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Superhydrophobic Surface with High Adhesive Forces Based Carbon/Silica Composites Films

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ABSTRACT

Glass substrates modified by carbon/silica composites are fabricated through a two-step process for the preparation of a superhydrophoboic surface (water contact angle ≥ 150°). Carbon nanoparticles were firstly prepared through a deposition manner on the glass using a hydrothermal synthesis route, then the glass was modified by SiO_2 were achieved using the hydrolysis reaction of tetraethylorthosilicate (TEOS) at room temperature. It is not only a facile method to create a superhydrophobic surface, but also form a multi-functional surface with high adhesive forces.

Key words: Superhydrophoboic surface; high adhesive forces; hydrothermal synthesis route; hydrolysis reaction.

1. INTRODUCTION

In recent years, bionics has been attracted considerable attention for its great prospect. After a rainy day, shining water drops keeping a nearly perfect spherical shape on lotus leaves which can be rolled off easily, is one of the most beautiful wonders of nature. This natural phenomenon is defined as lotus effect (Zhai et al 2004; Cha et al 2010; Hipp et al 2010), it is considered as the basic study of superhydropobic behavior of a surface. Now the study of superhydropobic behavior of various surfaces is not only for fundamental research, but also for practical applications in many fields, especially in daily life (Yang et al 2007; Zhang et al 2011; Ogihare et al 2012), industry (Li et al 2008; Xu et al 2011), and agriculture (Sheng et al 2009; Wang et al 2011). Cassie-Baxter (Cassie and Baxter 1994) as well as Wenzel (Wenzel 1936) proposed two mathematical models to explain the wetting phenomena on rough surfaces that lead to superhydrophobic property (Su et al 2009; Erbil et al 2009). Usually, any surface with water contact angle larger than 150o

can be defined as a superhydrophobic surface (Tuberquia et al 2010). Various materials and methods are made for the fabrication of superhydrophobic surfaces. Generally, these approaches to obtain superhydrophobicity which can be divided into two groups, one is to achieve superhydrophobicity by changing the structure and surface energy of substrates. For example, Meng et al (Meng et al 2008) created superamphiphobic surfaces on common engineering metals by immersed into perfluorocarboxylic acid and keeping few hours. Ishizaki et al (Ishizaki et al 2011) prepared color-tuned superhydrophobic magnesium alloy with corrosion resistance. Xiu et al (Xiu et al 2008) obtained superhydrophobic surfaces on silicon surfaces by hierarchical etching. Shen et al (Shen et al 2010) employed a flowerlike silicon particulates films by chemical etching and obtained superhydrophobicity.

Another one is by coating superhydrophoboic surface on the substrates. Such as, Tsai et al (Tasi et al 2007) employed a raspberry-like particulates film by layer-by-layer deposition and produced superhydrophobic surfaces. Yildirim et al (Yildirim et al 2011) prepared a superhydrophoboic surface by coating fluorinated mesoporous silica nanoparticles. Brassard et al (Brassard et al 2011) prepared superhydrophobic thin films by synthesizing of monodisperse fluorinated Silica nanoparticles. Manca et al (Manca et al 2009) obtained superhydrophobic surfaces by trimethylsilanized silica nanoparticles based sol-gel processing.

Recently, various ways have been fabricated to obtain superhydrophoboic surface, such as template method, spray painting, self-assemble way, and etching method. But for the most researches, just only one material was used to employ the superhydrophoboic surface, few researches about employing composites to create superhydrophoboic surface. Here, we report the design of superhydrophoboic surface with high adhesive forces by means of C/SiO2 composites which is simple and environmental. Especially, the high adhesive forces enhance the water retaining capacity of the surface which is very important for long distance transport of water. C nanoparticles were prepared through a deposition manner on the glass using a hydrothermal synthesis route, then TEOS dissolved in isopropanol (IPA) forming homogeneous solution, which was dropped onto the glass modified by C nanostructures and kept in a container for few days. The C/SiO2 composites were fabricated due to the hydrolysis reaction of TEOS. In order to reduce the surface energy, the glass was further treated by fluorosilicone. After that, the fabricated coatings exhibited superhydrophobic property because of their dual-size rough surface and low surface energy.

2. EXPERIMENTAL PROCEDURE

2.1. Materials. All chemicals were of analytical grade and used as received. Glucose, were purchased from Tianjin Henxing Chemical Reagent manufacturing Co., Ltd. TEOS were obtained from Tianjin Kermal Chemical Reagent Co., Ltd. IPA were purchased from Hangzhou Gaojing Fine Chemicals Co., Ltd. 1H,1H,2H,2H-Perfluordecyltrimethoxysilane (>97 wt%)

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were obtained from Nanjing Daoning Chemicals Co., Ltd.

2.2. Methods. 6 g of glucose was added into 60 mL of deionized water stirring few minutes, forming homogeneous solution. The resulting mixture was transferred to and sealed in a Teflon-lined autoclave, and a piece of glass was also putted into the autoclave. The autoclave was sealed and maintained at 160oC for 6 h. After the autoclave was cooled down to room temperature naturally, the glass was collected and washed with deionized water carefully and dried for 12 h. then TEOS dissolved in isopropanol (IPA) with different volume ratios forming homogeneous solution, which was dropped onto the glass modified by C nanostructures and kept in a container for few days. The C/SiO2 composites were fabricated due to the hydrolysis reaction of TEOS, followed by perfluorosilane deposition to obtain highly water-repellence.

2.3. Characterization. The microstructures of SiO2 and C/SiO2 composites were investigated by ULTRA-55 field-emission scanning electron microscopy (FE-SEM) and The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 spectrophotometer using. The wetability of the as-prepared C/SiO2 composites films was analyzed by measurement of the water angles using SL200B contact angle system at ambient temperature. Water droplets were dropped carefully onto the samples. The average contact angle was obtained by measuring at three different positions of the same sample; the accuracy of measurement is $\pm 1^{o}$C.

3. RESULTS AND DISCUSSION

Fig. 1 shows the field-emission scanning electron microscopy (FE-SEM) images of the resulting surface after the two-step process. Contrasting to network-like SiO2 nanostructures which has single particle chains (Fig. 1 B), the network-like C/SiO2 composites (Fig. 1 A) appears more roughness. FT-IR analyses are carried out on the thin films deposited on the glass to provide a description of covering silica layer onto carbon particles. The spectrum of C nano particles in Fig 2 C shows a broad band with a maximum around 3365 cm-1 is attributed to the O-H stretching. A small peak appearing around at 2925 cm-1 is associated to the stretching vibration of C-H bond in the form of CH2 (Wan et al 2008). The stretching at 1282cm-1 is associated to the C-O-C skeleton. The spectrum of C/SiO2 composites in Fig 2 B shows a broad band with a maximum around 3425 cm-1
is attributed to the O-H stretching. A strong peak appears at 1100 cm-1 due to the presence of Si-O-Si asymmetric bond stretching. Two small peaks appear at 950 cm-1 and 2926 cm-1 are associated to the stretching vibration of Si-OH bond and C-H bond, respectively. The peak at 2700 cm-1 is associated to the C-H stretching vibration. The spectrum of fluorinated C/SiO2 composites in Fig 2A shows a small peak appears at 960 cm-1 which associated to the stretching vibration of C-F bond in the form of CF3 (Brassard et al 2011).

Water contact angle tests are carried out on the thin films to obtain better understanding of wetability. 5μl water is dropped on the glass modified by SiO2, due to the presence of hydrophilic Si-OH bonds, exhibit hydrophilic property. After treatment with fluorosilicone, its WCA reaches to 133 (the inset of Fig 3 A). The wetability of glass modified by C nanoparticles is similar to the glass modified by SiO2. However, when the glass is modified by C/SiO2 composites, followed by treatment with fluorosilicone, its WCA is 152 (the inset of Fig 3 B) which indicates the surface of the glass has superhydrophoboic property. In addition, as IPA keeps increasing, the WCA increases firstly, and then decrease gradually. The possible reason for this phenomenon is the changing of the surface roughness at the different volume ratios of TEOS and IPA. As shown in Fig. 3, when the volume ratios of IPA and TEOS are 2:1 or 5:1, the surface exhibit superhydrophoboic properties. Furthermore, we also find when the drop is turned upside-down, it still adhere to the surface. As shown in Fig. 4, the C/SiO2 composites film modified by TEOS and IPA with volume ratio of is 1:5 has strong adhesive force that is similar to gecko's foot (Zeng et al 2009; Liu et al 2010; Bhushan 2012). The gecko feet possess superhydrophobicity and a high adhesive ability towards water, because its feet are covered with millions of well-aligned microscopic keratinous hairs called setae(20–70 mm in length and 3–7 mm in diameter), which are further split into hundreds of smaller nanoscale ends called spatulae (100–200 nm in diameter) (Liu et al 2012). The possible reason of suerhydrophobic surface with high adhesive force had been studied by many researchers, such as Liu et al (Liu et al 2011), Lai et al (Lai et al 2009), and Hong et al (Hong et al 2007). The carbon/silica composites films reported in this paper also exhibit strong adhesive forces. We suggest that the strong adhesion is attributed to van der Waals force and negative pressure generated by the air trapped in closed "liquid-solid" system when the drop is turned upside-down. The micro-fluctuant surface and hair-like fluorosilicone results in a large contact area when a droplet is placed on it that increasing the van der Waals force between water droplet and surface. When the droplet is turned upside-down, the direction of gravity has changed which lead to changing the surface energy of "liquid-solid" system and "liquid-air" system. Generally, the variation of surface energy result in generating negative pressure that is an important factor for the water droplet can adhere to the surface.

4. CONCLUSIONS

In summary, we designed a two-step process for the preparation of a superhydrophoboic surface. A binary structure forms after the combination of C nanoparicles and network-like SiO2 nanostructures, after treatment with fluorosilicone, the surface obtained with two functional areas that present different wetabilities and high adhesive force that enhance the water retaining capacity of the surface, for this feature can be used in some places need keeping water for a long time. The advantages of this methodology also include its simplicity and easy to control.

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List of Figures

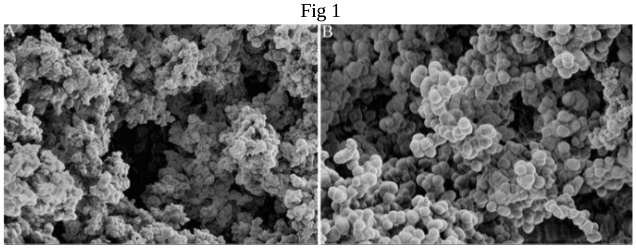
Fig. 1 FE-SEM images of the resulting surface after different processes (A) glasses were modified by C/SiO2 composites and (B) glass modified by SiO2. All the scale bars are 2 μm.

Fig. 2 FT-IR spectra of the thin films prepared with (A) fluorinated C/SiO2 composites; (B) C/SiO2 composites; and (C).C nano particles.

Fig. 3 FE-SEM images of glasses were modified by C/SiO2 composites with the different volume ratios of IPA and TEOS: 0 (A), 2 (B), 5 (C) and 10 (D); the insets are WCA images. All the scale bars are 2 μm.

Fig. 4 A 5 μl water drop hanging on the micro-fluctuant area that upside-down; the left is WCA image, the right is the schematic of a 5 μl water drop hanging on the rough surface.

Fig 1



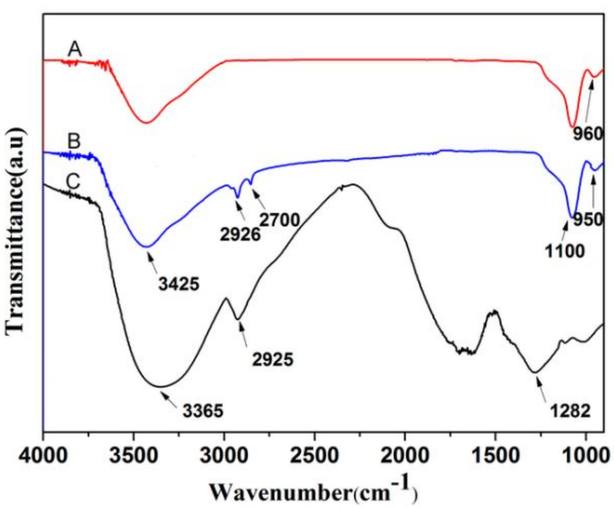


Fig 2

Fig 3

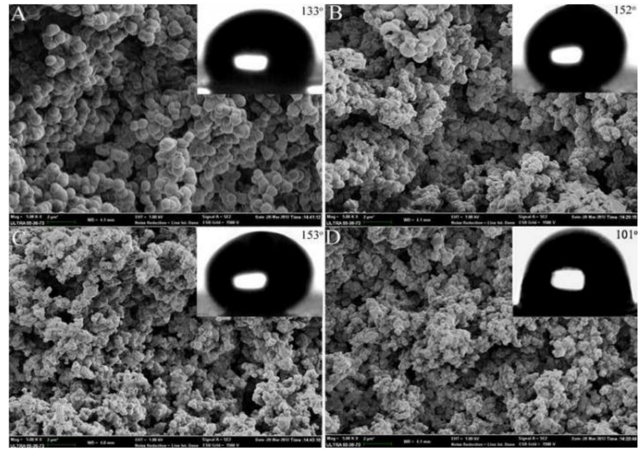


Fig 4