



Engineering durable hydrophobic surfaces on porous alumina ceramics using in-situ formed inorganic-organic hybrid nanoparticles



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ARTICLE INFO

Article history:

Received 12 May 2017

Received in revised form 22 June 2017

Accepted 24 June 2017

Available online 13 July 2017

Keywords:

Durable hydrophobic surface

Alumina

Polydimethylsiloxane

Pyrolysis

Inorganic-organic hybrid nanoparticles

ABSTRACT

Hydrophobic surfaces are required for a variety of applications owing to their water repellent and self-cleaning properties. In this work, we present a novel approach to prepare durable hydrophobic surfaces on porous ceramics. A polydimethylsiloxane (PDMS) film was applied to a porous alumina wafer, followed by pyrolysis at 400 °C in a non-oxidizing atmosphere (H₂:N₂ = 5:95), giving rise to nanoparticles. In these particles, Si, C and O elements formed amorphous networks to which methyl groups that had survived the pyrolysis were bonded. The as-modified porous alumina wafer was hydrophobic with a water contact angle of 136°, which is attributed to the presence of the methyl groups. The hydrophobicity was maintained after immersion in aqueous solutions in a pH range of 2–12 and acetone. The hydrophobicity was also retained after exposure to temperatures as high as 450 °C in an oxidative atmosphere (air) and after mechanical abrasion with sandpaper. The hydrophobic porous alumina ceramics developed in the present study are promising for use as membranes in various separation processes.

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1. Introduction

Preparation of durable hydrophobic surface on ceramics is vital for a variety of technical applications [1,2]. In particular, porous ceramics with a hydrophobic surface can be used as membranes for separation purposes [3–5]. Owing to the liquid water repellent property, solutes in the liquid water cannot transport through the porous ceramic membranes, while water vapor can permeate through these membranes. The hydrophobic porous membranes have been explored for desalination of water, concentration of waste water and liquid foods [6–8].

Ceramics are usually hydrophilic because of the presence of surface hydroxyl (–OH) groups tending to absorb water molecules [9–11]. Therefore, surface modification is required for rendering ceramics into hydrophobic. For this purpose, organic compounds with low surface energy such as chloroalkylsilanes, fluoroalkylsilanes (FAS) [2,12,13] and polydimethylsiloxane (PDMS) [14–16] are often applied to the ceramic surface. FAS, which possess a carbon chain composed of –CF groups and 3 hydrolysable groups, can react with hydroxyl groups present on the ceramic surface [17].

Larbot et al. [10] used FAS to create a hydrophobic layer on porous alumina and zirconia tubes, and applied them for membrane distillation. Gabino et al. [8] modified flat and tubular alumina with FAS, and used them for osmotic evaporation. It has to be noted that for practical applications the hydrophobic surface needs to be durable. Kujawa et al. [17] reported that the hydrophobicity of porous ceramics modified with perfluoroalkylsilanes (PFAS) was strongly reduced when kept in contact with water for 1 year. The hydrophobicity also deteriorated at elevated temperatures. Obviously, the hydrophobic surface of ceramics created using FAS might not be robust enough for practical applications.

Compared with FAS, PDMS has a better thermal stability (stable up to 300 °C in air) [15,18,19] and a lower cost. In the work of Pinheiro et al. [15], PDMS was used to modify porous γ -alumina ceramics, resulting in a water contact angle (CA) of 95°; however, the hydrophobic stability was not investigated. Huang et al. [14] coated a palladium/metal-organic framework (MOF) composite by using a facile CVD process with PDMS at 200 °C, converting the composite from hydrophilic to hydrophobic. Note that at the given temperature (200 °C), PDMS kept its initial structure, thus the coating layer was essentially polymeric. Consequently, the coating layer might not possess sufficient thermal and mechanical stability.

In order to obtain a more durable hydrophobic surface, we propose to modify a ceramic surface with inorganic-organic hybrid materials, where the organic component renders the surface into

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hydrophobic while the inorganic component enhances the durability. In the present study, the hybrid material was produced in-situ on the surface of alumina ceramics by pyrolysis of PDMS at elevated temperatures in inert atmosphere. The PDMS pyrolysis product was in form of nanoparticles comprising an inorganic core to which organic groups (methyl) were bonded. This paper reports the preparation, characterization of PDMS-derived nanoparticles on the porous alumina ceramics and resulting hydrophobic properties.

2. Experimental

2.1. Preparation

Alumina wafers were prepared by the phase inversion tape casting method as described in detail in [20]. In order to remove any impurities and to obtain more hydroxyl groups, these alumina wafers were ultrasonically cleaned in subsequently acetone, ethanol and water for 10 min and subsequently dried in an oven at 80 °C for 1 h. Hydroxyl-terminated polydimethylsiloxane (PDMS) (Mw = 14,000, 100 cSt) (ACROS, USA) was used for modifying the alumina wafers. First, a cross-linking agent of 3 wt.% tetraethyl orthosilicate (TEOS) (CP, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), the PDMS precursor (20 wt.%) and a dibutyltin dilaurate catalyst (DBTDL, 1 wt%) (CP, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were added to *n*-heptane (CP, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and stirred for 30 min at room temperature to obtain sufficient hydrolysis of TEOS. Then, the cleaned wafers were immersed in the polymer solution at room temperature and left for 15 min to allow the solution to fully penetrate into the pores and to cover the wafer surface under ultrasonic treatment. Afterwards the alumina wafers were pulled out from the PDMS precursor solution at a velocity of 0.2 mm/s and transferred to a tubular oven, heated at a rate of 3 °C/min to 200 °C and kept at 200 °C for 1 h, followed by heating to 400 °C at a rate of 3 °C/min and being held for 1 h and then cooled to room temperature naturally. The whole heating and cooling process were performed in a non-oxidizing atmosphere of H₂/N₂ (flow ratio H₂:N₂ = 5:95). After this temperature treatment the polymer-coated alumina wafers were ultrasonically cleaned in ethanol for 10 min. For comparison, the same type of alumina wafers were modified with fluoroalkylsilane (FAS) (DYNASYLAN F8261, Guangzhou, China) as described in [6].

2.2. Characterization

The morphology of the alumina wafers (before and after modification) was analyzed with scanning electron microscopy (SEM, JSM-6390LAF, JEOL, Japan), and with high resolution transmission electron microscopy (HRTEM, JEM, ARM-200F, JEOL, Japan), equipped with an energy-dispersive X-ray analyzer (EDS). Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet 8700) was used to examine the elemental composition and the chemical structure of the PDMS-modified alumina surfaces. The density of the alumina wafer was measured using the Archimedes method in mercury, and the porosity was calculated using the formula $(1 - \rho/\rho_{th}) \times 100\%$ where ρ_{th} is the theoretical density of the alumina. The porosity of the surface layer was estimated by calculating the percentage of pixels related to the pores as deduced from SEM images [20,21], and the pore size was determined with mercury porosimeter (PM60G7-17, Quantachrome Ins, USA). The water contact angles (CA) of the alumina wafers were measured using the contact angle meter (SL200B, Chenghui, China). The volume of a deionized water droplet was ~5 μ L. The contact angle value was calculated from 5 droplets at different positions on the same sample.

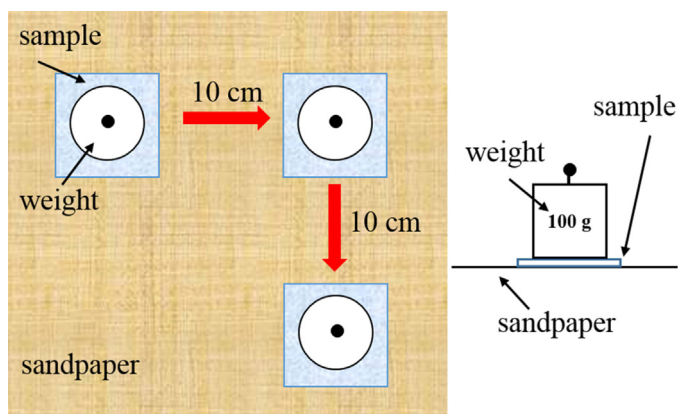


Fig. 1. Schematic diagram of sandpaper abrasion test: in each cycle, the sample is abraded for 10 cm transversely and longitudinally, respectively.

The decomposition of the PDMS coating on the alumina wafer was characterized by thermal gravimetric analysis (TGA, DTF-60H, Shimadzu, Japan) with a heating rate of 5 °C/min in N₂. The sample was prepared by immersing an alumina wafer in PDMS solution as described above but now only followed by drying at 200 °C in air for 1 h.

2.3. Durability tests

Both PDMS-modified and FAS-modified alumina wafers were treated at 100, 200, 300, 400, 450, 500 °C in air for 1 h, respectively. In order to investigate the chemical stability of the hydrophobic surface, aqueous solutions, with pH ranging from 2 to 12, or acetone were applied to treat the as-prepared hydrophobic alumina wafers for 24 h. After cleaning and drying, CAs for the wafers were measured again.

The sandpaper abrasion tests were carried out by placing the hydrophobic surfaces (PDMS-modified and FAS-modified alumina wafers) on sandpaper (standard glass paper, grit no. 320) and placing a weight of 100 g with diameter of 24 mm, which corresponded with a load of 0.98 N. One cycle included one move for 10 cm from left to right and another move for 10 cm perpendicular to the first move (Fig. 1). The CAs were measured after 20, 50, 100 and 200 cycles, respectively.

3. Results

3.1. Surface modification and characterization

The alumina wafer possessed a thin top layer and a thick support layer (Fig. 2a). The top layer consisted of well-sintered grains (Fig. 2b). The porosity of the top layer was estimated to be 25%, and the pore size was determined to be 1.2 μ m. Due to the presence of large finger-like pores in the support layer, the overall porosity of the wafer was as high as 56%. Fig. 2c shows the surface of an alumina wafer modified with pyrolyzed PDMS. It can be seen that sphere-like particles were grown on the surface of alumina grains. The HRTEM analysis revealed that these particles had a size of 150–200 nm (Fig. 3a). Fig. 3b shows the close-up image of the area marked by the first frame in Fig. 3a. The electron diffraction pattern consisted of two weak diffuse rings (Fig. 3b, inset), indicating that the particles were composed of an amorphous phase and crystallites. The crystallites could also be directly observed from the HRTEM image as marked by a red circle. Fig. 3c presents the close-up TEM image of the area marked by the second frame in Fig. 3a, showing that the particles were tightly adhered to the

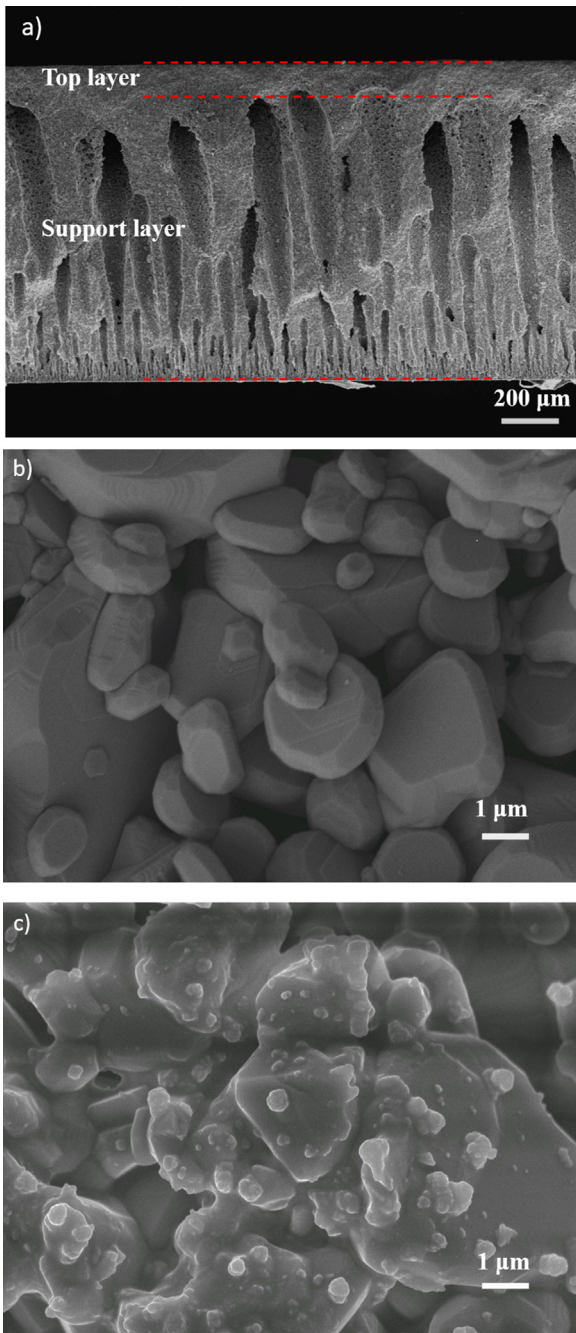


Fig. 2. SEM images of α -alumina: (a) cross-section along the thickness direction; (b) top surface of bare wafer; (c) top surface after modification.

underlying alumina grains. Elemental mapping revealed that the particles were mainly composed of Si, C and O elements.

Fig. 4 shows the IR spectra for a PDMS-modified alumina wafer. The intensities of the peaks assigned to the bonds involving Si or C were reduced strongly by the heat treatment at 400 °C. But, a significant amount of methyl groups survived the heat treatment. Fig. 5 shows the DTG and TGA curves of the PDMS-coated alumina wafer. A strong weight loss occurred in the temperature range ~350 to ~620 °C, with a maximum rate in weight loss at ~550 °C. This weight loss was related to the pyrolysis of PDMS and the removal of the methyl groups (demethylation) [18,19,22].

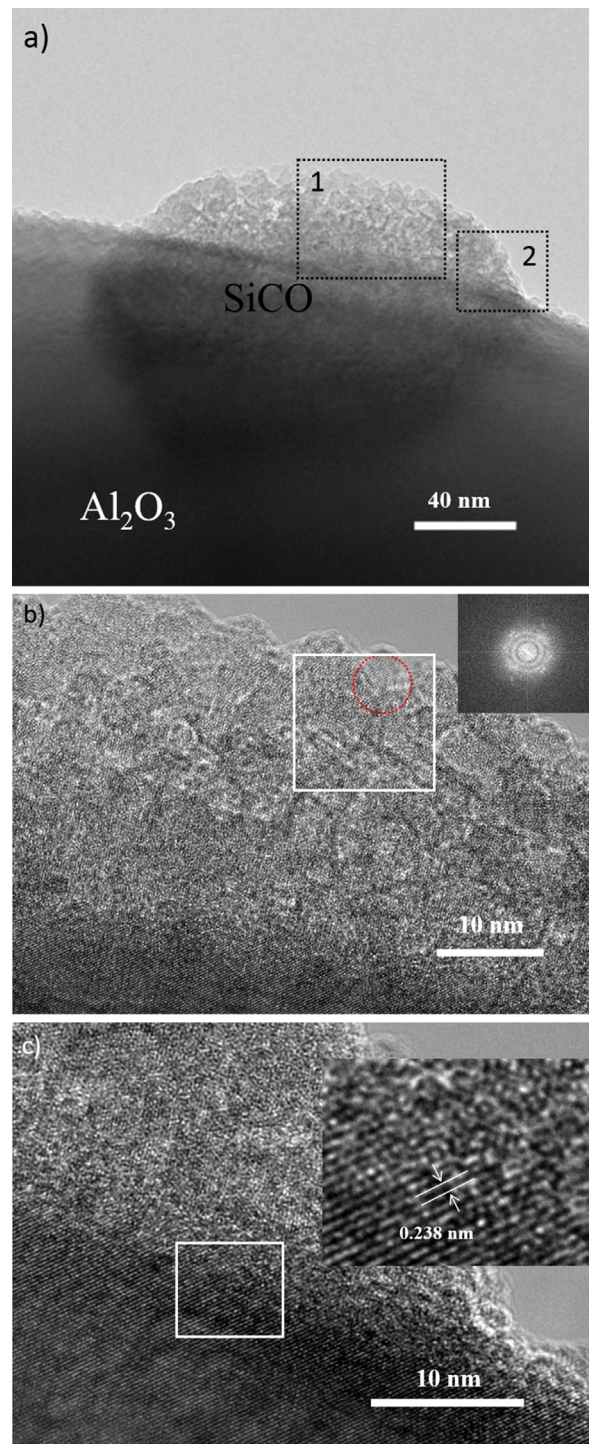


Fig. 3. (a) HRTEM image of a nanoparticle on the surface of Al_2O_3 grains in the PDMS-modified wafer; (b) Close-up image of area as labeled by the first frame from left in image (a) and inset ED patterns; (c) Close-up image of the boundary between an Al_2O_3 grain and a nanoparticle as labeled in the second frame in image (a).

3.2. Hydrophobicity and stability

The hydrophobic behavior of the PDMS-modified wafers is demonstrated by the results as given in Fig. 6. Fig. 6a shows the behavior of the PDMS-modified and bare wafers when kept in contact with water. Clearly, the bare wafer was hydrophilic and sank under the water, while the PDMS-modified wafer floated on the water without wetting as also demonstrated by the colored water

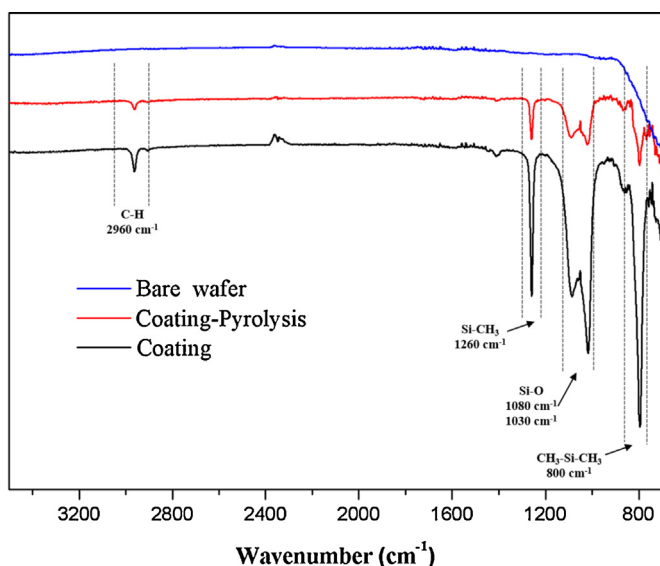


Fig. 4. IR spectra on the surface of bare and PDMS-modified alumina wafers.

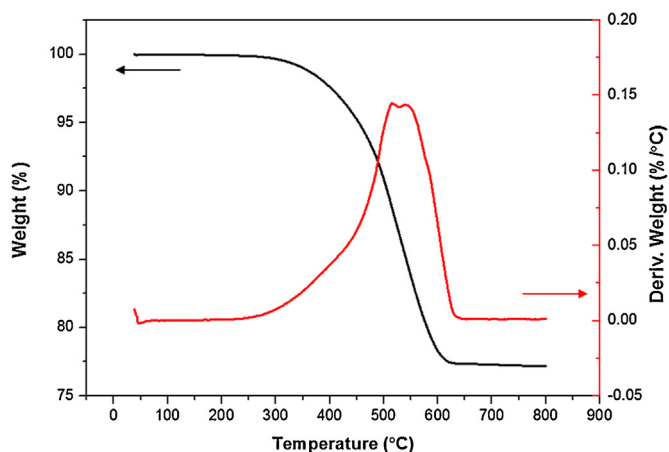


Fig. 5. DTG and TGA thermographs of the PDMS coating on alumina wafer. The sample was pre-treated at 200 °C with a heating rate of 5 °C/min in N₂.

droplets on its surface. The presence of $-\text{Si}-\text{CH}_3$ groups lowered the surface energy of the alumina wafer, rendering the surface hydrophobic. The water contact angle (CA) was determined to be $136^\circ (\pm 1)$ for the PDMS-modified wafer (Fig. 6b).

The results of the thermal stability of the PDMS-modified wafers are summarized in Fig. 7. In this experiment the surface contact angles (CAs) of PDMS-modified and FAS-modified alumina wafers were determined after a treatment in air for 1 h at different temperatures. For the FAS-modified wafer, the hydrophobicity reduced at 300 °C, and was totally lost after a temperature treatment at 400 °C. This was in agreement with the work of Kujawi [17] in which the hydrophobicity of the FAS-modified ceramics reduced when treated at 250 °C. The PDMS-modified wafer, however, remained hydrophobic after a temperature treatment at 450 °C, which demonstrated that PDMS-modified alumina wafers had a better thermal stability than FAS-modified ones.

Besides, no change in CA was observed after soaking the modified wafers for 24 h in 0.01 M HCl or 0.01 M NaOH solution. After soaking for 24 h in acetone the CA slightly decreased to $134^\circ (\pm 1)$ from the original value of $136^\circ (\pm 1)$, but this might also be within the experimental error. However, the CAs decreased from $138^\circ (\pm 1)$ to $132^\circ (\pm 1)$, $134^\circ (\pm 1)$ and $130^\circ (\pm 1)$ for the FAS-modified alumina wafer, after soaking for 24 h in 0.01 M HCl, 0.01 M NaOH and pure

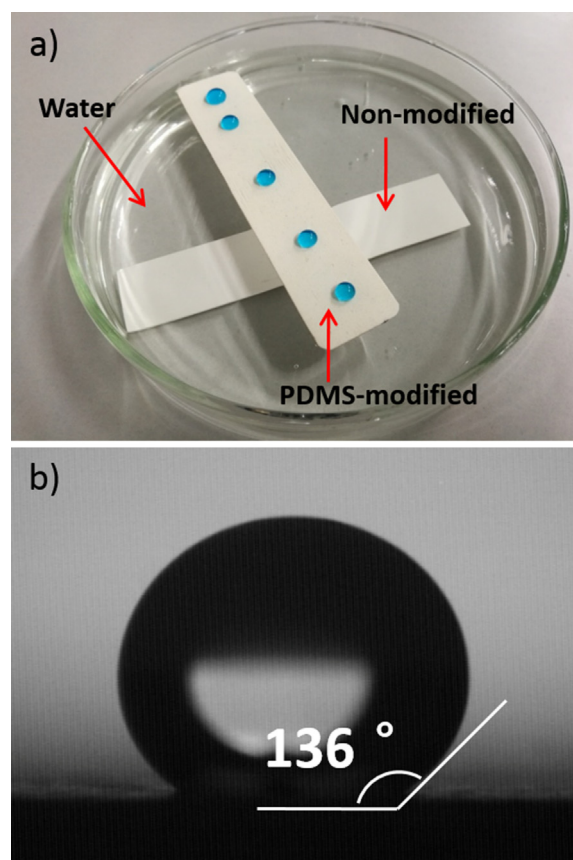


Fig. 6. (a) Status of the PDMS-modified and non-modified wafer when kept in contact with water: the PDMS-modified wafer is floating on the water and droplets (colored with methylene blue) are present on the wafer; (b) Water contact angle of the PDMS-modified wafer (a round wafer with diameter of 35 mm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

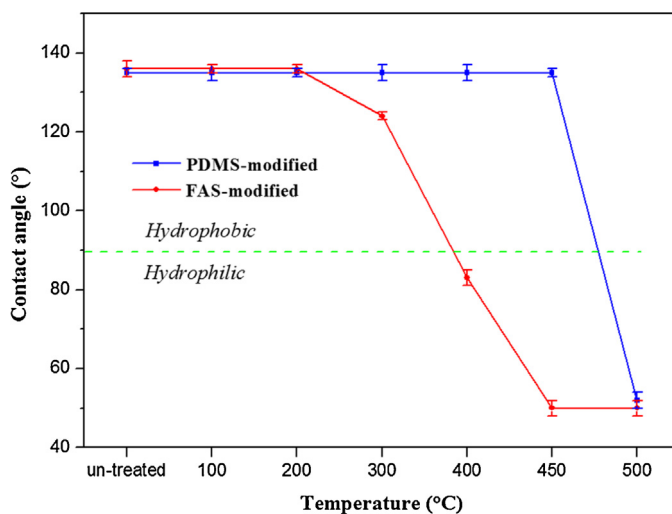


Fig. 7. Contact angles (CAs) of the FAS-modified and PDMS-modified alumina wafer after treated at various temperatures in air for 1 h.

acetone, respectively. Apparently, the PDMS-modified wafer showed a better chemical stability which was ascribed to the good stability of the PDMS-derived hydrophobic SiCO nanoparticles and the well attachment between the SiCO nanoparticles and the alumina grains.

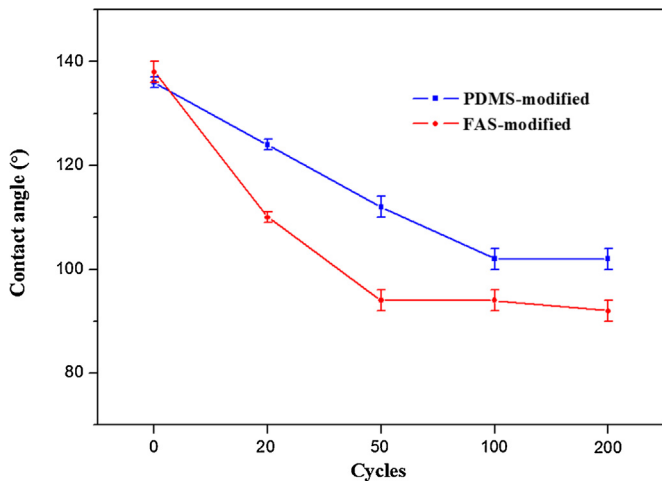


Fig. 8. Contact angles (CAs) of the PDMS-modified wafer after different cycles of sandpaper abrasion.

The influence of the sandpaper abrasion on the hydrophobicity is shown in Fig. 8. For the PDMS-modified wafers, the CAs dropped with increasing abrasion cycles until 100 cycles and then remained constant, and still hydrophobic after another 100 abrasion cycles. This decrease in CA can be caused by a decrease in surface roughness as a result of the sandpaper treatment and removal of some of the surface nanoparticles. As shown in Fig. 8, the CAs for the FAS-modified wafers decreased dramatically after abrasion with sandpaper. The wafer surface almost turned into hydrophilic after 50 abrasion cycles. Clearly, the PDMS-modified alumina wafers exhibited better mechanical stability because of the better stability of SiCO nanoparticles on the alumina surface than that of the FAS molecules. The IR spectra of the PDMS-modified wafer surfaces after abrasion tests are shown in Fig. 9. The intensity of both $-\text{Si}-\text{CH}_3$ and $-\text{Si}-\text{O}-$ decreased with increasing abrasion cycles. But, these characteristic peaks remained visible even after 200 cycles of abrasion. This indicates that mechanical abrasion could not completely remove the PDMS-derived SiCO particles from the surface, manifesting the high mechanical stability of the hydrophobic surface.

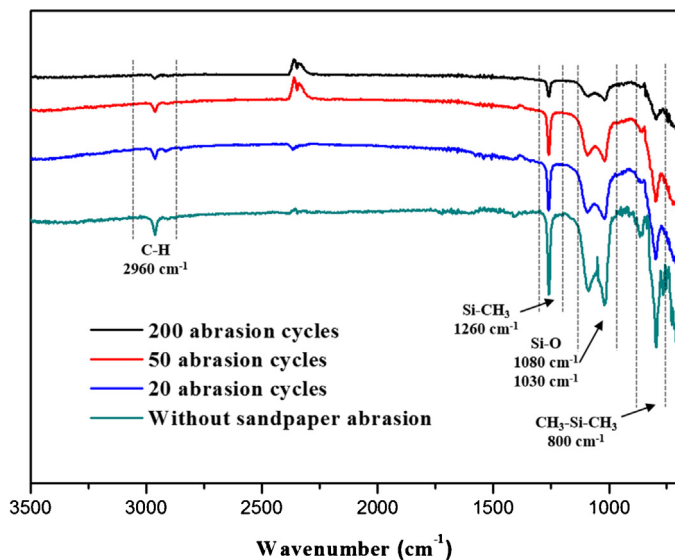
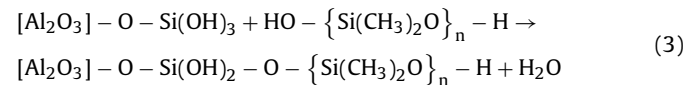
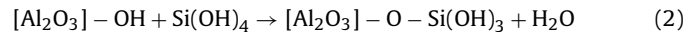
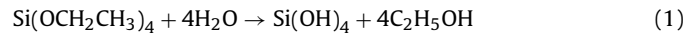


Fig. 9. IR spectra of PDMS-modified alumina wafer after abrasion.

4. Discussion

This work demonstrated that a hydrophobic surface can be obtained by modifying porous alumina ceramics with PDMS-derived nanoparticles. Based on the analysis of IR, TGA, SEM, HRTEM in combination of the results reported in literatures, the surface modification process involves a series of reactions. First, hydrolysis of TEOS occurs (Reaction (1)), which is catalyzed by the acetic acid which in turn is generated by reaction of DBTDA with water absorbed from the atmosphere [23]. The hydrolyzed TEOS then acts as a linker between PDMS and alumina surface via condensation reactions (Reactions (2)–(3)) [24]. Self-condensation of the silanol-terminated PDMS also take place, thereby extending the chains of PDMS [25–27].



The PDMS chains are then converted into nanoparticles via pyrolysis at elevated temperatures. In this process, part of the methyl groups in PDMS is removed [18] and the bonds in the remaining PDMS reorganize, leading to the formation of SiCO inorganic networks. Note that a large amount of hydrophobic methyl groups survive the pyrolysis, and are tightly bonded to the inorganic networks. Note also that the PDMS pyrolysis products are tightly adhered to the alumina substrate. Therefore, it is not surprising that the alumina ceramic wafer coated with PDMS-derived inorganic-organic hybrid nanoparticles exhibited far more durable hydrophobicity than the one grafted with FAS which is essentially organic.

The porous alumina ceramic wafer modified with the in-situ formed hybrid inorganic-organic nanoparticles exhibited much improved hydrophobicity and durability. It is expected that a detailed study on the chemical composition (Si/O, Si/C ratios), amount of methyl groups, degree of crystallization and microstructure of the nanoparticles will lead to further improvement of the hydrophobic property. The availability of stable hydrophobic porous ceramics makes it possible to explore various membrane distillation processes such as desalination of water, concentration of waste water and liquid foods. In fact, it has been shown recently in the authors' lab that the hydrophobic alumina membrane developed in the present study demonstrated much improved membrane distillation water desalination performance, which will be reported in a separate publication.

5. Conclusions

A novel method has been developed to render hydrophilic alumina ceramics hydrophobic. In this method, a PDMS film is applied to alumina ceramics, then subjected to pyrolysis at elevated temperatures in inert atmosphere, giving rise to the formation of nanoparticles comprising Si, C and O elements. The as-treated alumina ceramics are hydrophobic, which is attributed to the presence of the methyl groups bonded to the nanoparticles. The hydrophobicity can be retained after exposure to aqueous solutions in a pH range from 2 to 12, heat treatment in ambient atmosphere and sandpaper abrasion. The hydrophobic porous alumina ceramics developed in the present study are likely to be used as membranes in various separation processes.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant No. 21271164) and the CNPC-CAS Strategic Cooperation Research Program (2015A-4812).

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