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Fabrication of robust, transparent PMMA/SiO_2 nanocomposite superhydrophobic films with self-cleaning property

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Optically transparent poly(methyl methacrylate) (PMMA)/ SiO_2 nanocomposite superhydrophobic films were fabricated by a dip coating method for a small piece of specimen, and a spray-on coating method for a large specimen such as a glass panel. The PMMA molecules were incorporated to improve the film's robustness and adhesion between the substrate and the film. The coating precursor was prepared by mixing 0.1-0.3 wt.% PMMA with respect to the SiO_2 content into 2 wt.% fumed SiO_2 suspension. The hierarchical surface structure was fabricated by depositing a layer of micrometer-sized SiO_2 aggregate obtained from 2.0 wt.% fumed SiO_2 suspension followed by a layer of nanometer-sized SiO_2 aggregate obtained from 0.5 wt.% fumed SiO_2 suspension hydrophobized with trichloro (1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl) silane. Under the optimun condition, the dip-coated film exhibited water contact angle (WCA) of 160.4 degrees and transmittance of 95.0%. The spray-coated film exhibited slightly less WCA of 140.1 degrees and transmittance of 85.0%. The nanocomposite film had good adhesion based on a peel off test following the ASTM D 3359-02 standard, and good anti-dusting property making it feasible for self-cleaning coating of glass panel.

Key words: Superhydrophobic, Water repellent, Nanocomposite, Self-cleaning, Poly(methyl methacrylate), SiO_2 nanoparticle.

Introduction

Superhydrophobic surfaces are generally found in plant surfaces such as the surface of lotus leaf. Such surfaces exhibit self-cleaning property thanks to their unique hierarchical surface structure which consists of micrometer-scaled protrusions covered with natural wax-like nanoparticles. Electron microscopic investigation of these surfaces in the 1990s has triggered investigations both in fundamental and application aspects [1-2]. Biomimetic liquid-repellent surface exhibiting self-cleaning property similar to the phenomenon observed on the lotus leaf has been successfully realized by a variety of methods [3-11].

For optical coating application, SiO_2-based transparent liquid-repellent films have been fabricated by combining transparent property of the SiO_2 and low-surface energy molecules such as fluorohydrocarbon and alkyl groups [12-14]. It has been recently demonstrated that a robust and highly transparent superhydrophobic film comprising of polydimethylsiloxane (PDMS) and ethyl α-cyanoacrylate can be fabricated on the etched surface [15]. Micro/nano surface structure was created by selective flowing of the ethyl α-cyanoacrylate into the pits on the etched surface while the main body of the film was mainly constituted by the PDMS. The PDMS has also been employed as binding layer between the fluorosilane-modified SiO_2 layer and the substrate to fabricate a robust, transparent superhydrophobic coating [16]. A different approach to prepare transparent superhydrophobic films has been reported by melting polytetrafluoroethylene micro powder over a glass substrate [17].

In this present work, the robust and transparent superhydrophobic films of PMMA/SiO_2 nanocomposite were coated onto glass substrate by using a simple dip coating method. The PMMA was selected due to its high optical transparency and binding property that can enhance the film's robustness as well as adhesion between the film and the substrate. Aerosil® 200 fumed SiO_2 having an average particle size of 12 nm and specific surface area of 200 m^2/g was employed at different suspension concentration to create hierarchical structure comprising of both micrometer-scaled and nanometer-scaled roughness similar to surface of the lotus leaf. To realize its pratical use, a spray-on coaing method was employed to deposit the film onto large glass panel, and the film was tested for self-cleaning property.

Experimental Procedure

Fabrication of PMMA/ SiO_2 nanocomposite superhydrophobic film

Hierarchical hydrophobic film (Fig. 1) was fabricated

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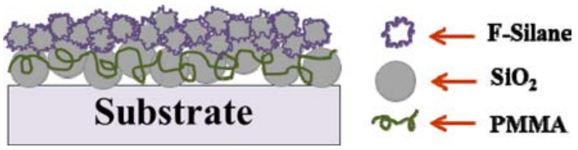

Fig. 1. Schematic depiction of the film's structure.

by depositing the first layer of micrometer-sized SiO_2 aggregate followed by depositing the second layer of fluorosilane-modified nanometer-sized SiO_2 aggregate. Coating precursor for the micrometer-sized SiO_2 aggregate was obtained by dispersing 2 wt.% fumed SiO_2 (Aerosil® 200, JJ-Degussa, an average particle size of 12 nm) in 2-propanol. To improve adhesion between the film and the substrate, 0.1, 0.2 or 0.3 wt.% PMMA with respect to the amount of the SiO_2 was added into the suspension. The precursor for submicrometer-sized SiO_2 aggregate was obtained from more diluted suspension by dispersing 0.5 wt.% fumed SiO_2 in 2-propanol. This submicrometer SiO_2 aggregate was modified with 0.4 v/v% (in 2-propanol) of trichloro (1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl) silane (TPFS, $CF_3(CF_2)_5CH_2CH_2SiCl_3$, 97%, Aldrich) to bear hydrophobic functionality. A typical procedure is as follow. 0.52 g of TPFS was dissolved in 100 ml of 2-propanol, and then 0.5 wt.% of fumed SiO_2 was added into the TPFS solution followed by vigorous stirring for 1 hr.

The substrate employed was a glass slide which was ultrasonically cleaned with ethanol, acetone and de-ionized water, respectively, followed by soaking in Piranha solution (a mixed solution of conc. H_2SO_4 and 30% H_2O_2 with volume ratio of 3 : 1) at room temperature for 30 min, washing with large amount of de-ionized water. This cleaning procedure would give rise to pristine glass surface with high hydrophilicity as observed by fully wet characteristics. For a small piece of glass substrate, the film coating was performed by dipping the clean glass slide into the coating precursors for 5 or 10 min and then withdrawing at a speed of 0.1 mm/sec. Finally, the specimen was dried in the oven at 120 °C for 1 h. A spray-on coating was employed for coating on a large glass panel.

Characterization

Surface morphology was observed by using a field-emission scanning electron microscope (FE-SEM, JSM 6301F) and an atomic force microscope (AFM, SPA 400) performed in a non-contact mode. Surface's wettability was evaluated by measuring water contact angle by using a goniometer (ramé-hart instrument). A 5-µl liquid droplet was mounted onto the specimen's surface using a microsyring. Photo of the liquid droplet was recorded using a CCD camera, and a curvature profile was created and the contact angle measured. The measurement was repeated on five locations covering the entire sample's area. The film's transparency was measured by using a UV-Visible spectrophotometer (PerkinElmer, Lambda 650) in the wavelength range of 400-800 nm. Self-cleaning property was tested as follow. Powder of black pigment was sprinkled over the 30 °-tilted specimen at both coated and uncoated portions. Then, water was continuously dropped and the pigment removal observed.

Adhesion between the film and the substrate was evaluated by means of a peel off test following the ASTM standard (D 3359-02) [18]. The adhesion test was conducted by applying an adhesive tape (3M Scotch® tape) over cuts made in the film, rubbing with uniform pressure, and then peeling off the adhesive tape. Images of the specimen before and after the tape test were taken using an optical microscope to determine the extent of film removal. A classification of 5B, 4B, 3B, 2B, 1B and 0B was assigned for a percentage of area removal of 0, < 5, 5-15, 16-35, 36-65 and > 65%, respectively.

Results and Discussion

Fig. 2 shows water contact angles of the dip-coated films on glass slides fabricated at various concentrations of PMMA and at 5- and 10-min soaking time during the dip coating process. In the absence of PMMA binder, the water contact angles of 118.0 deg. and 135.5 deg. were obtained at the soaking times of 5 and 10 min, respectively. In both cases, the water contact angle gradually increases with the increased concentration of PMMA, reaching 147.8 deg. for 5 min soaking and 163.6 deg. for 10 min soaking at the PMMA concentration of 0.2 wt.% and became constant afterward. This result suggests that sufficient time is required to allow complete attachment of aggregated SiO_2 nanoparticle to the glass substrate which can be enhanced by pre-coating the substrate with the PMMA binder. Thus, the PMMA

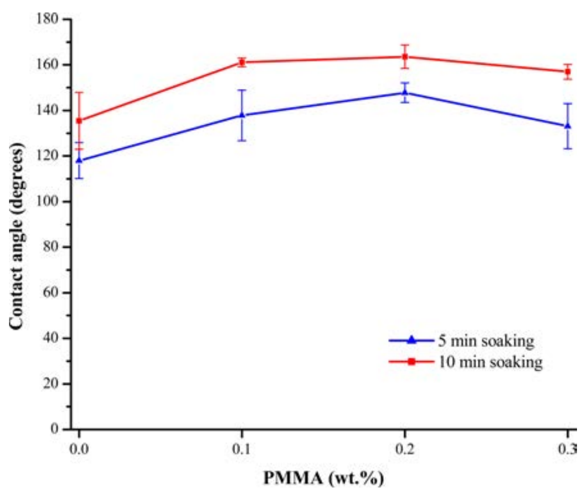

Fig. 2. Water contact angle of the dip-coated films on glass substrates fabricated at various concentrations of PMMA and soaking times.

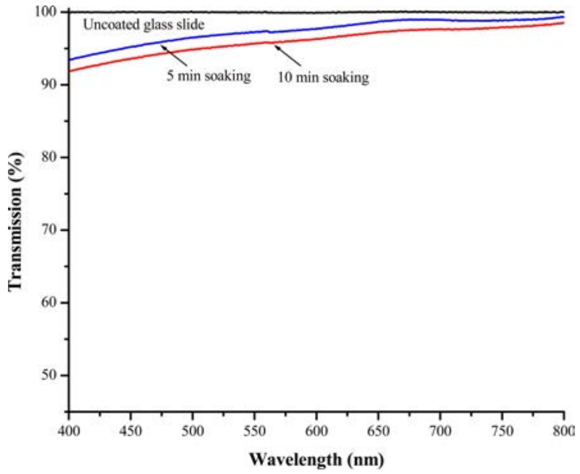

Fig. 3. Transmission spectra of the dip-coated films on glass substrates treated with and without the Piranha solution at soaking times of 5 and 10 min.

concentration of 0.2 wt.% was chosen for the next study.

To further investigate the effect of glass cleaning procedure on the film's quality, the glass substrate was cleaned just by ethanol, acetone and de-ionized water without subsequent soaking in the Piranha solution. The films deposited onto this substrate at PMMA concentration of 0.2 wt.% had water contact angles of 149.4 deg. for 5 min soaking and 160.4 deg. for 10 min soaking. It is thus obvious that both the films deposited onto the glass slides cleaned by both methods have comparable water contact angles. In the other word, the subsequent cleaning with the Piranha solution is not neccessary in this case. In our previous work, without the use of binding layer, the Piranha cleaning step is important in order to achieve a uniform coating. Therefore, the PMMA binder played the important role for the attachment aggregated SiO_2. This cleaning precedure would be appropriate for large glass panel coating by the spray-on method in which case cleaning by soaking it in the strong oxidizing Piranha solution is inconvenient. Fig. 3 is optical transmission spectra of the dip-coated films on the glass substrates, cleaned by ethanol, acetone and de-ionized water without subsequent soaking in Piranha solution, at soaking times of 5 and 10 min. All the specimens had the transmittance of approximately $95 \pm 1.5\%$ which was slightly less than that of the uncoated glass substrate indicating their good optical transparency. The film prepared by 5-min soaking is slightly more transparent than the 10-min soaking film due to its less thickness.

Fig. 4(a-b) shows SEM images of the spray-coated films consisting of 0.2 wt% PMMA in the first layer. A

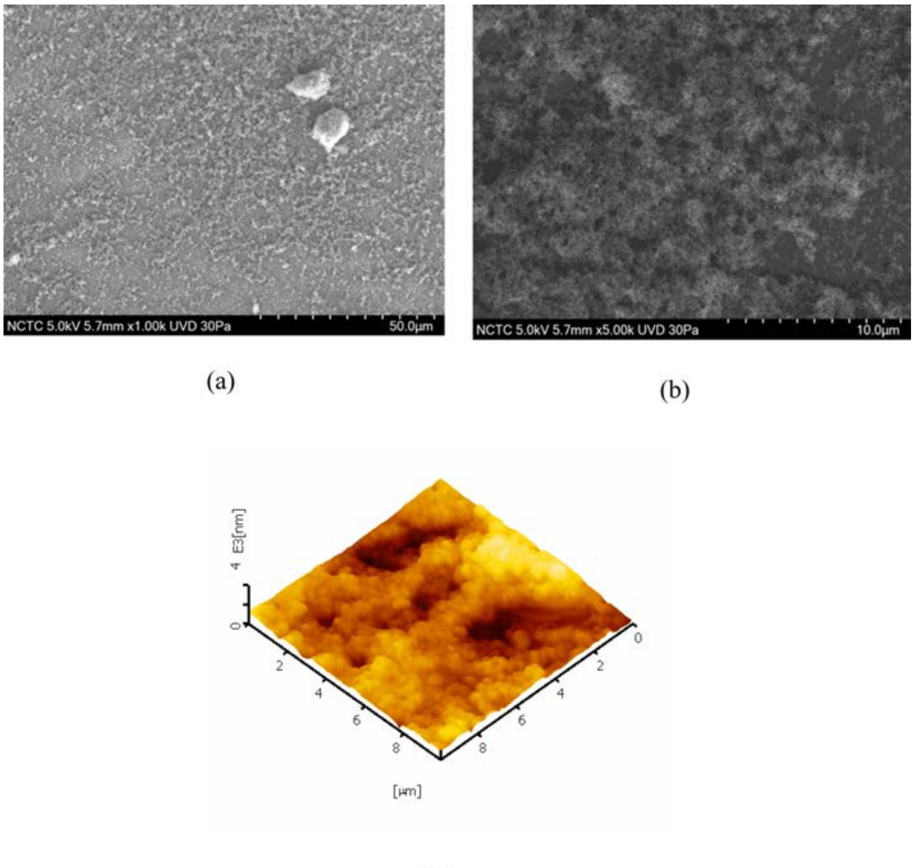

Fig. 4. SEM images of the spray-coated films consisting of 0.2 wt.% PMMA in the first layer.

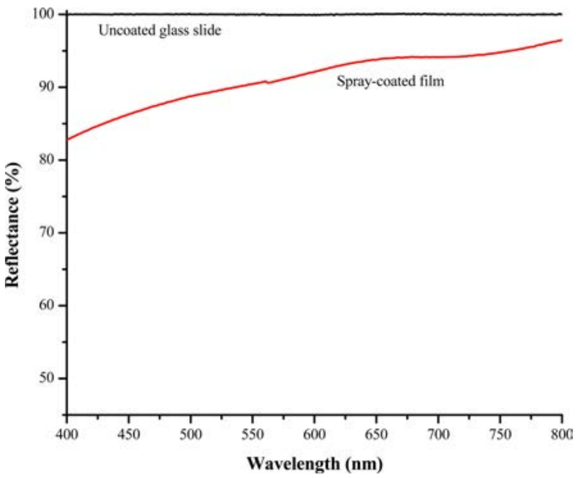

Fig. 5. Transmission spectra of the spray-coated film consisting of 0.2 wt.% PMMA.

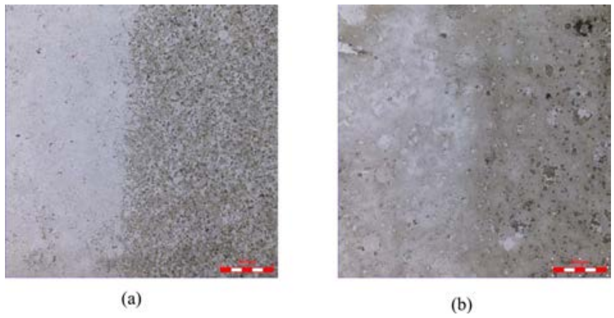

Fig. 6. Optical images of specimen after the tape test showing film removal area (left side) compared to the untested area (right side). (a) the films without the PMMA, and (b) the film consisting of 0.2 wt.% PMMA.

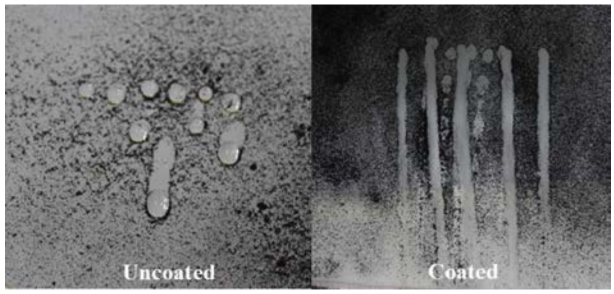

Fig. 7. Photographs taken after continuously dropping of water over the coated and uncoated portions cover with black pigment.

lower-magnification image (Fig. 4(a)) clearly reveals that the surface is covered with micrometer-sized aggregated SiO_2 particles, and a higher-magnification image (Fig. 4(b)) reveals the presence of submicrometer-sized aggregated SiO_2 particles with highly porous structure. Some large aggregated particles of approximately 10 microns is also observed. Such large aggregated particles was not observed in the films deposited by dip coating because such large aggregated particles had settled down to the bottom of the container during a dip coating step. An AFM image of the same specimen (Fig. 4(c)) shows better view for surface topography, revealing hills and valleys structure having double-scaled roughness similar to surface of the lotus leaf. That is, it comprises of a micrometer-sized roughness created by the deposition of large aggregated SiO_2 and a nanometer-sized roughness created by the primary SiO_2 nanoparticles. This surface has the RMS roughness of 168.6 nm, which is very high on the basis of enhancing surface roughness by means of deposition of oxide nanoparticle.

Fig. 5 is optical transmission spectrum of the spray-coated film on the glass substrate. The film has average transmittance of 85% and water contact angle of 140.1 degrees. The decrease of optical transparency compared to the uncoated glass is a good tradeoff for the gained superhydrophobic property. The optical transparency could be improved by employing more diluted SiO_2 suspension for the first layer, for example 1 wt.% instead of 2 wt.% as employed in a typical experiment. However, the resulting film showed less water contact angle. Thus, in practical, a good balance between the optical transparency and hydrophobicity can be manipulated for the spray-on coating method.

Results of a peel off test following the ASTM D 3359-02 standard revealed that film removal of around 75% was observed for the film without PMMA binder. It is classified to ‘0B’, which is poor adhesion. In contrast, the film consisting of PMMA binder shows slight removal of around 25%, and thus can be classified to ‘2B’. Additional testing was set aside to further compare the film’s adhesion. The adhesive tape was placed on only half portion of the specimen (left side in the images). Uniform pressure was applied, and then the adhesive tape was peeled off. Optical images of the films spray-coated from the suspension without the PMMA and the suspension consisting of 0.2 wt.% PMMA are shown in Fig. 6(a) and 6(b), respectively. It is obvious that significant film removal was observed on the film without the PMMA, and much less removal was observed for the film consisting of the PMMA. According to the adhesion test, the films fabricated in this work would be of sufficient adhesion for practical use.

Fig. 7 shows photographs after continuously dropping of water over the coated and uncoated portions cover with black pigment particles. The coated portion shows clear paths as a result of water droplets rolling off the surface and picking up the pigment particles along their paths. In contrast, water tended to spread out over the uncoated portion and did not roll off. Such self-cleaning result would be observed on the outdoor glass panel coated with this superhydrophobic film. Self-cleaning phonomenon by lotus effect of the superhydrophobic film can be attributed to air pockets in the film which consists of high fraction of pores as observed in the SEM image in Fig. 4(b). It has been described that liquid droplets cannot penetrate into micropores easily on the superhydrophobic surface because the air trapped in the micropores has greater floating force to liquid droplet, reflecting higher air resistance against wettability [19]. The deposition of aggregated SiO_2 fume created large amount of void in the film as well as at its surface, preventing liquid penetration into the film and therefore enhancing liquid roll off over its surface.

Conclusions

It has been demonstrated that durable, transparent, PMMA/ SiO_2 superhydrophobic film having self-cleaning property were fabricated by a 2-step coating; the deposition of micrometer-scaled SiO_2 aggregate mixed with PMMA binder followed by the deposition of nanometer-scaled SiO_2 aggregate modified with trichloro (1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl) silane to bear hydrophobic functionality at the outer most surface. Under the optimum condition, the dip-coated film exhibited water contact angle of 160.4 degrees and transmittance of 95.0% while the spray-coated film exhibited water contact angle of 140.1 degrees and transmittance of 85.0%. A slight decrease of water repellent and optical transparent properties is a good trade off for hydrophobicity considering that the spray-on is a versatile coating method that can be coated on variety of substrates with no size and line-of-sigth limitations. The film was robust and had good anti-dust effect, thus can be used for self-cleaning application.

Acknowledgments

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