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# A Novel Design Toward Understanding and Characterizing Transport Behavior of Composite Mesoporous Silica Thin Film

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## ABSTRACT

In this paper, we for the first time apply a so-called "bottom-up" approach in fabricating synthetic ion-channel by exploiting evaporation-induced self-assembly (EISA) to form highly ordered porous thin film silica structures with precisely defined pore size, connectivity and surface chemistry as well as mechanical/thermal robustness. Here we demonstrate a novel design to integrate the above porous and composite nanostructures into an electrochemical device in which transmembrane ion fluxes can be measured to characterize the transport behaviors of ions/molecules through our mesoporous silica thin film. The demonstration of DNA translocation indicates a possible application of the mesoporous thin film structure in low cost DNA sequencing.

## INTRODUCTION

In nature, various natural transmembrane proteins such as ion channels and aquaporins have exhibited outstanding transport properties such as high flux and exquisite selectivity to specific ions/molecules. For example, aquaporins conduct thousands of millions of water molecules per second (per channel), without conducting ions, and thus enable kidneys to process enormous quantities (150 liters) of water daily, out-performing the current desalination solution, reverse osmosis membranes. With the development of material science, there is current need to emulate such proven natural designs in robust engineering materials with known geometry and chemical structure using efficient, manufacturable processing approaches. While various so-called "top-down" solid-state materials such as silicon nitride or silicon dioxide with single nanopores have been fabricated to offer several potential advantages over biological pores including chemical, mechanical, and thermal robustness, there still remain some problems such as the difficulty to introduce functional ligands in hierarchical architectures resulting in optimized properties. In this paper, we, for the first time, apply a "bottom-up" approach in fabricating synthetic ion channels by exploiting evaporation-induced self-assembly (EISA) to form highly ordered porous thin film silica nanostructures with precisely defined pore size, structure and surface chemistry. The pore size (1nm to over 10nm) covers that of biological ion channels, but with much wider range. This synthetic system with well-defined and adjustable structure and surface chemistry is important for establishing structure/property relationships. Meanwhile, the EISA process allows us to use simple coating and printing procedures to integrate these porous and composite nanostructures into electronic, fluidic, photonic, and membrane platforms, thereby providing a means to characterize their transport behaviors.

Although bottom-up self-assembly provides an efficient route to form highly ordered membranes, the membranes have multiple repeating copies of pores, making it hard to understand transport at the individual pore level. In this paper, we are exploring a novel process with prospects for overcoming this limitation. First, we limit the amount of pores as open channels in the direction perpendicular to the membrane by employing focused ion beam (FIB) lithography to drill a single sub-100-nm aperture on a solid substrate support, which serves as a platform enabling both TEM and the characterization of trans-membrane behavior of ions/molecules. Second, we use EISA to form a cubic thin film silica mesophase spanning the FIB-drilled aperture. In one approach, we adapted our aerosol-assisted EISA, where fusion of liquid crystalline aerosol droplets creates a thin membrane spanning the substrate pore. In a second approach, we modified our synthetic protocol to form ultra thin (below 30nm) spanning films by spin-coating. Films with pore sizes ranging from 2nm to 7nm and surface chemistries including –OH, -COOH and –NH2 are prepared in this fashion and deposited as free-standing membranes spanning the FIB-drilled aperture, providing several hundred pores with highly controlled size and surface chemistry. Finally, we characterize the electrochemical behavior of the free-standing membrane by incorporating the platform as a membrane between two reservoirs in an electrochemical cell. Experiments are conducted to measure the change in ion fluxes due to conductance fluctuations during the translocation of selected molecules like DNA across the membrane under an external applied voltage, a method relevant to low cost DNA sequencing.

## EXPERIMENT

**Fabrication of single aperture on $Si_3N_4$ membrane.** Commercial 1 cm x 1 cm $Si_3N_4$ membranes of 200 nm thickness supported on the standard Si wafers with a back-etched "window" (Figure 1) are purchased from SPI Supplies and Structure Probe, Inc. Focused ion beam techniques (FIB) are then applied to make a single sub-100-nm aperture on the $Si_3N_4$ membrane above the open Si window (see inset of Figure 1).

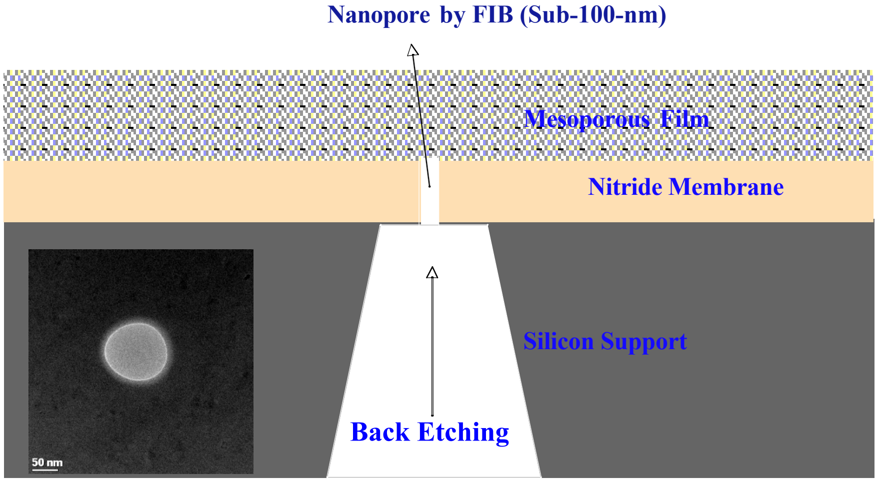

Figure 1. Schematic of the mesoporous thin film spanning the $Si_3N_4$ membrane with single aperture. Inset: TEM image of the sub-100-nm single aperture fabricated on the $Si_3N_4$ membrane by FIB

**Evaporation-Induced-Self-Assembly (EISA).** We adapted two EISA approaches to prepare mesoporous membranes spanning the single aperture on $Si_3N_4$ substrate. One is regular ethanol-based spin-coating and the other is aerosol-assisted EISA. For the first approach, the synthesis procedure to make highly ordered mesoporous thin films by spin or dip-coating technique is described in detail elsewhere[1,2]. Here we modify the recipe by diluting the original sol with ethanol to make thinner films. For the second approach, a water-based sol is nebulized to generate an aerosol using an ultrasonic humidifier. These liquid crystalline aerosol droplets are carried by a $N_2$ stream towards a substrate (anodisk with pore size ~0.1μm or $Si_3N_4$ membrane with single aperture in this case) and then deposited on the top surface after bypassing the substrate around its circumference, resulting in film formation after drying and self-assembly. The details about synthesis and instrument set-up are described elsewhere [3]. For both approaches films are first coated/sprayed on solid Si wafer and anodisks with pore size ~0.1μm for TEM/SEM demonstration prior to deposition on the $Si_3N_4$ membrane with single aperture.

The surfactant is removed from the film by either calcinations (425°C oven for 3hrs) or extraction (1N HCl in ethanol solution).

**Electrochemical cell design.** The electrochemical cell is made of teflon and composed of two separate chambers with capacities up to 3ml. The $Si_3N_4$ membrane with mesoporous thin film on top is mounted between the two chambers and sealed with O-rings. Ag/AgCl electrodes connected to an amplifier (Axopatch 200B, Axon Instruments, USA) are placed in both chambers to measure the ion flux across the membrane.

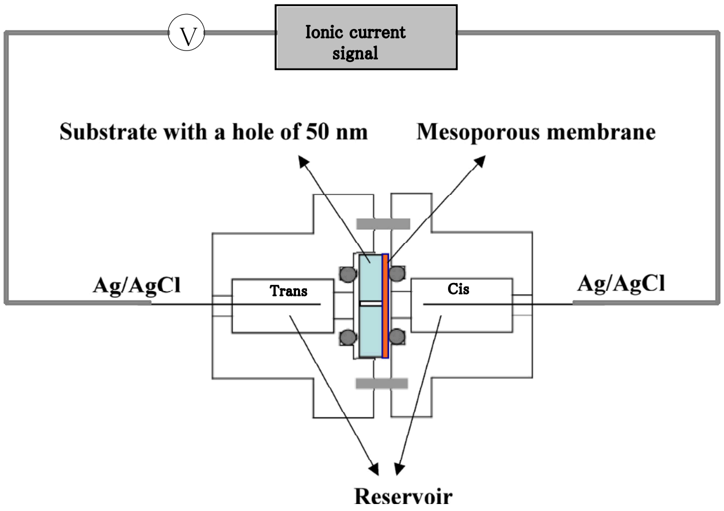

Figure 2. Schematic of electrochemical design.

**DNA solution.** Linear double stranded DNA solution made from pUC19 plasmid (3k bp) with concentration of 5 ng/μl in buffer solution (10 nM Tris-HCl, 1 nM EDTA, 1M KCl, pH 8.0) is loaded in –cis chamber while –trans chamber contains buffer solution only. Up to 200 mV external voltage is applied to drive DNA molecules across the membrane. In-situ ionic current with time is detected by Axopatch 200B amplifier and recorded on hard drive for further analysis.

## DISCUSSION

**Integration of thin film silica mesophase on the membrane with single aperture.** As mentioned before, we adapted two EISA approaches (aerosol-assisted EISA and regular ethanol-based spin-coating) to form highly ordered cubic thin film mesophases. Regular ethanol-based spin coating is a very simple and repeatable process to make homogenous and highly ordered thin film on solid Si substrates. The pore sizes can be varied from 2nm to 7nm depending on the chosen surfactant. Pore surfaces can be easily modified with different functional groups by either incorporation of the organosilane precursors with functional groups in starting sol before synthesis or post-grafting the functional ligands on the pore surfaces after synthesis. After diluting the original sol with ethanol, the resulting thin film structures are still highly ordered, while film thickness is decreased to below 30 nm (less than 1/10 of the original film thickness) (Figure 3). Thinner film thicknesses are beneficial for transport characterization of biomolecules like DNA through the membrane, because the connectivity of film structures by EISA is usually tortuous, meaning that the channel pathway exceeds the film thickness. A thinner membrane makes the pathway of translocation shorter, enhancing the chance that an individual channel remains connected from one side of the membrane to the other.

We choose aerosol-assisted EISA for film formation because this approach had been demonstrated as a good way to deposit highly ordered films on coarse-pore supports like anodisks [3]. For our research, it is important that the film can uniformly span the aperture without clogging in the pore. TEM images show that very ordered structures are formed by this approach on an anodisk with ~0.1μm pore size (data not shown here). Scanning electron microscope (SEM) cross section images of the sprayed thin film on the 100nm anodisk show that the thin films span the porous substrate uniformly (figure not shown in this paper).

Finally, we used either spin coating or aerosol spraying to deposit the nanoporous thin film on the $Si_3N_4$ membrane fabricated with a single sub-100-nm aperture. TEM images show that the films cover the apertures homogeneously yielding an ordered nanoporous free-standing membrane. We find that it is easier and more reliable to get ordered structures over the aperture using the aerosol approach. The film structure spin-coated on the single aperture is not as ordered and repeatable as that coated on a solid Si substrate, which implies that the support surface conveys order to mesoporous films prepared by standard EISA. In the case of aerosol deposition, interfacial effects between the liquid crystalline aerosol and the solid substrate are not as important as noted by the observation that the cubic thin film mesophases formed by the aerosol approach on both solid Si substrates and porous substrates are randomly oriented [3] whereas films formed by standard EISA during spin or dip-coating are always oriented with respect to the substrate.

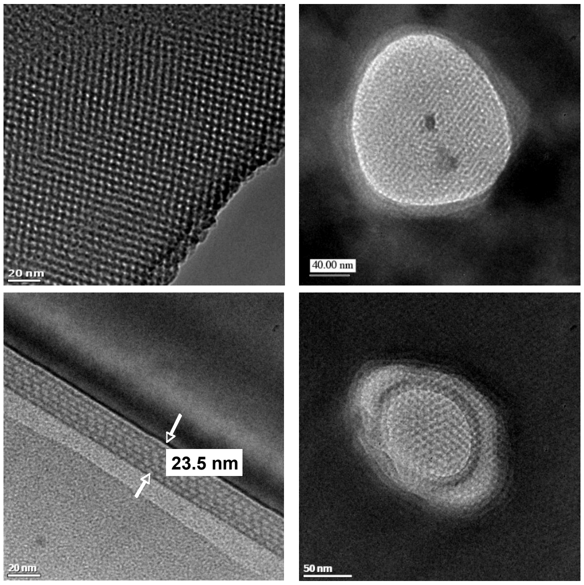

Figure 3. (left)TEM plan view (top) and cross section (bottom) of thin film spin coated on normal Si wafer with Brij56 as surfactant; (right) TEM plan views of thin films integrated on the $Si_3N_4$ membranes with single apertures by regular ethanol-based spin-coating (top) and aerosol-assisted EISA (bottom).

After trying both calcination and extraction for surfactant removal, we find the films formed by both approaches can survive the extraction treatment with their ordered structure maintained, while calcination treatment might cause cracking of the films spanning the aperture.

From Figure 3 we can see that there are still many nanopores spanning the single aperture, because the aperture diameter of the $Si_3N_4$ membrane is about 100nm. For the convenience of characterizing the transport behaviors of ions/molecules on a single pore basis, we need to make the aperture smaller or we need to block all but one nanopore. Currently, making a single aperture with a 20nm diameter is feasible. For our Brij56 based mesoporous films with a 5nm center-to-center spacing, there are around 70 pores on an aperture of 50nm, while there would be only 10 pores on a 20nm aperture.

**Detecting DNA translocation.** Sensing of DNA translocation at the single-molecule level was first demonstrated using the protein pore $\alpha$-hemolysin. When a voltage is applied, the negatively charged DNA in the vicinity of the nanopore are translocated through the nanopore from the negative side to the positive side according to a diffusional process that represents a balance between the electric driving force and viscous drag. As a result of the partial blocking of ionic current accompanying DNA translocation, we can measure transient reductions of the ion current, for which both time and amplitude of blockade can be used to analyze the transport characteristics of DNA. To accomplish the detection of single molecule translocation events, the nanopore dimensions must be small enough to avoid averaging over continuous single-molecule configurations induced by thermal fluctuations and large enough to pass the smallest dimensions of the molecule to be probed [4]. The super thin mesoporous membranes described above satisfy this requirement, having pore size and membrane thickness smaller than the molecule persistence length, 50nm for double stranded DNA and a pore diameter larger than the 2nm cross-sectional size of the molecule. Figure 4 plots a fix-length sweep of ionic current with time. It shows successive current blockades when DNA is located on the –cis side of the chamber and a negative voltage is applied. When the DNA solution is replaced with a buffer solution on the –cis side, no current blockades are detected, implying that the observed current blockade is caused by DNA translocation. Conducting the same experiments under different external voltages shows that the current blockades become more frequent as the applied voltage increases, implying that the electric field is the driving force for DNA translocation.

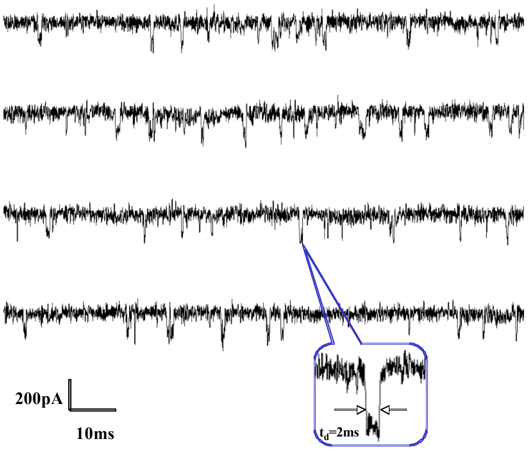

Figure 4. successive events of Current blockade as a function of time when DNA is translocated.

Interestingly, we only observe current blockade for membranes on $Si_3N_4$ substrate by spin-coating. For the membranes prepared by aerosol-assisted EISA, no current blockades are detected. One possible reason is that the randomly oriented cubic structure formed by the aerosol approach makes DNA translocation from one side of membrane to the other side extremely hard. This result implies that the mesoporous structure obtained by regular ethanol-based spin-coating is oriented in the direction perpendicular to the membrane surface.

As we expected, membrane thickness is a factor to influence the DNA translocation. Compared to the membrane of normal 300nm thickness, the current blockade frequency for the membrane formed from a highly diluted starting sol with thickness below 50nm is much greater.

The DNA translocation shown above is multiplexed resulting from the collective transport through many channels. This might be an advantage for DNA detection. However, in some cases, research on a single channel basis is necessary, which requires the efforts of decreasing the aperture diameter as well as blocking most of the pores.

## CONCLUSIONS

In this paper, we develop a novel design combining the EISA sol-gel approach for film formation, focused ion beam (FIB) lithography techniques and an electrochemical cell device toward characterizing transport behaviors of ions/molecules through composite mesoporous silica thin film. As the very first step, we demonstrate that, by using the above novel design, composite mesoporous silica thin film can be applied for understanding and characterizing the transport behaviors of selected molecules like DNA through the membrane. Next, we will utilize the availability of changing pore size or modifying pore surface charges/function (via introducing external stimuli functional groups like photoresponsive azobenzene ligands) to further understand structure/property relationship. By applying atomic layer deposition (ALD) technique, we can further decrease the pore size to a level where ion/water selectivity is available.

## ACKNOWLEDGEMENTS

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