



A novel method to fabricate superhydrophobic surfaces based on well-defined mulberry-like particles and self-assembly of polydimethylsiloxane

Jinxin Yang, Pihui Pi, Xiufang Wen^{*}, Dafeng Zheng, Mengyi Xu, Jiang Cheng, Zhuoru Yang

The School of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Guangzhou 510640, PR China

ARTICLE INFO

Article history:

Received 18 May 2008

Received in revised form 27 September 2008

Accepted 27 September 2008

Available online 18 October 2008

Keywords:

Superhydrophobic surface

Polydimethylsiloxane

CaCO₃/SiO₂ composite particle

Self-cleaning

ABSTRACT

A superhydrophobic surface was obtained by combining application of CaCO₃/SiO₂ mulberry-like composite particles, which originated from violent stirring and surface modification, and self-assembly of polydimethylsiloxane. Water contact angle and sliding angle of the superhydrophobic surface were measured to be about 164 ± 2.5° and 5°, respectively. The excellent hydrophobicity is attributed to the synergistic effect of micro–submicro–nano-meter scale roughness (fabricated by composite particles) and the low surface energy (provided by polydimethylsiloxane). This procedure makes it possible for widespread applications of superhydrophobic film due to its simplicity and practicability.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Superhydrophobic surfaces with water contact angle (WCA) larger than 150° and sliding angle (SA) lower than 10° have attracted increasing interest due to their outstanding properties of low flow resistance and self-cleaning [1–3]. These properties can be widely applied in industrial applications and daily life, such as stain resistant/water resistant protective coatings and anti-snow/anti-icing windows and antenna [4–6]. Inspired by many plant leaves in nature, notably lotus leaves and rice leaves, scientists recognize that WCA can be enhanced by two means: low surface energy material and suitable surface roughness [7–11]. Many superhydrophobic surfaces have been fabricated by means of combination of rough surface and low surface energy [12,13]. Up till now, many methods have been used to prepare superhydrophobic surfaces including etching and lithography [14,15], chemical vapor deposition [16,17], template synthesis [18,19], polymer reformation [20,21], phase separation and self-assembly [12,22], and rf-sputtering [23]. However, most of these reported methods involve strict conditions, complex step processes, time-consuming, expensive materials or low adhesion of the coating indicating that they cannot be easily scaled-up to practical systems. Therefore, the applications of the superhydrophobic surfaces so far have been limited.

Polydimethylsiloxane (PDMS) is one of the known low surface energy substances. Due to its excellent insulation property, flexibility and weatherability, PDMS is a potential and competitive material to replace porcelain and glass in housing and high-voltage outdoor insulator or as an anti-pollution flashover coating. However, WCAs higher than 120° only based on flat PDMS film is few reported in literatures [24]. The hydrophobicity of flat PDMS surface with the low WCA and high SA limits its wide application to a certain extent [25]. To our great knowledge, the methods to prepare superhydrophobic coating based on PDMS are still limited to laser-etching [26] or soft-lithographic imprinting [27]. In addition, it is difficult to fabricate superhydrophobic film on high-voltage outdoor insulator with these technologies. In this contribution, we present a simple, yet robust and effective procedure to fabricate superhydrophobic surfaces. First, mulberry-like composite particles were prepared by violent stirring and surface modification. Superhydrophobic surfaces were then obtained by means of self-assembly of PDMS after spraying the mixture of composite particles and PDMS onto the clean glass, which is just suitable to fabricate large scale superhydrophobic surface.

2. Experimental

2.1. Preparation of composite particles

Twenty gram CaCO₃ (0.8–1 μm, provided by Fujian Longpu Light Calcium Carbonate Factory, China) and 5 g SiO₂ (30 ± 5 nm, purchased from Zhejiang Hongsheng Nano-material Co. Ltd, China)

^{*} Corresponding author. Tel.: +86 20 87112057x805; fax: +86 20 87112057x804.
E-mail addresses: xfwen@scut.edu.cn, jinxiny_2003@yahoo.com.cn (X. Wen).

were introduced in homogenizer for a 10 min premixing at 1000 rpm, and then with violent stirring at 7000 rpm for 30 min [28] which leading to the precursor of composite particles. To graft $(\text{CH}_3)_3\text{Si}$ -group onto the composite particles, the precursor was transferred into a 500 mL flask and 9 mL hexamethyldisilazane (HMDS) was added at the same time. The mulberry-like composite particles were prepared after the mixture was stirred at 2000 rpm and 140°C for 5 h.

2.2. Preparation of superhydrophobic surfaces

A hundred gram PDMS with a viscosity of 6000–20,000 mPa s and various weight of composite particles were mixed homogeneously in a planetary mixer and admixed in succession with 15 g trimethylsilyl-terminated polydimethylsiloxane with a viscosity of 100 mPa s, 0.2 g dibutyl tin laurate, 5 g vinyltriethoxysilane (A-151) and 5 g γ -aminopropyl triethoxysilane (A-1100) at 100 – 150°C for 5 h. The components were then mixed for 20 min at a reduced pressure of about 20 mbar. Subsequently, 1–1.2 time gasoline (weight ratio to the mixture) was added into the mixture and mixed homogeneously. Superhydrophobic surfaces were obtained by means of spraying (paint spray gun, Model 30224, made by Harbor Freight Tools) the mixture onto the clean glass first, then curing at room temperature for 2 h and at 50°C for 24 h successively. Air pressure on compressor was 30–80 PSI. While spraying, keep the gun nozzle vertical to the object surface and the distance from the object being painted at $6''$ – $9''$. The smooth PDMS surfaces were procured as the similar process just without composite particles.

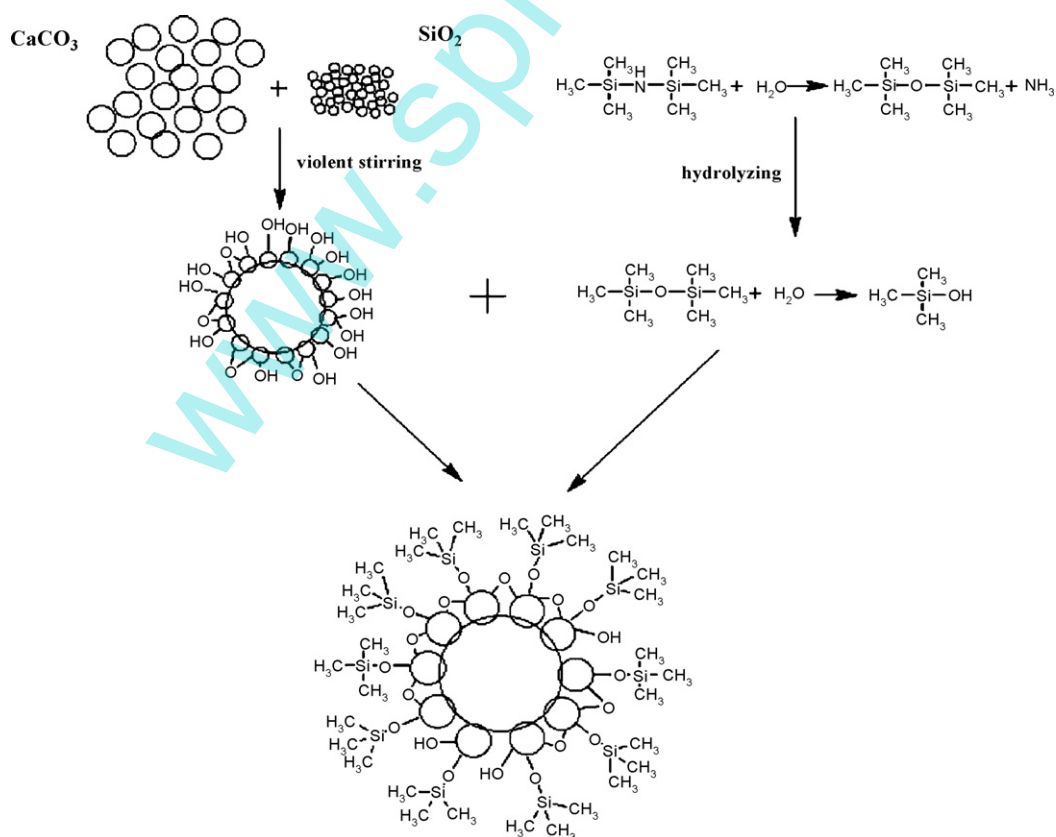
2.3. Characterization

The composition of the modified particles was studied by attenuated total reflectance Fourier transform infrared spectro-

meter (ATR-FTIR, Bio-Rad). The scanning electron microscopy (SEM) images were obtained on a LEO 1530VP SEM (Germany). Prior to measuring, the samples were coated with a thin gold film by means of a vacuum sputter to improve electrical conductivity. Elemental composition was characterized by energy dispersion spectrum (EDS) which is an attachment of the SEM. Atomic force microscopy (AFM) measurement was performed using CSPM5000 (Benyuan, China). The correlative roughness of the surfaces can be calculated from the AFM software. The WCAs were measured with a $5\text{-}\mu\text{L}$ water droplet at ambient temperature with an optical contact angle meter (Dataphysics Inc. OCA15). Reported WCA values were averages of 25 measurements made on five different district of the sample surface. The adhesion of coatings was measured according to GB/T-9286-1998 with 3 M Scotch 600# adhesive tape.

3. Results and discussion

As shown in Scheme 1, the composite particles with mulberry-like irregular structure were prepared. The CaCO_3 particles were studded by SiO_2 particles after violent stirring. HMDS could hydrolyze at the hydroxyl surface to generate silanol, and further reacted with the $-\text{OH}$ groups on the surface of SiO_2 particles, resulting in the formation of a network composing of $-\text{Si}(\text{CH}_3)_3$ groups. Then the interaction between CaCO_3 and SiO_2 was enhanced. The combination of the two particles is probably only a physical change [28], which can be proved by the IR spectrum (Fig. 1) analysis. The curves a, b and c are the IR spectra of SiO_2 , CaCO_3 and the precursor of $\text{CaCO}_3/\text{SiO}_2$ composite, respectively. Comparing curve c to a and b, neither new peak was observed, nor any existed one disappeared, indicating that there was no chemical bond between CaCO_3 and SiO_2 in the composite particles. In Fig. 1, curve d is the IR spectrum of $\text{CaCO}_3/\text{SiO}_2$ composite modified with



Scheme 1. The procedure for preparing composite particles.

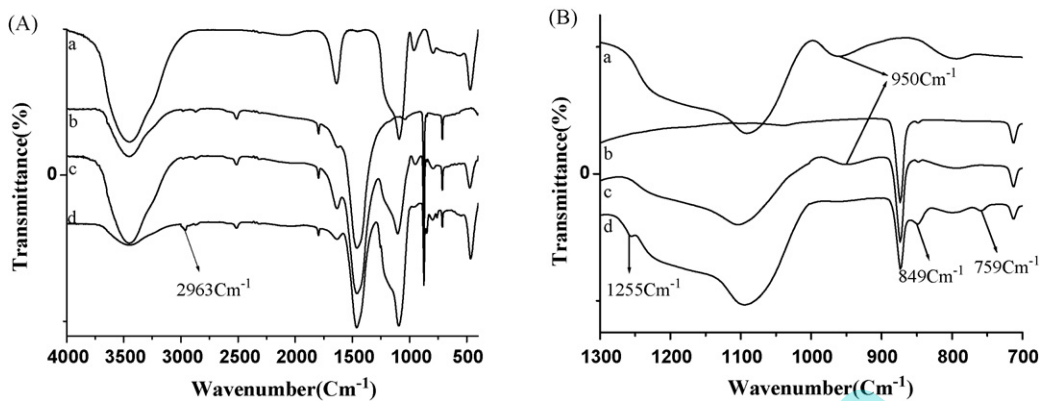


Fig. 1. FTIR of composite particles. (a) SiO₂, (b) CaCO₃, (c) CaCO₃/SiO₂ composite particles without modified, and (d) CaCO₃/SiO₂ composite particles modified with HMDS (II is a part of I).

HMDS. The intensity of bonds relating to Si–O–Si at around 1091 and 469 cm⁻¹ was increased noticeably. The absorption of methyl groups at 2963 and 1255 cm⁻¹ could be seen at the same time. At 849 and 759 cm⁻¹, the absorptions were attributed to Si–C bonds of –Si(CH₃)₃ groups. The Si–OH absorption (950 cm⁻¹) decreased sharply after modified with HMDS. From above data, it reveals that hydrophobic groups had been bonded onto the composite particles surface. Thereby, the absorption band of water absorbed on the composite particles around 3500 and 1637 cm⁻¹ decreased after modified with HMDS. In Fig. 2, the hydrophobicity of CaCO₃/SiO₂ composite particles and its precursor can be seen optically. The emulsion was formed when the precursor was put into the water. On the contrary, the composite particles still floated on water even after violent stirring.



Fig. 2. Hydrophobicity of composite particles (right) and its precursor (left).

It can be seen from Fig. 3 that mulberry-like composite particles with 4–10 μm diameter were fabricated by assembling small SiO₂ particles on the big CaCO₃ particles. EDS was performed to ascertain it was CaCO₃ inside the composite particles and the results are listed in Table 1.

Table 1
Component of CaCO₃/SiO₂ composite particles.

	C	O	Si	Ca
wt%	55	32	3	10
at%	66	29	2	3

The wettability of the surfaces was evaluated with the WCA and SA on the surfaces. Fig. 4a shows the shape of a water droplet on the surface of the PDMS self-assembly with composite particles hybrid. The WCA is about 165°, yet more importantly, the SA of this rough surface is ultra-low about 4°. In the contrast, the flat PDMS, while still hydrophobic, shows a significantly lower WCA (about 109°, Fig. 4b) and a 5 μL water drop could not slide from its surface even when the surface was completely vertical.

magnified for 5000 times, the surface still looks smooth. The similar information can be obtained from the AFM image. When the mulberry-like composite particles are doped into the PDMS system, the topographic image shows a two-level structure. The micrometer-level convexes are attributed to composite particles

To find out the effect of the surface structure on the wettability of film, SEM and AFM were used to examine the films with and without CaCO₃/SiO₂ composite particles. Fig. 5a1 shows a SEM image of the flat PDMS film without composite particles. Though

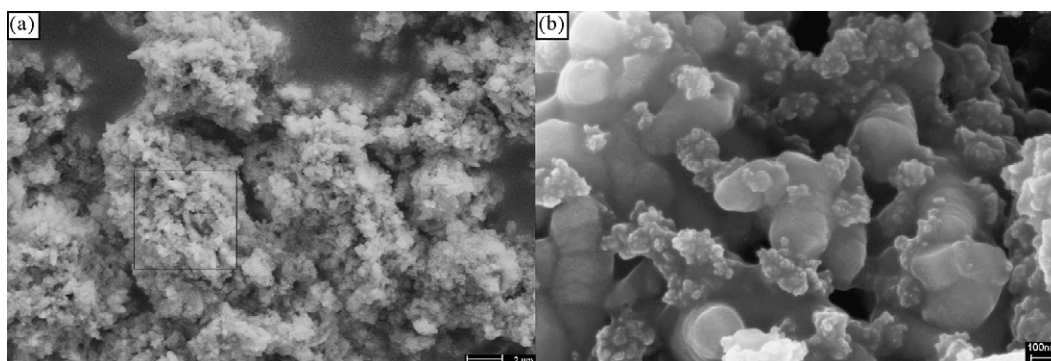


Fig. 3. SEM images of composite particles (b is the magnified image of a).

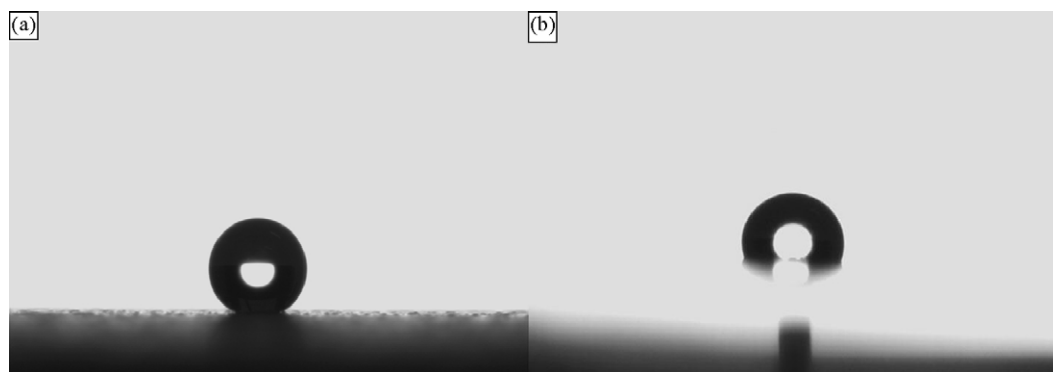


Fig. 4. Water drop profiles on PDMS surfaces with (a) and without (b) composite particles.

(Fig. 5a2). The magnified SEM image of the microconvexes (Fig. 5a3) shows that the microconvexes consist of many submicrometer or nanometer particles and pores. The particles were SiO₂ or their aggregate, and the pores were generated during the solvent volatilization.

In combination with WCA data, we believe that the surface roughness factor (r), which is the ratio of actual area of rough surface to the geometric projected area, plays a pivotal role in governing the surface wettability. And the surface roughness factor can be enhanced by the micro-submicro-nano-meter structure. The Wenzel model [29] and the Cassie model [30] have been proposed to explain this phenomenon. The Wenzel model describes a roughness regime in which both WCA and CA hysteresis increase as r increases (water penetrates into the surface cavity). The Cassie model describes that, as r further increases passing a critical level, the water receding angle also increases dramatically (water does not penetrate into the surface cavity; there is an air pocket between the water droplet and the

solid surface), thus minimizing the CA hysteresis [31]. Surface roughness factors were obtained from AFM software analysis. The WCA and roughness parameters of the film prepared in optimal composition are listed in Table 2. The roughness factor was calculated to be 2.2. The apparent WCA calculated from the Wenzel model (135.6°, based on the WCA of flat PDMS 109°) is much lower than experimental value (164°), which indicates that r had passed the critical value and there was a transition from the Wenzel regime to the Cassie regime. A composite surface had been formed to allow air pockets to exist between the water droplet and the solid face. In this case, WCA is described by the Cassie-Baxter equation as following:

$$\cos \theta_r^c = f \cos \theta + f - 1$$

where f is the area fraction of the solid in contact with liquid. θ_r^c and θ are the WCA on PDMS surface with rough and flat structures, respectively. The air trapped in the rough surface can significantly decrease the contact area between water and the solid surface of

Table 2

Statistical data of WCA and roughness parameters.

District		WCA (°)	SA (°)	Sa (nm)	Sq (nm)	Sdr	r	f	Calculated WCA (°) by Wenzel equation
A	1	165	4	201	261	117	2.17	0.053	134.95
	2	163							
	3	166							
	4	165							
	5	164							
B	1	163	5	217	269	119	2.19	0.0589	135.48
	2	160							
	3	165							
	4	165							
	5	166							
C	1	166	5	220	275	118	2.18	0.0492	135.21
	2	167							
	3	164							
	4	163							
	5	166							
D	1	162	7	189	258	121	2.21	0.0808	136.01
	2	159							
	3	160							
	4	161							
	5	163							
E	1	164	4	205	266	123	2.23	0.0404	136.55
	2	167							
	3	167							
	4	165							
	5	167							
Arithmetical mean		164.12	5	206.4	265.8	119.6	2.196	0.0566	135.64

^a The maximum WCA of flat PDMS is 109; $r = 1 + \text{Sdr}/100$ [32]; Sa, Sq and Sdr are roughness average, root mean square, and surface area ratio, respectively.

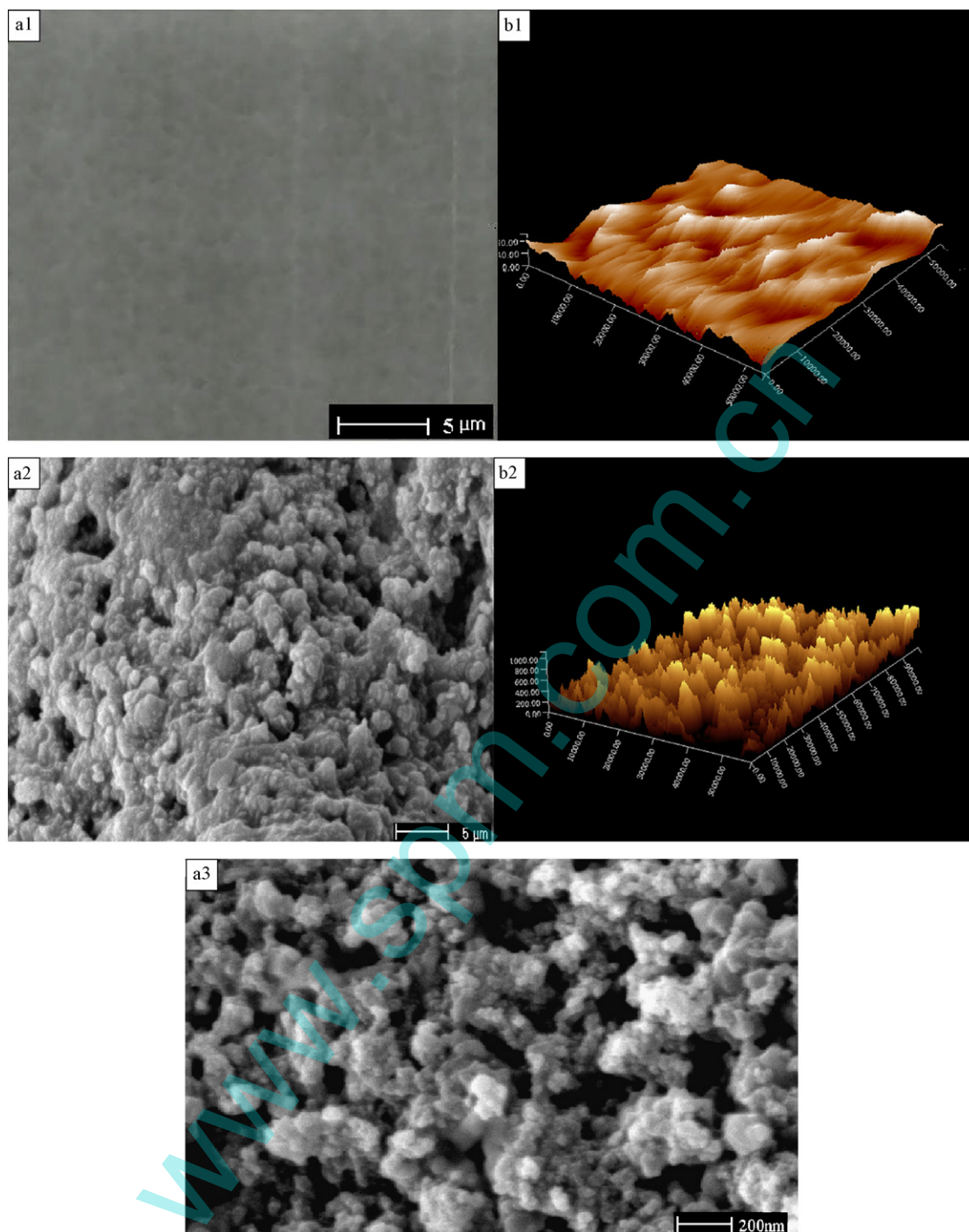


Fig. 5. SEM and AFM images of PDMS surfaces with (a2 and b2, a3 is magnified image of a2) and without (a1 and b1) composite particles.

PDMS, and thus, make the surface exhibit the high WCA and small SA. The value of f was calculated to be 0.057. This result implies that water does not penetrate the surface grooves on the films. Water droplet on the coating surface actually contacts with the extreme top portion of nano-protrusion so that water droplet has high static WCA and slides easily on the surface [31,33].

It cannot always lead to a useful superhydrophobic surface with well-defined particles [34]. In order to evaluate the effect of the concentration of composite particles on surface wettability, the WCAs of PDMS surfaces with various particles content were analyzed and the results are shown in Fig. 6. From the Fig. 6 curve a,

it can be seen that the WCA on PDMS surface changed insignificantly with the increase of particles content when the latter is lower than 40 g. The reason is likely that roughness constructed by composite particles was filled with PDMS due to surface migration of PDMS [31]. Thus the hydrophobicity of the surface was only attributed to the low surface energy of PDMS. When the content of particles is greater than 90 g, the values of WCA are higher than 150° and superhydrophobic surfaces can be fabricated by the combination of surface roughness and low surface energy. Samples with more than 110 g composite particles may show a higher hydrophobicity but a lower mechanical

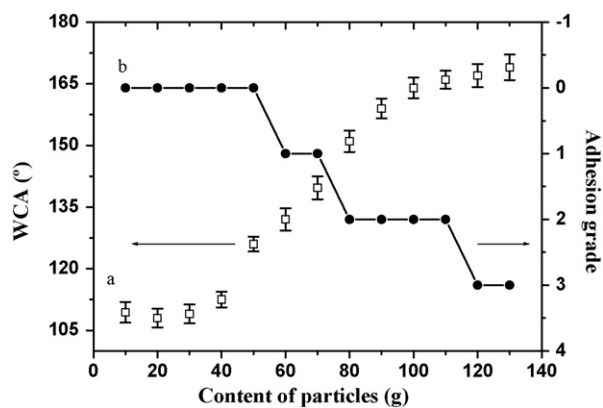


Fig. 6. The relationship between WCA and content of particles.

properties and adhesive attraction (Fig. 6 curve b). The adhesion is an important parameter of coating. The superhydrophobic surface based on PDMS has excellent adhesion on glass due to the glass has plenty of hydroxyls which can react with the hydroxyls of PDMS. So the adhesion was up to zero grade when the $\text{CaCO}_3/\text{SiO}_2$ composite particles content was lower than 50 g. However, the adhesion was found to be decreased with the increase of composite particles ratio successively, possibly because of the decreased reactive point, PDMS hydroxyls, reacted with the hydroxyls of substrate surface. According to GB/T-9286-1998, the adhesion can meet the requirement in practical application when it is not lower than second grade. A value of 110 g can be picked out as the most satisfying composite particles content, which simultaneously contained comprehensive properties of adhesion and hydrophobicity.

4. Conclusion

This paper has demonstrated a convenient and effective method to prepare superhydrophobic films by means of employing mulberry-like $\text{CaCO}_3/\text{SiO}_2$ composite particles and self-assembly of PDMS. Compared with other complex processes, this procedure is simple and potentially usable to fabricate large-area superhydrophobic surfaces for practical self-cleaning applications. More importantly, such surface is superhydrophobic with WCA higher than 160° and SA lower than 10° .

Acknowledgements

The authors thank the financial support of this work by Natural Science Foundation of China (no. 20506005). Thanks go to Dr. Ailan Qu and Master Tuo Li for their beneficial discussions and assistance in experiment.

References

- [1] R.P. Garrod, L.G. Harris, W.C.E. Schofield, J. McGettrick, L.J. Ward, D.O.H. Teare, J.P.S. Badyal, *Langmuir* 23 (2007) 689.
- [2] Y. Li, X.J. Huang, S.H. Heo, C.C.H. Li, Y.K. Choi, W.P. Cai, S.O. Cho, *Langmuir* 23 (2007) 2169.
- [3] W. Chen, Y. Fadeev, M.C. Heieh, D. Öner, J. Youngblood, T.J. McCarthy, *Langmuir* 15 (1999) 3395.
- [4] H. Yamashita, H. Nakao, M. Takeuchi, Y. Nakatani, M. Anpo, *Nucl. Instrum. Meth. B* 206 (2003) 898.
- [5] J.M. Lim, G.R. Yi, J.H. Moon, C.J. Heo, S.M. Yang, *Langmuir* 23 (2007) 7981.
- [6] Y. Yu, Z.-H. Zhao, Q.S.H. Zheng, *Langmuir* 23 (2007) 8212.
- [7] W. Barthlott, C. Neinhuis, *Planta* 202 (1997) 1.
- [8] I. Woodward, W.C.E.V. Roucoules, J.P.S. Badyal, *Langmuir* 23 (2007) 8212.
- [9] X.J. Feng, L. Feng, M.H. Jin, J. Zhai, L. Jiang, D.B. Zhu, *J. Am. Chem. Soc.* 126 (2004) 62.
- [10] H.M. Shang, Y. Wang, S.J. Limmer, T.P. Chou, K. Takahashi, G.Z. Cao, *Thin Solid Films* 472 (2005) 37.
- [11] T.L. Sun, G.J. Wang, L. Feng, B.Q. Liu, Y.M. Ma, L. Jiang, D.B. Zhu, *Angew. Chem. Int. Ed.* 43 (2004) 357.
- [12] H.Y. Erbil, A.L. Demirel, Y. Avci, *Science* 299 (2003) 1377.
- [13] J.P. Youngblood, T.J. McCarthy, *Macromolecules* 32 (1999) 6800.
- [14] K. Teshima, H. Sugimura, Y. Inoue, O. Takai, A. Takano, *Appl. Surf. Sci.* 244 (2005) 619.
- [15] H. Notsu, W. Kubo, I. Shitanda, T. Tatsuma, *J. Mater. Chem.* 15 (2005) 1523.
- [16] Y. Wu, H. Sugimura, Y. Inoue, O. Takai, *Chem. Vap. Deposition* 8 (2002) 47.
- [17] H. Li, X. Wang, Y. Song, Y. Liu, Q. Li, L. Jiang, D. Zhu, *Angew. Chem.* 113 (2001) 1793.
- [18] L. Feng, S. Li, H. Li, J. Zhai, Y. Song, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* 41 (2002) 1221.
- [19] C. Guo, L. Feng, J. Zhai, G. Wang, Y. Song, L. Jiang, D. Zhu, *Chem. Phys. Chem.* 5 (2004) 750.
- [20] X. Lu, C. Zhang, Y. Han, *Macromol. Rapid Commun.* 25 (2004) 1606.
- [21] Q. Xie, J. Xu, L. Feng, L. Jiang, W. Tang, X. Luo, C.C. Han, *Adv. Mater.* 16 (2004) 302.
- [22] H. Yabu, M. Takebayashi, M. Tanake, M. Shimomura, *Langmuir* 21 (2005) 3235.
- [23] D.K. Sarkar, M. Farzaneh, R.W. Paynter, *Mater. Lett.* 62 (2008) 1226.
- [24] H. Murase, T. Fujibayashi, *Prog. Org. Coatings* 31 (1997) 97.
- [25] M.T. Khorasani, H. Mirzadeh, *J. Appl. Polym. Sci.* 91 (2004) 2042.
- [26] M.H. Jin, X.J. Feng, J.M. Xi, J. Zhai, L. Kilwon Cho, L. Feng, *Macromol. Rapid Commun.* 26 (2005) 1805.
- [27] B. Liu, Y.N. He, Y. Fan, X.G. Wang, *Macromol. Rapid Commun.* 27 (2006) 1859.
- [28] F.S. Li, Y. Yang, *Composite Technology of Micrometer/Nanometer Materials and Its Application*, National Defence Industry Press, Beijing, 2002.
- [29] R.N. Wenzel, *J. Phys. Colloid. Chem.* 53 (1949) 1466.
- [30] A.B.D. Cassie, S. Baxter, *Trans. Faraday Soc.* 40 (1944) 546.
- [31] A.L. Qu, X.F. Wen, P.H. Pi, J. Cheng, Z.R. Yang, *Appl. Surf. Sci.* 253 (2007) 9430.
- [32] P. Jouko, J. Mikael, A. Sami, *Langmuir* 20 (2004) 9428.
- [33] C.H. Su, J. Li, H.B. Geng, Q.J. Wang, Q.M. Chen, *Appl. Surf. Sci.* 253 (2006) 2633.
- [34] W. Li, A. Amirfazli, *Soft Matter* 4 (2008) 462.