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# Fabrication of a superhydrophobic and oleophobic PTFE membrane: An application to selective gas permeation

Eun Ji Park[1], Dae Han Kim[1], Ju Ha Lee, Seonggyun Ha, Changsik Song, Young Dok Kim*

*Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Republic of Korea*

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ABSTRACT

A superhydrophobic and oleophobic film was fabricated on polytetrafluoroethylene (PTFE) using $SiO_2$ nanoparticles and *1H,1H,2H,2H*-perfluorooctyltrichlorosilane (FOTS). The surface of the bare PTFE sheet was first coated with $SiO_2$ nanoparticles by the dip-coating method, and FOTS was subsequently deposited on the $SiO_2$-coated PTFE by either dip-coating or vapor deposition. Both of the FOTS-coated PTFE samples prepared using either dip-coating or vapor deposition initially showed high repellence towards water and hexadecane droplets. The FOTS-PTFE prepared by vapor deposition gradually absorbed hexadecane. By contrast, the dip-coated FOTS-PTFE displayed a durable non-wetting property, even after exposure to acidic/basic solutions and UV light irradiation. Gas permeability of the prepared superhydrophobic and oleophobic PTFE sheets towards $CO_2$ and dimethyl methylphosphonate (DMMP) vapor was also determined. We suggest that our superhydrophobic and oleophobic membrane could be used as the shielding layer of a gas sensor, to repel various liquids and only allow transmission of gases.

## 1. Introduction

Superomniphobic (superhydrophobic and superoleophobic) surfaces display a specific wetting property to both water and low surface tension liquids with a contact angle over 150° in conjunction with a low contact angle hysteresis (the difference between the advancing and receding contact angles). In order to achieve such a surface property, substrate surfaces are modified with a combination of hierarchical surface geometric structure and low surface energy functionality [1–5].

Hierarchically structured surfaces possess more than one scale roughness to reduce the contact area between liquid droplets and solid substrates. Over the past decade, various strategies to generate hierarchical structures on various solid surfaces have been reported [6–11]. Among them, patterning of solid surfaces based on lithography is widely used to make dual-scale roughness, which is generated by micro- and nano-scale texturing [12,13]. However, lithography systems are generally expensive and the patterning process can be regarded as being complex. The random distribution of nanoparticles on a substrate surface can be an alternative method for the facile fabrication of hierarchical surface structures; nano-scale texture caused by the intrinsic size of nanoparticles is combined with micro-scale structures formed by aggregation of nanoparticles, resulting in dual-scale roughness [14–18].

Not only surface morphology of a substrate, but also a low surface energy is required for non-wetting properties. A C-F termination is known to have a much lower surface energy in comparison with those of C—H and C—C bonds, and thus, substrate surfaces are generally functionalized with fluorinated alkylsilanes (FAS) to inhibit dispersion of water and low surface tension liquid droplets on the surface [19–21].

To date, much effort has been extended in numerous application fields of superomniphobic surfaces including self-cleaning [22,23], stain-free clothing, spill-resistant protective wear [24], enhancement of solvent-resistance [25], anti-biofouling [26,27], and drag reduction [28–30]. Apart from these commercial applications, (super)omniphobic materials can be used as a shielding layer of chemical gas sensors. In general, it is known that many gas sensors are easily contaminated by a variety of liquids and dust, resulting in reduction of intrinsic sensitivity towards target material [31]. In order to prevent these unexpected situations, gas sensors should be protected from such contaminants. Herein, (super)omniphobic shielding layers can be introduced at the aperture of gas sensors, to allow selective permeation

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* Corresponding author.
*E-mail address:* ydkim91@skku.edu (Y.D. Kim).
[1] These authors contributed equally to this work.

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of gas from a gas/liquid mixture, while repelling aqueous and non-aqueous liquids.

In the present work, the surface of polytetrafluoroethylene (PTFE) sheets was modified with $SiO_2$ nanoparticles to make dual-scale roughness on PTFE surface. Then, *1H,1H,2H,2H*-perfluorooctlytrichlorosilane (FOTS) was coated on the modified PTFE surface using two different methods, vapor deposition and dip-coating, for the preparation of an omniphobic (hydrophobic and oleophobic) surface property that repels both water and hexadecane. It was found that our omniphobic PTFE sheets have potential use as a protective layer of gas sensors, based on the results of gas permeability tests of $CO_2$ and dimethyl methylphosphonate (DMMP) vapor.

## 2. Experimental

### 2.1. Sample preparation

A PTFE (pore size = 0.2 μm, Meari) sheet was used as a substrate of the omniphobic coating. Prior to the FOTS (97%, Sigma-Aldrich) coating of PTFE sheets, $SiO_2$ nanoparticles (Aerosil 200, particle size = 24 nm, Degussa) were physically attached to the PTFE sheets (3 cm × 3 cm) to generate a hierarchical surface morphology. In detail, $SiO_2$ nanoparticles (0.2 g) were dispersed in hexane (29 mL, 95%, Daejung) with an adhesive solution (1 mL) that consisted of fluidic polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning), curing agent, and hexane in a volume ratio of 1:0.1:8. The PTFE was dipped in the aforementioned $SiO_2$ solution for 30 s and was then dried for 10 min under atmospheric conditions. The dip-coating process was repeated three times (Fig. 1a).

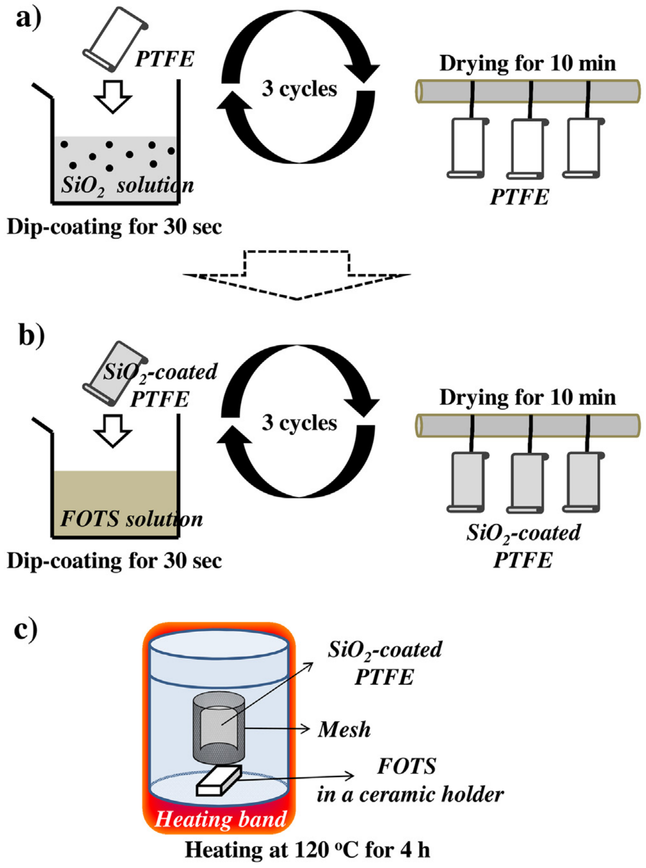

**Fig. 1.** Schematic diagram of the experimental procedures for a) preparation of the dip-coating of $SiO_2$ nanoparticles on bare PTFE sheets, b) preparation of dip-coated FOTS layers, and c) preparation of vapor-deposited FOTS layers on the prepared $SiO_2$-coated PTFE sheets.

In order to fabricate FOTS layers on the $SiO_2$-coated PTFE sheet, the dip-coating method was introduced (Fig. 1b). The FOTS solution, which consisted of FOTS (1 mL) and hexadecane (29 mL), was prepared, and the $SiO_2$-coated PTFE sheet was dipped into the FOTS solution for 30 s and was subsequently dried for 10 min under atmospheric conditions. This dip-coating process was repeated three times for each sample.

The vapor deposition method was also used for fabrication of FOTS layers on the $SiO_2$-coated PTFE sheet. As shown in Fig. 1c, FOTS (500 μL) in a ceramic holder (2.5 cm × 2.0 cm) was located at the center of a stainless steel reactor that was wrapped with a heating band. The $SiO_2$-coated PTFE fixed to a stainless steel mesh was placed on the ceramic holder. Subsequently, the reactor was completely sealed and heated at 120 °C for 4 h. The temperature of the reactor was monitored using a K-type thermocouple that was attached to the sidewall of the reactor.

### 2.2. Characterizations

The wettability of FOTS-coated PTFE surfaces for water and hexadecane was determined by measuring static contact angles using a Theta optical tensiometer (KSV Instruments, Ltd.) equipped with a digital camera connected to a computer; Young-Laplace curves were employed for the fitting process required for contact angle determination. Contact angle measurements were performed with 3 μL of either a water or hexadecane droplet and were repeated on three different sites on each sample surface to obtain an average value of the contact angle. The surface morphology of each sample was analyzed with scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS, JSM-7100F, JEOL) and atomic force microscopy (AFM, NTEGRA Spectra Raman-AFM, NT-MDT). For characterization of the chemical structure of the sample, studies using Fourier transform infrared (FT-IR, Optics/vertex 70, BRUKER) spectroscopy were carried out in the range of 600–4000 $cm^{-1}$. Each spectrum was collected for 64 scans with a resolution of 4 $cm^{-1}$ and was corrected for atmospheric $H_2O$ and $CO_2$ peaks.

### 2.3. Chemical and optical durability

In order to evaluate the chemical durability of the FOTS layers, changes in the static contact angles for water and hexadecane were monitored as a function of immersion time of the FOTS-coated PTFE samples in acidic/basic solutions. Aqueous HCl (pH = 1) and NaOH (pH = 10) solutions were used for the chemical durability tests. Samples were also exposed to ultraviolet (UV) light generated from an UV lamp (λ = 254 nm, 4 W, VILBER LOURMAT), and the optical resistance of FOTS layers to UV light was evaluated with respect to the change in water and hexadecane contact angles.

### 2.4. Gas permeability test

Information regarding gas permeability of the prepared PTFE sample could be qualitatively obtained using a simple $CaCO_3$ precipitation reaction (Eq. (1))

$$Ca(OH)_2\ (aq) + CO_2\ (aq) \rightarrow CaCO_3\ (s) + H_2O \quad (1)$$

When $CO_2$ gas molecules react with $Ca(OH)_2$ in the aqueous solution, they form white solid precipitate, $CaCO_3$, and therefore, originally clear $Ca(OH)_2$ solution becomes turbid. In order to qualitatively verify gas permeability of the PTFE samples, 20 mL of aqueous $Ca(OH)_2$ solution (4 mM) was placed in a 30 mL-volume vial with printed letters attached at the back side, and the mouth of