

Investigating the Effect of Hierarchical Carbon Micro/Nano Spheres on the Surface Wettability: Experimental and Theoretical Study

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(Received 26 Sep. 2020; Revised 29 Oct. 2020; Accepted 18 Nov. 2020; Published 15 Dec. 2020)

Abstract: Carbon spheres with controllable structures (i.e., nano and microstructure) were prepared by using a hydrothermal method. By adjusting the concentration of glucose solution at a both constant temperature and constant process time in a sealed autoclave, the total size of carbon spheres (CSs) was changed from nano to microscale. Then micronanobinary carbon spheres structure (MNCS) was successfully obtained by coating colloidal solution of carbon nanospheres (CNSs, average diameter of 186 nm) and microspheres (CMSs, average diameter of 5 μm) on the FTO substrates. It was realized that by annealing of the carbon spheres under vacuum condition, their functional groups were reduced, therefore, this effected on the wetting behavior of carbon spheres. The effect of hierarchical roughness as a beneficial factor on the superhydrophobicity of CSs was analyzed by the investigation of the contact angle (CA). The highest CA was measured for the mixture structures containing both the micro and nanoscale spheres. Based on the new research, CA of the surface with micronanobinary structure is larger than the nanostructure and the nanostructure is larger than the microstructure and above all, theoretical calculations confirmed the experimental measurements.

Keywords: Micro/nano Carbon Sphere Structures, Carbon Hierarchical Sphere Structure, Contact Angle, Superhydrophobic

1. INTRODUCTION

These days, superhydrophobic surfaces have attracted a considerable amount of attention due to their wide range of potentials not only in fundamental research but also in many practical applications such as self-cleaning, aerospace

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industry, low-friction coatings, oil/water separation, and controlling corrosion [1-4]. The superhydrophobic solid surface is characterized by a macroscopic Water Contact Angle (WCA) larger than 150° . Generally, the wettability of a surface is governed by both surface tension and surface geometrical structure [5]. In principle, it can be said that by enhancing the surface roughness or with deposition of low surface energy materials, wettability's property can be changed. Lotus leaf is a strong superhydrophobic surface because of its hierarchical micro/nanostructure and also has a low surface-energy material that covers its structure [6-8]. Besides the plants, the surface of some insects such as butterfly, water strider, and spider show superhydrophobic behavior, too [6]. Therefore, with this nature inspiration, designing superhydrophobic surfaces can be very practical. Carbon spheres because of having spherical shape, low surface energy, anti-corrosion property, non-toxicity, inexpensive, controllable sizes, and its morphology can be suitable to be used for fabrication superhydrophobic coatings [9]. Therefore, the fabrication of superhydrophobic carbon spheres surfaces with a micro-nano hierarchical structure seems to be expected for having wide practical applications. Until now, considerable works have been developed to format hierarchically structured surfaces inspired by the natural surface structures [10]. In recent years, many numbers of methods for forming hierarchical structures on different materials have been reported such as Creation of hierarchical surface structures by combining colloidal self-assembly and sputter deposition [11], plasma treatment [12], utilizing the reaction between the hydrolyzed solution and metallic surfaces [13], replication of micropattern and self-assembly of hydrophobic alkanes [14], electrodeposition [15], lithography [5,16], lotus and rice leaf template [14], self-assembling under hydrothermal conditions [17], and so on. Although, a few numbers of methods have been suggested for fabricating micro-nano hierarchical spheres structures [18,19]. The hierarchical structure of ZnO film in micro-nano scale, including first layer of ZnO microspheres array (about $1.0\ \mu\text{m}$ in average particle radius) and second layer of ZnO spheres (about $0.1\ \mu\text{m}$ in average particle radius) by controlling pH in the $\text{Zn}(\text{gray}) + \text{H}_2\text{O}_2$ reaction is reported by Zhang et al. [19]. Their approach concentrated on low cost and facile way although the morphology of ZnO spheres micro-nano hierarchical structures were not controllable. Many methods have been developed to produce superhydrophobic surfaces with a modifying surface tension by using silanes [18]. However, most of these surfaces fabricated were expensive, or could not be easily applied to large scale application. The use of silanes limited the application of this method. Superhydrophobic research on the hierarchical carbon micro/nanospheres composite films has never been carried out. Here, we reported a facile and economic two-step method to prepare superhydrophobic films with micro-nano

hierarchical carbon spheres coating. This method is low cost and can be applied on a large scale. In addition, the morphology of carbon sphere micro-nano hierarchical structures is controllable. Also, the fabricated thin films without any chemical surface modification show a stable and complete superhydrophobicity. A model for describing wettability of the micro-nano hierarchical spheres are is also applicable for the fabricated thin films.

2. EXPERIMENTAL

A. Materials

The materials which have been used consisted of Glucose powder purchased from Merck Co (Germany) and absolute ethanol 99% for washing the product and it was also supplied by Merck Co.

B. Chemical process

For this study, proper amounts of glucose powder were dissolved in Di-Ionized (DI) water to prepare the glucose solutions for having two different concentrations of them, 0.75 and 2.5 M, respectively. The resulting solutions were transferred into a 75 ml cylindrical Teflon located in a stainless-steel autoclave. The autoclave was maintained at 160 °C for 18 h and then they cooled down to room temperature, naturally. The hydrothermal conditions and the nomination of the samples are listed in Table 1. After the hydrothermal process in an autoclave, the obtained products (brown or black color) were centrifuged at 9000 rpm and were washed with DI water, absolute ethanol and acetone several times and then they were dried at 80 °C for 5 h. All of the experiments were carried out at room temperature (~21 °C).

TABLE I
HYDROTHERMAL TREATMENT CONDITIONS AND NOMINATION FOR DIFFERENT SAMPLES

Sam ple no.	Hydrother mal time (h)	Hydrotherm al temperature (°C)	Concentrat ion (M)	Structur e Scale
a	18	160	0.75	nanometer
b	18	160	2.50	micrometer

C. Preparation of thin film with the hierarchical structure of Carbon spheres

Micro-nano hierarchical structure carbon spheres coating was made by a simple and low-cost method. Uniform and stable film for the hierarchical structures of carbon spheres containing both the micro and nanoscale spheres

was made by drop-casting of mixture colloidal solution of the micro (sample b) and nanoscale (sample a) spheres in DI water on FTO substrate.

At first, equal amounts (100 mg) of the prepared CMSs (about 5 μm in average diameter) samples (sample b) and also equal amounts (100 mg) of the prepared CNSs (about 186 nm in average diameter) samples (sample a) were dissolved in 10 ml of DI water. In the next step, the hierarchical structure was obtained by drop casting of prepared colloidal solution of CNSs and CMSs in DI water on the FTO as a substrate. The as-prepared films were annealed at 350 $^{\circ}\text{C}$ for 5 min under vacuum condition in order to remove carboxyl and hydroxyl functional groups. In recently research [20], it was shown that under such conditions the functional groups of the surface of the carbon spheres had the greatest reduction without the carbon spheres being decomposed. The formation mechanism of micro-nano hierarchical structured carbon spheres coatings is illustrated schematically in Fig. 1.

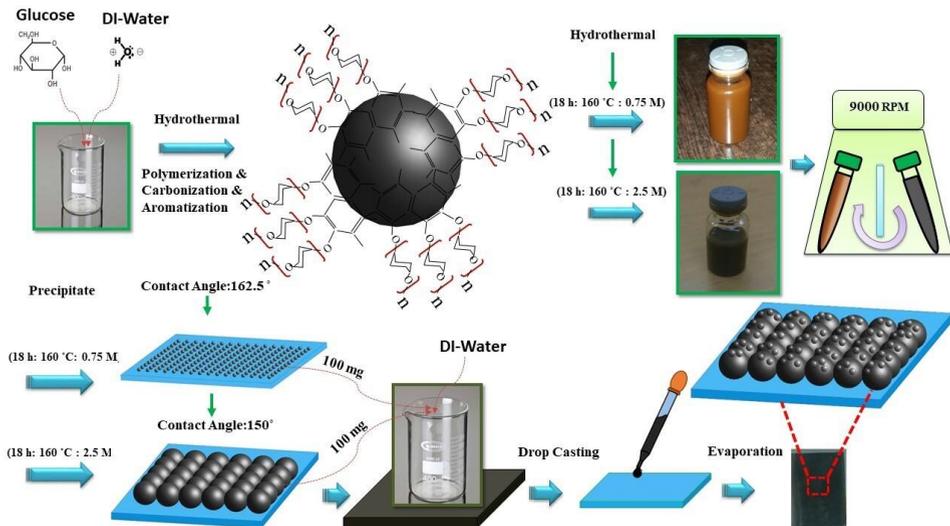


Fig. 1. The formation process of the superhydrophobic micro-nano hierarchical carbon sphere coating.

D. Characterizations

The morphology and composition of samples were characterized by field emission scanning electron microscopy (FESEM) Mira 3-XMU model equipped with an energy dispersive spectroscopy (EDS). In order to study the crystal structure, the X-ray diffraction (XRD) patterns were recorded from 10 to 80 $^{\circ}$ on an X'Pert MPD X-ray diffractometer with Cobalt Tube $K\alpha$ ($\lambda=1.78897 \text{ \AA}$)

radiation at 40 kV and 40 mA. Static water contact angles were measured on the surface of different samples by an OCA 15 plus type contact angle (CA) measuring system by using the distilled water (the volume of 4 μL) in three random spots for each surface to measure the average value and then the shape of the droplets was recorded by a Canon camera after 20 s.

3. RESULTS AND DISCUSSION

A. FESEM/EDS and XRD analysis

The effect of hydrothermal treatment on the morphology and chemical composition of CSs was studied by FESEM/EDS analyses. Fig. 2 shows the FESEM micrographs images of prepared micro, nano, and micro-nano hierarchical structures. Fig. 2a and 2b show the carbon spheres arrays with nano and microstructures, respectively. This form of surface morphology has been also reported in the previous researches [20,21]. Fig. 2c shows the FESEM image of as-prepared micro-nano hierarchical structures. As can be seen, impressively, the total surface of carbon microspheres is well covered by carbon nanospheres.

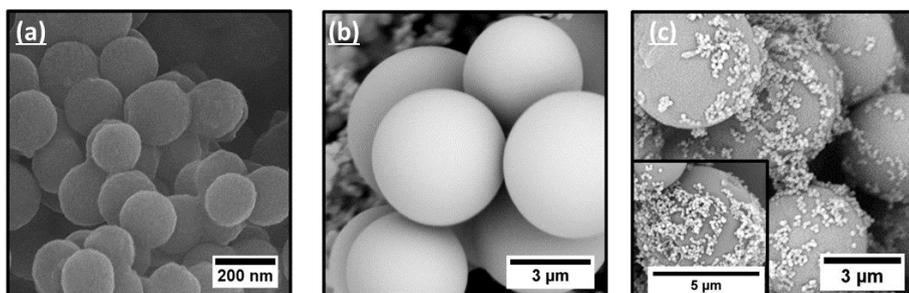


Fig. 2. Typical FE-SEM micrographs of a, b and c film final products. a) nano scale carbon sphere structure (sample a), b) microscale carbon sphere structure (sample b) and c) micronanobinary carbon sphere structure (microscale sphere and nanoscale binary structure, (sample c).

According to Fig. 2, it can be seen that the products of a, b, and c have different structures. It is obvious that after hydrothermal treatment, the carbon spheres with a regular spherical shape with averages diameters 186 nm and 5 μm (samples a and b, respectively) have been formed. Changing the concentration of glucose solution from 0.75 to 2.5 M causes a transformation from nanometer to micrometer scale. Increasing of the initial concentration of glucose in the hydrothermal process leads to an increase in the diameter of carbon spheres without any changes in the CSs' morphologies. Fig. 2c shows that the product of the sample has both microscale spheres structure and

nanoscale spheres structure (i.e., the product of sample c is depicted by micronanobinary structure). As shown in Fig. 2c, carbon spheres surface is in the micro-nano scale exhibiting typical hierarchical structure with a first film of microscale in the form of spheres (CMSs) and with a second layer of nano-scale spheres (CNSs). The presented structure in Fig. 2c shows the concept of inspire from nature very well. Due to the morphology of sample 2c, it indicates similarity to the natural lotus leaves which consists of hierarchical micro/nanostructures.

The elemental composition of the samples was reported in Table 2. As depicted in Table 2, the spheres are formed from carbon and oxygen and the amount of carbon is higher than oxygen. The O peak would be originated due to several reasons including [20,21]:

1. The incomplete decomposition of glucose
2. Existence of carboxyl and hydroxyl functional groups
3. Adsorption of water on the carbon sphere surfaces.

TABLE II

C AND O CONTENTS DETECTED BY EDS ANALYSIS ON VARIOUS SAMPLES		
Sample	C (%)	O (%)
a	73.8	26.2
b	73.1	26.9
c	76.1	23.9

In Fig. 3, XRD pattern of the sample a (18 h: 160 °C: 0.75 M) is shown. Two broad and weak diffraction peaks near the diffraction angles of 24.5° and 43° correspond to the diffractions of graphite crystal face (002) and (100), respectively which can be indexed as graphite (JCPDS File No.040836) [20]. The existence of these two weak peaks confirms that the crystallinity of the samples is low. The distance between planes (002) calculated from the X-ray diffraction data is about 4.2 Å. The value obtained is greater than the distance between graphite plates (3.56 Å) and it represents the considerable disorder in the synthesized carbon structure.

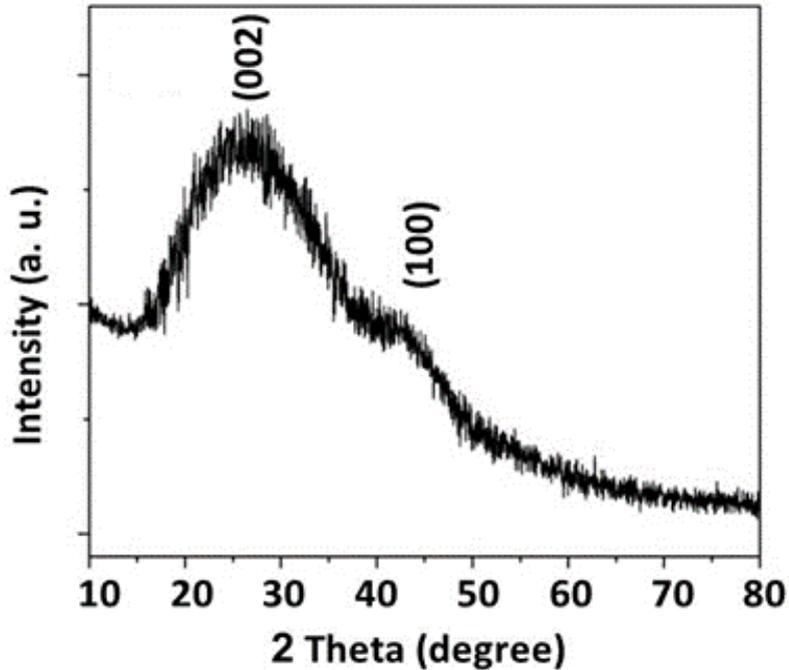


Fig. 3. XRD pattern of sample a (18 h:160 °C: 0.75 M).

B. Experimental Considerations

The wettability behavior of the synthesized different structures was investigated by static WCA. The CA of the as-prepared samples with nano and micro structure were measured to be 162.5° and 150° (Fig. 4a and b), respectively, and exhibit superhydrophobicity. But, the micro-nano hierarchical structure of CSs (MNCS) showed perfect superhydrophobicity behavior with extraordinary contact angle, so we could not measure the WCA. Because the surface was so superhydrophobic, the drop which has been fallen on the surface was unable to find a balance point and, therefore, it moved on the surface. As a result, taking a shot of the drop at a fixed moment was quietly impossible. So, we decided to take photo of the drop when it was in contact with the needle. The results for WCA were the average of the values measured at three different points for each sample. Under heat treatment, condition was investigated recently [20], nano and micro structures of carbon spheres showed hydrophobicity and superhydrophobicity. It was seen that the water contact angle of a film of carbon microspheres without any nanostructure was 150°. The most stable contact angle was measured for the hierarchical structures of carbon spheres containing both the micro-and nanoscale spheres, moreover, the surface

of MNCS showed superhydrophobicity. It was found that the nanospheres significantly contribute to the increase of hydrophobicity.

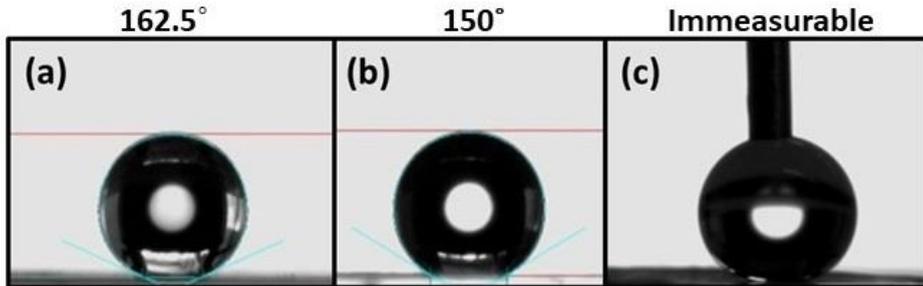


Fig. 4. (a) Optical photographs of the wetting for about a 4 μL water droplet on the nano structured surface from side view direction. (b) Side view of a 4 μL water droplet on the micro structured surface and (c) Side view of a 4 μL water droplet on the hierarchical structured surface, respectively.

The WCA was possible to significantly change under switching from nano or microstructures to hierarchical structures, however, it exhibited superhydrophobicity when the nanostructure was appeared and it covered the entire microspheres (Fig. 4a, b and c). The WCA of the samples was dramatically increased. So, it can be added that surface structure played a key role in controlling the wettability of the solid surface. Generally, the results revealed that, the WCA of the surface of carbon spheres followed the order $\text{WCA}_{\text{micronanobinary}} > \text{WCA}_{\text{nanostructure}} > \text{WCA}_{\text{microstructure}}$.

Recently, in our previous work [20], positive effect of heat treatment on the hydrophobicity of carbon spheres has been investigated. As it has been mentioned, via combining of nano and microscale structures as a specific morphology usually named micronanobinary structures, carbon spheres can be produced superhydrophobic thin film. Due to the micronanobinary roughness, the coated surfaces could exhibit perfect superhydrophobic properties.

It can be clearly seen that the CA of the samples gradually increased as the structure of a sample from micro to nano and then micro-nano changed. Therefore, the topography had a considerable influence on the wettability of the surface.

C. Theoretical Considerations

The effect of two key factors including surface chemistry and surface roughness in controlling wettability has been evaluated by Wenzel theory and Cassie–Baxter theory models [22] which are the well-known. In the Wenzel model, the effect of roughness on the wettability evaluated by the following equation (1):

$$\cos\theta_w = r_w \cos\theta_Y \tag{1}$$

Where r_w is the roughness factor defined as the ratio of the actual surface area to its horizontal projection. In the Cassie-Baxter model theory, interaction actions and reactions between the liquid and the solid should be weak, in which the deposited liquid is supposed to sit on the solid/air interface [22]. This model was introduced by following equation (2):

$$\cos\theta_{CB} = f_1 \cos\theta_Y - f_2 \tag{2}$$

where θ_{CB} and θ_Y represent the water contact angle on rough and smooth surfaces, respectively. In this equation, is the f_1 fraction of the projected area of the solid surface has been wetted by the liquid and f_2 is the surface area fraction of the air-liquid interface (i.e., $f_1+f_2=1$).

Herein, in order to respond to this question: Why does the micronanobinary or hierarchical structure improve the surface hydrophobicity to the greatest limit? We have used the model which was proposed by Nakae et al at first [23]. Han's group a few years later applied this model for describing the wettability of the hierarchical structure of ZnO spheres [19]. In this regard, the equations used together with the results for carbon spheres with different structures are listed in Table 3. The used factors R , R' , r and r' are depicted schematically in Fig. 5a, b and c.

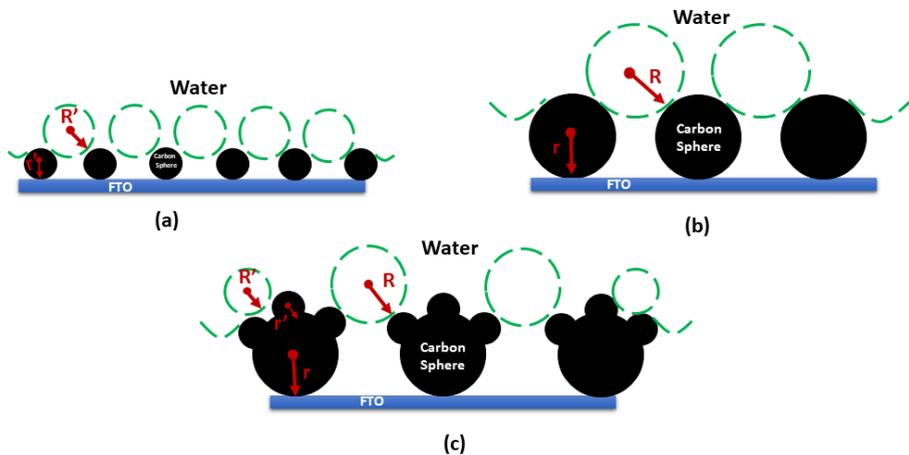


Fig. 5. Schematic images of the shapes of water on the surface of carbon spheres with different structures. (a) nanostructure, (b) microstructure and (c) micronanobinary structure.

Where r' , r , R' and R are the average nano spheres radius, the average micro spheres radius, the average curvature radius on nanostructure surface and

average curvature radius on microstructure surface, respectively. According to these this model the contact angles for thin films prepared in our experimental are reported in Table 3.

As can be seen in Table 3, for three different structures of carbon spheres, different values for contact angles and f_2 parameter by theoretical and experimental consideration were achieved. It is clear that higher air fraction (f_2) resulted in a significant increase of CA and increase repellent water.

TABLE III

WATER CONTACT ANGLES, DOMINATED SURFACE STRUCTURES, AND F_2 VALUES FOR DIFFERENT SAMPLES OF CARBON SPHERES AND SUMMARY OF WETTABILITY MODELS ON THE VARIOUS STRUCTURES AS DESCRIBED FOR DIFFERENT STRUCTURES.

Sample	a	b	c
Structure Scale	nanometer	micrometer	micro-nanometer
f_2 [24]	$\frac{R'}{R'+r'}$	$\frac{R}{R+r}$	$\frac{R+R'}{R+R'+r'}$
Contact Angle exp (deg)	162.5	150.0	Immeasurable*
f_2 (exp)	0.942	0.843	Incalculable
R' (μm)	1.45	non	1.45
r' (μm)	0.93	non	0.93
R (μm)	non	13.15	13.15
r (μm)	non	2.5	2.5
f_2 (theo)	0.939	0.845	0.993
Hydrophobicity	Sample c > Sample a		
Ordering	>Sample b		

* Due to unbalance position of the drop and not staying on the surface, capturing a shot of the drop in contact with surface and measuring its contact angle isn't possible.

By using experimental data's, it is calculated that $f_{2_nano}= 0.942 > f_{2_micro}=0.843$. Because the drop did not fix on the surface of micronanobinary structure, we could not measure the angle of drop contact with the surface, and consequently could not calculate the experimental value of f_2 for this surface. The reason for these conditions could be the large amount of air/liquid contact

friction of this structure. It can be clearly seen that the contact angle of the samples increases as the structure of sample from micro to nano and then micronano changes. Using the same procedure as in Ref. ([19]) for calculating theoretical parameters, by considering "hemispherical close-packed model" [22] and expressing R and R' as $R=A(1-e^{-Br})$ & $R'=A(1-e^{-Br'})$, the average curvature radiuses R and R' calculated as $R= 13.15 \mu\text{m}$ and $R'=1.45 \mu\text{m}$. Using the values of the radius of curvatures and the radius of the sphere of surface structures (r, r'), theoretical values for f_2 were obtained as they are shown in Table 3. The value of $f_2=0.993$ for the micronanobinary structure indicates that this surface is perfect superhydrophobic. This phenomenon can be a justification for our inability (Failure of fixation of drops on the surface) to measure the angle of water drop contact with this surface. So, theoretical considerations are entirely in agreement with the experimental results which mean that the used model can explain the effect of structures on the wetting behavior. As a result, the topography has a considerable influence on the wettability of surface in this structures.

4. Conclusion

In summary, a facile technique to fabricate superhydrophobic artificial surfaces has successfully investigated. The artificial surfaces were fabricated by drop casting of mixture colloidal solution of the micro and nanoscale spheres in DI water on the FTO substrate. The morphologies of the provided artificial surfaces exhibited typical hierarchical structure in micro-nanoscale, composed of CMSs about $5 \mu\text{m}$ diameter as the first substrate and CNSs array about 186 nm diameter as the second layer. These structures were similar to those of the natural lotus leaves which consisted of rough micronanobinary structure, (i.e., hierarchical micro/nanostructures) and thus the surfaces exhibited strong superhydrophobicity with a high CA after the heat treatment for removing functional groups. Substrates coated with Carbon micro-nanospheres showed perfect superhydrophobicity and also theoretical calculations confirmed completely the experimental measurements. In fact, complete superhydrophobic surfaces were designed by morphological engineering technology without using of any low-energy material like silanes, and indicated stable and complete superhydrophobic behavior which can be applicable in a variety of fields such as medicine, aircraft industry and etc.

ACKNOWLEDGMENT

The authors would like to thank Research Council of Tarbiat Modares University for financial supports and of Mr. V. Barough for his help in experimental measurements.

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