysis of FePc was performed under flow of Ar/H_2 (1:1 v/v) 55–60 cm^3/min. When the temperature of region where the quartz-glass plate was placed was heated to 900 °C, the carbon resource FePc in the quartz boat reached about 550 °C. After heating for 15 min, aligned carbon nanotubes grew out on the substrate surface. The morphology and structure features of the ACNTs were characterized by scanning electron microscopy (SEM) (JEOL JSM-6700F, AMRAY 1910FE), and transmission electron microscopy (TEM) (JEM-200CX), and atomic force microscopy (AFM) (SPA-400). Contact angles and sliding angles were measured by an optical contact angle meter (JY-82) at room temperature after SEM observation. Contact angles and sliding angles of five different positions of the sample were measured and the average was adopted.

Results and Discussion

Honeycomb-like ACNT film structure was observed by SEM. The SEM photographs of ACNTs deposited on the quartz substrates were shown in Figure 1. These images revealed special honeycomb-like patterns composed of ACNTs. Figure 1a demonstrated the as-synthesized CNTs surface morphology in low magnification. The diameter of the honeycombs ranged from 3 μm to 15 μm. The honeycombs were mainly composed of hexagon and pentagon structure, blending a few triangle, quadrangle, and polygon patterns. Figure 1b was the tilting image of the sample. The "walls" of the honeycomb were composed of carbon tubes aligned in a direction nearly normal to the substrate surface. The nanotubes were measured to be about 10 μm in length, the nanotube length would be controlled via adjusting the reaction time. Figure 1c was higher magnification image, and showed perfectly honeycomb-like structures clearly, CNTs lay closely together in honeycomb and oriented grew in radial patterns from the bottom cave. Figure 1d was higher magnification tilting view of honeycomb-like patterns along the peeled edge and showed carbon tubes part in honeycomb were at certain oblique angle with substrate surface.

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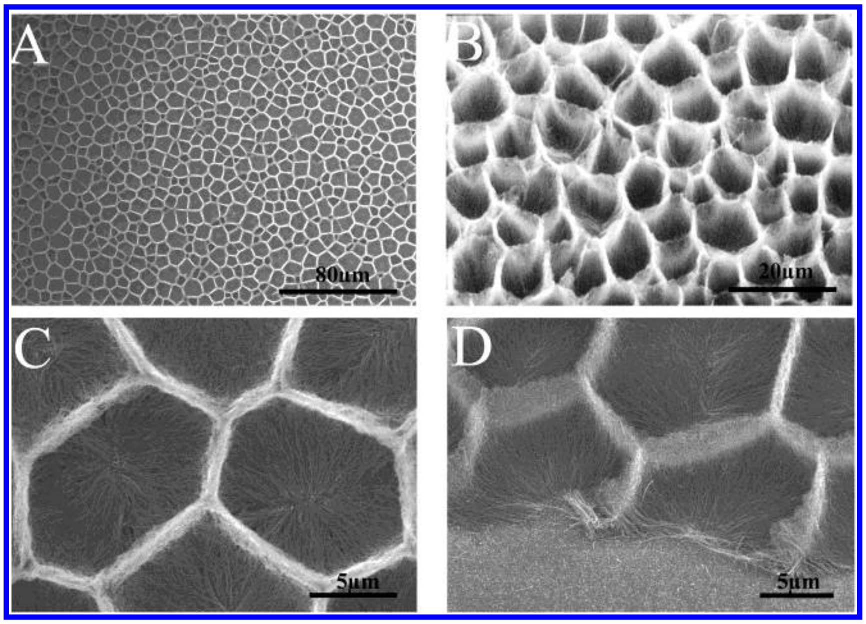

Figure 1. (A) SEM image of large-area honeycomb pattern aligned carbon nanotubes (ACNTs), carbon nanotubes formed honeycombs, the shape and size of honeycomb were different. (B) Enlarged view of honeycomb-like aligned carbon nanotubes film from a certain gradient. (C) Higher magnification SEM image of typical honeycomb-like pattern, hexagon honeycomb was composed of carbon nanotubes. (D) Higher magnification tilting view of honeycomb-like patterns along the peeled edge.

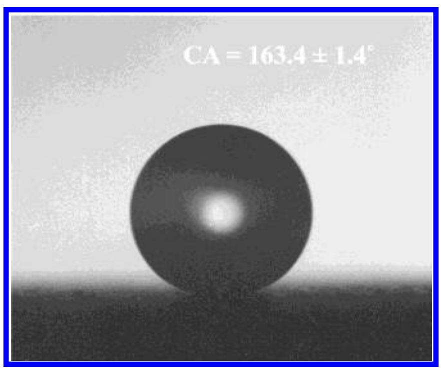

Figure 2. The shape of a water droplet on honeycomb-like ACNT film surface with contact angle 163.4 ± 1.4° and sliding angle less than 5°.

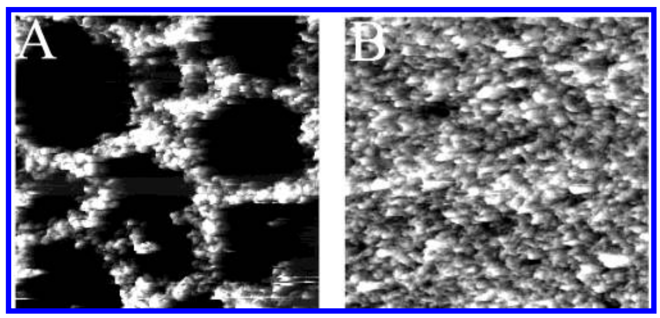

Figure 3. (A) AFM image (20 μm × 20 μm) of a honeycomb pattern on the aligned carbon nanotube film surface, the image showed the surface consisted of a few aligned carbon nanotubes. (B) AFM image (20 μm × 20 μm) of densely packed aligned carbon nanotube film surface.

At the initial stage of carbon nanotubes growth, the carbon tubes radiated from the center of honeycomb caves, and oriented nearly parallel to substrate. Then carbon tubes gradually turned their growth direction upward till vertical to the substrate, the wall of honeycomb was formed. It was suggested that honeycomb-like structure formation was a self-assembly process. TEM investigation suggested that the materials were consisted of multiwall nanotubes with a hollow inside, the diameter of a single carbon tube was about 25−50 nm.

The wettability of honeycomb pattern ACNT surface was studied. It was found that as-grown honeycomb-like ACNT film were super-hydrophobic surface, the shape of a water droplet on the film was shown in Figure 2. The contact angle (CA) for water was 163.4 ± 1.4°. In our previous report the CA for water on densely packed ACNT films was 158.5 ± 1.5°, but the sliding angle, which is also a very important criterion for hydrophobic surface, was higher than 30° for water on this ACNT films.[6] Q. Chen et al. also reported sessile CA = 146° for untreated ACNT film, but the difference between advancing CA and receding CA was 33°.[5] However, a much smaller sliding angle was obtained on honeycomb-like ACNT film, which was less than 5° for a 3 mg water droplet, this implied that the water droplet moved easily even when there was little tilt of the surface. In comparison with densely packed ACNT films, honeycomb pattern ACNT film exhibited a larger water CA and a smaller sliding angle.

It has long been known that the air trapped in the surface is important to hydrophobicity, and Cassie and Baxter[10] proposed an equation

$$\cos \theta_c = f_1 \cos \theta - f_2 \tag{1}$$

to describe the contact angle θ_c of a hydrophobic surface composed of solid and air. Here, f_1 and f_2 were the fraction of solid surface and air in contact with liquid, respectively. while θ was the equilibrium CA on a flat solid surface. It was reported that the CA for water on a flat graphite surface was 86°.[11] The CA of super hydrophobic honeycomb-like ACNT film surface was 163.4 ± 1.4°. According to the related data, f_2 value calculated by eq 1 was about 0.96, which was larger than that of densely packed ACNT film ($f_2 = 0.93$). Here, the AFM was used to compare the surface structure of two kinds of ACNT films. Figure 3a,b showed the AFM images (20 μm × 20 μm) of honeycomb-like ACNT film and densely packed ACNT film, respectively. From the image of Figure 3a, it was observed directly that the bright part was honeycomb "wall" composed of CNTs, the dark part was honeycomb cave. Figure 3b showed that the ACNT film consisted of densely packed CNTs. It was

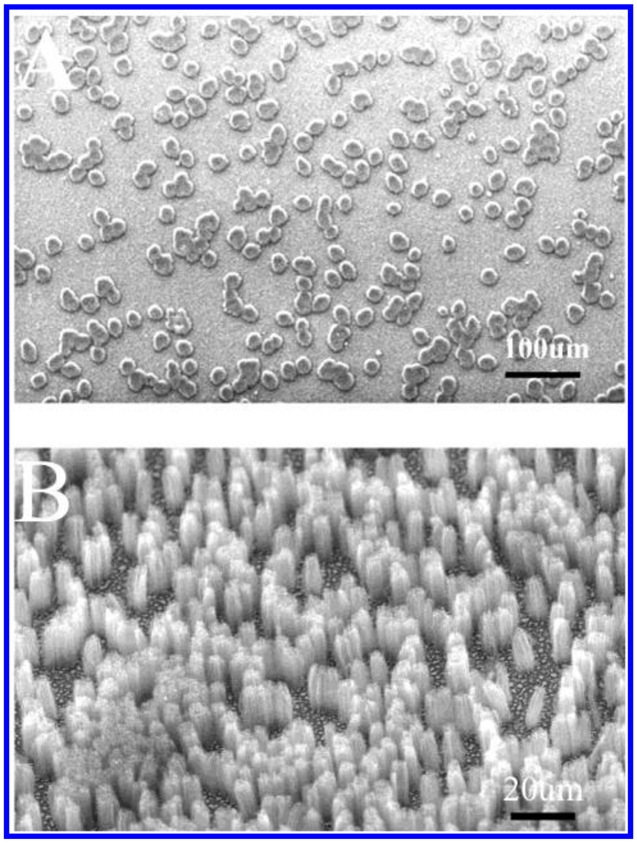

Figure 4. (A) SEM image of island-like ACNT film with CA 166.4° and sliding angle about 3°. (B) SEM image of post-like ACNT film, with CA 166.1° and sliding angle about 2°.

reported that water could not intrude into the film when hydrophobic microstructure scale was less than 50 μm,[1b] therefore, water did not intrude into the micrometer scale (3 μm−15 μm) honeycomb of super-hydrophobic film surface—the water droplet was riding only on the extreme top portions of the honeycomb-like ACNT film. The air trapped in the honeycomb cave of the ACNT film plays an important role in enlarging the contact angle and lowering the sliding angle. On the other hand, the sliding angle was also strongly affected by the three-phase (solid−liquid−air) contact line structure (shape, length, continuity of contact, amount of contact).[1b] In general, an unstable contact line can generate a lower energy barrier for advancing and receding of the water droplet. Therefore, the existence of an unstable contact line was very important for a small sliding angle. The surface structure of a honeycomb-like ACNT film was one with various honeycomb shapes (hexagon, pentagon, triangle, etc., polygon), wide honeycomb size distribution (3 μm−15 μm), and random oriented honeycomb "wall", all these resulted in the contact line with water droplets contorted and discontinuous. In this case, the contact line was less stable, thus, water droplets move easily on this surface.

In conclusion, large area (2 cm × 1 cm) honeycomb-like ACNT films were grown. The film surface showed super-hydrophobic with higher CA (163.4 ± 1.4°) and lower sliding angle (less than 5°). The results indicated that microstructure in CNT film is important to create a lower sliding angle. This phenomenon can be verified in other samples (e.g., island structure, post structure ACNT film, see Figure 4). The information was useful for designing a bio-mimetic hydrophobic surface structure for a variety of applications; these surfaces may provide very effective water-repellent and anti-adhesive properties against particular contamination (such as for transportation of an ultra-small amount of liquid).[12]

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References and Notes

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