

Facile Fabrication of Superhydrophobic Polymer Membranes with Hierarchical Structure for Efficient Oil/Water Separation

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Abstract: Superhydrophobic polymer membranes provide highly promising methods for efficient oil/water separation because of their cost effectiveness, and environmental friendliness. A variety of polymers have been widely used for the membrane fabrication, among which polyurethane acrylate (PUA) presents strong advantages of excellent mechanical strength with high deformability and chemical stability. In this study, we present a facile and rapid method for the fabrication of PUA-based superhydrophobic membranes with hierarchical structure, enabling efficient oil/water separation. For this work, PUA membranes with uniform pores were prepared via soft lithography, on which silica nanoparticles were deposited. The nanoparticles were preferentially functionalized with a silane coupling agent to lower the surface energy, and then spray-coated onto the PUA membrane supports to spontaneously form the hierarchical structure possessing superhydrophobic properties and excellent wettability to oil. Efficient oil/water separation was successfully demonstrated using a mixture of hexane and water with a separation efficiency of ~97 %, and the membranes could withstand a high pressure of ~2.0 kPa. We anticipate that these results will significantly contribute not only to the fabrication of superhydrophobic membranes with uniform pores but also the development of more diversified polymer-based membranes and separators leading to a wide range of applications.

Keywords: Polymer membranes, Silica nanoparticles, Surface functionalization, Hydrophobicity, Oil/water separation

Introduction

Recently, water pollution from accidental ship leakage and industrial wastewater has threatened not only the ecological environment but also human health [1-3]. Regulations to prevent water pollution have been strengthened, and thus finding an efficient method for oil/water separation is crucial [4,5]. Oil/water separation can be achieved via various routes based on physical methods [6,7], bio-inspired methods [8,9], and electrochemical methods [10,11]. These techniques have significant potential; however, the issues associated with laborious fabrication processes and recontamination still need to be improved for practical applications [12-14]. In this context, superhydrophobic materials have been considered as a promising class of materials, offering interesting scope for oil/water separation with high efficiency. Superhydrophobicity is characterized by a water contact angle of greater than 150 ° and an oil wetting angle close to 0 ° at the surface [15,16]. Superhydrophobic materials thus have a high affinity for oil and repel water, enabling selective filtration of oil/water mixtures [17,18]. In addition, low surface energy and rough surface structure leading to low wettability of water can greatly improve the separation

efficiency. Various types of superhydrophobic materials, such as polymer membranes [19,20], metal meshes [21,22], nanoparticles [23,24], and porous gels [25,26], have been studied for the selective filtration of oil/water mixtures. Considering cost effectiveness and environmental friendliness [27-29], polymer membranes can satisfy necessary requirements, such as facile and rapid fabrication processes and low recontamination/defect rates [30-32]. A variety of polymers can be used for the membrane fabrication [12,33-36], among which polyurethane acrylate (PUA) presents strong advantages of excellent mechanical strength with high deformability and chemical stability. In particular, ultraviolet (UV) curable PUA mixtures enable rapid and efficient polymerization where soft lithography techniques to fabricate membrane structures can be directly applied at low cost [37-40]. However, despite these advantages, only few studies have been conducted on PUA-based superhydrophobic membranes thus far [36].

For the realization of PUA-based superhydrophobic membranes, the hydrophobicity of PUA should be significantly enhanced. Since a lower surface energy is essential to improve the hydrophobicity of PUA, low-surface-energy materials can be employed as additives for surface functionalization decreasing the surface energy [41-43]. Thus, developing effective and efficient methods for the surface functionalization is critical to the fabrication of PUA-based superhydrophobic membranes enabling further

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applications. In addition, according to the Wenzel and Cassie-Baxter models, hierarchical structures at the micro- and nanometer scales can also provide superhydrophobicity to surfaces [44,45]. Such hierarchical structures greatly increase hydrophobicity by entrapping air at the solid/liquid interfaces, which can be prepared by confined aggregation of nanoparticles on templates [46,47]. Various processes have been proposed to fabricate the hierarchical structures consisting of nanoparticles [48-52]. Among these fabrication methods, spray coating has great potential because of its simplicity, high processability, and quick coating speed (i.e., short processing time), facilitating the preparation of superhydrophobic surfaces with micro/nanoscale layered structures [53].

Here, we present a facile and rapid method for the fabrication of PUA-based superhydrophobic membranes with hierarchical structure, enabling efficient oil/water separation. For this work, PUA membranes with uniform pores were prepared in a thin-film form via soft lithography, on which silica (SiO_2) nanoparticles were subsequently deposited. SiO_2 nanoparticles used in this work were functionalized with a silane coupling agent to further lower the surface energy [54,55], and spray-coated onto the PUA membrane supports to spontaneously form the hierarchical structure possessing superhydrophobic properties. Thus, low surface energy and rough surface structure, which play decisive roles in superhydrophobicity, were both achieved by one-step spray coating of the functionalized nanoparticles for a few seconds. The PUA-based superhydrophobic

membranes, of which a water contact angle was found to be greater than 150° , exhibited excellent wettability to oil. In addition, efficient oil/water separation was successfully demonstrated using a mixture of hexane and water with a separation efficiency of $\sim 97\%$, which is attributable to the excellent oil wetting and water resistance of the membranes. These results indicate that soft lithography techniques can be directly applied to the fabrication of superhydrophobic membranes with uniform pores via proper selection of components, suggesting great potential for the further applications including separation and filtration of mixtures.

Experimental

Materials

Dehydrated toluene, trichloro(hexyl)silane, ethanol, and SiO_2 nanopowder (10-20 nm particle size) were purchased from Sigma-Aldrich, and used as received. Hexane was purchased from J. T. Baker (USA). Polydimethylsiloxane (PDMS) elastomer (SYLGARD 184), hexane, and methylene blue solution (1 %) were purchased from DOW, J. T. Baker, and Samchun Chemicals, respectively.

Preparation of PUA Membrane Supports

PUA membrane supports were prepared as schematically illustrated in Figure 1. A UV curable PUA mixture, synthesized in accordance with previous reports [56,57], was drop-dispensed onto a pre-patterned PDMS mold, and then covered with another flat PDMS mold. The pre-

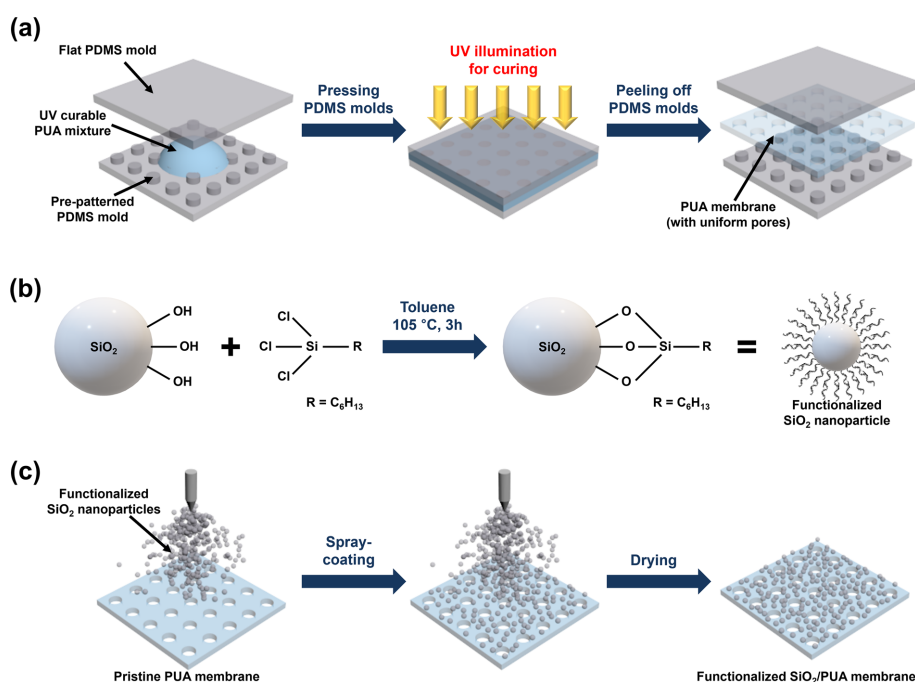


Figure 1. Schematic illustration for (a) fabrication of PUA membrane, (b) preparation of SiO_2 nanoparticles functionalized with silane coupling agent, and (c) spray-coating of SiO_2 nanoparticles onto PUA membrane.

patterned PDMS mold used in this work was embossed with regularly arranged pillars of which diameter and height were designed to be 50 μm , following a conventional soft lithography method [38,39]. The excess amount of the PUA mixture between the two PDMS molds was squeezed out using a roller until the embossed PDMS pattern was brought into contact with the flat PDMS mold. The sample was exposed to UV light ($\lambda \sim 365$ nm, 34.0 W m^{-2}) for 8 min, and the PUA mixture could be cured through the UV transparent molds. After the UV curing, the two PDMS molds were easily detached from the sample owing to the low surface energies of PDMS (~ 21.6 mJ m^{-2}) and PUA (~ 23 mJ m^{-2}), and thus a freestanding PUA film was prepared with the perforated pattern. Since the perforated pattern of the cured PUA film was negatively replicated from the pre-patterned PDMS mold, the PUA film could serve as a membrane support possessing uniform pores with a diameter of 50 μm . A size of the fabricated membrane support was 15 mm $\times$ 15 mm.

Preparation of SiO₂ Nanoparticles Functionalized with Silane Coupling Agent

SiO₂ nanoparticles were functionalized with a silane coupling agent (i.e., trichloro(hexyl)silane) to lower the surface energy. SiO₂ nanopowder (1 g) was added to a mixture of dehydrated toluene (20 ml) and trichloro(hexyl)silane (1 ml), and then refluxed in a round-bottom flask at 105 $^{\circ}\text{C}$ for 3 h. In this process, trichloro(hexyl)silane reacted with hydroxy groups terminating the surface of SiO₂ [58], leading to the surface modification (see Figure 1b). To evaporate the solvent, it was subsequently heated at 70 $^{\circ}\text{C}$ for 10 h on a hot plate in a fume hood, and completely dried in a convection oven at 70 $^{\circ}\text{C}$ for 24 h.

Spray Coating of SiO₂ Nanoparticles on PUA Membranes

For the preparation of a fully dispersed solution, the functionalized SiO₂ nanoparticles (1 g) in an ethanol solvent (20 ml) were sonicated for 1 h, and further stirred for 30 min. The prepared solution was spray-coated onto the PUA membrane supports at a rate of 19 $\mu\text{l s}^{-1}$ and a pressure of 1.5 bar. The SiO₂-coated PUA membranes were then placed in a convection oven at 180 $^{\circ}\text{C}$ for 1 h for drying. For comparison, the pristine SiO₂ nanoparticles were also used following the same procedure.

Measurements

The surface morphology was investigated using scanning electron microscopy (SEM; EM-30AX, COXEM). Dynamic light scattering (DLS; ELSZ-2, Otsuka) analysis was also performed to examine size distribution of SiO₂ nanoparticles.

Results and Discussion

SEM measurements were performed to analyze the morphology of the PUA membrane and functionalized SiO₂

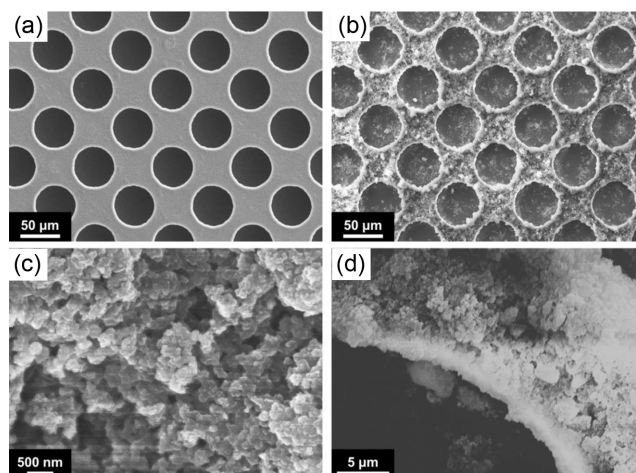


Figure 2. SEM images of (a) pristine PUA membrane and (b) functionalized SiO₂/PUA membrane. Spray volume for (b) was 1.5 ml. (c) A magnified SEM image of the functionalized SiO₂ clusters in (b), indicating the formation of micrometer-sized random networks in a hierarchical manner. (d) A magnified SEM image of the functionalized SiO₂ clusters on edge of a PUA membrane pore.

nanoparticles. Figure 2 shows SEM images of the PUA membrane, before and after spray-coating with the dispersed solution of the SiO₂ nanoparticles, and spray volume was 1.5 ml. As shown in Figure 2a, the PUA membrane was neatly perforated along the pre-patterned PDMS mold. Since remaining unsaturated acrylate in the PUA membrane provided adhesive properties [37–40], the coated SiO₂ nanoparticles could be tightly bound to the membrane. The SEM observations clearly indicated that the spray-coated nanoparticles were well distributed on the membrane surface. The SiO₂ nanoparticles preferentially aggregated into clusters in the dispersed solution, as will be discussed with the DLS analysis, and the clusters spontaneously formed micrometer-sized random networks in a hierarchical manner. Since these hierarchical structures can greatly increase hydrophobicity, i.e., water resistance, by entrapping air at the solid/liquid interfaces [46,47], the surface of the PUA membrane with consistent roughness was highly expected to provide superhydrophobic properties.

To elucidate the roles of the silane coupling agent, the cluster sizes of pristine SiO₂ nanoparticles and functionalized SiO₂ nanoparticles were initially analyzed via DLS measurements. For the measurements, the dispersed solution of each component was individually prepared with the same content ratio as described in the Experimental section. As shown in the DLS diagram (see Figure 3), the clusters of functionalized SiO₂ nanoparticles were overall larger than that of the pristine SiO₂ particles. The DLS result implies that alkyl chains on the functionalized SiO₂ nanoparticles enhanced van der Waals interaction [59], leading to a higher

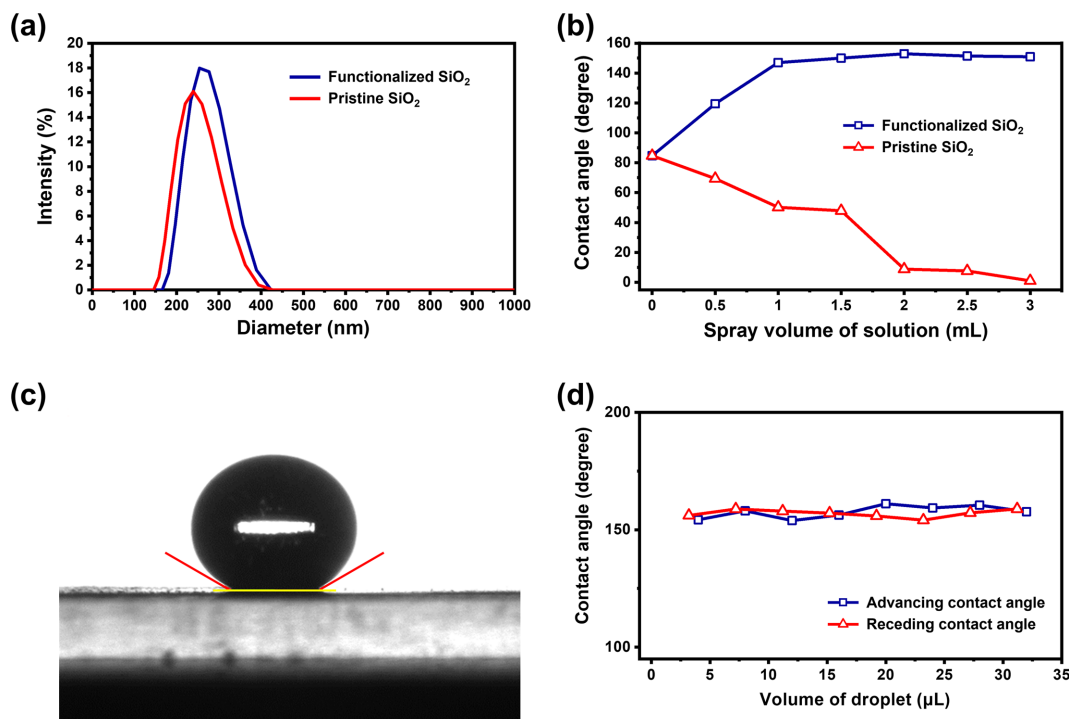


Figure 3. (a) DLS diagram showing size comparison of pristine SiO₂ and functionalized SiO₂ clusters. (b) Static contact angles of water on SiO₂/PUA membranes corresponding to varied spray volumes (i.e., 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mL). (c) Static contact angle of water stabilized on the functionalized SiO₂/PUA membrane (prepared with spray volume of 1.5 mL). Red and yellow lines indicate the angle of 150°. (d) Water contact angles on the functionalized SiO₂/PUA membrane (prepared with spray volume of 1.5 mL) in both advancing and receding modes, corresponding to varied water volumes.

aggregation propensity of the nanoparticles. For further investigation of the effects of the silane coupling agent on the hydrophobicity, each dispersed solution was individually spray-coated onto the PUA membrane, and then the static contact angles of water were measured corresponding to varied spray volumes (i.e., 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mL), as shown in Figure 3b. When the pristine SiO₂ nanoparticles were coated on to the membrane, the measured contact angle gradually decreased as the spray volume increased. The water contact angle converged to 0° as the spray volume increased up to 3.0 mL, which was possibly originating from a significant amount of hydrophilic hydroxyl groups terminating the SiO₂ surface. This result is consistent with a previous work reporting the change of the water contact angle according to the loading amount of SiO₂ [60]. On the other hand, the water contact angle of the functionalized SiO₂/PUA membrane rather increased with the spray volume. When the spray volume exceeded 1.0 mL, the water contact angle was maintained at ~150° (see Figure 3c). Since the oxygen atoms in SiO₂ nanoparticles became covalently bonded with the silane coupling agent, the surface energy could be significantly lowered by the functional groups [61]. It should be noted that the water contact angles in both advancing and receding modes were

also measured on the functionalized SiO₂/PUA membrane corresponding to varied water volumes (see Figure 3d and Supplementary Video 1). Any significant change in the contact angle was not observed for both modes of operation, compared to the static contact angle of ~150°. Thus, no contact angle hysteresis occurred, implying that the functionalized SiO₂ nanoparticles were well stabilized on the PUA membrane without water spreading effects [62]. These results indicate that the superhydrophobic properties originating from low surface energy and rough surface structure can be efficiently and stably imparted by one-step spray coating of the functionalized nanoparticles.

To examine the behaviors of oil (hexane) and water on the PUA membranes, hexane and water were individually dropped onto the functionalized SiO₂/PUA membrane, and the pristine PUA membrane as prepared before spray coating (see Figure 4). On the functionalized membrane, the hexane spread over a relatively larger area (spreading diameter of ~11 mm) in comparison with the pristine membrane (spreading diameter of ~6 mm), indicating improved oil wettability (see Figure 4a and b). In addition, the functionalized membrane exhibited the water contact angle of greater than 150°, which was significantly larger than ~85° observed on the pristine membrane (see Figure 4c

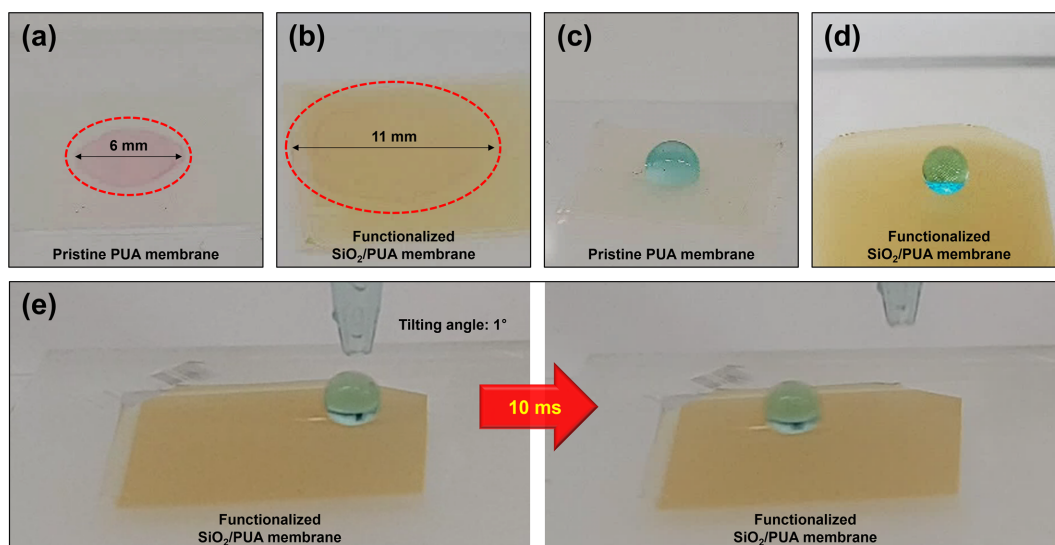


Figure 4. Photographs of hexane (stained with oil red O) and water (stained with methylene blue) on membranes. (a, b) Hexane droplets on the pristine PUA and functionalized SiO₂/PUA membranes; (c, d) water droplets on the pristine PUA and functionalized SiO₂/PUA membranes. (e) Sliding motion of a water droplet on the functionalized SiO₂/PUA membrane with 1 ° slope.

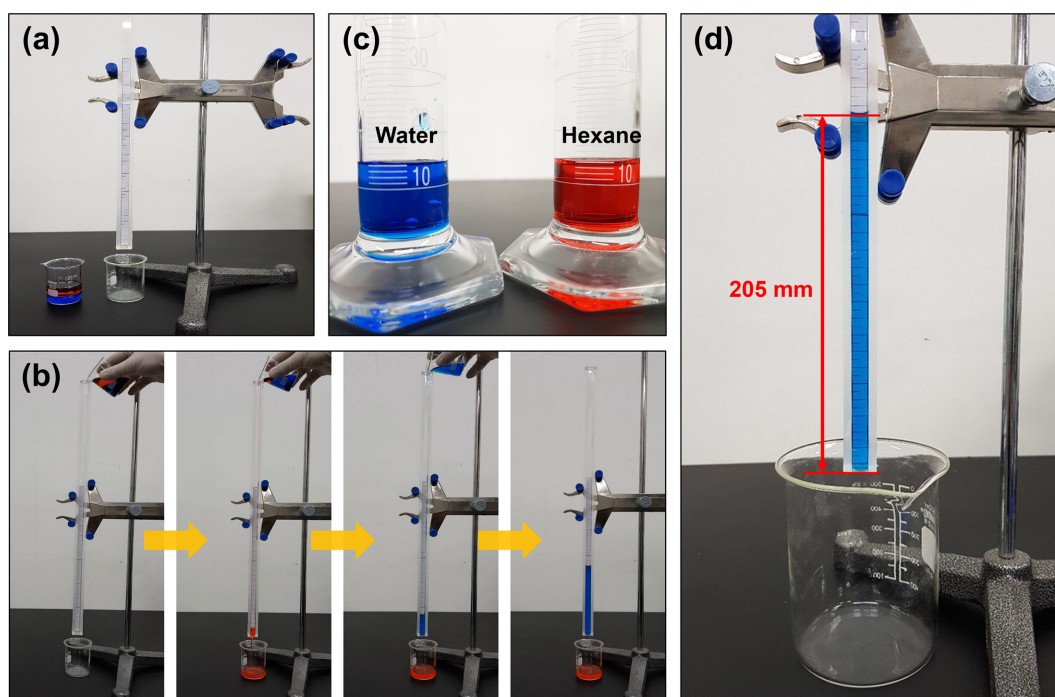


Figure 5. Photographs of oil/water separation process (hexane was stained with oil red O, and water was stained with methylene blue). (a) Experimental set-up for oil/water separation. (b) Sequential steps of the water/oil separation process. (c) Separation results, i.e., separated hexane and water after (b). (d) Measurement of water penetration pressure.

and d). The sliding angle of water, which refers to the angle at which water begins to roll, was also found to be less than 1 ° on the functionalized membrane (see Figure 4e). When the functionalized membrane was tilted to 1 °, the water droplets only rolled within 10 ms. Considering that the

sliding angle is less than 10 ° on a typical superhydrophobic material, the functionalized membrane exhibited excellent superhydrophobicity. Due to the oil/water selectivity (i.e., hexane interpenetrates the membrane, but water does not), these results can be applied to the design of various polymer-

based membranes and separators.

Figure 5 shows a demonstration of oil/water separation using the functionalized SiO₂/PUA membrane. The superhydrophobic membrane was fixed at the bottom of acrylic tube, and a mixture of hexane (15.0 ml stained with oil red) and water (15.0 ml stained with methylene blue) was prepared. As the prepared solution was poured into the tube, only the hexane instantly passed through the membrane, while the water was blocked by the membrane and remained in the tube (see Figure 5b and Supplementary Video 2). As a result, the two materials were completely separated (see Figure 5c), and the separation efficiency was calculated using the volume ratio of hexane before and after permeation. After the separation process, ~14.5 ml of hexane that passed through the membrane was collected, indicating a separation efficiency of ~97%. A small amount of loss (~0.5 ml) possibly occurred during the collection process, and a sufficient separation efficiency could be solely achieved with gravitational force. In addition, the penetration pressure of water was measured to determine how much pressure the membrane could withstand [63,64]. Figure 5d shows the maximum water height that the membrane could withstand. The membrane withstood the pressure exerted by 205 mm of water, which corresponds to ~2.0 kPa in consideration of the area of the membrane. It is worth noting that the functionalized SiO₂/PUA membrane is robust without losing its superhydrophobic properties against long-term contact with water. Since water cannot penetrate in the superhydrophobic nanoparticle layer coated on the PUA membrane, the nanoparticles are rarely removed from the membrane by water treatments. However, it was found that hexane treatments could damage the nanoparticle layer. When the membrane (15 mm×15 mm) was fabricated with a spray volume of 1.5 ml, the separation efficiency was constantly maintained until a total of 75 ml of hexane passed through the membrane, and then sharply decreased above that. Because hexane possibly penetrated in the nanoparticle layer, weakening the bonding forces between the nanoparticles, the nanoparticles could be desorbed from the membrane along with flowing hexane, leading to a decrease in hydrophobicity of the membrane.

Conclusion

We have introduced a facile and rapid method for the fabrication of PUA-based superhydrophobic membranes with hierarchical structure, enabling efficient oil/water separation. The PUA membrane supports with uniform pores can be easily prepared in a thin-film form using a soft PUA mixture. Because the PUA membrane supports intrinsically provide adhesive properties originating from unsaturated acrylate, SiO₂ nanoparticles can be rapidly and tightly deposited via one-step spray coating. SiO₂ nanoparticles also can be functionalized with a silane coupling agent to

lower the surface energy, which spontaneously form hierarchical structure upon spray coating onto the PUA membrane support. Thus, both low surface energy and rough surface structure can be simultaneously achieved by one-step spray coating of the functionalized nanoparticles for a few seconds, leading to the superhydrophobic properties. The PUA-based superhydrophobic membranes exhibited the water contact angle of greater than 150°, and the sliding angle of water was found to be less than 1°, indicating excellent superhydrophobicity. In addition, the wettability of oil was significantly improved by the functionalized SiO₂ nanoparticles, providing the oil/water selectivity. Based on these findings, efficient oil/water separation was successfully demonstrated using a mixture of hexane and water. A sufficient separation efficiency of ~97% could be solely achieved with gravitational force, and the membrane could withstand a high pressure of ~2.0 kPa. It is anticipated that these results will significantly contribute not only to the fabrication of superhydrophobic membranes with uniform pores but also the development of more diversified polymer-based membranes and separators leading to a wide range of applications.

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Conflict of Interest

The authors declare no conflict of interest.

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