Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Online Material for

Light Transmission Technique for Pore Size Measurement in Track-Etched Membranes

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EXPERIMENTAL SECTION

Materials. PET (polyethylene terephthalate) membranes (diameter = 3 cm, thickness = 12 μm) that had been irradiated with heavy ions of 2.2 GeV kinetic energy to create a multi damage track through the membrane were obtained from GSI, Darmstadt, Germany and referred to as the "tracked" membranes. Sodium Hydroxide (NaOH) and Potassium Chloride (KCl) were purchased from Beijing Chemical Reagent Company (Beijing, China). All of the chemicals were of at least analytical grade. The water used throughout all experiments was purified by a Milli-Q system (Millipore, Bedford, MA, USA).

Preparation of Track-etched Membrane and SEM Imaging. Polyethylene terephthalate films (PET, 12 μm thick) irradiated with heavy ions Au with energy of 11.4 MeV/nucleon were purchased from GSI, Germany. One hour treatment of each side of the polymer membrane with UV light (4 mW/cm^2) allows the activation of the polymer foil. Polymer membrane was dipped into the high concentrated NaOH (2M) with different etching time, leading to cylindrical nanopore formation. In the presence of sodium hydroxide, polyethylene terephthalate (PET) was gradually hydrolyzed to p-phthalic acid and ethylene glycol, the pore size evolutions along the tracks are highly time dependent. The larger pore size, the greater scattered light intensity. The etching temperature was maintained at 65℃, which lead to much more successful etching than lower etching temperature. After chemical etching, the membranes were thoroughly washed with purified water and dried under nitrogen flow. The images of cylindrical nanopores in polymer membrane were obtained with field-emission scanning electron microscopy (ESEM

XL-30), the average pore size corresponding to each etching time were calculated from more than 20 measurements of the same membrane, if not specifically noted. The rough etching rate calculated from this study is 20±7 nm/min at 65℃ for one step etching. Data plots derived from SEM images (Figure. S2) show that for single membrane, the pore size showed good linear relationship with etching time, and however for different batches of membranes, the pore size evolutions with etching time were quite different.

UV/Vis Measurement and Analysis Cary 60 UV/Vis Spectrophotometer (Agilent, USA) was used to quantify the light scattering and reflection intensity via track-etched membrane. We directly used air or 0.1 M PBS buffer solution (pH =7.0, 500 mM NaCl) as baseline measurement. Polymer membrane with multi-tracks ($5*10^7$ tracks/cm^2 or $3*10^6$ tracks/cm^2) before etching was transparent under visible light wavelength, showing strong absorption below 300 nm wavelength. The surface plane of polymer membrane was placed in a vertical position relative to the UV/Vis light path. The absorption spectra of the membranes were measured in the wavelength range from 800 nm to 250 nm.

Measuring the UV-Vis spectra in air was pretty straightforward just by simply gluing the membrane onto the UV/Vis cuvette holder (Figure S12). As for measurement in buffer solution, the membranes dipped into the buffer were inclined to fold and were not in perfect vertical position, which caused the measured 'absorption value' to slightly deviate from the true value and slightly degraded the linear relationship. Nevertheless, this did not prevent the successful measurement in solution, which paved a promising foundation for further usage in industrial on-line monitoring.

In orde to avoid confusion, light transmisson percentage(%T), namely percent transmission, was used x axis instead of Abs. %R representing the ligh scattering percentage plus %T is equal to one unit.

AFM Imaging and Analysis of Surface Roughness. All the membrane samples with various etching times were flatly glued onto the metal plate with smooth surface. A Multi-mode 8 Atomic Force Microscope (Veeco) equipped with NanoScope V controller and with pyramidal shaped silicon nitride cantilever was employed for imaging the samples. Several AFM images obtained from separate locations across the PET membrane were to ensure the reliability of our results. All the images were analyzed using Nanoscope Analysis 1.20.

DISCUSSION ON SEVERAL CRITICAL ISSUES

What kind of track-etched membrane can this technique be used for and what is the smallest diameter that can be measured? Except that light transmission technique can be used for PET membrane, it can also be used for polycarbonate membrane (PC), according to data shown in Figure S10. Furthermore, UV-Vis spectra are highly diameter dependent and the SEM image also shows that the surface area close to the pore is bright. For kapton membrane with track density of 1×10^6 tracks/cm^2, the surface after etching is much smoother than PET and PC membrane, As shown in Figure S11, the UV-Vis spectra show only slight change after long time etching in 13% NaOCl solution at 50 degrees. Therefore, this technique is not suggested for kapton membrane. However, it has to be noted that majority of commercial track-etched membranes are fabricated with PET and PC sheets instead of kapton membrane. This technique should not be used for track-etched membrane with low track density (Figure S7). The smallest diameter we can measure was around 60 nm for track density of 5×10^7 tracks/cm^2. For higher track density, the smallest diameter which can be measured should be smaller.

The influence of pure transmission, film thickness reduction and surface roughness and structure underneath the Part II surface on the efficiency of light transmission technique. Figure S7C and D show the track-etched PET membrane with single track and low track density almost had no perceivable change in the UV-Vis spectra after long time etching. Therefore, in combination with very good linear fitting of the experimental data in Figure S13, it can be confidently concluded that pure transmission and film thickness reduction did not play conspicuous effect in the efficiency of light transmission technique. Nevertheless, if the pore evolution reaches a certain point, the pure transmission and film thickness reduction may begin to exert significant leverage on our light transmission technique. Unfortunately, this kind of membrane is fragile to prevent further investigation. After systematical analysis in the main manuscript, surface roughness and structure underneath the Part II surface were considered to play significant effect on the light transmission technique.

Why the Part II area near the pore is bright and what happened to this area? The bright area was due to electron charging, and one thing for sure is that Part II surface was different from Part I. If the bright is due to the high aspect ratio, then this should be observed via AFM images. Therefore, we conducted an analysis of AFM of PET membrane after 30 minutes etching. As shown in the following AFM images (Figure S14), there are clear pores on the PET membrane. The line profile along two pores did not show distinct difference in height profiles for surface close to the pore and surface far away from the pore. Therefore, high aspect ratio feature is probably not the explanation.

Since we already proved that the etching on PET membrane with single pore did not lead to opaque color and UV-Vis spectra did not have distinct change. This may be the reason that we did not observe distinct influence of film thickness reduction. Along with the surface roughness close to the pore and inside the pore, the change in structure underneath the Part II surface altogether contributed to the light scattering since the etching solution can penetrate into the amorphous inside, leading to partial inside degradation.

How to calculate the statistical deviation of the pore with certain average diameter. The average pore size measured by SEM versus scattered light intensity can be fitted with linear equation. As shown in Figure S13A, the fitting equation is y=a+bx, where y represents the pore size, x represents the negative log value of percent transmission (%T), a is the intercept and b is the slope. Once the negative log value of percent transmission (%T) for the membrane after etching is known, we can calculate the average pore size and the standard error.

If we try to know the statistical deviation of pore size for certain negative log value of percent transmission (%T), The first step is to calculate the average pore size. For example, when the negative log value of percent transmission (%T) is 1.4, the average pore size is calculated by following this procedure, y=(-223)+(631.7)*1.4=661 nm. The second step is to calculate the statistic deviation, namely error bar. The statistical deviation can also be calculated easily. If we plotted a curve (Figure S13B) from the data in Table S1 with standard error (Sd) as y axis and the negative log value of percent transmission (%T) as x axis. The fitting has pretty good linear relationship with R^2=0.99. Therefore, the error bar (statistical deviation) for each pore size can be calculated. For value of 1.4, ±y=-4.2+35.7*1.4=45.8 nm.

The final pore size value is 661±45.8 nm.

FIGURE CAPTIONS

Figure S1 Picture of PET membrane with track density of $5*10^7$ tracks/cm^2 after 30 minutes etching. The area with tracks is much more opaque than that without tracks.

Figure S2 SEM of pores in PET membrane with effective track density ($5*10^7$ tracks/cm^2) derived from different etching time (A)10 min, (B)20 min, (C)30 min, (D)40 min, (E)50 min and (F)60 min. Etching conditions: 2M NaOH and 65℃.

Figure S3 Calibration curve of pore size of track-etched membranes versus etching time at wavelength 600 nm. Black curve and red curve represent fitted curve of data derived from two batches of membrane, respectively. Etching conditions: 2 M NaOH and 65℃.

Figure S4 Calibration curve of the negtive log value of percent transmission (%T) at wavelength 600 nm versus etching time. Etching conditions: 2 M NaOH and 65℃.

Figure S5 Cartoons of PET surface.The surface of track-etched PET membrane is divided into three parts: Part I comprises the surface area located at certain distance D away from the pore in the membrane; Part II comprises the surface areas located between two concentric circles. The first circle is the pore with radius of R and the second circle has the radius of R+D; Part III is defined as the inside surface of the pore in the membrane.

Figure S6 SEM of pores in PET membrane with effective track density ($3*10^6$ tracks/cm^2) derived from different etching time (A)15 min, (B)35 min, (C)45 min and (D)55 min. All membranes were etched via single step.

Figure S7 UV/Vis absorption spectra of track-etched PET membranes with different track density after different etching time. Measurements were carried out in air. Etching conditions: 2M NaOH and 65^{o}C.

Figure S8 Calibration curve of pore size versus the negative log value of percent transmission (%T) of track-etched membranes ($5*10^7$ tracks/cm^2) at wavelength 600 nm. Black curve represents the measurement in air; Red curve represents the measurement in buffer solution (pH 7.4, 100 mM PBS, 500 mM NaCl).

Figure S9 Calibration curve of pore size in track-etched membranes with effective track density ($3*10^6$ tracks/cm^2) versus the negative log value of percent transmission (%T) at wavelength 600 nm. Etching conditions: 2M NaOH and 65^{o}C.

Figure S10 (A) UV-Vis spectra for commerical polycarbonate membrane. (B) SEM image of polycarbonae membrane (http://www.2spi.com/catalog/spec_prep/filter6.shtml).

Figure S11 UV-Vis spectra for Kapton membrane. Etching solution is 13% NaOCl.

Figure S12 PET membrane in vertical position relative to the light orientation.

Figure S13 (A) Calibration curve of pore size versus the negative log value of percent transmission (%T) of track-etched membranes ($5*10^7$ tracks/cm^2) at wavelength 600 nm. Fitted curve represents the absorption measurement in air. (B) Calibration curve of standard error versus the negative log value of percent transmission (%T).

Table S1 Each value for scattered light intensity has certain average pore size (counting 20pores in SEM images) and one standard error.

Figure S14 (A) AFM image of PET membrane with track density of 5×10^7 tracks/cm^2 after 30 minutes etching. (B) top and bottom line profiles corresponding to (a) and (b) lines in A, respectively.

Figure S1

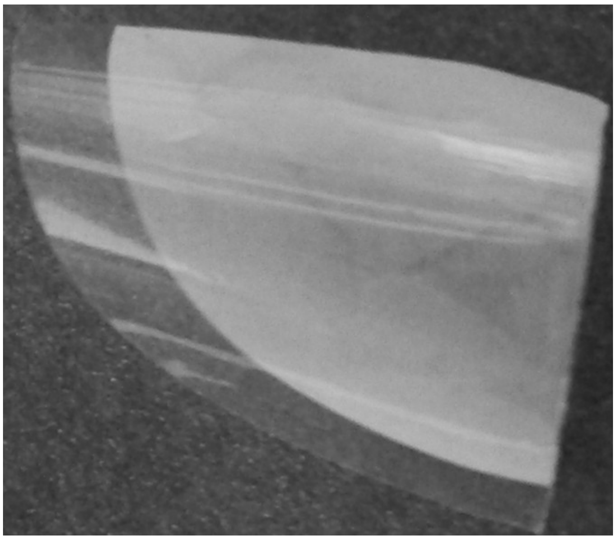
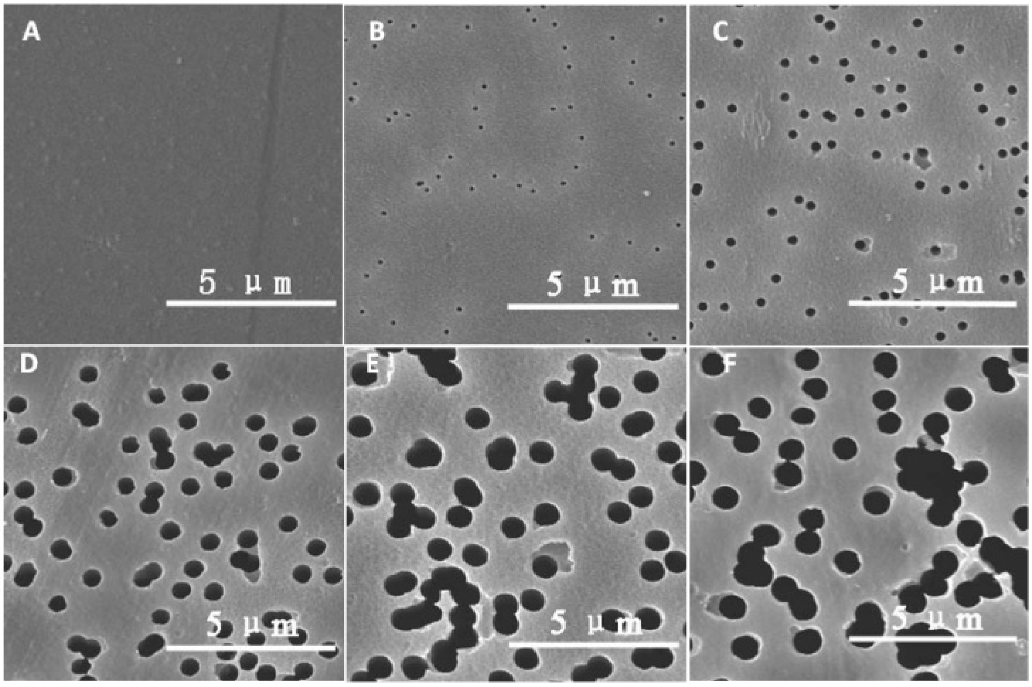


Figure S2



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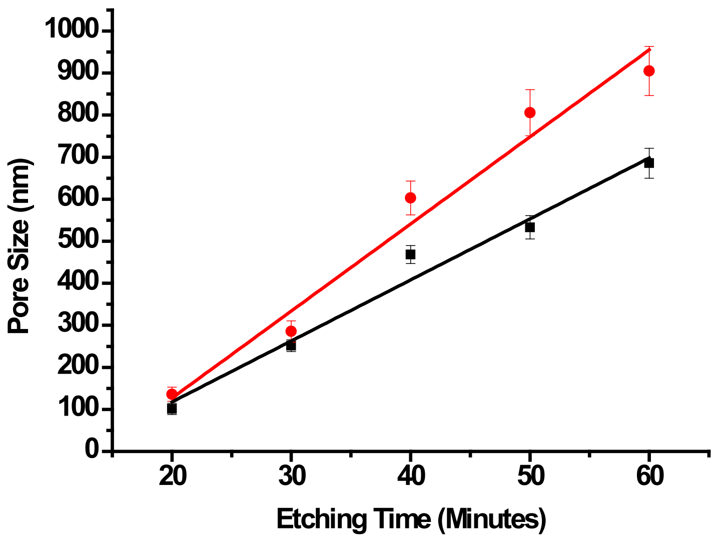

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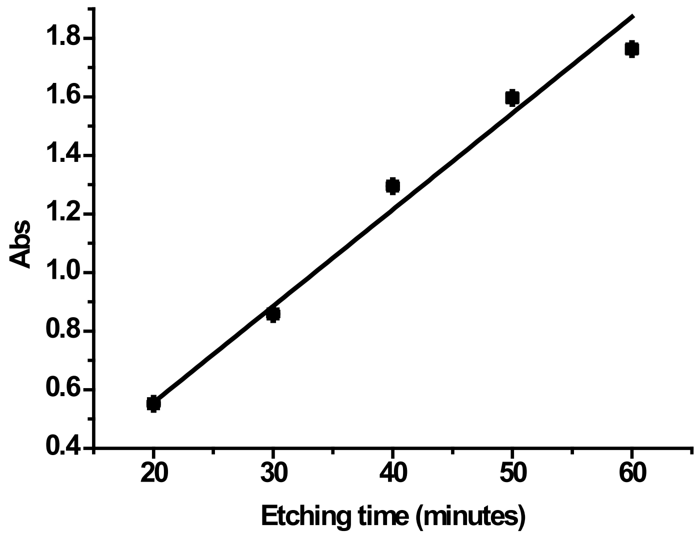

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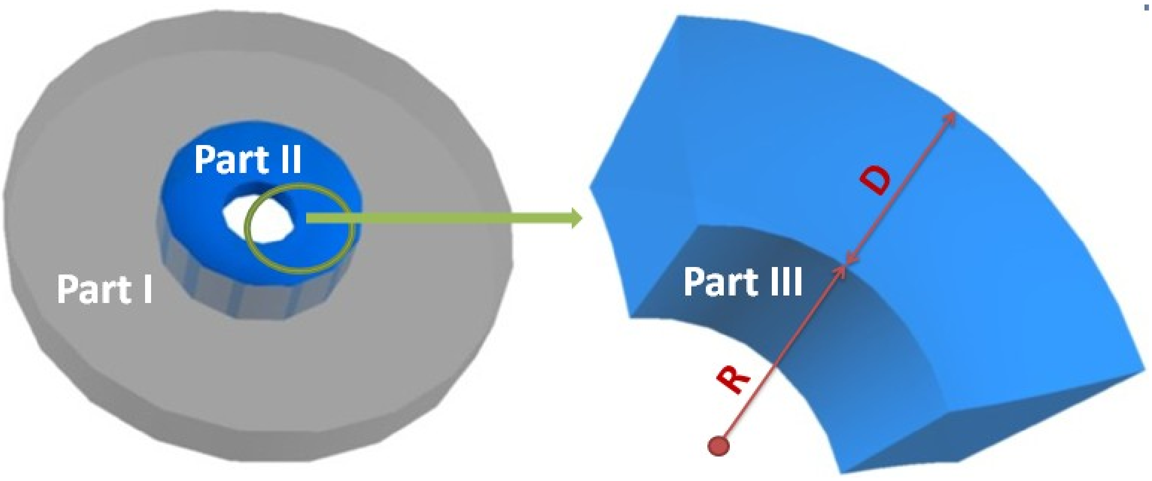

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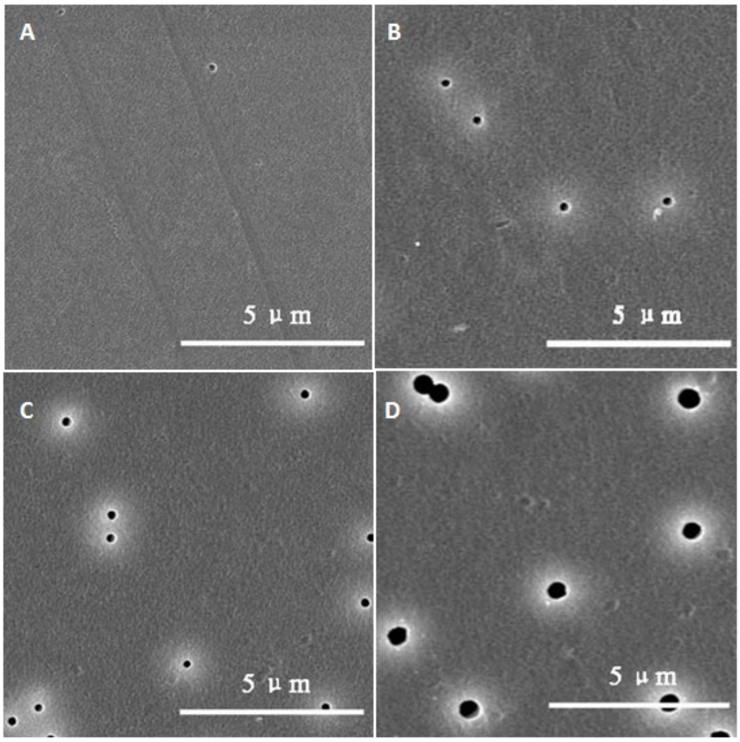

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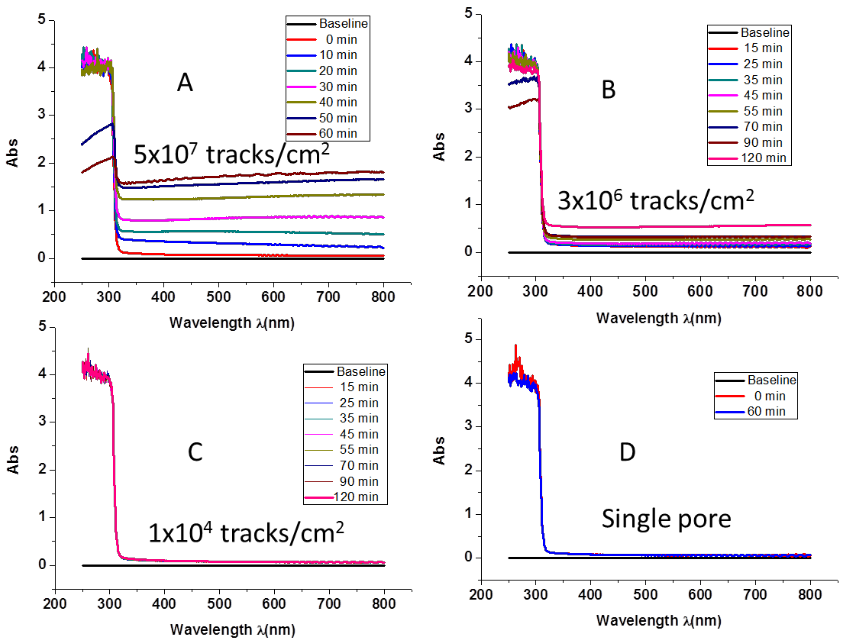

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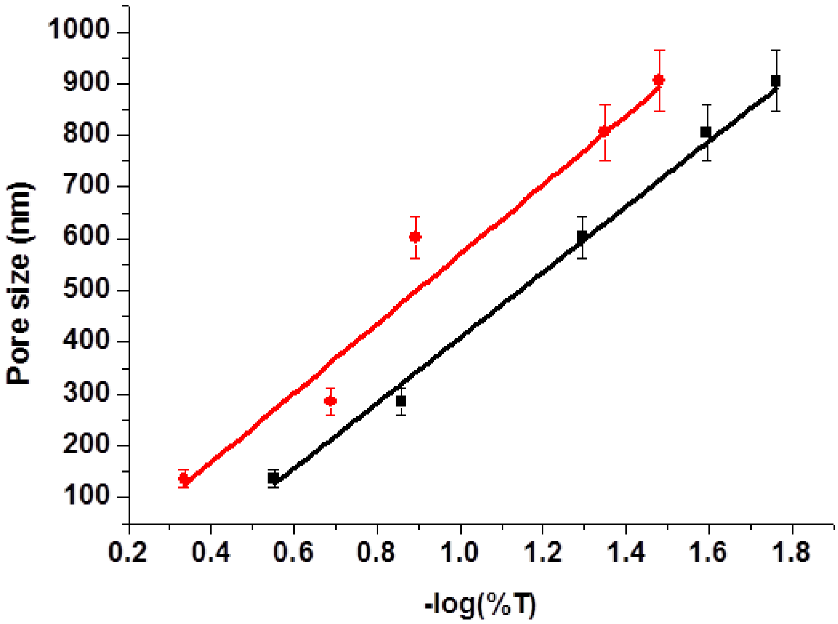


Figure S9

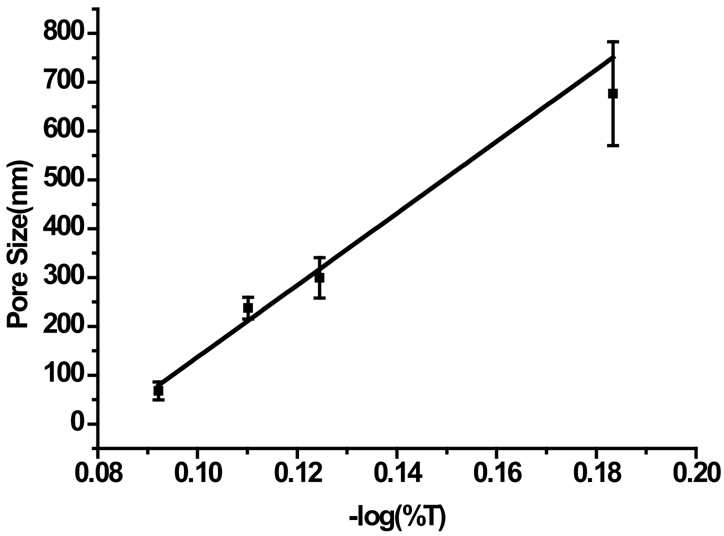


Figure S10

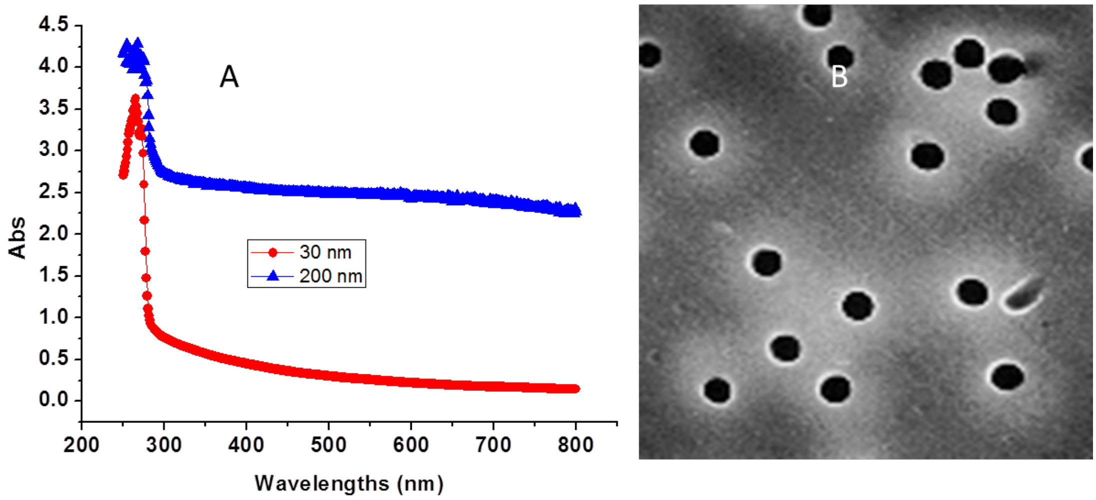
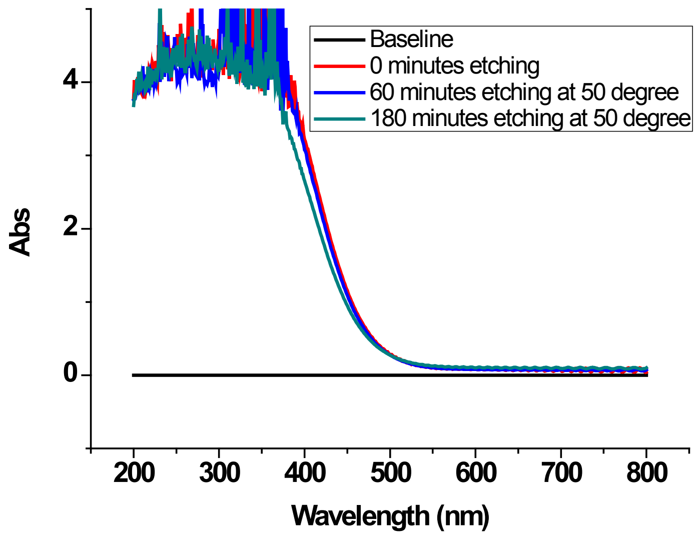


Figure S11



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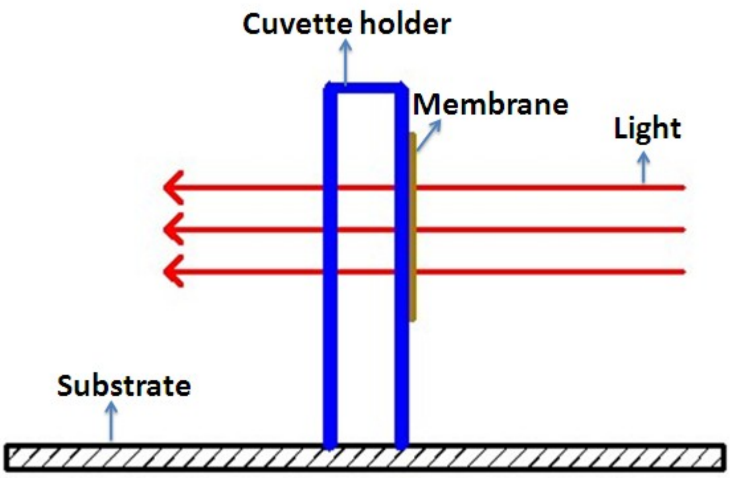

Figure S13

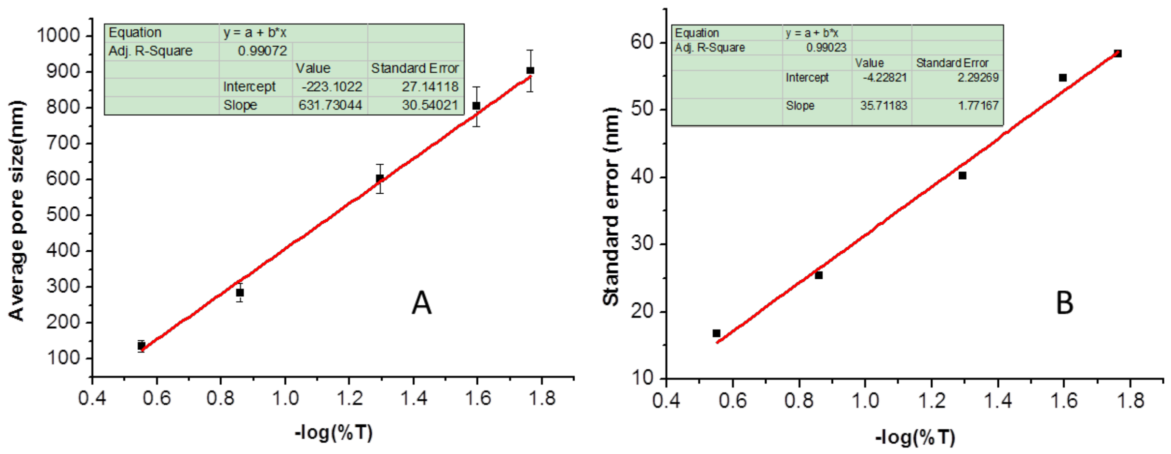

Table S1

Negative log value of percent tansmission (%T)	Average pore size (nm)	Standard error (nm)
0.55235	136.0	16.7
0.85859	285.4	25.3
1.29516	603.1	40.2
1.59599	805.6	54.6
1.76249	905.2	58.4

Figure S14