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## Self-supporting hybrid silica membranes with 3D large-scale ordered interconnected pore architectures

Chang Han<sup>a</sup>, Meng-Ya Li<sup>a</sup>, Ying-Ning Li<sup>a</sup>, Han-Lan Liu<sup>a</sup>, Ping Wang<sup>a</sup>, Maryanne M. Collinson<sup>\*b</sup>, and Zhe-Xue Lu<sup>\*a</sup>

<sup>a</sup> College of Science, Huazhong Agricultural University, Wuhan 430070, China

<sup>b</sup> Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284-2006, United States

### Abstract

A simple and versatile method to form transferrable self-supporting membranes with hierarchically ordered arrangement of nanometer size pores has been developed. The method relies on the formation of a ordered 3D arrangement of latex spheres on a sacrificial support, proper infusion of a suitably prepared organic-inorganic hybrid sol, followed by template removal without membrane destruction. To begin, the mechanical properties of self-supporting membranes prepared by combining a bi-functional silane (i.e., dimethyldimethoxysilane, DMDMOS) with tetramethoxysilane (TMOS) in different mole ratios were studied by nanoindentation. As the amount of DMDMOS increased, the hardness and Young's modulus decreased while the ratio of the two first decreased and then increased. The surface morphology and roughness as evaluated by Atomic Force Microscopy (AFM) also increased with the DMDMOS to TMOS ratio. Using a mole ratio of 1:1 and a close-packed 3D array of polystyrene spheres as a template, a flexible and transferrable membrane containing an ordered arrangement interconnected pores of well-controlled size was constructed. The diameters and number of layers of the 3D pore architectures were manipulated by changing the microsphere diameter and concentration. Surface pore diameters ranged in size from 110-300 nm while the diameters of the internal pores ranged from 60-140 nm depending on the size of the original template. The number of layers ranged from two to five. Such self-supporting membranes, with their uniquely hierarchical, interconnected pore architectures over a large length scale, can be transferred to other surfaces for potential and promising applications in the fields of filtration, sensing and catalysis.

### Introduction

Self-supporting nanoporous membranes of macroscopic size and nanometer thickness have attracted considerable attention because of their prospective applications in nanofiltration devices,<sup>1-2</sup> sensors,<sup>3-7</sup> and dye sensitized solar cells.<sup>8-10</sup> Ion channels and other transport systems in biological membranes are ideal in this respect. However, because of the fragility of the biological membranes, it seems unlikely that practical nanofiltration or sensing devices will result from such membranes. Thus, many researchers have turned to the design and fabrication of synthetic membranes.<sup>1-2, 6, 11-12</sup> For such applications, the membranes need to be defect-free, uniform, and macroscopically robust with high

permeability. The transferability of such membranes allows them to be used with unconventional supports, such as those that are microscopically rough and chemically heterogeneous.<sup>8</sup>

Several efforts have been made to obtain uniform, self-supporting membranes with pores in the nanosized range.<sup>2, 11-14</sup> For instance, Baun et al described the multi-step fabrication of a transferrable porous titania photonic film onto dye-sensitized solar cells<sup>8</sup>. Feng et al.<sup>2</sup> reported the synthesis of free-standing mesoporous carbon films by a simple coating-etching approach. These mesoporous carbon films have an intact morphology with variable sizes as large as several square centimeters and a controllable thickness of 90 nm to ~ 3  $\mu\text{m}$ . Velleman et al.<sup>11</sup> used the electrochemical etching of silicon to produce membranes with controlled structure and pore size close to molecular dimensions. Moreover, with such electrochemical etching method, Yang et al.<sup>12</sup> demonstrated a simple, low-cost, effective method to fabricate free-standing porous membranes related to silicon by in situ conversion of porous silicon films. Also, biomolecule-directed assembly was exploited to form self-supported nanoporous single-walled carbon nanotube scaffolds.<sup>13</sup>

In addition to these methods, the combination of sol-gel polymerization with templating has been shown to be a promising method for the fabrication of self-supporting thin membranes with pores in the nanosized region.<sup>15-18</sup> Sol-gel technology offers several advantages including processing under mild conditions, ease of manipulation of the structure and chemical characteristics of the inorganic matrices, and chemical inertness.<sup>19-21</sup> In previous work,<sup>17-18</sup> we showed that sol-gel processing can be merged with template-based processing to fabricate self-supported nanoporous silica membranes. In one example, polystyrene latex spheres were used as the template to create a membrane with asymmetric nanopores;<sup>17</sup> in the other, micron-sized bacteria were used to create micron-sized channels.<sup>18</sup> The pore size and shape of the self-supporting membranes were modified through changes in the size and shape of the templates (*i.e.*, polystyrene spheres or bacteria).

One of the main limitations associated with our early work<sup>17</sup> was the inability to form a close-packed layer of spheres on the polymer coated support with any degree of long-range order. This ultimately prevented the formation of a self supporting membrane with an ordered arrangement of pores over a large length scale, which is often a necessity for applications in catalysis, sensing, and especially filtration. Furthermore, it was also not feasible to form a 3D ordered arrangement of spheres and thus a self-supporting membrane with a defined 3D arrangement of interconnected pores of a controlled size. An additional challenge also lies in the fabrication of a membrane that is stable, not brittle, and does not undergo a high percentage of shrinkage during drying leading to random microscopic cracks. Traditional sol-gel precursors such as tetramethoxysilane or tetraethoxysilane often yield brittle materials.

In this work, these challenges have been addressed and solved using a two-step approach. First, the mechanical properties of sol-gel derived membranes prepared from dimethyldimethoxysilane (DMDMOS) and tetramethoxysilane (TMOS) were studied. Hardness (H), Young's modulus (Er), and brittleness were investigated using nanoindentation coupled with atomic force microscopy (AFM). With this knowledge in hand, we were then able to pick the most stable composition to construct the self-supporting and transferrable membrane. Second, ITO-coated glass was used as the sacrificial support instead

polystyrene-coated glass. Both 2D and 3D lattices of colloidal spheres could easily be formed on ITO, particularly in conjunction with the vertical deposition route.<sup>22-24</sup> By infiltrating the colloidal crystal with the appropriate DMDMOS/TMOS sol and dissolving the underlying ITO layer followed by template removal, a self-supporting and transferrable membrane with a unique architecture consisting of an ordered arrangement of interconnected pores of well-controlled sizes was made. The method described provides a means to easily tailor the mechanical properties of the self-supporting membranes to improve stability and transferability. It also provides a means to manipulate the diameters and the number of layers of the highly ordered pores. The obtained large, self-supporting, hierarchical ordered porous membrane can be transferred to other surfaces such as a sensor/chip surface for sensing or the surface of a filtration device for separation/filtration. Improvements in selectivity can be potentially obtained by trapping reagents into the porous network, by chemically modifying the silica surface,<sup>11</sup> and/or introducing molecularly imprinted sites into the silica framework.<sup>25</sup>

## Experimental

**Reagents.** TMOS was purchased from TCI Shanghai. Methyltrimethoxysilane (MTMOS), phenyltrimethoxysilane (PTMOS) and dimethyldimethoxysilane (DMDMOS) were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Chloroform (AR), hydrochloric acid (AR), 2-propanol (AR) and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Aqueous suspensions of polystyrene microspheres with diameters ranging from 0.2  $\mu\text{m}$  to 0.4  $\mu\text{m}$  were obtained from Invitrogen Corporation. Water was purified with an ultrapure water purification system.

**Preparation of Self-Supporting Membranes.** ITO coated glass (obtained from Zhuhai Kaivo optoelectronic Technology Co., Ltd.) were cut into 1.2 cm  $\times$  1.2 cm squares and cleaned by successive sonication in soap, ethanol and water, and then spin coated with a silica sol. Silica sols with different DMDMOS/TMOS mole ratios ranging from 0:1 to 3:1 were prepared by mixing 100  $\mu\text{L}$  TMOS, DMDMOS (0, 46, 92, 138, 184 and 276  $\mu\text{L}$ ), 200  $\mu\text{L}$  2-propanol, 30  $\mu\text{L}$  water, and 30  $\mu\text{L}$  0.1 M hydrochloric acid followed by stirring for 30 min. The sol was then aged for one day at room temperature. For the experiments using a diluted sol, dilution was done by mixing 100  $\mu\text{L}$  of the original aged sol with 0, 100, 200, 300 or 400  $\mu\text{L}$  of 2-propanol, respectively. The sols were then spin cast on ITO coated glass substrate at *ca.* 3000 rpm for 30 s using a commercial spin coater. The thin membranes supported on ITO coated glass were allowed to dry for 2 days at room temperature. The mechanical properties and surface morphology of such membranes were characterized by using a TI 750 Ubi nano-indenter and an AFM system integrated on it (Hysitron, USA). In the nanoindentation experiments, a pyramid-shaped Berkovich-type diamond tip whose radius of curvature is 50 nm was used. Multiple unloading-reloading processes were performed by a displacement controlled load function with 20 cycles, which ranging from 10 nm to 210 nm. For each sample, nine indentations were made and the results presented are an average of these indentations. To avoid the substrate effect when measuring the mechanical properties of the membrane made from the pure TMOS sol, several microliters of the TMOS sol were dropped on the ITO coated glass to make the membrane thicker than what could be achieved via spin

coating. To detach the film from the substrate, the membrane supported on ITO glass was immersed into 6 M hydrochloric acid. Approximately 30 min later, the membrane (DMDMOS/TMOS mole ratio ranging from 1:1 to 2:1) separated from the substrate and floated to the top where it was then transferred onto a clean glass substrate for film thickness measurement via profilometry (Form Talysurf Profiler-S4C, Taylor Hobson, U.K.).

### **Preparation of Self-Supporting Membranes with Highly Ordered 3D Pore Architectures.**

A 3D layer of closely-packed microspheres on ITO coated glass was prepared using the vertical deposition method.<sup>22-24</sup> A slide was vertically placed into a vial containing the solution of polystyrene spheres diluted in ultrapure water. The concentration of the spheres solution ranged from 0.025% to 0.35% w/v. The vial was kept in a temperature-controlled mini-incubator at 45 °C for about 30 hrs. After the completion of the drying process, the 3D closely-packed microspheres were obtained on the ITO coated glass substrate. A one-day aged sol diluted with 2-propanol (in a 1:1 ratio for the 0.29 μm and 0.4 μm spheres or 1:2 ratio for the 0.2 μm spheres) was spin coated onto the 3D array of closely-packed microspheres at *ca.* 6000 rpm for 30 s. The thin membranes formed were then allowed to dry for 2 days at room temperature. To detach the membrane from the glass substrate and remove the template (polystyrene microspheres), the membrane was immersed into 6 M hydrochloric acid for 1 h and then immersed into chloroform for 1 h. The self-supporting membranes with ordered 3D pores were then coated with gold to reduce charging effects and then imaged using a field emission scanning electron microscope (FE-SEM, SIGMA, ZEISS, Germany).

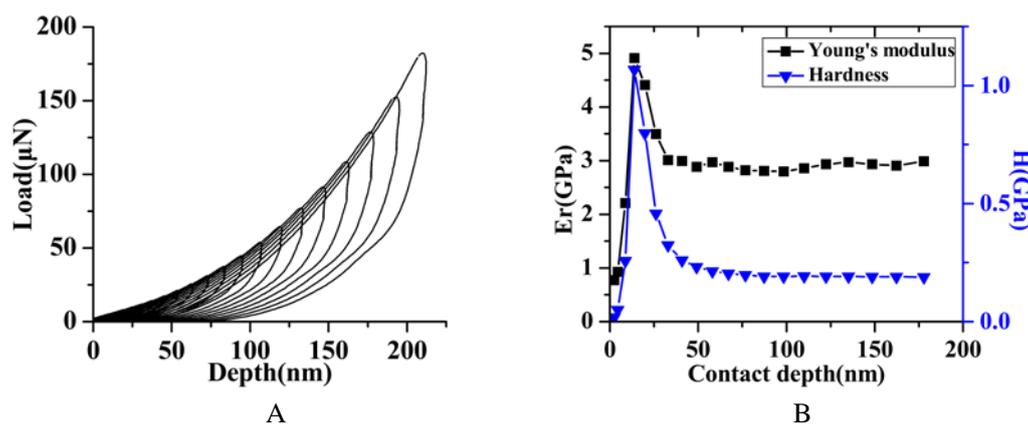
## **Results and Discussion**

### **Membrane Preparation and Characterization**

Sol-gel processing<sup>19-21</sup> provides an important and valuable means to form thin films on insulating and conducting surfaces and in some less typical cases, self-supporting membranes.<sup>15, 17, 26-29</sup> To be of use in any meaningful investigation, it is critical that the self-supporting membranes be stable and not easily fragmented into tiny pieces.<sup>17</sup> However, when such membranes are prepared solely from traditional precursors such as tetraethoxysilane or TMOS, the thin membranes are fragile. To introduce more flexibility into the matrix, organoalkoxysilanes can be used.<sup>30</sup> In this study, a number of organoalkoxysilanes was evaluated as a means to create intact, self-supporting thin films that can be detached from a surface without fracturing including methyltrimethoxysilane (MTMOS), phenyltrimethoxysilane (PTMOS), and DMDMOS. Specifically, the organoalkoxysilane was mixed with the traditional tetrafunctional silane, TMOS, in different mole ratios. The resultant hybrid silica sol was then spin coated on a ITO coated glass after a one-day aging time. By dissolving the underlying ITO layer after a two-day film drying period, the membrane detached and floated to the surface. The results showed that, no matter what the ratio of MTMOS or PTMOS to TMOS, these membranes were not stable and broke into tiny pieces once they detached from the ITO coated glass. This result was consistent with our earlier investigation.<sup>17</sup> When using DMDMOS, however, large, intact, self-supporting membranes could be obtained with DMDMOS/TMOS mole ratios between 1 and 2, thus confirming that DMDMOS is an excellent organoalkoxysilane to create stable self-supporting membranes using ITO as the sacrificial support.

The mechanical properties of the self-supporting membranes are critical to many applications and particular attention should be paid to the hardness, Young's modulus ( $E_r$ ), and brittleness of the membranes. In the first part of this investigation, quantitative information on the mechanical and surface properties of hybrid self-supported membranes prepared with different DMDMOS/TMOS mole ratios were obtained by using a nanoindentation technique combined AFM and surface profilometry. Nanoindentation is a convenient method to evaluate the mechanical properties of thin films. It involves nanoindentation testing, nanoscratch testing, and scanning wear testing. In nanoindentation testing, by employing small loads and an indenter with a geometry known to high precision, various parameters such as load and depth of penetration can be measured.<sup>31</sup> A record of these values can be plotted on a graph to create a load-displacement curve, and then the mechanical properties of the materials can be extracted from the curve.<sup>31-32</sup> This method was exploited here to detect the hardness and Young's modulus ( $E_r$ ) of the membranes made with different DMDMOS/TMOS mole ratios.

Figure 1A shows a typical load-displacement curve in the multiple unloading–reloading nanoindentation experiments with a displacement control ranging from 10 nm to 210 nm. According to this curve and the methods proposed by Oliver and Pharr,<sup>32</sup> the hardness and  $E_r$  with different contact depth were obtained and plotted in Figure 1B. Figure 1B showed that the hardness first increased sharply at small indentation depth, and then decreased in a rather meandering manner. Eventually it reached a constant value at a moderate indentation depth. As explained by Jian and *et al.*,<sup>33</sup> the hardness values obtained at the constant-value stage can be regarded as the intrinsic properties of the films. Therefore, the values of hardness and  $E_r$  in Table 1 were obtained at the depth around 100 nm, which is lower than one-tenth the thickness of the hybrid membrane as measured via surface profilometry. Therefore, substrate effects would be minimal.



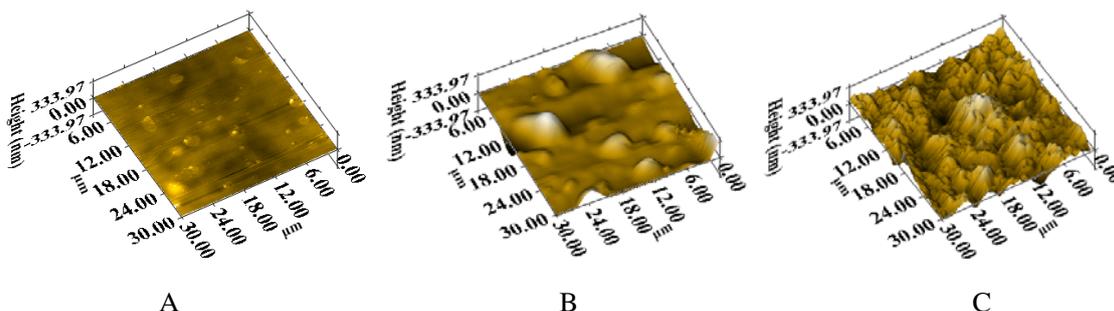
**Fig. 1** (A) A load-displacement curve obtained by using a multiple unloading-reloading progress; (B) Plot of hardness (H) and Young's modulus ( $E_r$ ) versus contact depth. The membrane was prepared with a DMDMOS/TMOS ratio of 1:1

**Table 1:** Hardness (H), Young's modulus ( $E_r$ ), and the brittle index of the membranes with different DMDMOS/TMOS ratio measured by nanoindentation

The mole ratio of DMDMOS to TMOS	0	0.5	1	1.5	2
H(GPa)	0.652	0.62	0.18	0.056	0.032
Er(GPa)	5.07	4.83	2.53	0.65	0.339
H/Er	0.129	0.128	0.071	0.086	0.094
Thickness/ $\mu\text{m}$	N/A	1.04	1.20	1.24	1.32

As seen in Table 1, the hardness and Er decreased as the amount of DMDMOS increased, which is consistent with the report of Mackenzie *et al.*<sup>34</sup> With the hydrolysis/condensation of DMDMOS, polydimethylsiloxane (PDMS) chains would form and incorporate into the SiO<sub>2</sub> network formed by hydrolysis/condensation of TMOS. The hardness and Er of the SiO<sub>2</sub> network would be expected to decrease. What is interesting is that, with increasing DMDMOS content, the ratio of hardness to Young's modulus (H/Er), which was reported as the index of brittleness,<sup>35-36</sup> first decreased and then increased. The reason we think is that, with the increasing of the amount of DMDMOS, the amount of PDMS chains would increase. The PDMS chains would break up the continuity of the SiO<sub>2</sub> network and contribute some degree of deformability, which would thus reduce the membrane brittleness. At some point, however, the reduced degree of cross-linking of the SiO<sub>2</sub> network that inevitably takes place with the continued addition of DMDMOS, will play an important role and membrane brittleness will increase at a certain critical amount. From Table 1, this appears to take place at a DMDMOS/TMOS mole ratio of  $\sim 1.5$ . However, with DMDMOS/TMOS mole ratios between 1 and 2, the value of H/Er of the membrane was much lower than that of the membrane made from pure TMOS, which demonstrate such membranes are more flexible and stable, consistent with direct observation by eye. The results show that flexible, self-supporting hybrid silica membrane with different mechanical properties can be obtained.

As studied by Oh and *et al.*,<sup>37</sup> the processing conditions and the component content can also affect the microstructure of the silica membranes. In this study, atomic force microscopy (AFM) integrated on the nanoindenter was used to obtain surface images of the membranes with DMDMOS/TMOS in the ratio of 1, 1.5 and 2. Figure 2 shows the surface morphology of the three different membranes and Table 2 reports surface roughness data obtained from  $30 \times 30 \mu\text{m}^2$  images. It was found that upon increasing the DMDMOS content in the film, more protrusions appeared on the surface and the surface roughness increased accordingly. As described above, the extent of cross-linking in the SiO<sub>2</sub> network would decrease as the DMDMOS content increases. When the DMDMOS content exceeds a certain critical amount, the SiO<sub>2</sub> network becomes such that SiO<sub>2</sub> clusters are isolated from one another, but are connected largely by the PDMS chains. The net result is in an increase in surface roughness.



**Fig. 2** AFM three-dimensional images in topographic mode of the membranes made from the sol with different DMDMOS/TMOS mole ratio: (A) 1:1; (B) 1.5:1; (C) 2:1. Image sizes:  $30 \times 30 \mu\text{m}^2$

**Table 2:** RMS roughness and average roughness measured by the AFM system integrated on the nanoindenter

The mole ratio of DMDMOS to TMOS	1	1.5	2
RMS roughness/nm	4.83	63.98	78.80
Average roughness/nm	3.56	41.96	61.70

In addition to the mechanical properties and surface morphology, membrane thickness and wettability are also important factors. By dissolving the underlying ITO layer, the membrane detached and floated to the surface while the glass substrate falls to the bottom. The self-supporting membrane can then be transferred onto a piece of clean glass for membrane thickness characterization by using profilometry. As shown in Table 3, the self-supporting membranes with thickness from approximately 160 nm to 1200 nm could be easily acquired by changing the viscosity of the original sol with a DMDMOS/TMOS mole ratio of 1 by dilution with 2-propanol. Because the membranes contained DMDMOS, they are expected to be slightly hydrophobic. Contact angle measurements on similar spin coated composite films yielded a contact angle of approximately  $82^\circ$ .<sup>38</sup>

**Table 3:** Thickness of the membranes made from the sol with a DMDMOS/TMOS mole ratio of 1:1 and with different dilution by using 2-propanol

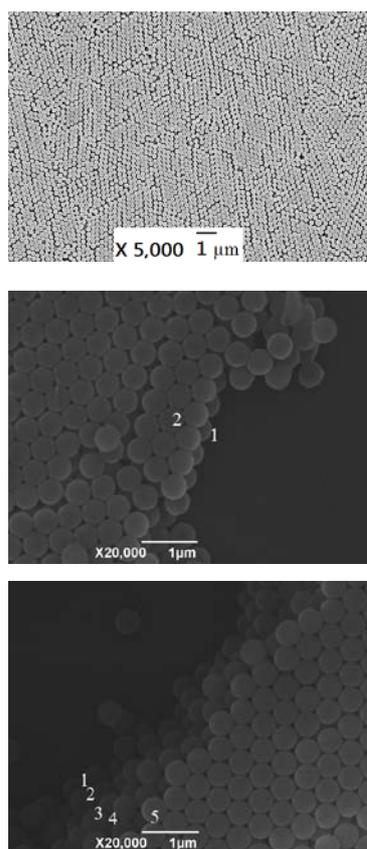
Different dilution ratio (2-propanol: original sol)	0	1	2	3	4
thickness/nm	1200	450	400	200	160

### Introduction of Highly Ordered, Interconnected, 3D Pores

As described above, large, flexible, self-supporting membranes with different mechanical properties and thickness can be obtained from DMDMOS/TMOS hybrid sols. If an ordered arrangement of nanosized pores can be introduced into such self-supporting membranes, it will greatly extend their usefulness in applications related to separation and filtration. In previous work,<sup>17</sup> single asymmetric nanopores or localized arrays of asymmetric nanopores

were created in silica membranes. In this case, a polystyrene coated glass was used as the sacrificial substrate. A much more challenging problem, however, is to fabricate three-dimensional (3D) architectures with highly ordered interconnected nanopores. Nature has developed routes to produce materials with complex structures and multifunctional properties and thus offers great inspiration for scientists to engineer similar materials.<sup>39-41</sup> For example, the nanoporous microsilia shells of Diatoms were exploited as mask to fabricate self-supporting gold microstructures with 3D pores.<sup>39</sup> However, since the 3D pores are inherited directly from the biological template of diatoms, the pore size and number of layers can't be manipulated, and large-sized self-supporting membranes, which have more practical applications in filtration and sensing, can't be obtained.

In the present study, to facilitate the fabrication of large, flexible, self-supporting flexible membranes with ordered and interconnected 3D pore architectures, ITO coated glasses were used in conjunction with the vertical deposition<sup>22-24</sup> to fabricate a close-packed 3D array of spheres.<sup>42-45</sup> Figure 3 shows SEM images (top view and side view) of polystyrene latex spheres on the ITO substrate. The number of layers can be controlled by the concentration of spheres in the deposition solution. Some small defects/dislocations can be seen in all three images, which is not uncommon in such materials.<sup>46</sup>

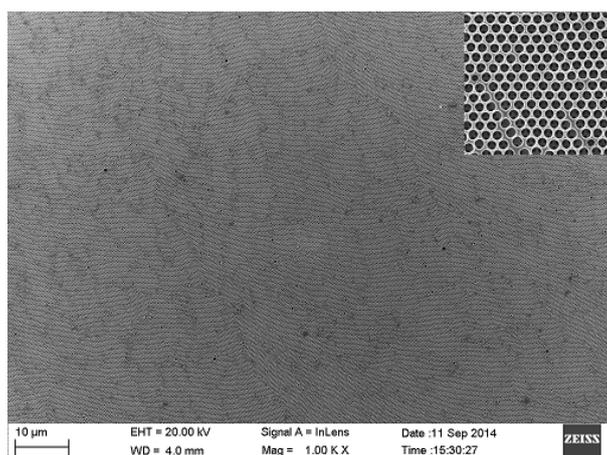


**Fig. 3.** SEM images of the multilayer spheres prepared from the 400 nm diameter spheres with different spheres concentration, which show different number of layers estimated to be 2 and 5.

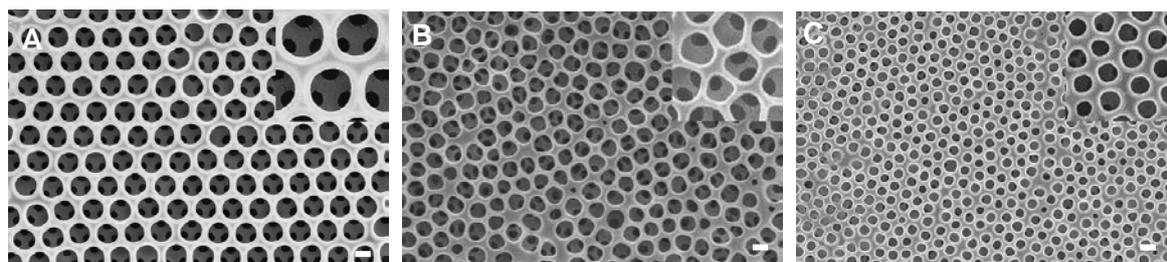
The close-packed 3D spheres arrays were then used as a template to introduce an ordered

3D arrangement of pores defined by the diameter of the latex spheres into the self-supporting membranes. To form a self-supported silica membrane from the assembled template, a DMDMOS/TMOS hybrid sol in isopropanol was spin coated onto them. We chose a mole ratio of 1:1 for this part of the study because this composition resulted in a flexible membrane with the smallest surface roughness. When the underlying ITO support was dissolved in acid, the membrane detaches and floats to the surface. Upon exposure to chloroform, the polystyrene spheres dissolve yielding a nanoporous self-supporting membrane. It is unlikely that the colloidal crystal array has a layer of silica over the top because the spheres can be easily removed by soaking the membrane (either before or after detachment from the ITO) in chloroform. The membrane can then be transferred onto a glass substrate for subsequent SEM characterization.

Figure 4 shows a low magnification SEM of a self-supporting membrane with ordered 3D pores prepared from 290 nm spheres. The long range order is good, but as noted earlier, some intrinsic defects in the films can be seen. As seen in the high magnification SEM images in Figure 5, the internal pores generated at the connect points of the close-packed 3D spheres are ordered and uniform in size. The surface pores are also ordered and have uniform pore size different than that of the internal pores. Moreover, the pores are interconnected to each other, not independent to each other as constructed by Velleman et al.<sup>11</sup> and Yang et al.<sup>12</sup> Thus, self-supporting silica membranes with unique architectures consisting of highly ordered 3D pores were obtained. When using 400 nm microspheres as template, the diameter of surface pores is ~ 300 nm and the diameter of internal pores is ~ 140 nm. When using smaller microspheres (290 nm and 200 nm), the diameter of surface pores is ~ 240 nm and 140 nm respectively, and the diameter of internal pores is ~ 110 nm and 60 nm respectively. The results showed that, the pores diameters are dependent on the diameter of the microsphere templates used. The larger the diameter of the spheres, the larger the diameter of both the surface and internal pores in the self-supporting membranes.

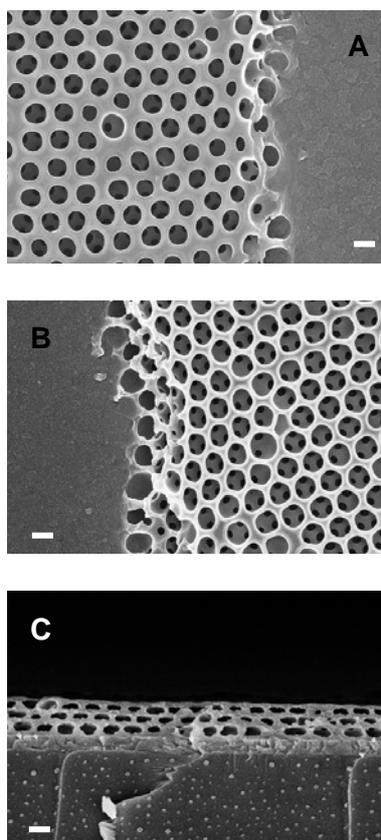


**Fig. 4.** Low magnification SEM image of the hybrid membrane with ordered pores prepared from the spheres with diameter of 290 nm. The scale bar is 10  $\mu\text{m}$ . The inserted images represent the expanded views of the pores.



**Fig. 5.** SEM images of the hybrid membranes (mole ratio of DMDMOS/TMOS is 1:1) with ordered pores prepared from the spheres with different diameters: (A) 400 nm; (B) 290 nm; (C) 200 nm. The scale bar is 200 nm. The inserted images represent the expanded views of the pores.

Beside the pore sizes, the number of pore layers also can be manipulated easily by changing the number of layers of the 3D spheres templates by using sphere solution with different concentrations in the vertical deposition step. In this study, the original 400 nm diameter microspheres solution was diluted into different concentrations to produce closely-packed 3D microspheres with different layers. By using such closely-packed 3D microspheres as templates (i.e., Figure 3), the self-supporting, ordered porous membranes with different number of layers were obtained. Figure 6 shows SEM images of two typical membranes with different number of layers estimated to be 2 and 5 along with a cross-sectional image of a porous membrane that is 3-layers thick.



**Fig. 6.** SEM images of the hybrid membranes (mole ratio of DMDMOS/TMOS is 1:1) with ordered pores prepared from the 400 nm diameter spheres with different spheres concentration: (A) 0.025% (w/v); (B) 0.035% (w/v); (C) 0.03 % w/v captured on ITO glass. The scale bar is 200 nm.

## Conclusion

In summary, a simple and versatile method to form easily transferable self-supporting hybrid silica membranes with an ordered and interconnected, 3D pore architectures has been developed after first examining the mechanical properties of hybrid films formed from DMDMOS and TMOS. The method relies on the formation of a ordered 3D arrangement of latex spheres on a sacrificial support using the vertical deposition approach, proper infusion of a hybrid sol containing a 1:1 mole ratio of two silanes, followed by template removal and release from the underlying support. One unique aspect of such self supporting membranes is the presence of a ordered interconnected arrangement of nanosized pores that are multiple layers thick. The thickness of the membranes can be altered by changing the viscosity of the sol. The ordered pore sizes and number of pore layers can be manipulated by changing the microspheres diameter and the microspheres concentration respectively. Furthermore, the mechanical properties of the membranes can be manipulated by changing the DMDMOS/TMOS ratio. Since the membranes were made using a silica sol-gel process, it is possible to chemically modified the surface fairly easily as well as trap molecules in the pores or fabricate molecular imprinting sites on the pore walls, which will be able to react with specific analytes passing through the pores. Because these self-supporting membranes are also transferrable, they can be used on nonconventional surfaces and thus have promising applications in the area of filtration, separations, and biological and chemical sensing.

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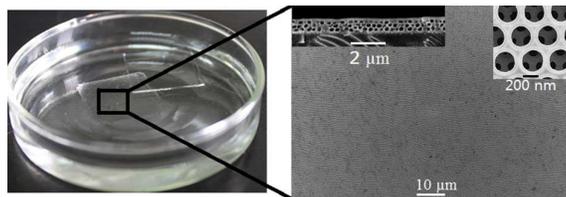
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## Table of Contents



Transferrable, self-supporting membranes with uniquely hierarchical, interconnected pore architectures over a large length scale, has been developed.