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Imaging flow distribution through nanoporous polymer films using bright-field nanoscopy

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ABSTRACT

Bright-field nanoscopy (BFN), an optical visualization technique using standard diffraction-limited microscopy, has been used in the past to visualize nanoscale objects such as grain boundaries in single layer graphene and water transport across nanomembranes. Here, we show how BFN can be used to visualize and gather information about water transport networks in porous polymer membranes. We were able to visualize a sub-100 nm network of pores in a polyelectrolyte multilayer using this technique. The extracted pore diameter distribution fitted well to an exponential distribution. Further, the time evolution of pore diameter displayed two distinct regimes consistent with expectations.

INTRODUCTION

Understanding fluid transport in microporous and nanoporous systems is crucial for developing future devices with applications like water filtration and separation membranes, where high salt rejection porous supports/polymer composites are widely used.¹ Porous materials can be imagined as a bunch of hollow pipes or pathways through which molecules are transported. The statistical distribution of the porous network affects the flow through it. It was recently shown that with increased disorder of the porous transport network, the flow velocities have an exponential distribution, changing to a gaussian and a delta distribution with increasing order.²⁻⁶

Experimental measurement of flow rate distributions is typically carried out using sand columns or microbead packs with fluorescent tracer particles, which allow the flow velocities to be characterized using particle image velocimetry (PIV) and the more recently used X-ray tomography.⁷ Such measurement approaches are challenging to adopt for microporous or nanoporous systems which may not be optically transparent. We had previously reported an optical technique called bright-field nanoscopy (BFN) for visualization of nanoscale features such as grain boundaries in graphene using standard diffraction-limited optical imaging.⁸ Subsequently, we had also demonstrated the visualization of water transport through nanomembranes using this technique.⁹ BFN works on the principle of interference, producing thickness dependent color responses from ultrathin germanium films on optically thick gold supports. Owing to the dissolution of Ge in water (hence, thickness change), any modulation of the water permeability arising due to the presence of nanostructures or nanoscale porosity produces a replica of the modulation pattern in the underlying Ge film. These patterns are observed with a high color contrast using a regular optical microscope. However, this technique “detects” only sparsely distributed features and does not necessarily resolve them. In this article, we extend the utility of BFN to extract information on the statistical distribution of pore networks in a microporous or nanoporous system. We demonstrate the use of BFN in extracting pore statistics using a nanoporous system composed of polyelectrolyte multilayers (PEMs), which have been extensively explored as polymer supports in combination with graphene for filtration and desalination applications. In our previous work, we were able to measure bulk (average) differences in water transport fluxes using this technique. In the present work, by tuning the etch rate of the Ge film, we show that not only the average difference but also local differences in water transport fluxes arising from the geometry of the pore network can also be visualized using BFN. The PEMs were fabricated on a thin film device, described previously, consisting of ultrathin films (25 nm) of germanium on optically thick gold films. As described previously, germanium films isotopically etch in water.⁹ The etch rate can be further increased by adding hydrogen peroxide.
(H₂O₂), which is also the etchant of Ge. Water permeation in such polymer membranes occurs through continuous pore tracks. Differential distribution in water fluxes arises due to randomness in the porous networks. The distribution of pore sizes estimated the flow distribution, which required very precise control on the H₂O₂ concentration. Hence, water flux rates and, consequently, germanium etch rates are related to the pore size distribution. The BFN technique allows one to monitor the local water fluxes through pore tracks in polymer membranes due to the strong color response arising from the local etch rate differences in the supporting Ge devices. The presence of nanoscale pores (sub-100 nm) in the PEM results in the formation of a specklelike pattern, which is an imprint of the porous water transport network on the germanium surface, observable by an optical microscope under a bright-field illumination condition. Pores much smaller (∼35 nm) cannot be visualized using this method, and such PEMs do not produce any observable patterns on germanium. By tracking the time evolution of the diameter of the patterns in germanium, one can extract the dynamical parameters of the transport process as well as the statistics of a pore network structure because the diameter of the pattern on germanium is directly related to the water flux through the pore, which, in turn, is related to the degree of disorder in the pore network.

EXPERIMENTAL METHODS

To cross-validate the numerical predictions, we first experimentally analyze the transport/percolation of water through the pores in PEMs. PEMs are assembled by electrostatic interactions between the oppositely charged polyelectrolytes (PEs) and were deposited by the layer-by-layer (LbL) process established by Decher. By the dip coating mechanism, with a controlled 1 min dip in the respective polyelectrolyte solutions (with intermittent wash steps to remove the unbound polymer chains), one can fabricate polyelectrolyte multilayers of varying thickness from a few nanometer to micrometer sizes. Here, we investigated a weak polyelectrolyte system consisting of positive PE, namely, poly (allylamine hydrochloride) (PAH) and a negative PE, namely, sodium salt of poly (acrylic acid) (PAA-Na⁺), with an average molecular weight of 17 500 Da and 15 000 Da, respectively. All polyelectrolytes used for our experiments were procured from Sigma Aldrich. The polymer solution was a 0.1 M NaCl solution in 18 MΩ cm Millipore deionized water, maintained at pH 5.5. The BFN device consisted of an ultrathin film of Ge (∼25 nm) deposited on optically thick Au on Si substrates. All depositions were carried out in a Tecport Sputter tool post Si wafer cleaning in a 1:3 Piranha solution. The PEM stack was fabricated on the BFN device by the process mentioned above. All imaging was carried out in an upright optical microscope by Olympus, BX51 M in the bright-field mode. The associated topographical images of all the samples were obtained using a tapping mode tip, namely, TESPA-V2, in an atomic force microscope (AFM), Bruker Dimension ScanAsyst. Germanium also etches in water, and the etch rates can be enhanced by the presence of H₂O₂ diluted in the water. All the experiments performed here are with a 5% H₂O₂ diluted in water (which is considered significantly large). The experimental times were reduced to 15 min with this concentration of the etchant.
RESULT AND DISCUSSION

Polyelectrolyte systems are nanoporous systems with pore sizes varying in few tens of nanometers, depending on the choice of polyelectrolytes. Here, PEM layers stacked on the BFN device were used as the nanoporous system for study. We carried out experiments with a 6 bilayer PEM consisting of PAH and PAA-Na⁺ alternately, with surface terminating with PAA-Na⁺. This will be denoted as (PAH/PAA-Na⁺)₆ further in the text. In order to compare the influence of the terminating layer, a PAH solution was drop casted on (PAH/PAA-Na⁺)₆. The pore tracks (not to scale) in bulk PEMs are the pathways that transport the etchant to the underlying Ge films as shown in Fig. 1. With the addition of 5% v/v of H₂O₂ to deionized (DI) water, the etch rate of germanium was enhanced to about 1.5 nm/min from 0.3 nm/min with pure DI water. We had previously reported that the usage of 0.02% v/v of H₂O₂ diluted in DI water can be used to distinguish the influence of the terminating polyelectrolyte layer and hence making the odd-even effect evident. However, this concentration of H₂O₂ was not sufficient enough to serve the intended motive of this work. The etch rates mentioned were estimated from the length of the experiment times in the presence of the etchant reservoir on the surface of (PAH/PAA-Na⁺)₆ deposited on Ge substrates. The gold layer serves as an etch stop allowing for accurate determination of the germanium etch rate. Etching experiments were carried out under a water immersion lens in an optical microscope.

In order to etch the underlying Ge, the water (etchant will be referred to as water further on in the text) has to propagate from the surface of the PEM to the Ge film through the pore tracks in the PEM. This process was monitored using optical microscopy. The etch rate of germanium was determined by measuring the length of the etch pits evolved with time. The etch rates were calculated from the length of the etch pits evolved with time. The etch rates were calculated from the length of the experiment times in the presence of the etchant reservoir on the surface of (PAH/PAA-Na⁺)₆ deposited on Ge substrates. The gold layer serves as an etch stop allowing for accurate determination of the germanium etch rate. Etching experiments were carried out under a water immersion lens in an optical microscope.

![Optical micrographs](image1.jpg)

**FIG. 2.** Evolution of etch pits in Ge at the PAA-Na⁺ terminated PEM. (a) Optical micrographs from the PEM deposited Ge surfaces imaged as the etching progressed. With an etchant reservoir on the surface, germanium is seen to etch to form etch pits which correspond to the flow rate associated with propagation of water in the respective pore tracks. The time stamps and scale bar are mentioned in the optical micrographs. (b) Cumulative distribution function (CDF) is plotted from 3 representative images similar to the last image in the sequence shown in (a). The CDF of EPA follows an exponential distribution. (c) A cropped and magnified image of the boxed region in (a). An image cropped and magnified from the PAA-Na⁺ terminated PEM region is shown. Image processing algorithms were carried out on this image to enhance the visual clarity on the etch pits evolved with time. The processed image is presented on the right.
bulk of the PEMs. This polymer system was tested with different concentrations on \( \text{H}_2\text{O}_2 \). A low concentration of 0.02\% \( \text{H}_2\text{O}_2 \) was sufficient to resolve the bulk transport properties but obscured the visibility of the details in the PEMs. However, on the usage of 5\% \( \text{H}_2\text{O}_2 \), the lateral etching is controlled to an optimum extent making the etch patterns visible.

The evolution of irregular etch patterns in Ge was seen in the time-lapse optical images as the experiment progressed [Fig. 2(a)]. However, such patterns were not observed when the PEM was terminated with PAA instead of PAA-\( \text{Na}^+ \) as shown in Figs. 1(b) and 2(a). The critical role of the terminating layer in polyelectrolyte multilayers has been described in our previous report. Etch patterns observed in the optical images are etch pits resulting from the isotropic etching of the germanium film by water. The etch pits effectively amplify the porous architecture of the PE near the germanium surface. More importantly, the etch patterns also give information of the flow rate (velocity) distribution of the water along the pore tracks, which directly controls the etch rate. The etch pit area (EPA) distribution was quantified from the last optical micrograph. Image processing steps, namely, background subtraction, thresholding, and despeckle, were carried out for EPA analysis using the software ImageJ. The EPA has an exponential distribution, as evidenced by the close match between the experimentally observed cumulative distribution function (CDF) and an exponential CDF with a \( \mu \) of 0.23\( \mu \text{m}^2 \) as shown in Fig. 2(b).

EPA analysis was carried out on processed images like the one shown in Fig. 2(c), which is cropped and magnified from the region terminated with PAA-\( \text{Na}^+ \). For a better perception, only the red color channel is presented here. The contrast of this image was enhanced slightly for visual clarity of the individual etch pits. The distribution of the EPA is an indicator of the flow rate distribution through the pore network. Earlier models describe how the pore size distribution governs the flow distribution in porous networks. In our system, the amount of germanium film etched, leading to the formation of a pore that is directly related to the total flow over that pore, which, in turn, is related to the flow rate over that pore. Therefore, based on this previous work, we would expect to find the volume of the etched region (product of EPA and etch depth) to have an exponential distribution. We plot the EPA distribution at a condition close to when the germanium film is fully etched [Fig. 2(a), last image]. Then, the etch depth is constant (equal to the original germanium film thickness) for all the pores in the image, and EPA would be expected to have an exponential distribution which is confirmed experimentally in Fig. 2(b). This result shows that our technique is capable of retrieving information consistent with previous findings and provides confidence in the use of our technique to understand aspects of fluid flow in nanoporous films. To further quantify the range of porosity and randomness in the pore arrangement in our system, surface topography of the PEM film was mapped using an atomic force microscope (AFM) in the tapping mode. AFM measurements of the interface of the terminating polymer surfaces were made at 3 instances, namely, before etch, intermediate etch, and after etch, which are marked as 0, 5, and 15 min, respectively, in the
ins in Fig. 3(a). From multiple measurements in AFM, the mean pore area measured increased from 35 nm² to 100 nm² as the etch progressed as seen in Fig. 3(a). This observation implies that the dissolution of the underlying germanium layer induces tensile stresses in the PEM causing it to stretch, thereby increasing the pore diameters with progressive etching of the germanium film.

We measured the temporal evolution of the EPA and mapped the evolution to a simple scaling relation of EPA ∼ $t^{\alpha}$. We found two distinct scaling regimes for the EPA. Initially, the EPA scaled with exponent $\alpha = 2/3$, followed by a faster increase in the pore area with exponent $\alpha = 3/2$. The $\alpha = 2/3$ regime may be explained by considering a constant flow rate through the PEM pore network and a hemispherical etched volume as shown in Fig. 3(b). The volume of the hemisphere scales as $r^3$, and we assume it to be directly proportional to the total volume of the etchant $Q t$ flown in at a constant flow rate $Q$ during time $t$. Equating these two factors, $r \sim t^{1/3}$. Thus, EPA ∼ $r^3$ scales as $t^{3/2}$ as seen in Fig. 3(c). After the etch-stop layer, namely, gold, is reached, the etched volume would scale as $r^2$ (in the limit of a cylindrical shape $V = \pi r^2 h$; where $h$ is the germanium film thickness). In this regime, one would expect EPA to scale as time, $t$, which is faster than the previous regime. However, the observed exponent is 3/2 and not 1, as expected. The higher exponent observed in the regime two in experiments is due to the enlargement of the pore diameters caused by lateral stretching of the porous membranes as a result of the etching of the underlying Ge film as described in the previous paragraph [Fig. 3(a)]. This is schematically represented as $R_{\text{pore}}$ and $R_{\text{pore}}'$, respectively, in Fig. 3(b). The large flow rates in the regime two are attributed to increased pore dimensions as seen from the AFM images [Fig. 3(a)]. Here, the flow rate is dependent on time, unlike the constant flow rate of Q as assumed in regime 1. The experimentally observed exponent of 3/2 implies that flow rate $Q \sim t^{1/2}$ in regime 2. The reason why this effect does not occur in regime 1 is because of the effect of stretching may be significant only when the germanium film is fully etched to gold, causing lateral etching of the film to apply tensile stresses on the polymer film. Thus, we see that the simple scaling argument we describe above correctly predicts the existence of a slow etch rate regime followed by a fast one, although the exponent for the faster regime needs more precise estimation, taking into account effects such as pore stretching.

CONCLUSION

To summarize, we have demonstrated how BFN can be used to visualize sub-100 nm pores in a polymer membrane and extract single pore resolved flow rates by tracking the evolution of etched pore areas in our thin film device observed with a standard diffraction-limited optical microscope. Using this technique, we were able to observe an exponential distribution of flow rates across the pores. We observed stress-induced stretching of our polymer films using AFM and detected two geometry-dependent regimes in the time-evolution of etched pore areas. The BFN technique can thus provide valuable insights into the transport properties of water through nanomembranes.

REFERENCES