

# **Bonding Nafion<sup>®</sup> with Polydimethylsiloxane: A Versatile Approach towards Ion-exchange Membrane Microfluidic Devices**

Minh-Hao Pham & Dominik P. J. Barz\*

Department of Chemical Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada

\*Electronic address: dominik.barz@queensu.ca

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**Abstract:** Polydimethylsiloxane (PDMS) is one of the most widely used materials for the fabrication of microfluidic devices. The uncomplicated integration of ion-exchange membranes, such as Nafion<sup>®</sup>, would facilitate manifold electrochemical processes in microfluidics. However, the Nafion ionomer does not directly bond with cross-linked PDMS and the assembly of the membrane and PDMS substrate still remains a technological challenge. This work reports a straightforward procedure using a simple bifunctional silane as crosslinking agent to directly integrate Nafion membranes into PDMS structures. The procedure applies a plasma treatment for both Nafion membrane and PDMS substrate to generate reactive surface functional groups that covalently bond with the functional groups of the silane, resulting in the formation of a strong chemical bonding across the interface. Peel tests prove the robust and uniform bonding that is also stable in acidic solutions. The ion conductivity of the bonded Nafion is comparable to that of the commercial Nafion.

## **1. Introduction**

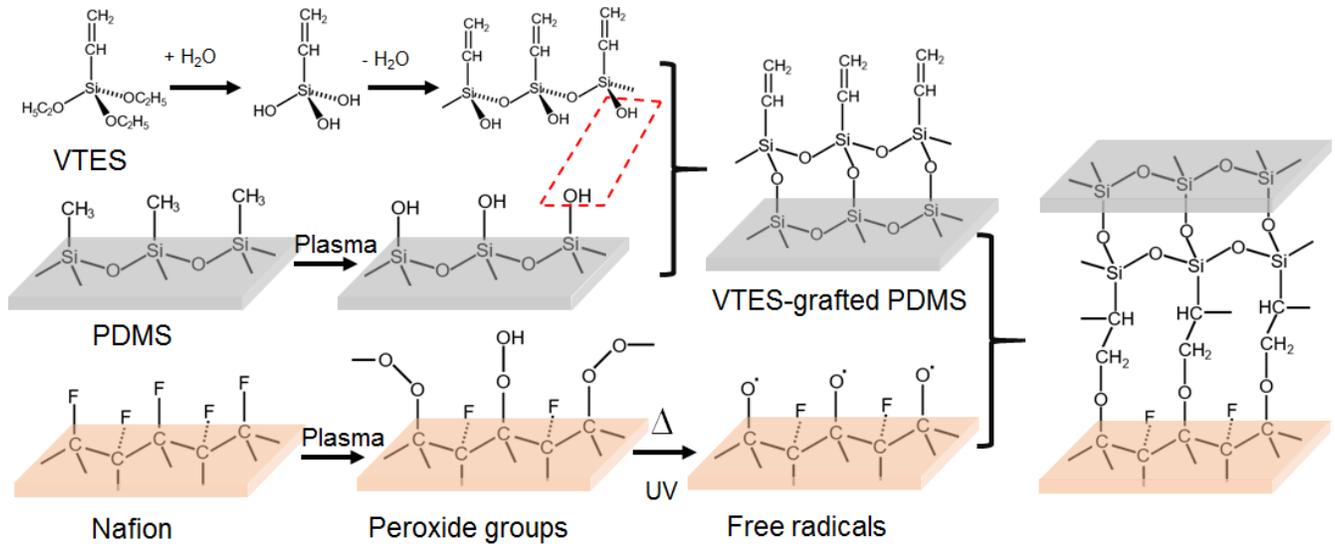
Progress in the fabrication of miniaturized systems has established different microfluidic concepts such as Lab-on-a-Chip (LOC), Micro-Total-Analysis-Systems ( $\mu$ TAS) and Point-of-Care-Testing (POCT) [1-4]. These systems offer the advantages of compactness and portability, easy operation and low reagent consumption as well as low manufacturing costs. However, many different materials, which are desirable as microfluidic substrates, cannot be easily combined by conventional integration mechanisms

such as diffusion, van der Waals interaction or direct chemical interaction due to their incompatible physical properties and/or chemical inertness [5, 6]. Device assembly from such incompatible materials requires the use of additional external casings such as cover plates along with holders such as screws or rivets. This makes the devices rather bulky which is contrary to the concept of miniaturization and unnecessarily complicates mass production [7-10].

The ionomer Nafion® and the moldable polydimethylsiloxane (PDMS) are the most popular ion-exchange membrane and microfluidic material, respectively [11-15]. Nafion is especially well suited for the transfer of small cations, such as protons and sodium ions, and has excellent thermal, chemical and mechanic stability. However, the tetrafluoroethylene ( $-\text{CF}_2-\text{CF}_2-$ ) based backbone of Nafion has a high chemical inertness which makes the adhesion to other materials difficult [16]. Likewise, PDMS is cross-linked by a curing agent during the fabrication of microfluidic structures. The cross-linked PDMS surface features a very low surface energy that results in an incompatibility with various materials including Nafion. Indeed, Slouka *et al.* emphasized in their review that one of the main challenges of microfluidic device fabrication is the integration of ion-exchange membranes such as Nafion [17].

Significant efforts have been made to integrate Nafion membranes into microfluidic devices [18-20]. One common strategy is the physical entrapment of Nafion inside the micro-holes of a PDMS thin-film scaffold [21-23]. Micro-holes are produced by means of a microfabricated mold and then filled with Nafion precursor. After curing, these PDMS-Nafion composite membranes can be bonded to other PDMS, silicon or glass-based components by plasma treatment but this fabrication strategy has several disadvantages. On the one hand, the fabrication of the composite membranes comprises several expensive microfabrication steps. On the other hand, the active ion conducting part of the membrane is much lower than its entire area due to the non-conductive PDMS portion. Moreover, the porous PDMS scaffolds are of rather delicate nature and due to the lack of adhesion between Nafion and PDMS, the composite membranes can be relatively easily damaged.

Therefore, the present research aims to develop a straightforward procedure using an alkoxy silane coupling agent in order to directly combine commercial Nafion membranes with cross-linked PDMS substrates, as illustrated in Fig. 1. In detail, the bifunctional alkoxy silane molecule possesses both hydrolysable alkoxy groups (R–O–Si–), that react with various forms of hydroxyl groups (–OH), and non-hydrolysable organic moieties that can form covalent bonds with other organic compounds [24]. The alkoxy groups, most typically methoxy (–O–CH<sub>3</sub>) and ethoxy (–O–C<sub>2</sub>H<sub>5</sub>), are hydrolyzed in the presence of water to generate reactive silanol groups (–Si–OH) that can undergo subsequent partial condensations forming oligomers. The air plasma treatment of cross-linked PDMS substrates also generates silanol groups on its surface. The plasma-treated PDMS substrate is then immersed in the pre-hydrolyzed alkoxy silane solution and a silane layer with free organic moieties is grafted covalently on the surface upon the condensation of the silanol groups.



**Fig. 1.** Scheme of the bonding between Nafion and PDMS via vinyltriethoxysilane (VTES) linkages.

Air plasma treatment also creates peroxide (–C–O–O–C–) and hydro peroxide (–C–O–O–H) groups on the tetrafluoroethylene skeletons of the Nafion polymer chains located on the membrane surface [25–28]. Under thermal initiation or UV irradiation, the peroxide groups decompose to form reactive free

radicals that are able to add to the double bonds of organic domains (e.g., vinyl, maleimide or acryloxy) [25, 26, 29, 30]. If the unsaturated organic moieties of the silanes grafted on the PDMS are put in contact with the treated Nafion surface, the covalent bonding between Nafion and PDMS is formed via free radical addition. As a result, the silane molecules induce strong linkages between PDMS and Nafion interface.

## 2. Experimental

*2.1. Bonding Nafion with PDMS:* In a typical experiment, a 4.0 wt. % aqueous solution of the silane coupling agent vinyltriethoxysilane (Sigma-Aldrich®, 97 %) in ethanol containing 10 vol. % of water was stirred for 1 h at room temperature to create the silanol groups. PDMS substrate was made by casting of PDMS precursors (Sylgard® 184, mix ratio of 10:1) and subsequent curing at 80 °C for 2 h. Air plasma treatment of the PDMS substrate was performed with a BD-20AC handheld corona producer for 10 minutes. The treated PDMS substrate was then dipped in the VTES solution for 2 minutes to allow the migration of the silanes to the surface. Then, the PDMS was dried in air and heated at 100 °C for 15 minutes to form siloxane linkages between the silanes and PDMS.

According to a common cleaning procedure, as-received Nafion® 117 membrane was first boiled in 3 wt. % hydrogen peroxide solution for 1 h, rinsed with DI water to remove organic impurities from its surfaces and then dried over night at ambient temperature. Next, the membrane was treated with corona for 10 minutes to generate (hydro) peroxide groups. The VTES-grafted PDMS substrate and the plasma-treated Nafion membrane were put in contact and firmly pressed between two glass slides using paper clamps. The sample was cured at 100 °C for 2 h and then cooled down to ambient temperature. The glass slides were removed for the test of the mechanical and electrical characteristics.

*2.2. Ion Conductivity Measurements:* Impedance spectroscopy of a two Pt-electrode cell with an Autolab Potentiostat/Galvanostat PGSTAT302N was used for the measurement of the membrane impedance in

aqueous solutions at frequencies from 100 Hz to 1 MHz and room temperature. Prior to the measurement, the membrane had been soaked in the respective solution for 24 h. Each measurement was repeated at least three times to determine mean value. First, the impedance of the cell was measured in absence of the membrane to determine the intrinsic resistance (cell constant) of the electrolyte system. The resistance value was derived from the intercept of the Nyquist plot with the real axis. Then, the impedance of the cell was measured with the PDMS-Nafion membrane assembled in the cell. The membrane resistance is thus the difference of the resistance measured with and without membrane installed in the cell. The specific conductivity of the membrane  $\sigma$  was calculated using the following equation:

$$\sigma = \frac{l}{R A}$$

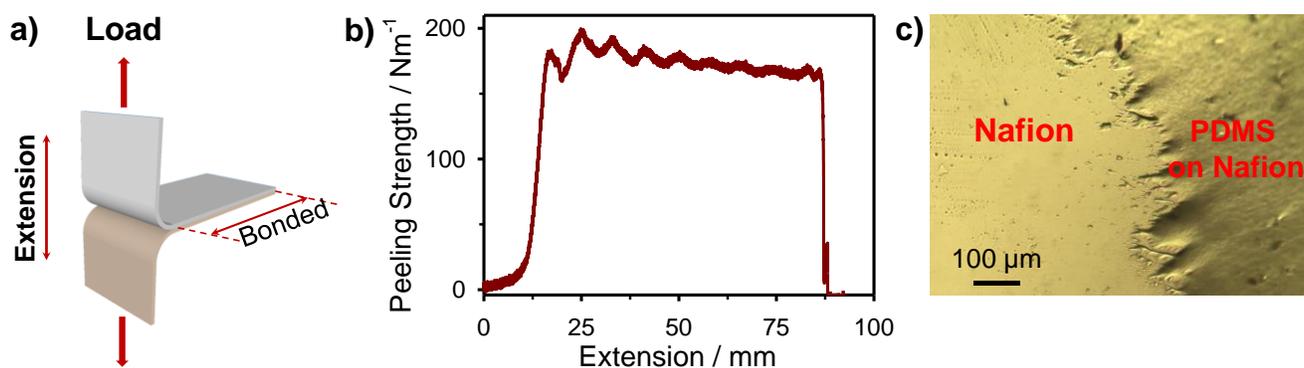
where R is the measured ohmic resistance of the membrane, A is the active conducting area of the circular opening of 8.0 mm in diameter,  $A = 0.5 \text{ cm}^2$ , and  $l = 210 \text{ }\mu\text{m}$  is the thickness of the fully hydrated Nafion 117 membranes which was measured with a thickness gage.

### 3. Results and Discussion

In order to bond Nafion with PDMS substrate, VTES coupling agent and PDMS substrate were, respectively, hydrolyzed in an aqueous ethanol solution and treated with corona discharge to create silanol groups. The treated PDMS was then dipped in the VTES solution and subsequently dried to form siloxane linkages between the silanes and PDMS. The (hydro) peroxide groups on the surface of Nafion membrane were also generated using a corona treatment. The VTES-grafted PDMS substrate and the plasma-treated Nafion membrane were put in contact and then heated to initiate the free radical addition reaction between the (hydro) peroxide groups and the vinyl groups of VTES.

The peel test is the common technique to evaluate the adhesion between two substrates. In order to determine the peeling strength, a PDMS sheet with size of 25 mm x 75 mm x 1.5 mm and a narrower

Nafion sheet were bonded together as described above. The width of the PDMS sheet is larger than that of the Nafion sheet to avoid tearing the PDMS sheet from its edges. The corona treatments were only implemented on half of the sheets. The T-peel testing was then carried out using an Instron® 3369 Universal Testing System with a peeling speed of 5 mm/min, as illustrated in Fig. 2a.



**Fig. 2.** a) Illustration of T-peel testing method; b) Peeling strength of the bonded PDMS-Nafion vs. extension; and c) Optical microscope image at the boundary between the non-bonded (labelled Nafion) and the bonded (labelled PDMS on Nafion) areas of the Nafion membrane after the peel test.

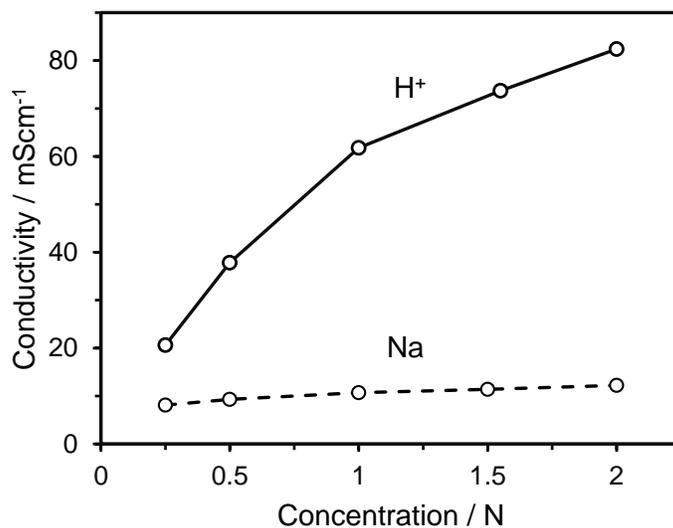
Fig. 2b shows a typical result of the T-peel test. We can clearly distinguish between two different regimes. At the beginning and up to an extension of around 10 mm, the peeling strength is close to zero and the two sheets even separated before the measurement could be performed. This regime corresponds to the non-bonded area without the corona treatment. These observations confirm the inability to bond Nafion and cross-linked PDMS without modifications. In contrast, the peeling strength in the bonded region, where the corona treatments were applied, reached a peak value of around 200 N/m. This value proves the robust bonding between the two initially incompatible materials. Moreover, the plateau-like trend of the peeling strength in the bonded region indicates a uniform chemical adhesion across the interface.

After the mechanical peel-off, a thin layer of residual PDMS completely covers the bonded area of the Nafion sheet, as shown in Fig. 2c. In some of the peel tests, the PDMS sheets were even torn apart

right after the peeling strength had reached a value of around 225 N/m (Fig. S1, Supporting Information). These results exhibit that the bonding via the silane linkages is stronger than the fracture of the PDMS substrate. Therefore, it is inferred that the actual bonding strength could be higher than the measured value of 200 N/m and this value could correspond to the tearing strength of the PDMS substrate. In order to clarify this assumption, the tearing strength of the PDMS substrate was measured using the trouser tear testing method as illustrated in Fig. S2 of the supporting information [31]. The measurement exhibits that the PDMS substrate features a tearing strength of about 165 N/m to 190 N/m (Fig. S2, Supporting Information). The tearing strength is very similar to the measured peeling strength of the bonded PDMS-Nafion, which strengthens the above inference.

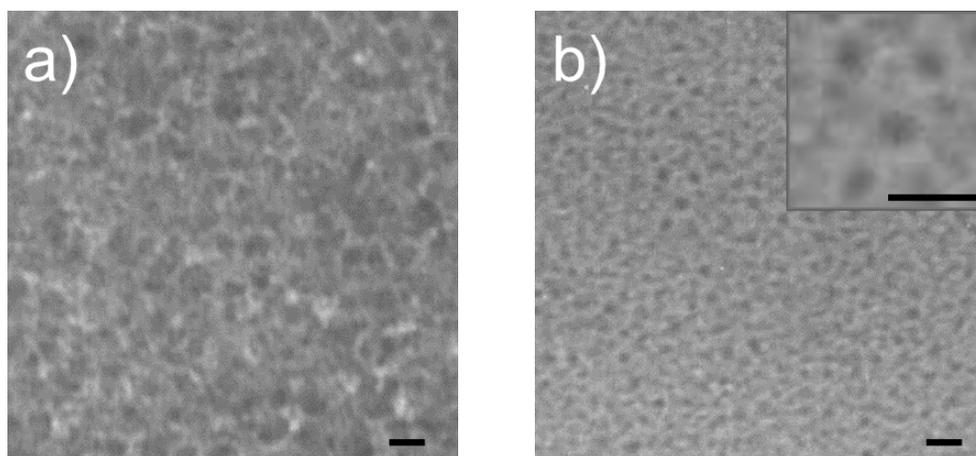
Microfluidics is one of the applications where Nafion membranes have to be integrated into PDMS structures. Contrary to PDMS, the Nafion ionomer significantly swells when exposed to aqueous solutions which can cause considerable mechanical stress at the interface of the bonded materials [32]. Hence, the stability of the adhesion in aqueous solutions needs to be assessed over a certain time period as well. The PDMS-Nafion samples were first soaked in different aqueous solutions, namely 1.0 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and 1.0 M sodium chloride ( $\text{NaCl}$ ), for one week at room temperature. Subsequently, excess liquid was wiped off and the samples were allowed to dry in air. After soaking, the Nafion and PDMS parts in the untreated area of the soaked specimens were detached due to the Nafion swelling. In contrast, in the plasma-treated area, excellent adhesion between the different substrates was observed and the measured peeling strength in the range of 170 to 218 N/m matches that of the non-soaked samples (Fig. S3, Supporting Information). Again, tearing of the PDMS substrates was observed rather than failure of the PDMS-Nafion bonding. This demonstrates that our method results in excellent irreversible bonding despite of being subjected to strongly acidic solution. The stability of the adhesion can be attributed to the formation of the strong covalent bonds of the linking silanes with both Nafion membrane and PDMS substrate.

In order to evaluate through-plane ion conductivity in the membrane, a Nafion sheet with a size of 2.5 x 2.5 cm<sup>2</sup> was bonded onto a cross-linked PDMS sheet with a circular opening of 8.0 mm in diameter. The inferred conductivities for the bonded Nafion membrane in aqueous H<sub>2</sub>SO<sub>4</sub> and NaCl solutions at various concentrations and ambient temperature are plotted in Fig. 3. Details about the results are presented in the Supporting Information. As can be seen in Fig. 3, the ion conductivities increase with an increase in the ion concentrations. As the concentrations change from 0.25 N to 2.0 N, the proton and sodium conductivities rise from 20.6 mScm<sup>-1</sup> to 82.4 mScm<sup>-1</sup> and from 8.1 mScm<sup>-1</sup> to 12.2 mScm<sup>-1</sup>, respectively. The conductivity of the bonded membrane is only 71 to 75 % of the Nafion 117 membrane after the H<sub>2</sub>O<sub>2</sub> cleaning (Tables S1,S2, Supporting Information). This lower conductivity can probably be attributed to the air plasma treatment and the thermal initiation/curing of the bonding procedure. Similar results were found by Ramdutt *et al.* who measured the proton conductivity of Nafion 117 membrane after a thermal treatment at 100 °C to be around 70 % of a H<sub>2</sub>O<sub>2</sub> cleaned membrane [34]. It is assumed that the treatments induce a structural change of the Nafion ionomer resulting in a distortion and shrinkage of pores that lowers the conductivity [33, 34].



**Fig. 3.** Proton (solid line) and sodium (dashed line) conductivities of the bonded PDMS-Nafion membrane.

In order to distinguish between the effect of the plasma and the heat treatment, the membrane ion conductivity after the air plasma exposure was measured and compared to that of a membrane after H<sub>2</sub>O<sub>2</sub> cleaning and after H<sub>2</sub>O<sub>2</sub> cleaning and bonding. The measured proton and sodium conductivities of the plasma-treated membrane in 1 M solutions are 96.1 mS<sub>cm</sub><sup>-1</sup> and 12.3 mS<sub>cm</sub><sup>-1</sup>, respectively. These values approximately correspond to 81 and 87 % of the membrane conductivity after H<sub>2</sub>O<sub>2</sub> cleaning. Recall that the respective values of the cleaned and bonded membrane are only 71 and 75 % of the membrane after H<sub>2</sub>O<sub>2</sub> cleaning. Hence, we conclude that both the plasma and the heat treatment contribute to the decrease of the ion conductivity but the plasma treatment is the dominating factor.



**Fig. 4.** Cross-section TEM images of the Nafion membranes after a) H<sub>2</sub>O<sub>2</sub> cleaning and b) after bonding; scale bars are 10 nm.

To further evaluate the impact of the bonding process on the pore structure, cross-section Transmission Electron Microscopy (TEM) images of a H<sub>2</sub>O<sub>2</sub> cleaned and a H<sub>2</sub>O<sub>2</sub> cleaned and bonded membrane were taken. Prior to the TEM imaging, the membranes were embedded between two polystyrene plates and sliced with an ultramicrotome to fabricate very thin specimens with a thickness of around 50 nm to ensure electron transparency. Fig. 4 shows the cross-section TEM images of both membranes. We find a random distribution of ionic clusters in the polymer matrix, indicated by the dark domains, which is consistent with the nanostructure of Nafion in dry state, cf. Refs. [35, 36]. It should be noted that, due to TEM operation at high vacuum, the obtained images characterize the Nafion membranes in a dry state

rather than a hydrated state. Nevertheless, as can be clearly observed in Fig. 4, the cluster size of the bonded membrane, given in part b), is significantly smaller than that of the cleaned membrane, depicted in part a). This comparison clearly demonstrates the structural change and shrinkage of the pores due to the bonding process.

The thermal initiation of the covalent bonding formation between the peroxide and vinyl groups was also tested at lower temperatures and different treatment times to minimize the impact on the pore structure and the performance of the bonded membrane. In detail, Nafion was bonded with PDMS at a curing temperature of 75 °C and the treatment time was either 2 h or 6 h. Curing with the shorter time results in a measured peeling strength range of 60 – 90 N/m, which is considerably lower than the peeling strength that is achieved for bonding at 100 °C and the same duration. This value is also smaller than the tearing strength of the PDMS substrate. The extension of the curing time to 6 h results in a peeling strength range of 62 – 105 N/m, indicating that there is no significant influence of longer curing times, at least at this low temperature. Moreover, bonding at 75 °C results in larger variations of the peeling strength across the PDMS-Nafion interface, as can be seen in Fig. S4 of the Supporting Information. Such behavior indicates an inhomogeneous adhesion. We conclude that a bonding process at lower temperatures is not suitable to form a secure adhesion between PDMS and Nafion membrane.

#### **4. Conclusion**

In summary, we developed a straightforward procedure using a simple silane as a coupling agent to directly bond Nafion polymer membranes to cross-linked PDMS substrates. The bifunctional silane molecules serve as linkages across the interface between the Nafion and the PDMS substrate. The bonding is achieved through strong covalent bonds of the functional groups of the pre-hydrolyzed silanes and the pre-created reactive groups on the surfaces of both Nafion membrane and PDMS. Since the fluoropolymer backbones of Nafion and the cross-linked PDMS do not possess any intrinsic functional groups for covalent bonding, the air plasma treatment is an essential requirement to create

the desired surface functional groups. The measured peeling strength for the bonded PDMS-Nafion substrates proves a robust and irreversible chemical adhesion. But for substrate surfaces without any plasma treatments, it is very close to zero; i.e., there is no bonding. The PDMS-Nafion membrane features ion conductivity characteristics comparable to a commercial Nafion ionomer which is beneficial for applications.

It should be possible to modify the current procedure for the combination of non-adhesive fluoropolymer membranes with other substrates. In principle, an appropriate conditioning, such as plasma treatment or ozonisation, can generate chemically active surface functional groups on membrane and substrate. And therefore, linking molecules possessing functional groups that are able to bond covalently with the created active surface groups can be used to form strong crosslinking bridges across the interface between two materials. The developed bonding procedure is thus expected to be a potential technique for the integration of other non-adhesive functional materials, such as fluoropolymers membranes, with various substrates based on silicon materials or metal oxides;

### **Supporting Information**

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2017.xx.xxx.

### **Acknowledgements**

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