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A FACILE APPROACH FOR THE FABRICATION OF SUPERHYDROPHOBIC SURFACE WITH CANDLE SMOKE PARTICLES

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Abstract: The aim of this communication is to explore a simple and efficient method for fabrication of superhydrophobic surface by candle smoke particles (CSPs). The properties of CSPs before and after the calcination process has been studied by SEM, TEM, TG-DSC, FT-IR and contact angle measurements. The results show that there is a complex mixture of elemental carbon and a variety of hydrocarbons in association with amorphous nanomaterial in CSPs, whose structure and composition leads to superhydrophobic properties. The wetting properties of CSPs can turn from superhydrophobic into superhydrophilic due to characteristic group changes by calcination process. Thus, it is a simple and efficient method to fabricate superhydrophobic or superhydrophilic surface by CSPs at low cost.

Keywords: *superhydrophobicity, carbon, candle smoke particles, calcination*

Introduction

The newly functionalized materials play an important role in interfacial engineering fields (Horiuchi et al. 2011; Yan et al. 2008), because the interaction between water and solid surface is an active research area. Especially in these years, considerable attention has been paid to the artificial superhydrophobic materials owing to its self-cleaning effect (Nishimoto et al. 2009; Goncalves et al. 2009). These studies indicate that material's surface self-cleaning properties strongly depend on the surface energy and microstructure of artificial superhydrophobic materials (Furstner et al. 2005; Jiang et al. 2004). Many naturally occurring self-cleaning surfaces such as lotus leaves suggest that a combination of low surface energy materials and a nanoscale architecture which repels water are required to create a superhydrophobic surface, which water contact angle is approximately 180^{o} (Zhai et al. 2004). Microscale and nanoscale hierarchically structured surfaces of the materials have proven to be vital structures in generating the superhydrophobic surface properties (Han et al. 2005; Lim

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et al. 2006). Hence, the construction of a nanostructure is indispensable for the design of a superhydrophobic surface.

Various methods have been proposed to fabricate superhydrophobic surface mimicking the lotus leaf surface nanostructure, including layer-by-layer assembly (Lin et al. 2006), electrodeposition (Shi et al. 2005), lithographic patterning (Furstner et al. 2005), chemical vapor deposition (Liu et al. 2004). The most of the above methods involve strict preparation conditions, high raw materials cost and low productivity. Therefore, the applications of superhydrophobic surface have been limited so far (Bao et al. 2011).

The candle is generally composed of paraffin, which is made of heavy straight-chain hydrocarbons consisting of linear n-alkane and branched iso- and cyclo-alkanes with carbon lengths ranging from C_{16}~C_{30} and higher (Sun et al. 2006; Saber et al. 2011; Kuszlik et al. 2010; Luyt et al. 1999; Zaky et al. 2010). The candle flames present a simple example of a diffusion flame. Its burning is still complicated by the nature of its finite cylindrical wick (Sunderland et al. 2011). Some studies found the size of smoke particles produced from the candle flames, which are hydrocarbons in origin, to be around 30 nm in diameter (Pagels et al. 2009; Li et al. 1993). These candle smoke particles (CSPs) contain organic compounds and can be assembled into nanostructured superhydrophobic surface. Some studies suggest that many of the particulate organic compounds emitted in candle smoke consist of unburned wax components. The heavy alkane predominance in organic compounds of the paraffin candle smoke can be explained by volatilization of the mostly alkenes wax material and subsequent condensation into the CSPs (Fine et al. 1999).

The objective of this study is to explore a simple and efficient procedure to fabricate superhydrophobic surface through the CSPs from candle flames. Although, there have many excellent studies on the fabricate superhydrophobic surface with candle soot, some studies made the soot as a template (Deng et al. 2012; Maxime et al. 2014), other studies used paraffin wax-fixed candle soot for improving durability (Kwangseok et al. 2014) or paid attention to the optical absorption and fluorescence properties of the soot (Campbell et al. 2014). The emphasis of this work is to take advantage of the relationships before and after calcinations of CSPs, which allow the surface properties to be transformed. The proposed mechanism of observed superhydrophobicity surface properties due to calcination is discussed in detail. The paper offers a new perspective on CSPs in surface properties application.

Materials and methods

Materials

The candle used in this study was purchased from a commercial shop in Suzhou, China and used without further purification. It is a column in shape (1.5 cm in diameter ×17 cm in height) and white in color. The FT-IR results indicate that the candle is made of paraffin.

Methods

Preparation of deposition surface

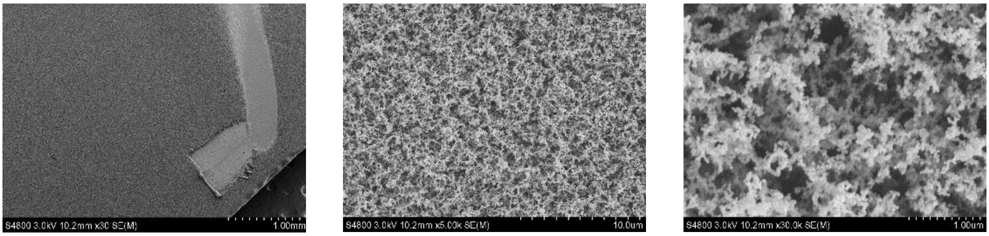
The candle was placed in a simple laboratory fume cupboard. The candle is lit with a match and allowed to burn. It burns steadily about 1 min later, then a flat glass was placed above the flame of the candle to collect (by deposition) candle smoke particles (CSPs) emitted from the candle flame (the distance between the top of flame and glass is about 0.5 cm). The CSPs deposited on the glass were coded as CSPs, the deposition time was 3 min (the thickness of the CSP's layer is about 200 nm). When the CSPs have been deposited on the glass, it was placed in a muffle furnace, then heat up to 500 ^{o}C with heating rate at 10 ^{o}C/min. The resultant CSPs on the glass were coded as CSPs(500) and their color was black.

Characterization

The thermal properties of the candle smoke particles (CSPs) before and after calcination was estimated by thermogravimetric analysis (TA, Q600). The samples were heated from room temperature to 1000 ^{o}C under air atmosphere with heating rate of 10 ^{o}C/min. The wettability (water contact angle) of CSPs deposited on the glass was measured by video-based optical contact angle measuring instruments (Dataphysics, OCA-20) at ambient temperature. Water droplets of about 3.0 μL in volume were dropped carefully onto the CSPs deposition surface, and the average value of five measurements at different positions of the sample was adopted as the contact angle. The contact angle was calculated from the images by the instrument software. The morphology and size of CSPs were investigated by transmission electron microscope (FEI, TecnaiG220), and the surface morphology of CSPs and CSP's deposition layer was examined by scanning electron microscope (Hitachi, S4800).

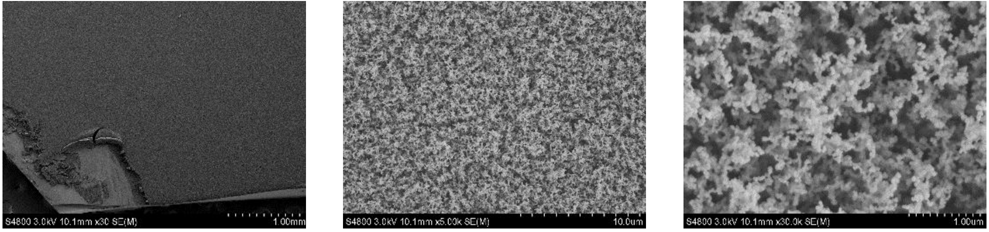
Results and discussion

The SEM micrograph of candle smoke particles (CSPs) deposited on the glass before and after calcination process is presented in Fig. 1a and 1b. The surface morphology of the CSPs is seen to be non-uniform and extremely small with a majority of the particles about 30 nm in diameter, which were formed by burning the candle. The SEM micrograph shows that the CSPs are deposited on the glass placed above the flame of the candle. A higher magnification of the micrograph shows that the particles of matter as irregular particles, all joined together, without any carbon nanotubes or nanowires among the particles (Fig. 1a). When the CSPs are heated up to 500 ^{o}C, formation of CSPs(500), the morphology and dimension of the CSPs have not changed. The heated particles are also irregular and joined together. Furthermore, there are no carbon nanotube or nanowire forms due to calcination process (Fig. 1b).



CSPs (×30) CSPs (×5k) CSPs (×30k)

(a)

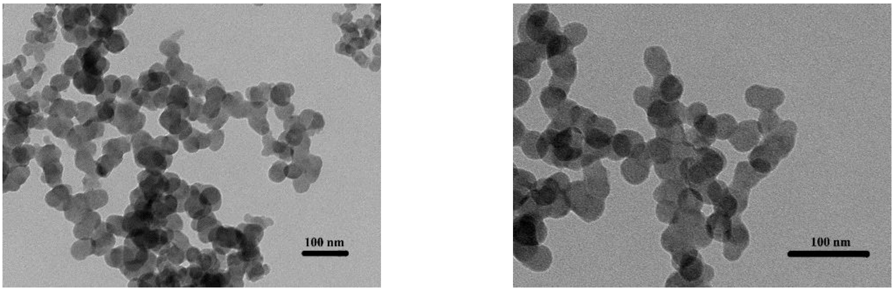


CSPs(500) (×30) CSPs(500) (×5k) CSPs(500) (×30k)

(b)

Fig. 1. The SEM micrograph of candle smoke particles deposited on the glass before and after calcination

Figure 2a is a typical TEM micrograph of the CSPs from candle flame, which is similar with the CSPs(500) (Fig. 2b). They show that the samples contain small non-uniform spherical particles. The equivalent diameter of the CSPs is about 30 nm, which is as big as the CSPs(500) samples. Meanwhile, there are not any carbon nanotubes or nanowire in the CSPs and CSPs(500) samples. The above results are all in agreement with the SEM micrograph of the CSPs. It indicates that the CSPs emitted from the candle flame are non-uniform spherical particles (about 30 nm in equivalent diameter), which maintain morphology and dimension after the calcination process at 500 ^{o}C. The following research has focused on the chemical properties of the CSPs and CSPs (500) samples.



(a) CSPs (b) CSPs(500)

Fig. 2. TEM micrograph of candle smoke particles deposited on the glass before and after calcination

The 4000~400 cm^{-1} wave-number range of the FT-IR spectra measured for the CSPs and CSPs(500) samples are compared in Fig. 3. The process of burning a candle flame to obtain CSPs is a thermal decomposition process, in which the candle flame breaks up to form CSPs. The particles, formed from the atmospheric combustion of a candle flame, are a complex mixture of elemental carbon and a variety of hydrocarbons. The composition of particles has a strong impact on the chemical properties of the CSPs and CSPs(500) (Shooto et al. 2011). According to Figs 1 and 2, the equivalent diameter of the CSPs is extremely small (nanoscale) having a large surface area. The functional groups on the particle surface have an important influence on its chemical properties. As expected, the intensities of the CSPs and CSPs(500)'s FT-IR absorption bands are weak for the most of amorphous carbon is non IR-active modes. Only small features centered around 3029, 2926 and 2853 cm^{-1} are evidenced in the CSPs sample, which are attributed to the presence of stretching vibration of methylene groups. They have been identified and observed on the CSP's FT-IR spectra in comparison with the CSPs(500)'s spectra. No band in the stretching mode range of the carbonyl groups (1600~1800 cm^{-1}), and hydroxyl groups (3000~3600 cm^{-1}) was observed in the CSPs samples, indicating that the CSPs are free of usual group functionalization during the candle burning process (thermal decomposition process). A very broad and complex feature centered around 1250 cm^{-1} band is also found in the FT-IR spectrum of the CSPs, which is agreement with the large amount of amorphous carbon present in the CSPs (Bantignies et al. 2006). Interestingly, the bands with respect to the A_{2u} (868 cm^{-1}) and E_{1u} (1590 cm^{-1}) IR-active modes of graphite are observed in CSPs(500)'s spectra (Kuhlmann et al. 1998). Furthermore, the 1720 cm^{-1} presence stretching mode range of carbonyl groups in CSPs(500)'s spectra indicates that the methylene groups reacting with oxygen formation of carbonyl groups when the CSPs are heated up to 500 ^{o}C. At the same time, during the calcination process, complex mixture of elemental carbon and a variety of hydrocarbons in the CSPs have been transformed into polar groups or decomposed in the CSPs(500) sample. For example, the carbonyl group is strongly polar in the CSPs(500), which would lead to the CSPs deposited on the glass's surface properties turn into hydrophilic after the calcination process.

The TG and DSC curves of the CSPs and CSPs(500) samples (under air atmosphere) are presented in Figure 4. The TG curves of the CSPs show that most the weight loss, related to the decomposition of hydrocarbons. It occurs at temperatures lower than 620 ^{o}C. During CSP's thermal decomposition processes, the disappearance of branch and backbone structure in CSPs is associated with different exothermal temperature, formation of two exothermal peaks at 593 ^{o}C and 616 ^{o}C, respectively. Interestingly, there is a little weight increasing appearance at 200~400 ^{o}C when the CSPs are heated up under air atmosphere. This phenomenon indicates that the methylene groups react with oxygen formation of carbonyl groups during the CSPs heating from 200 to 400 ^{o}C under the air atmosphere. For the CSPs(500) samples, there is no weight increase on the TG curves under the air atmosphere. It is so because the methylene groups, reacting with oxygen formation of carbonyl groups, have been completed during preparation of the CSPs(500) by the calcination process. From a different perspective, the decomposition of carbonyl groups creates an additional exothermal peak (593 °C) in CSPs(500)'s DSC curves, which demonstrates that methylene groups were oxidized into carbonyl groups during the calcination process. From room temperature to 200 °C the weight of the CSPs(500) is decreasing slowly, which indicates that before the decomposition of backbone structure the hydroxyl groups already decompose below 200 °C.

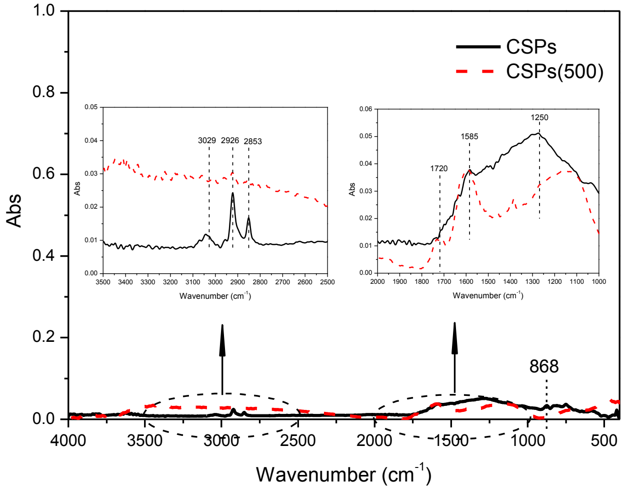


Fig.3 The FT-IR spectra of candle smoke particles deposited on the glass before and after calcination

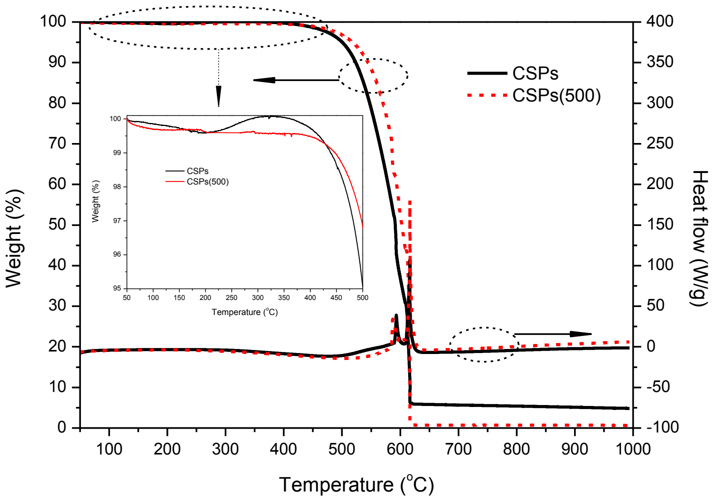
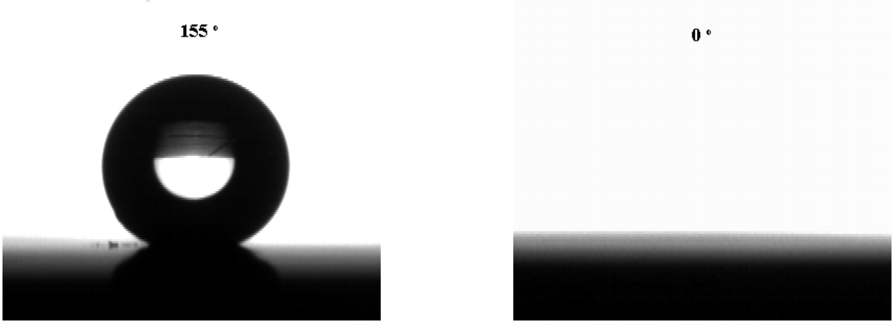


Fig. 4. TG-DSC curves of candle smoke particles deposited on the glass before and after calcination

The FT-IR spectra and TG-DSC curves reveal that the most important chemical properties' difference between CSPs and CSPs(500) samples. During the calcination process, the complex mixture of elemental carbon and a variety of hydrocarbons in the CSPs, such as methylene groups, have turned into carbonyl groups, leading to chemical properties variation. The objective of this communication is to study the surface properties of the CSPs from candle flames and to fabricate either superhydrophobic or superhydrophilic surface with a simple and efficient method. So it is interesting to investigate the wetting properties of the CSPs and CSPs(500) samples.

Wetting properties of the CSPs and CSPs(500) samples were evaluated by water contact angle measurements, The water contact angle is the average value of five measurements at different positions. Photographs of water droplets are shown in Figs 5(a-b) and the results of water contact angle measurements are 155^o and 0^o respectively. Interestingly, the results of the water contact angle indicate that the glass surface hydrophobic properties improved dramatically with the CSP's deposition. The water contact angle reached 155^o, showing the formation of superhydrophobic surfaces from a candle flame. The method, CSP's deposition on glass surface, is very simple and of low cost. Before calcination up to 500 ^{o}C, the CSPs deposition on glass surface exhibited superhydrophobic properties accounted for their specific composition and structures. The CSPs contain a complex mixture of elemental carbon and a variety of hydrocarbons, which provide a large amount of hydrophobic groups. Based on the SEM and TEM investigation, the CSPs deposition on glass surface is expected to exhibit two types of microstructure, that is, the relatively large pores formed through the interconnection of the CSPs, and the smaller nanoscale structure within the individual nanoparticles. The above microstructures of the CSPs increase their surface roughness, which can trap air to form superhydrophobic surfaces.

The calcination of the CSPs, which forms CSPs(500) samples, led to a dramatic decrease of water contact angles from 155^o to 0^o. The result suggests that surface properties of the CSP's deposited on glass have been successfully converted into superhydrophilic. Given that the complex mixture of elemental carbon and a variety of hydrocarbons in the CSPs produce superhydrophobic surface, it can be removed due to calcination process. The defect sites in the carbon network of the CSPs (500) samples, which form during the calculation process, produce surface hydroxyl groups, and carbonyl groups acted as a strong adsorption site of water molecules. The carbonyl groups in the relatively large pores, which were formed through the interconnection of the CSPs, can absorb water molecule. So the water is made to spread over the surface structure of the CSPs and its aggregation, leading to water contact angles equal to 0^o. The above results lead to the change of the surface properties of the CSPs from superhydrophobic to superhydrophilic by calcination at 500 ^{o}C.



(a) CSPs (b) CSPs(500)

Fig. 5. Photographs of water droplets on candle smoke particles deposited on glass before and after calcination

Conclusion

The candle smoke particles (CSPs) emitted from the candle flame has superhydrophobic properties without any additional treatment. The special properties results from the unique structure and composition of the CSPs, for SEM and TEM micrographs provide a clear indication that the particles are nanoscale in size (about 30 nm in equivalent diameter). Furthermore, the FT-IR spectra and TG-DSC investigation show the presence of a complex mixture of elemental carbon and a variety of hydrocarbons in association with amorphous nanomaterial in the CSPs. Interestingly, the CSPs can turn into superhydrophilic after calcination at 500 ^{o}C without dramatic morphology and dimension variation, for the CSPs(500) have different functional groups compared with the CSPs. So the CSPs from the candle flames provide a simple and efficient procedure of fabrication of superhydrophobic and superhydrophilic surfaces at low cost.

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