Fabrication of Silica Nanoparticle-Based Transparent Superhydrophobic Coatings

Xinde Tang[a], Xiuying Hu, Haichuan Jia, Xiaoman Sun and Hongtao Ling

School of Material Science and Engineering, Shandong Jiaotong University, Jinan 250357. China

[a]xdtang8033@163.com

Keywords: Silica nanoparticle; hexadecyltrimethoxysilane; transparent superhydrophobic coating

Abstract. One-step dip-coating process was employed to fabricate transparent superhydrophobic coating on the glass surface by using the mixture of silica nanopartilces and hexadecyltrimethoxysilane in anhydrous ethanol using triethylamine as hydrolysis catalyst. The water contact angle and optical transmittance were measured for samples using all particle-substrate combination. The results indicate that the superhydrophobicity and transparency of the obtained coatings depend on the aggregation states of silica nanoparticles, which are determined by the concentration of silica nanoparticle in the suspensions.

Introduction

Hydrophobic surfaces have attracted significant attention due to extensive applications such as self-cleaning, anticorrosion, anti-icing, and so forth [1-3]. It is now well-known that superhydrophobic surfaces result from the combination of a low surface energy and high surface roughness, and they have been achieved through the control of both chemical composition and morphological structure [4]. Various research groups have tried to develop fabrication techniques for superhydrophobic surfaces based on a variety of top-down and bottom-up approaches [5,6].

Recently, there has been increasing interest in transparent superhydrophobic coatings for optically transparent applications including solar cells, lenses, and windows [7-9]. However, the fabrication of such surfaces has often involved complex or expensive processes, required techniques that were not suitable for a variety of substrates and particles, required surface pre- or post-treatment, or lacked wear resistance [10]. More recently, on-step coating technique of hydrophobic silane-treated nanoparticles that yield transparent superhydrophobic properties has been reported and the effect of the surface structures on the hydrophobicity and transparency has been described [9,11].

In this paper, a facile method by using silica nanoparticles for the fabrication of transparent superhydrophobic coatings is presented. This method does not require additional surface treatments to enhance the adhesive force between the substrate and the coated materials. A simple approach to confer significant superhydrophobic and transparent coatings by easily tuning the surface morphology, which can be controlled by varying the concentration of silica nanoparticles in the solution.

Experimental

Materials. Fumed silica nanoparticle was kindly offered by Prof. Feng's group of Shandong University of China. The silane coupling agent hexadecyltrimethoxysilane (HDTMS) was purchased from Aladdin Reagent Company. The other reagents were used as received without further purification.

Preparation of silica hybrid nanoparticles. Silica nanoparticles (0.4 g) were dispersed in anhydrous ethanol (9.6 g), and then HDTMS (0.2 g) was added into the silica solution under ultrasonication, resulting in a modified silica dispersion solution with a concentration of 4 wt%. Following the procedure, the other modified silcia dispersion solutions with concentration of 2 wt%, 1 wt%, 0.5 wt%, and 0.25 wt% were prepared, respectively. Triethylamine (0.05 mL) was injected to each of the above-mentioned solutions under ultrasonication and the resultant solutions were allowed to react for 12 h at ambient temperature.

Dip-coating of silica nanoparticles on glass substrate. The glass slides (1 cm×4 cm) without pre-treatment were immersed in the dispersion solution for 30 seconds, and taken out by vertical lift, then dried at room temperature overnight.

Characterization. The morphologies of the samples were examined with a scanning electron microscope (SEM, Hitachi S-4800) at 8 kV. The water contact angles were measured on CA100A instrument, and the droplet size of deionized water was controlled to be 5 μL. The optical transparencies of the coated substrates were measured with UV−vis spectrophotometry (Cary-5000, Varian).

Results and Discussion

Fabrication of superhydrophobic coatings. The content of silica nanoparticles was adjusted by dilution in anhydrous ethanol. In this work, five systems with different concentration of silica nanoparticles formed. The dependence of water contact angle on the content of silica nanoparticle is shown in Fig. 1. The original glass surface displayed a water contact angle of 92.3^o. With an increase of silica content, the water contact angle increases, while the higher value occurred between the concentration of 0.5-1 wt%. Thereafter the water contact angle decreased slightly with an increase in concentration. This can be attributed to the combination of low surface energy materials and micro/nano hierarchical structures [5,12]. This result also indicates that the optimal silica nanoparticle concentration plays an important role for the fabrication of superhydrophobic coatings.

The surface superhydrophobicity derives from low surface energy material and surface roughness, which resulted from silane coupling agent (HDTMS) and silica nanoparticles. Under ambient temperature, with triethylamine as hydrolysis catalyst, HDTMS transforms form silane to silanol, which can interact with the hydroxyl groups on the surface of silica nanoparticle and glass slide, resulting in the stacking of modified silica nanoparticles on the surface. SEM images of resulting coatings on the glass surface are shown in Fig. 2. In the original state, the glass surface shows smooth. With 0.25wt% of silica nanoparticles was applied, a continuous film with a few small protuberances was observed with a water contact angle of 143.6^o. When the concentration of silica nanoparticle increases to 0.5 wt%, microscale island-like structured aggregates formed, which provides enough surface roughness to achieve the large water contact angle of 152.6^o. Further increasing the concentration, no obvious increase of water contact angle can be observed. On the other hand, with an increase of concentration, the coatings become thicker and denser, maybe resulting in crack and other negative effect on the surfaces. This indicates that high concentration of silica nanoparticles is unfavorable for such coatings. Therefore, the optimal concentration is of 0.5-1 wt% in this case.

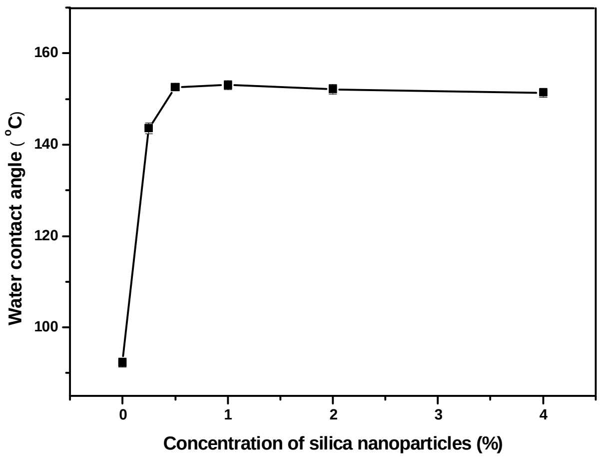

Fig. 1 Dependence of water contact angle on the concentration of silica nanoparticles.

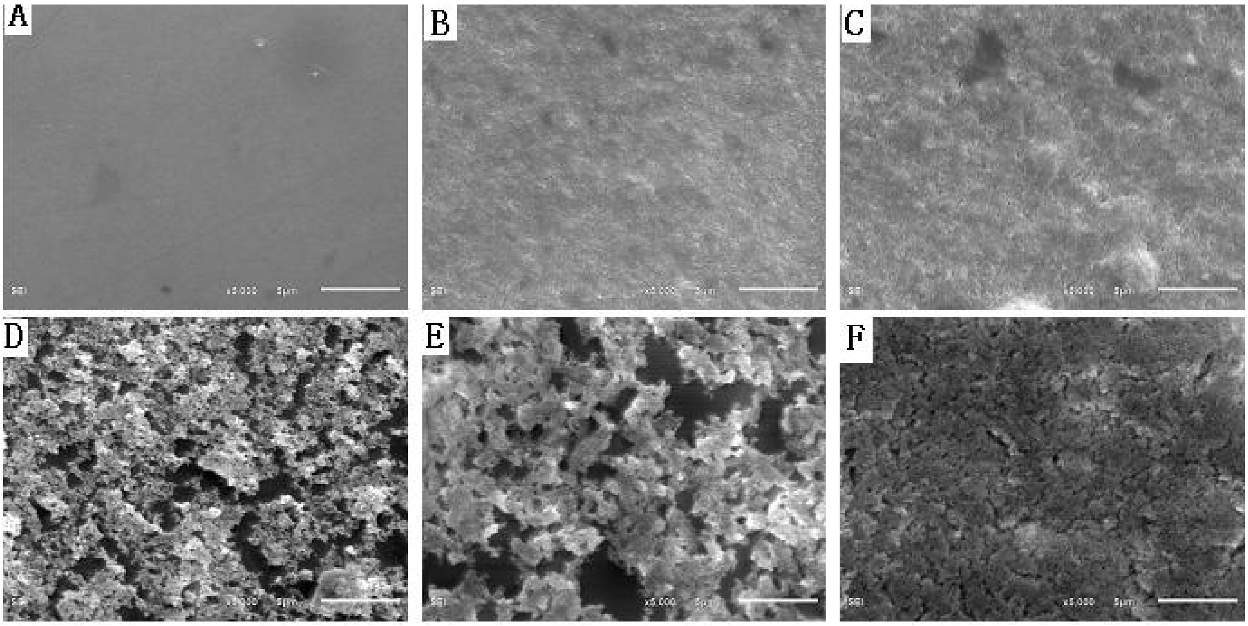

Fig. 2 SEM images of the initial glass surface (a) and the modified glass surfaces by different concentration of 0.25 wt% (b), 0.5 wt% (c), 1 wt% (d), 2 wt% (e), and 4 wt% (f) of silica nanoparticle. Scale bar: 5 μm.

In addition to the superhydrophobic properties, we investigated the transperancy of the silica-coated glass substrates with UV-vis transmittance spectra, with a view to assessing the potential applications in window treatments or optical devices. The transmittance profiles of the samples with increasing the concentration of silica nanoparticles are shown in Fig. 3. When the concentration of the silica nanoparticles is of lower than 0.5 wt%, the transmittance of the coated glass is over 60%, being comparable to bare glass. When the concentration is greater than 0.5 wt%, both the surface roughness and the film thickness are higher. As a result, light scattering increases, leading to reduced transparency. In general, superhydrophobicity and transparency are mutual contradiction, the enhanced superhydrophobicity derived from surface roughness maybe gives rise to dereased transparency. To some extend, an increase of silica concentration can lead to increased hydrophobicity and dereased transparency. The optimal concentration is one of the key factors for the fabrication of transparent superhydrophobic surfaces. Taken all factors into consideration, the concentration of 0.5 wt% is suitable for his case.

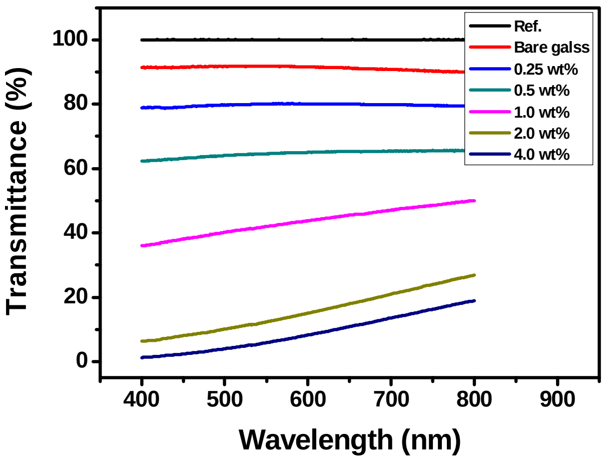

Fig. 3 Transmittance spectra of coatings on glass substrates with various concentration of silica nanoparticles.

The durability of the prepared transparent superhydrophobicity coatings under ambient conditions was tested. The properties of the coated surface with the concentration of lower than 0.5 wt% are durable without obvious change within one month.

Summary

A facile technique for the fabrication of transparent superhydrophobic coatings by dip-coating method without pre- or post-treatment of the substrate. No further surface modification was required in the method, which can be applied to large-scale fabrication on various substrates. The effects of varying the concentration of silica nanoparticles on the water repellency and on the transparency of the coated glass substrates. Increased concentration of silica nanoparticles facilitates the transition between the superhydrophobic and transparent states. The resulted coatings can also display high durable stability. The facile strategy, with no expensive instruments, multi-step procedure, complicated conditions, or special reagents, has some advantages for preparation of transparent superhydrophobic film or coatings. It is anticipated that the present technique has various practical applications in the fabrication of transparent superhydrophobic coatings.

Acknowledgements This work was financially supported by Shandong Provincial Science and Technology Development Plan Project of China (2014GGX102013).

References

[1] K. Liu, L. Jiang: Annu. Rev. Mater. Res. Vol. 42 (2012), p. 231

[2] Y. Zhu, J.C. Zhang, Y.M. Zheng, Z.B. Huang, L. Feng and L. Jiang: Adv. Funct. Mater. Vol. 16 (2006), p. 568

[3] L. Cao, A.K. Jones, V.K. Sikka, J.Z. Wu and D. Gao. Langmuir Vol. 25 (2009), p. 12444

[4] Y. Lai, Y. Tang, J. Gong, L. Chi, C. Lin and Z. Chen: J. Mater. Chem. Vol. 22 (2012), p. 7420

[5] T.L. Sun, L. Feng, X.F Gao and L. Jiang: Acc. Chem. Res. Vol. 38 (2005), p. 644

[6] S.G. Lee, H.S. Lim, D.Y. Lee, D. Kwak and K. Cho: Adv. Funct. Mater. Vol. 23 (2013), p. 547

[7] J. Bravo, L. Zhai, Z.Z. Wu, R.E. Cohen and M.F. Rubner: Langmuir Vol. 23 (2007), p. 7293

[8] S.G. Lee, D.Y. Lee, H.S. Lim, D.H. Lee, S. Lee and K. Chok: Adv. Mater. Vol. 22 (2010), p. 5013

[9] H. Ogihara, J. Xie, J. Okagaki and T Saji: Langmuir 28 (2012), p. 4605

[10] D. Ebert and B. Bhushan: Langmuir Vol. 28 (2012), p. 11391

[11] X.D.Tang, S.Q Nan, T.S Wang, Y. Chen, F.Q. Yu, G.Y. Zhang and M.S.Pei: RSC Adv. Vol. 3 (2013), p. 15571

[12] X. Gao and L. Jiang: Nature Vol. 432 (2004), p. 6