Superhydrophobicity of hierarchical nanostructure of candle soot films

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Abstract. Candle soot containing carbon nanoparticles can form hierarchical structure films. We prepared soot films by using glass slides blocking candle flame in the middle of the flame. The hierarchical nanostructures of the carbon nanoparticles films were confirmed by scanning electron microscopy and transmission electron microscopy. Carbon nanoparticle size was 49.2±9.0 nm from SEM, which agrees to 37.9±8.5 nm from TEM. The contact angles of water droplets on these films are more than 150˚, indicating superhydrophobic surface. Decrease contact angles of water droplets were observed with an increase deposition time. The decrease of contact angle was saturated at about 150˚ when the deposition time reaches 180 s. Cassie-Baxter state was attributed to describe superhydrophobicity of carbon nanoparticles films because the hierarchical nanostructures of the surface provide a large fraction of hollows on the surface. We proposed that the contact angle dependence on deposition time was governed by the increase of the distance between nanopillars in carbon nanoparticles films.

1. Introduction

Candle soot is typically one of the undesired byproducts from candle flame. These soot were produced by incomplete combustion processes of hydrocarbon in the candle flames [1]. The soot can be collected by using a desired substrate to block the flame in the middle or to be held on the top of the flame. When the substrate is held for longer than a few seconds, a black film of candle soot will be visible on the substrate. The soot film consists of many carbon nanoparticles (CNPs) connecting into complex networks, which are hierarchical or multiscale structures [2]. An interesting property of the CNPs film is its superhydrophobic surface, defined by a line of liquid-air interface and a line of liquid-solid interface exceeding 150˚. The superhydrophobic surface has a unique biomimetic application, i.e. self-cleaning effect. This phenomenon can be observed when water droplets rolling on lotus leaves makes the leaves clean. The contact angle of a liquid droplet on a flat surface can be described by Young’s equation. For a non-flat surface, a modified Young’s equation is needed by Wenzel as follows:

\[ \cos \theta' = r \cos \theta \]  

(1)

, where \( r \) is a ratio of the actual area of a rough surface to the geometrically projected area or called roughness factor, \( \theta \) is a contact angle on a flat surface and \( \theta' \) is an apparent contact angle on a rough surface. \( r \) is typically larger than 1. Wenzel’s equation can be applied when droplets intrude into the hollows of a rough surface, i.e. no available gap between droplets and the surface. For a droplet on a surface consisting of two material phases, solid and air, we have to use Cassie-Baxter’s equation as follows:

\[ \cos \theta' = f \cos \theta + (f - 1) \]  

(2)

, where \( f \) is an area fraction of solid and liquid and therefore \( (f - 1) \) is that of solid and air.
Hierarchical or multiscale roughness structure is an important factor in natural surfaces to achieve superhydrophobicity. Low adhesion surface energy is not sufficient, such as wax coated on flat substance obtaining contact angle of about 103° [3], which is less than the contact angle of superhydrophobicity. The roughness surface, unlike flat surface, provides a composite interface of solid and air for water droplets. In this interface, the hollows between asperities can trap air. The convex features in multiscale structure pin the liquid-air interface of the droplets, resulting in energetic stability of the droplet and surface [4]. In this paper, we present the contact angle of water droplets decreases with increased deposition time for evolving CNPs layers. Scanning electron microscope and transmission electron microscope were employed to measure surface morphology and to analyze particle size. The film thickness at various deposition times was measured. Descriptions of contact angle dependence on fabrication time of CNPs were given.

2. Sample preparation
CNPs were prepared from candle soot. CNP films were prepared by blocking the flame of a candle. The glass slides were held in the middle of the candle flame, and moved gradually in the horizontal to cover the whole glass slide with CNP film. The deposition time is defined by the total time spending to deposit CNPs on the moving glass slide. The contact angles of the water droplet and the prepared CNP films were measured by a home-made contact angle measurement device. The CNP films were characterized by a JSM 6335F field emission-scanning electron microscope (FE-SEM) and an FEI Tecnai G2 transmission electron microscope (TEM) for surface morphology and particle analysis.

3. Results and discussion
3.1 Water droplet contact angles and thickness of CNP films
Contact angles of droplet were measured on CNP films with varying deposition time. Figure 1 illustrates the contact angle decreasing with CNP deposition time. The short deposition time of 2 s yields the highest contact angle of 161.3°. The contact angle decreases when deposition time increases. The relation between contact angle and deposition time seems to be fit with an exponential function. The decline of contact angle was saturated at ~157° with the threshold of deposition time at 180 s. The thickness of CNP films was measured from SEM cross section images. EDS line scans were conducted in SEM images to distinguish CNP films from SiO$_2$ glass slides. Figure 1(b) displays the increase of CNP thickness with a function of deposition time. It is difficult to determine the thickness for the samples of CNP film with deposition time less than 10 s. We assume that the wetting nature of CNP is similar to hydrophobic graphite and its hierarchial nanostructure has many gaps on the surface. These gaps can trap air to creating liquid-air interface underneath water droplets. These two factors are favorable for the superhydrophobicity of CNPs films. For Wenzel state, there is an only liquid-solid interface at the supported area for water droplets. From Wenzel’s equation in (1), the contact angle of the liquid droplet is larger as roughness factor (r) increases. The surface of CNPs film with long deposition time has a high degree of roughness as observed by SEM images. However, our results of contact angle do not agree with the expectation from Wenzel state. Evolution of contact angles can be explained by Cassie-Baxter state, which water droplets do not intrude into hollows in the nanostructure of CNPs film. Thus, water droplets have two interfaces, i.e. liquid-solid and liquid-air, with CNP films.
3.2 Film thickness

Figure 2 (a)-(c) shows the SEM images of evolving CNPs agglomeration in the films for deposition times of 2 s, 10 s and 2 min. Particle size from SEM images was $49.2 \pm 9.0$ nm. The hierarchical nanostructure of CNP networks can be observed. Interconnections of CNPs network were revealed by TEM images as displayed in Figure 2 (d). The particle size of CNP was $37.9 \pm 8.5$ nm. This is consistent with particle size measured from TEM images. Also, from the TEM images, it is evident that CNPs are assembled from amorphous carbon. These CNPs originated from soot precursors by formation of polycyclic aromatic hydrocarbons (PAHs) [1]. These soot were extended by surface growth and coagulation of hydrocarbon and acetylene molecules.

3.3 Discussion

To explain the dependence of the contact angle on the deposition time, CNPs nanostructures can be viewed approximately by pillar-like structure [5]. We do not know the exact distance between CNPs nanopillars but this quantity relates to the roughness of the surface. Measuring surface roughness by atomic force microscope (AFM) would provide important information of gaps in the CNPs network. However, obtaining AFM images on CNPs film is a challenging task. Because each CNP bonds weakly with other, scanning the AFM tip could move CNPs or make CNPs attaching to the tip.
causing a blurring image. Instead, we made a simple model for CNPs network based on its formation. Initial deposited CNPs starts to agglomerate on the glass slide, forming clusters of the small nanopillar-like structure. However, at this stage, CNPs do not cover the entire surface. Many parts of flat glass substrate still remain unaffected as seen in Figure 2(a). Then, more CNPs were added to the previous CNPs structures, resulting in higher nanopillars. From the characteristic of hierarchical structure similarly appearing in some plant surfaces, the width of nanopillars would be smaller as the nanopillars grow higher. Therefore, the additional deposition of CNPs can lead to a substantial increase of nanopillar spacing.

Simulations of water microdroplets on a hierarchical structure with the lattice Boltzmann method by Bo Zhang and co-workers [6] indicate that contact angle decreases with larger nanopillar spacing. Thus, the decrease of water contact angle on CNPs films can be understood in term of the increase spacing in CNPs nanopillar-like structures. This growth is possible via hierarchical pattern, where a new higher-level structure resembles previous structure. According to the wetting in Cassie-Baxter state, the contact angle is predicted to increase with an increase in nanopillar length. However, this effect would have small contributions. Furthermore, for the deposition times beyond 180 s, the contact angle is constant at ~151°. It suggests the spacing of nanopillar-like CNPs would be constant. Longer deposition time would produce more CNPs with repeating structure adding on the top of the previous hierarchical structure. The level of hierarchical structure would saturate when the deposition time is long enough.

4. Conclusions
We reported that the dependence of deposition time of contact angle for water droplets on carbon nanoparticles film produced by candle soot. Carbon nanoparticles films exhibit a superhydrophobicity with the maximum contact angle of 161.3°. The superhydrophobic surface of films was explained by Cassie-Baxter state. The decrease of contact angle as an increase of deposition time was found. Assembling of irregular nanopillars was modeled for constructing hierarchical nanostructures of carbon films. We proposed that the decrease of the contact angle occurs from the increase of the nanopillar-like carbon nanoparticles spacing, leading to contact angle decreases. The complexity of hierarchical nanostructures would be constant when deposition time reaches 180 s. This reflects from the saturation of contact angle at ~151°. This work may provide an insight of the influence of nanostructure of carbon nanoparticles film on its superhydrophobicity.

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