



Available online at www.sciencedirect.com



CERAMICS INTERNATIONAL

Ceramics International 41 (2015) 3017-3023

www.elsevier.com/locate/ceramint

Superhydrophobic coatings prepared from methyl-modified silica particles using simple dip-coating method

Annaso B. Gurav^{a,b}, Qingfeng Xu^a, Sanjay S. Latthe^c, R.S. Vhatkar^b, Shanhu Liu^{a,c,*}, Hyun Yoon^d, Sam S. Yoon^{d,**}

^aInstitute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, P.R. China ^bDepartment of Physics, Shivaji University, Kolhapur 416 404, Maharashtra, India

^cPhotocatalysis International Research Center, Research Institute for Science & Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan ^dSchool of Mechanical Engineering, Korea University, Seoul 136-713, Republic of Korea

> Received 7 October 2014; received in revised form 13 October 2014; accepted 23 October 2014 Available online 30 October 2014

Abstract

A simple and time-saving approach for preparing self-cleaning superhydrophobic silica coatings using a dip-coating technique is reported in this study. Commercially available silica particles were modified with methyl groups using methyltrichlorosilane as a modifying agent. By adopting a multi-layer deposition process, a superhydrophobic silica coating with a water contact angle of $153^{\circ} \pm 2^{\circ}$ and roll-off angle of $8^{\circ} \pm 1^{\circ}$ was obtained. The prepared silica coating exhibited excellent self-cleaning performance; moreover, it was able to maintain superhydrophobicity under the impact of a water jet. This method could be an effective strategy for fabricating self-cleaning superhydrophobic surfaces for promising industrial applications.

© 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Superhydrophobic; Dip coating; Silica; Interface; Self-cleaning

1. Introduction

Many biological surfaces, particularly some plant leaves [1,2], exhibits remarkable water repellence (superhydrophobicity). As a result, they are highly self-cleaning. The wellknown high water repellency and self-cleaning properties of lotus leaves [3] have attracted a lot of attention and have generated much interest in fundamental research, as well as in industrial applications. In the practical design of multifunctional surfaces, artificially mimicking the functionalities of the lotus leaf surface for solid surfaces could help meet the increasing need for self-cleaning materials in daily real-world and industrial applications. It is well known that the wettability of a solid surface can be controlled by its chemical

E-mail addresses: Shanhuliu@henu.edu.cn (S. Liu), skyoon@korea.ac.kr (S.S. Yoon).

http://dx.doi.org/10.1016/j.ceramint.2014.10.137

composition and morphological structure (i.e., surface roughness) [4]. An appropriate combination of the surface roughness and low surface energy is one of the key criteria for preparing artificial superhydrophobic surfaces. Numerous methods for developing artificial superhydrophobic surfaces and their possible applications have been summarized in recent review articles [5-10]. Many studies have attempted to synthesize rough or patterned solid surfaces to obtain superhydrophobic properties using expensive equipment and tedious procedures. Moreover, some methods for creating superhydrophobic surfaces require the repetition of the entire experimental process, which can be time-consuming and laborious reducing their applicability [11]. Therefore, the development of a simplified synthetic method for preparing superhydrophobic surfaces has remained a challenge. Therefore, in this article, we discuss a simple, economical, and time-saving method for preparing superhydrophobic silica coatings on glass substrates using dip coating. Silica was chosen as the coating material because it exhibits excellent intrinsic characteristics such as non-toxicity, high

^{*}Corresponding author.

^{**}Co-corresponding author.

^{0272-8842/© 2014} Elsevier Ltd and Techna Group S.r.l. All rights reserved.

thermal and mechanical stability, and easy structural regulation [12]. Hence, it becomes very popular and is widely used in the field of coating technology, especially for preparing superhydrophobic silica coatings. Different hydrophobic organosilane compounds, in combination with silica precursors, have been applied to various substrates for preparing superhydrophobic silica coatings using different methods [13-18]. Gao and McCarthy [19] prepared a perfectly hydrophobic surface with a water contact angle of $> 170^{\circ}$ on a silicon wafer by submerging it in a toluene solution of methyltrichlorosilane (MTCS) at room temperature. Khoo and Tseng [20] described in detail the hydrophobic engineering of three-dimensional nano-architectures with various shapes, morphologies, and sizes using the phase separation of MTCS on glass and silica substrates. Khalilabad and Yazdanshenas [21] demonstrated a dip-pad-dry coating method for depositing graphene oxide on cotton fibers. When combined with a subsequent reaction with MTCS, the method vielded polymethylsiloxane (PMS) nanofilaments on the fiber surface, which converted highly water-absorbing insulator cotton fabrics into textile-based substrate conductors with superhydrophobic properties. Shirgholami et al. [22] recently reported the deposition of polymethylsilsesquioxane (PMSQ) nanostructures onto the surface of cotton fabric and adopted the subsequent modification in a toluene solution of MTCS at room temperature with different duration times to achieve superhydrophobic cotton fabrics. The present work offers an effective and simple method for preparing self-cleaning superhydrophobic coatings on glass substrates. In our experiment, silica particles were easily modified by methyl groups using MTCS as a modifying agent; they were then applied to a glass substrate using a simple dip-coating technique.

2. Experimental

2.1. Materials

Silicon dioxide (SiO₂) particles (~99%) with diameters in the range 0.5–10 μ m (~80% in the range 1–5 μ m), MTCS (\geq 97%), and toluene (anhydrous, 98.8%) were purchased from Sigma Aldrich, U.S.A., and all the chemicals were used as received without any further purification. Glass micro-slides (Blue Stars^(R)) were purchased from Polar Industrial Corporation (India).

2.2. Preparation of superhydrophobic silica coating

Prior to coating, the glass micro-slide substrates were cleaned thoroughly using the procedure described in our earlier report [23]. The method employed for preparing the superhydrophobic silica coating was as follows: initially, 1 g of pristine SiO₂ particles was dispersed in 20 ml of toluene and ultrasonicated for 15 min. In the next step, 0.6 ml of MTCS was added slowly to this mixture, which was again ultrasonicated for another 2 h to obtain homogenous solution. Finally, the coatings were prepared using a simple dip-coating method at room temperature (~ 27 °C). A schematic of the dip-coating process is shown in Fig. 1. A well-cleaned glass substrate was dipped into the coating solution for 5 s and then

withdrawn at a constant speed of ~5 mm/s after which was kept in air at room temperature for 5 min. The same coating procedure was repeated two more times under a fixed condition with the same sample to obtain a uniform and rough-textured silica coating. All the prepared coatings were first kept in room temperature for an hour to enhance the adhesion of the coating material to the substrate, and then annealed in air at 150 °C for 5 h with a ramping rate of 2 °C/min to eliminate the residual solvent. Finally, silica coatings prepared after one, two, and three dips were characterized in detail by suitable techniques.

2.3. Characterizations

The surface morphologies of the coatings were analyzed using a field emission scanning electron microscope (FE-SEM) (Hitachi, S-4800), and surface chemical analyses of the coatings were performed using the energy dispersive X-ray (EDX) method for a sample area of $100 \,\mu\text{m}^2$. The surface topographies and roughness values of the prepared coatings were analyzed using laser microscopy (KEYENCE, VK-X200 series). Here, the surface roughness of each coating was measured for a $50 \times 50 \ \mu\text{m}^2$ planar area in the non-contact mode. The surface roughness of each coating was measured in at least ten different areas, and the average value of these measurements was taken as the final value. Optical photographs were obtained using a Canon digital camera (G 15 series). The static water contact angles and sliding angles were measured over five different areas on a sample using a contact angle meter (Ramehart Instrument Co., USA), and the average value of these measurements was selected as the final value. The angle at which a placed water droplet started to move from the coated surface was recorded as the sliding angle value.

3. Results and discussion

3.1. Surface morphology and chemical composition

In general, rough-textured solid structures with a low surface energy demonstrate strong non-wetting characteristics. Fig. 2(a-c)



Fig. 1. Schematic showing simple dip-coating process for deposition of methyl-modified silica particles on glass substrate.



Fig. 2. FE-SEM images of the silica coatings prepared from (a) 1, (b) 2, and (c) 3 dips.

shows the FE-SEM images of the silica coatings prepared after one, two, and three dips, respectively. A fairly homogeneous distribution of small-diameter silica particles was observed to be deposited on the substrate after one dip (Fig. 2a). Because the coating solution was composed of silica particles with diameters ranging from 0.5 to 10 µm, at the outset, smaller-diameter silica particles were uniformly dispersed and deposited on the substrate during the dip-coating process. These smaller-diameter particles, rather than the larger-diameter particles, first randomly occupied all the available sites and adhered to the substrate by weak van der Waals forces. In the next dipping process, an increasing number of silica particles with miscellaneous sizes from the solution adhered to the already deposited silica particles. Consequently, a rough surface morphology was observed after two dips, as compared to the morphology after the single dip coating (Fig. 2b). Further, with additional dips, more silica particles are attached to the previously deposited silica particles on the substrate. As a result, a dense layer of silica particles was formed after three dips (Fig. 2c) that increased the surface roughness considerably. This surface morphology was partially analogous to the surface micro/nanostructure of a lotus leaf. An electron microscope image of a lotus leaf surface shows a rough hierarchical structure with cuticles arranged at

regular intervals [3], which produces a high water contact angle $(>150^{\circ})$ on the surface, and causes droplets to roll-off the surface at a very small sliding angle $(\le 5^{\circ})$ with slight disturbance. From Fig. 2c, we can observe that the coated surface has a rough morphology, which allows a large amount of air to be entrapped in the rough protrusions; this is a principal requirement of super-hydrophobicity. Thus, it is clear from the FE-SEM images that increasing the dipping steps allows a larger number of silica particles to assemble gradually on the substrate surface and produce a rough surface morphology.

Surface roughness is considered a critical parameter for determining the degree of surface wettability. Threedimensional (3-D) laser microscope images of the silica coatings prepared after one, two, and three dips are shown in Fig. 3 (a–c), respectively. Based on these images, it is clear that the coating surfaces exhibited different topographical features after each dip. Fig. 3a shows the surface topography of the silica coating prepared after one dip; the surface roughness of the coating formed after one dip was mostly due to the deposition of low-diameter silica particles, which may be the reason for the low surface roughness. Fig. 3b and c



Fig. 3. Three-dimensional laser microscope images of silica coatings prepared after (a) one, (b) two, and (c) three dips.

shows the surface topographies of the silica coatings prepared after two and three dips; the surface roughness values increased to 0.527 and 1.118 μ m, respectively. During the second and third dips, an increasing number of silica particles with different sizes were deposited on the substrate. As a result, the surface roughness of the coating is also increased. Hence, we can conclude that the surface roughness is dependent on the number of dips. In particular, the surface roughness obtained after three dips could increase the water repellence of the coating.

The EDX spectrum of the silica coating prepared after three dips was recorded to investigate the elemental composition of the coated material, as shown in Fig. S1 (Supplementary Information); Si, O, and C elemental peaks were observed. The presence of the C peak in the spectrum was due to the MTCS, which implied the existence of methyl groups. The presence of the Si, O, and C elements could be attributed to the strong interaction between carbon containing groups, that is –CH₃, and the silica particles. This formed Si-O-CH₃-oriented groups on the surface contributed to improve the water repellence of the coating. The absence of a chlorine peak in the spectrum

suggests that the MTCS was fully hydrolyzed during the reaction.

3.2. Surface wettabilities of the coatings

The ultimate tests to prove the formation of superhydrophobic surfaces is static and dynamic water contact angle measurements. The wetting properties of surfaces are commonly described by Young's equilibrium contact angle equation [24], which is applicable to smooth solid surfaces. However, most of the solid surfaces are intrinsically rough and often have micro-nano scale roughness. Therefore, the effect of the surface roughness on the contact angle is defined using the Wenzel model, which describes a fluid droplet pinned to the rough features of a surface [25], while, in the Cassie-Baxter model, air is entrapped in the rough texture underneath the droplet that forms a composite air and solid interface [26]. Fig. 4 shows the variation in the static water contact angle with respect to the number of dips, where the insets are optical images of the water droplets on the respective coating surfaces. The coatings prepared from unmodified silica



Fig. 4. Variation in static water contact angle with number of dips.

particles exhibited complete wetting with a water contact angle of almost 0° . This observation was expected because the pristine silica particles were hydrophilic in nature because of the immediate formation of Si-OH sites when water molecules interact with silica particles. Fig. 4 shows that the water contact angle is dependent on the number of dips. As the number of dips increased, the water contact angle increased. The coating prepared after one dip exhibited a hydrophobic behavior, with a static water contact angle of $113^{\circ} + 4^{\circ}$. When the coating was prepared after two dips, the water contact angle increased to $128^{\circ} \pm 2^{\circ}$, which could be attributed to the increased surface roughness. The water contact angle reached $153^{\circ} \pm 2^{\circ}$ for the silica coating prepared after three dips, indicating the formation of a superhydrophobic surface. This high contact angle indicated a low surface energy in conjunction with a high surface roughness—a large amount of air was trapped within the interspaces of the coated surface, which pushed the water droplet off. A further increase in the number of dips (>3) did not increase the water contact angle, which remained the same. The study on the sliding angle showed that water droplets rolled-off the silica coatings prepared after one, two, and three dips at angles of $43^{\circ} + 5^{\circ}$, $27^{\circ} + 3^{\circ}$, and $8^{\circ} + 1^{\circ}$, respectively. This indicates that as the number of dips increased, water droplets started to lose their adhesion to the surface, imparting a self-cleaning capability to the coatings. Conversely, in the case of coatings prepared by dipping the substrate for a prolonged time of 1 min, instead of preparing the coatings by changing the number of dips, it was observed that the coated surface was white and opaque, and the coating material could be completely removed from the substrate simply by gentle air blowing.

Fig. 5a shows an image of water droplets on the superhydrophobic silica-coated glass substrate; the water droplets resemble spherical balls. These water droplets were colored blue using methylene blue (MB) to obtain a clear optical image of them. As shown in Fig. 5b, large-volume water droplets (around 1 ml) were created by adding water to water droplets ($\sim 10 \ \mu$ l) that were already on the coated surface. In this study, the substrate was intentionally adjusted to be perfectly horizontal because the surface was highly water repellent, and a small tilting angle could also cause the water droplets to



Fig. 5. Optical images of (a) water droplets ($\sim 10 \ \mu$ l) and (b) large-volume water droplets ($\sim 1 \ m$ l) on superhydrophobic silica coating prepared after three dips.

roll-off the surface. When the droplet volume reached about 1 ml, the droplet still maintained a spherical shape. This was because, up to this volume, the droplet size was comparable to the capillary length, and the gravitational effect was negligible. However, with the further addition of water, the hydrostatic force exerted on a small area of the droplet–air interface at the bottom dominated the capillary force, and the gravitational force tended to flatten the droplet. Thus, the spherical-shaped water droplet acquired an elliptical shape owing to its increased volume. It was difficult for this large-volume water droplet to remain on the coating surface because on hydrophobic surfaces, droplets are more sensitive to gravitational force.

Glass surfaces quickly get dirty owing to the accumulation of dust and dirt particles from the environment. They could be made self-cleaning by applying a superhydrophobic coating. The self-cleaning performance of the silica coating was investigated using carbon powder as contaminant dust particles. Fig. 6a shows the self-cleaning functionality of the silica coating. A thin layer of carbon powder was sprinkled onto the superhydrophobic silica coating prepared after three dips, and then, a water droplet was gently placed on this contaminated surface. The contaminant particles were immediately adsorbed on the surface of the water droplet as soon as they came into contact with the water droplet. After several sliding and rolling processes, the water droplet completely adsorbed the contaminant particles, and the carbon powder was easily removed from the surface by simply rolling the water droplets, which confirmed the excellent self-cleaning ability of the prepared silica coating.

When considering real-world practical applications, it is essential for superhydrophobic surfaces to maintain their water repellent properties under the high-speed impact of water droplets and water jets. The continuous bombardment of high-speed water droplets or jets can destroy or squeeze out the air trapped within the rough structure of a



Fig. 6. Optical images of (a) self-cleaning behavior and (b) water-jet impact on superhydrophobic silica coating prepared after three dips.

superhydrophobic coating owing to their impact, which subsequently causes wetting of the surface. In addition, most superhydrophobic surfaces are found to be fragile and can be easily damaged by the impact of a high-speed water jet, causing them to lose their superhydrophobicity. This restricts the practical application of superhydrophobic coatings. Therefore, it is essential to consider the impact dynamics of a water jet to acquire a precise understanding of the non-wetting properties of superhydrophobic surfaces. This could be one of the most important aspects for determining the self-cleaning capability of a superhydrophobic coating. Fig. 6b shows a jet of water produced under normal pressure that impinges on a superhydrophobic surface at an angle $\sim 45^{\circ}$. It was observed that the jet was completely repelled by the surface and reflected at the same angle of $\sim 45^{\circ}$, without leaving a trace of water on the surface. The water jet impacted the entire coating surface. Further, the surface remained clean and superhydrophobic, with no damage to the coating surface, even after the continuous impact of water on the surface for 30 min from a height of ~ 10 cm. Thus, such hydrophobic coatings can be expected to satisfy future demands of practical applications of superhydrophobic surfaces for self-cleaning technology.

4. Conclusions

We have successfully fabricated self-cleaning superhydrophobic silica coatings by applying a simple dip-coating method. The methyl-modified silica particles provided a typical surface roughness and low surface energy coatings, which yielded characteristics such as high water repellency, self-cleaning capability, and sustainability under a water-jet impact. The results of this study can significantly contribute to the development of superhydrophobic coatings over large surface areas for practical applications.

Acknowledgments

Mr. Annaso B. Gurav is highly grateful to the Council of Scientific and Industrial Research-Human Resource Development Group (CSIR-HRDG), New Delhi, Government of India, for providing financial support by awarding the Senior Research Fellowship (SRF) [File no. 09/816(0036)/2012-EMR-I, Dated 30/03/2012]. He also would like to express his gratitude for extending the SRF for a third year. We greatly appreciate the support of the National Natural Science Foundation of China (21101056, 21105021). This work was partly supported by KETEP (No. 20133030010890), NRF-2013R1A2A2A05005589, and NRF-2013M3A6B1078879.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint. 2014.10.137.

References

- K. Koch, W. Barthlott, Superhydrophobic and superhydrophilic plant surfaces: an inspiration for biomimetic materials, Philos. T. Roy. Soc. A 367 (1893) (2009) 1487–1509.
- [2] S.S. Latthe, C. Terashima, K. Nakata, A. Fujishima, Superhydrophobic surfaces developed by mimicking hierarchical surface morphology of lotus leaf, Molecules 19 (4) (2014) (4256-83).
- [3] W. Barthlott, C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, Planta 202 (1) (1997) 1–8.
- [4] X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang, D. Zhu, Reversible superhydrophobicity to super-hydrophilicity transition of aligned ZnO nanorod films, J. Am. Chem. Soc. 126 (1) (2003) 62–63.
- [5] Z. Guo, W. Liu, B.-L. Su, Superhydrophobic surfaces: from natural to biomimetic to functional, J. Colloid Interface Sci. 353 (2) (2011) 335–355.
- [6] Y.-K. Lai, Z. Chen, C.-J. Lin, Recent progress on the superhydrophobic surfaces with special adhesion: from natural to biomimetic to functional, J. Nanoeng. Nanomanuf. 1 (1) (2011) 18–34.
- [7] S.S. Latthe, A.B. Gurav, S.M. Chavna, R.S. Vhatkar, Recent progress in preparation of superhydrophobic surfaces: a review, J. Surf. Eng. Mater. Adv. Technol. 2 (2) (2012) 76–94.
- [8] Y.-L. Zhang, H. Xia, E. Kim, H.-B. Sun, Recent developments in superhydrophobic surfaces with unique structural and functional properties, Soft Matter 8 (44) (2012) 11217–11231.
- [9] E. Celia, T. Darmanin, E. Taffin de Givenchy, S. Amigoni, F. Guittard, Recent advances in designing superhydrophobic surfaces, J. Colloid Interf. Sci. 402 (0) (2013) 1–18.
- [10] N. Valipour M, F.C. Birjandi, J. Sargolzaei, Super-non-wettable surfaces: a review, Colloid Surface A 448 (0) (2014) 93–106.
- [11] Y.S. Choi, J.S. Lee, S.B. Jin, J.G. Han, Super-hydrophobic coatings with nano-size roughness prepared with simple PECVD method, J. Phys. D: Appl. Phys. 46 (31) (2013) 315501.
- [12] D. Membreno, L. Smith, B. Dunn, Silica sol-gel chemistry: creating materials and architectures for energy generation and storage, J. Sol-Gel Sci. Technol. 70 (2) (2014) 203–215.
- [13] C.-T. Hsieh, F.-L. Wu, S.-Y. Yang, Superhydrophobicity from composite nano/microstructures: carbon fabrics coated with silica nanoparticles, Surf. Coat. Technol. 202 (24) (2008) 6103–6108.

- [14] S.S. Latthe, C. Terashima, K. Nakata, M. Sakai, A. Fujishima, Development of sol-gel processed semi-transparent and self-cleaning superhydrophobic coatings, J. Mater. Chem. A 2 (15) (2014) 5548–5553.
- [15] L. Xue, J. Li, J. Fu, Y. Han, Super-hydrophobicity of silica nanoparticles modified with vinyl groups, Colloid Surface A 338 (1–3) (2009) 15–19.
- [16] A. Venkateswara Rao, S.S. Latthe, D.Y. Nadargi, H. Hirashima, V. Ganesan, Preparation of MTMS based transparent superhydrophobic silica films by sol–gel method, J. Colloid Interf. Sci. 332 (2) (2009) 484–490.
- [17] A. Yildirim, T. Khudiyev, B. Daglar, H. Budunoglu, A.K. Okyay, M. Bayindir, Superhydrophobic and omnidirectional antireflective surfaces from nanostructured ormosil colloids, ACS Appl. Mater. Interf. 5 (3) (2013) 853–860.
- [18] N. Wang, D. Xiong, Influence of trimethylethoxysilane on the wetting behavior, humidity resistance and transparency of tetraethylorthosilicate based films, Appl. Surf. Sci. 292 (0) (2014) 68–73.
- [19] L. Gao, T.J. McCarthy, A perfectly hydrophobic surface ($\theta A/\theta R = 180^{\circ}/180^{\circ}$), J. Am. Chem. Soc. 128 (28) (2006) 9052–9053.

- [20] H.S. Khoo, F.-G. Tseng, Engineering the 3D architecture and hydrophobicity of methyltrichlorosilane nanostructures, Nanotechnology 19 (34) (2008) 345603.
- [21] M. Shateri-Khalilabad, M. Yazdanshenas, Preparation of superhydrophobic electroconductive graphene-coated cotton cellulose, Cellulose 20 (2) (2013) 963–972.
- [22] M.A. Shirgholami, M. Shateri-Khalilabad, M.E. Yazdanshenas, Effect of reaction duration in the formation of superhydrophobic polymethylsilsesquioxane nanostructures on cotton fabric, Text. Res. J. 83 (1) (2013) 100–110.
- [23] A.B. Gurav, S.S. Latthe, R.S. Vhatkar, J.-G. Lee, D.-Y. Kim, J.-J. Park, S.S. Yoon, Superhydrophobic surface decorated with vertical ZnO nanorods modified by stearic acid, Ceram. Int. 40 (5) (2014) 7151–7160.
- [24] T. Young, An essay on the cohesion of fluids, Philos. T. Roy. Soc. London 95 (1805) 65–87.
- [25] R.N. Wenzel, Resistance of solid surfaces to wetting by water, Ind. Eng. Chem. 28 (8) (1936) 988–994.
- [26] A.B.D. Cassie, S. Baxter, Wettability of porous surfaces, T. Faraday Soc. 40 (0) (1944) 0546–0550.