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Robust super-hydrophobic ceramic coating on alumina with water and dirt repelling properties

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Abstract

Artificial super-hydrophobic surfaces are required for various applications. The super-hydrophobic surfaces are usually made by applying a low surface-energy organic coating on a highly textured substrate. A major problem with the as-created surfaces is their poor durability. This problem is even severer for the surfaces created by applying the organic coating on inorganic substrates. The present study reports for the first time the all-inorganic super-hydrophobic surface created by modifying the inorganic substrates with polymer-derived inorganic coating. A polydimethylsiloxane (PDMS) film was applied to an alumina substrate having flower-like hierarchal micro-nano surface texture, and then subjected to pyrolysis at 400°C in a nonoxidizing atmosphere. As a result, a $Si_r C_v O_z$ ceramic coating with low-surface energy methyl groups was formed on the alumina substrate. The as-modified alumina exhibited super-hydrophobicity with a water contact angle of 170° and a sliding angle of 5°. The super-hydrophobicity was well retained after abrasion with sandpaper and exposure to boiling water and acidic solution. The super-hydrophobic alumina demonstrated desired water repelling and self-cleaning function. The method explored in this study could also be used for super-hydrophobic surface modification of other inorganic materials such as glass and metals.

KEYWORDS

ceramics, coating, self-cleaning, super-hydrophobic, textured surface

1 | INTRODUCTION

In nature, many super-hydrophobic surfaces exist such as lotus leaves,^{1,2} butterfly wings,^{3,4} rice leaves.¹ Biomimetic super-hydrophobic surfaces have attracted great attentions due to its potential applications such as self-cleaning,^{5–8} an-tifogging,^{9,10} anti-icing¹¹ and oil/water separation.^{12,13} These surfaces are usually made by modifying highly textured (rough) substrates with a low-surface tension organic coating such as perfluoroalkylsilanes (PFAS),^{14,15} fluoroalkylsilanes (FAS),^{16,17} or polydimethylsiloxane (PDMS).¹⁸ The major drawback of the as-prepared super-hydrophobic surfaces

is their poor durability. Due to the similar chemical nature, the organic polymer coating adheres better to the polymer substrate. Likewise, the hydrophobic inorganic (ceramic) coating, if available, would adhere better to the inorganic (ceramic) substrate.

Ceramics (carbides, nitrides, and oxides) can be prepared using various polymer precursors via pyrolysis process. Note that the preceramic polymer precursors usually consist of low-surface tension organic groups such as methyl groups. By conducting the pyrolysis at intermediate temperatures and in the inert atmosphere, some of the organic groups could be preserved in the pyrolytic product. Consequently, the derived ceramics would be hydrophobic.¹⁹ Our previous study showed that the porous alumina disk modified with pyrolytic PDMS was hydrophobic with a water contact angle of 136°.²⁰

The hydrophobicity of a surface, which is primarily determined by its surface chemical composition, is affected by its roughness as well. As illustrated by the two distinct models developed by Wenzel²¹ and Cassie-Baxter²² respectively, the apparent contact angle of a hydrophobic surface increases with increasing roughness. The roughness can be enhanced by constructing hierarchical micro-nano structure on the surface. For alumina, a variety of micro/nano structures including fibers,^{23,24} rods,²⁵ tubes,²⁶ wires,²⁷ and sheets^{2,28,29} have been synthesized, which could be converted into super-hydrophobic by modification with low-surface energy materials.³⁰

In this paper, we report for the first time the all-ceramic super-hydrophobic surface by modifying ceramic substrates with a polymer-derived ceramic coating. An alumina substrate having a flower-like hierarchal micro-nano surface texture was coated with a PDMS film, and then subjected to heat treatment at elevated temperatures in a nonoxidizing atmosphere. The heat treatment converted the PDMS film into an amorphous ceramic coating to which low-surface energy methyl groups were bound. The as-treated alumina exhibited durable super-hydrophobicity and water and dirt repelling properties, promising for practical applications.

2 | EXPERIMENTAL PROCEDURE

2.1 | Preparation and surface modification of alumina

Disk-shape alumina was prepared using the phase-inversion tape casting/sintering method, as described elsewhere.^{31,32} Then a γ -Al₂O₃ layer was grown on the alumina disk by using the hydrothermal method as follows.³³ A solution was prepared by dissolving 5 g of Al(NO₃)₃·9H₂O and 0.2 g NaOH in 35 mL deionized water, to which 0.1 g hexamethylenete-tramine was added under stirring. The solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and mixed using a magnetic stirrer for 10 minutes. Finally, the alumina disk was put into the above-mixed solution, and the autoclave was sealed and maintained for 24 hours at 200°C.

The surface of the alumina disk was modified using the procedure as follows. A solution was prepared by adding the PDMS precursor, TEOS, and a DBTDL catalyst to n-heptane and stirred for 30 minutes at room temperature. An alumina disk was immersed into the as-prepared solution and kept for 20 minutes at room temperature. Then, the alumina disk was removed from the solution, and transferred to a tubular oven, heated to 400°C and held for 2 hours. The whole heating and cooling process was conducted in a nonoxidizing atmosphere of H_2/N_2 (flow ratio $H_2:N_2 = 5:95$). For comparison,

the surface of another alumina disk was modified by immersing it in the PDMS solution followed by curing at 130°C for 2 hours in air atmosphere.

2.2 | Characterization

X-ray diffraction measurements were performed using Cu (K) radiation on a powder X-ray diffractometer (XRD, BrukerD2phaser) to analyze the phase composition of the alumina disks. The microstructure of the alumina disks was observed with scanning electron microscopy (SEM) (ZEISS, GeminiSEM500, Germany) and high-resolution transmission electron microscopy (HRTEM) (JEM, ARM-200F, JEOL, Japan). Fourier transform infrared spectroscopy (FT-IR) (Thermo Nicolet 8700, USA) were used to determine the chemical composition of the coating on the alumina disks. The sessile-drop method was applied to measure the water contact angles of the modified alumina disks using contact angle meters (SL200B, Chenghui, China; G100, KRUSS, Germany) with drop volume of 5 µL. The contact angles were taken as an average of at least five measurements at different positions on the same sample. A high-speed camera (FASTCAM SA5 1000K-M3, Photron, Japan) was used to observe the behavior of the droplets after reaching the surface, which was either placed horizontally or tilted at 5°.

2.3 | Durability and self-cleaning tests

The durability of the as-modified alumina disks was examined by immersing them in aqueous solutions of pH 2 and 12, boiling water for a certain period. After cleaning and drying, the water contact angles of the disks were measured again. Abrasion tests were carried out by placing them on sandpaper (No. 240, Shanghai Grinding Wheel Factory, China) under a weight of 100 g (Figure 1); in one cycle, the disks were abraded for 10 cm transversely and longitudinally, respectively. Self-cleaning tests on the as-modified alumina disks were conducted. The disks were inserted into water dyed with methylene blue and then taken out. MnO_2 with a particle size of 50 nm was placed on the disks and then removed with running water.



FIGURE 1 The scheme of the abrasion test. The wafer weighted 100 g was faced down to the sandpaper [Colour figure can be viewed at wileyonlinelibrary.com]

3 | RESULTS

Alumina disks were obtained by the phase-inversion tape casting/sintering method. To increase the surface roughness of the alumina disks, a flower-like layer of thickness 53 μ m was grown on the surface using the hydrothermal method (Figure 2A,B). The XRD patterns of the layer were indexed to γ -Al₂O₃ (Figure 2C). The disks were then modified with a PDMS film and subjected to different heat treatment. For the sample heat-treated at 130°C in the air for 2 hours, its surface was obscured by the PDMS polymer film (Figure 3A). In

contrast, for the sample heat-treated at elevated temperature of 400°C in nonoxidizing atmosphere for 2 hours, the flower-like feature of the γ -Al₂O₃ layer comprising nano-needles of length 300-400 nm and width 40-50 nm remained clearly visible (Figure 3B). The surface of the alumina nano-needles was covered by a thin film as shown by the HRTEM image (Figure 3C). The film was composed of Si, C and O elements as revealed by EDS mapping (Figure 3D). The Si_xC_yO_z film itself was amorphous while the underlying alumina needle was crystalline, and the former adhered to the latter tightly (Figure 3E).

FIGURE 2 (A) Top surface SEM image of the substrate, (B) cross-sectional image of the substrate, (C) XRD patterns of the γ -Al₂O₃ layer [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 3 (A) SEM image of the cured sample, (B) SEM image of the pyrolytic sample, (C) HRTEM image of the alumina needles in the pyrolytic sample, (D) the corresponding EDS elemental mapping, (E) Close-up image of the area marked in image (C), insets are the HRTEM image and the electron diffraction pattern of the alumina needle [Colour figure can be viewed at wileyonlinelibrary.com]





3200 2800 2400 2000 1600 1200 800 Wavenumber (cm⁻¹)

FIGURE 4 IR spectra of PDMS on alumina heat-treated under various conditions [Colour figure can be viewed at wileyonlinelibrary. com]

The IR spectra for the samples heat-treated under different conditions are shown in Figure 4. The peaks at 2960 and 1260 per cm corresponded to asymmetric CH₃ stretching and CH₃ deformation, respectively. The peaks at 1030 and 1080 per cm were associated with the symmetric Si-O-Si stretching, and the peak at ~800 per cm was related to the Si–C stretching (and the CH₃ rocking in Si–CH₃).^{20,34,35} For the sample heat-treated at 130°C, the PDMS polymer was cured, resulting in the crosslinking of the polymer chain. The CH₃ peaks of the cured sample were strong and comparable to the original PDMS. In contrast, for the sample heat-treated at elevated temperature of 400°C, the pyrolysis of the PDMS polymer occurred. The pyrolytic sample showed a much weaker CH₃ peaks, indicating that a large number of methyl groups had been removed from the PDMS. The pyrolytic sample exhibited the characteristic peaks for the Si–O and Si–C bond observed in amorphous $Si_xC_yO_z$, demonstrating that the PDMS polymer had been converted into ceramic.

The cured sample was hydrophobic with a water contact angle (CA) of 117° (Figure 5A), while the pyrolytic sample was super-hydrophobic with a CA of 170° (Figure 5B). Note that for the alumina substrate without the application of flower-like hierarchal micro-nano γ -Al₂O₃ layer, modification with the pyrolytic PDMS yielded a much lower CA (136°).²⁰ The pyolytic sample demonstrated a sliding angle (SA) of 5° (Figure 5C,D). When a water drop stroked the horizontal surface of the pyrolytic sample, it rebounded twice from the surface, converting kinetic energy into vibrational one (Figure 6A). As to the sample titled at an angle of 5°, the drop rolled down easily, and the surface remained dry (Figure 6B).

The pyrolytic sample showed a much better hydrophobic durability than the cured sample. The CA for the former remained almost unchanged after 100 cycles of sandpaper abrasion, while the CA for the latter decreased from 117° to 96° after 10 cycles of abrasion (Figure 7A). The CA for the pyrolytic sample was retained after immersion in boiling water for 48 hours, while the CA for the cured sample was decreased from 117° to 92° by the same treatment (Figure 7B). Soaking in acidic solution of pH = 2 for 48 hours also did not affect the CA for the pyrolytic sample, while it reduced the CA for the cured sample from 117° to 106° (Figure 8A). Immersion in alkaline solution of pH = 12 for 48 hours decreased the CA for the pyrolytic sample from 170° to 160°, while it lowered the CA for the cured sample from 117° to 97° (Figure 8B). It has been reported that the methyl groups in siloxanes



FIGURE 5 (A) Water contact angle of the cured sample, (B) the pyrolytic sample, and (C) the water drop before sliding, (D) after sliding [Colour figure can be viewed at wileyonlinelibrary.com]



FIGURE 6 (A) High-speed photography images of a water droplet bouncing on alumina placed horizontally, (B) tilted at an angle of 5°



FIGURE 7 (A) Change of water contact angles with abrasion, (B) with immersion in boiling water [Colour figure can be viewed at wileyonlinelibrary.com]

could be stripped off from the silicon nuclei in the presence of strong base.³⁶ Similarly, for the PDMS-derived $Si_xC_yO_z$ ceramic coating immersed in the alkaline solution, some of the methyl groups were removed as well, resulting in a substantial decrease in the CA.

Since the pyrolytic sample possessed super-hydrophobic surface, it would exhibit water and dirt repelling properties. After immersion in water dyed with methylene blue (Figure 9,9), no blue traces were left on the surface (Figure 9). As a contrast, the surface of the cured sample was water-logged with blue water (Figure 9). Abundant amounts of MnO₂ powders on the pyrolytic sample were effectively washed away (Figure 9,9). Contrarily, the cured sample remained wet and

contaminated by the MnO_2 powder after washing with water (Figure 9,9).

4 | DISCUSSION

This work demonstrated that polymer-derived ceramic coating could be applied to converting ceramic substrates (having hierarchical micro/nano surface texture) from hydrophilic into super-hydrophobic. The ceramic coating was formed via pyrolysis of preceramic precursors on the ceramic surface. The pyrolysis was carried out at intermediate temperatures and in inert atmosphere, thus some of the methyl groups in



FIGURE 8 (A) Change of water contact angles with exposure to acidic solution (pH = 2), (B) alkali (pH = 12) solution [Colour figure can be viewed at wileyonlinelibrary.com]

the polymer precursor was preserved, reducing the surface energy of the ceramic coating and giving rise to the superhydrophobicity. Note that the ceramic substrate modified with the polymer-derived ceramic coating exhibited a much higher water contact angle than the one modified with the cured polymer. The polymer-derived ceramic coating possessed less methyl groups than the cured polymer, thus the former would be expected to exhibit a lower water contact than the latter. This contradiction could be explained by the observation that the ceramic substrate remained highly textured and rough after formation of the polymer-derived ceramic coating (Figure 3B), while the surface of the substrate became smoother after applying cured polymer (Figure 3A).

This work showed that the alumina substrate with the polymer-derived ceramic coating remained intact after mechanical abrasion and exposure to boiling water and acidic solution, while the one with cured polymer coating degraded rapidly. This could be explained as follows. Ceramics are



(A1) The pyrolytic sample and (B1) the cured sample before inserting into the methylene blue dyed water, (A2) the pyrolytic FIGURE 9 sample and (B2) the cured sample after taking out from the water. (C1) The pyrolytic sample and (D1) the cured sample with MnO₂ powder, (C2) and (D2) after washing with water [Colour figure can be viewed at wileyonlinelibrary.com]

known to possess much higher mechanical strength, chemical and thermal stability than polymers, thus coating made from the former is more durable than the one made from the latter. Moreover, the interface between the polymer-derived ceramic coating and the ceramic substrate is more robust than the one between the polymer coating and the ceramic substrate.

The application of artificial super-hydrophobic surfaces is hindered by their poor durability. The all-ceramic super-hydrophobic surface developed in the present study exhibited excellent durability with water and dirty repelling properties, making it very suitable for use in antifogging, anti-icing, oil/water separation, and self-cleaning. The preparation method explored in this study could also be used to convert other materials (glass and metals) into super-hydrophobic.

5 | CONCLUSIONS

A ceramic coating can be formed on a highly textured ceramic substrate via pyrolysis of polymer precursors at intermediate temperatures and in nonoxidizing atmosphere. The as-formed all-ceramic surface exhibits super-hydrophobicity, which is attributed to the presence of low-surface energy methyl groups in the polymer-derived ceramic coating and the high roughness of the ceramic substrate. The super-hydrophobicity is well retained after mechanical abrasion and exposure to boiling water and acidic solution. It is likely that the method explored in the present study could also be used for hydrophobic surface modification of other inorganic materials such as glass and metals.

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