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

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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.

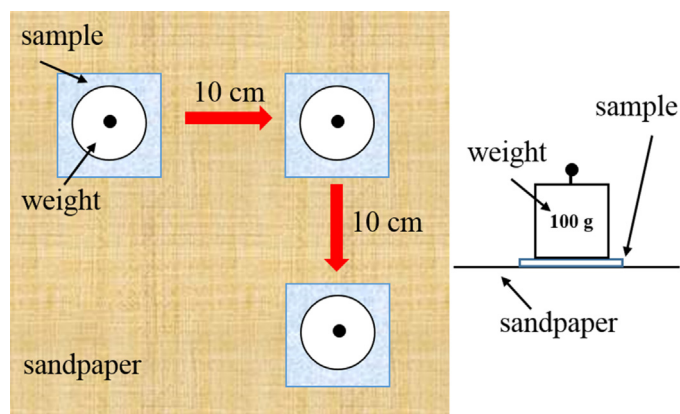


Fig. 1. Schematic diagram of sandpaper abrasion test: in each cycle, the sample is abraded for 10 cm transversely and longitudinally, respectively.

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

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