Electronic Supplementary Information

Electrically Gated Nanoporous Membranes for Smart Molecule Flow Control

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1. Molecular structure of ethacrynic acid and timolol maleate and UV-vis characteristics

The molecular structures of ethacrynic acid and timolol maleate are shown in Figure 1. Also, the molar mass and the charge at pH 7.4 are shown in Table 1. UV-vis spectroscopy was used to measure the concentration of the drug molecules in solution. The absorbance spectrum of ethacrynic acid solution with 0.015 mg/mL and timolol maleate solution with 0.1 mg/mL in 0.01x PBS are shown in Figure 2. For ethacrynic acid, the absorption peak was observed at 209 nm in 0.01x PBS solution. Timolol maleate has an absorption peak at 215nm in 0.01x PBS solution. Hence, we scanned from 205nm to 240nm. The maximum absorbance units measured in the experiment was 0.35 for ethacrynic acid and 0.60 for timolol maleate. We observed linear relationship between absorbance and the concentration under 0.35AU range for ethacrynic acid and under 0.60 AU for timolol maleate.

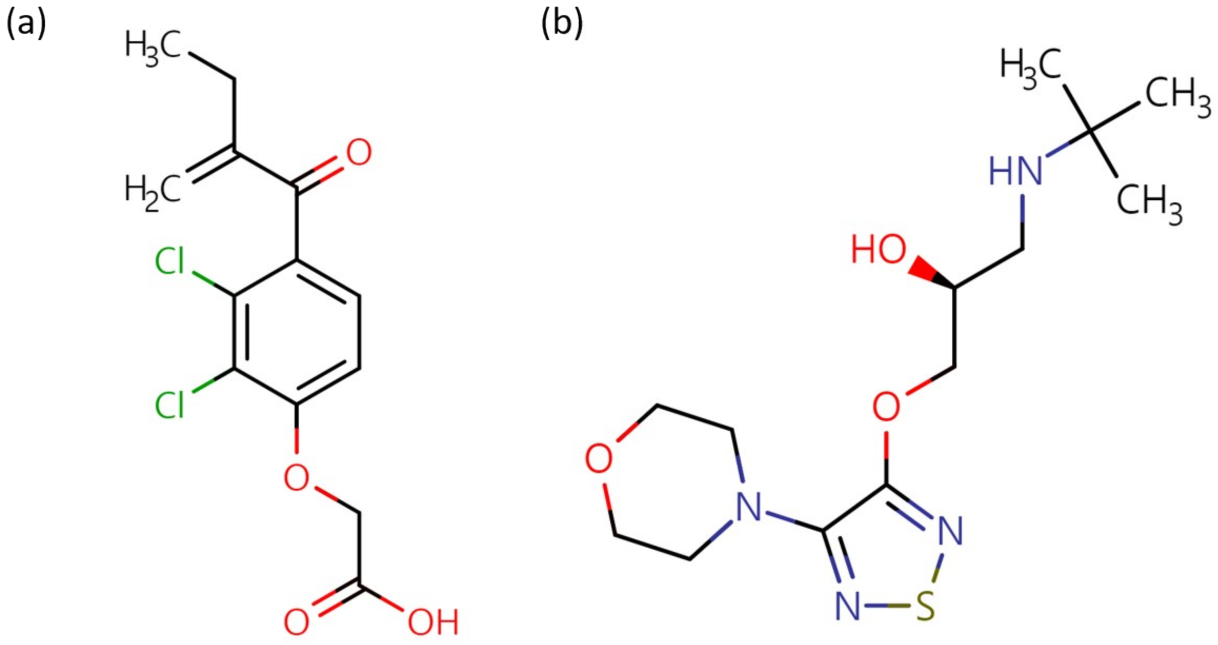

Figure 1(a) Molecular structure of ethacrynic acid (b) Molecular structure of timolol maleate[1]

Table 1 Material characteristics of ethacrynic acid and timolol maleate[1]

	Ethacrynic acid	Timolol maleate
Molar mass	303.14 g/mol	316.42 g/mol
Net charge at pH 7.4	-1.602×10^{-19}C (-1e)	$+1.602\times10^{-19}$C (+1e)

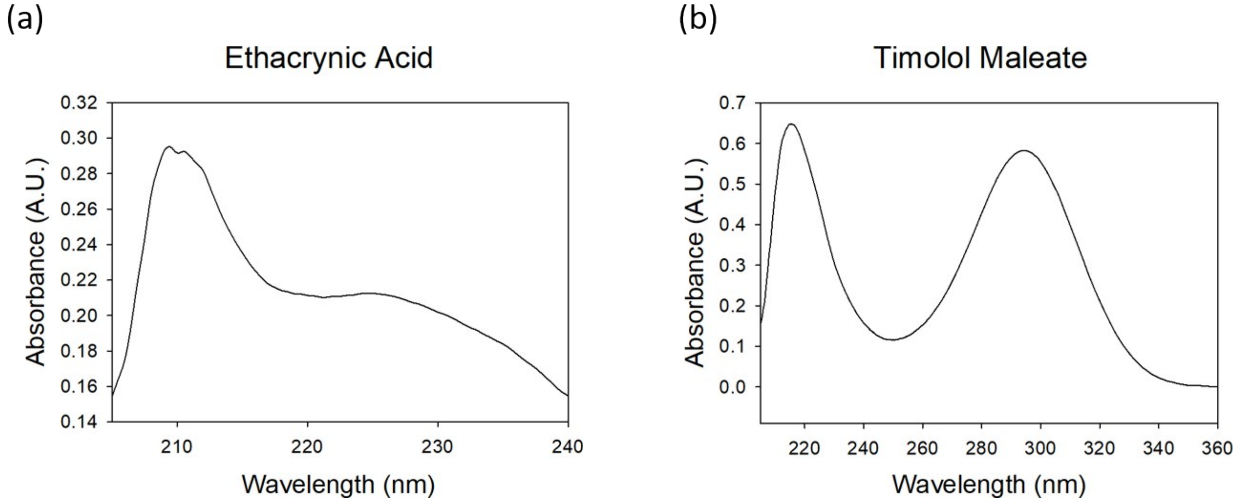

Figure 2 UV absorbance spectrum of (a) Ethacrynic acid (0.015mg/mL) and (b) Timolol maleate (0.1mg/mL) in 0.01x PBS solution

2. Characterization of the AAO membrane

The SEM image of the bare AAO membrane is shown in Figure 3. The image has a high noise because of the non-conducting characteristics of the bare AAO membrane. This image was processed with ImageJ as shown in Figure 4 to characterize the pore size and distribution. The measured pore size was 77.7nm in average with 19.9nm standard deviation. The average pore size measured by the manufacturer was 80nm in diameter, which is in line with our measurement.

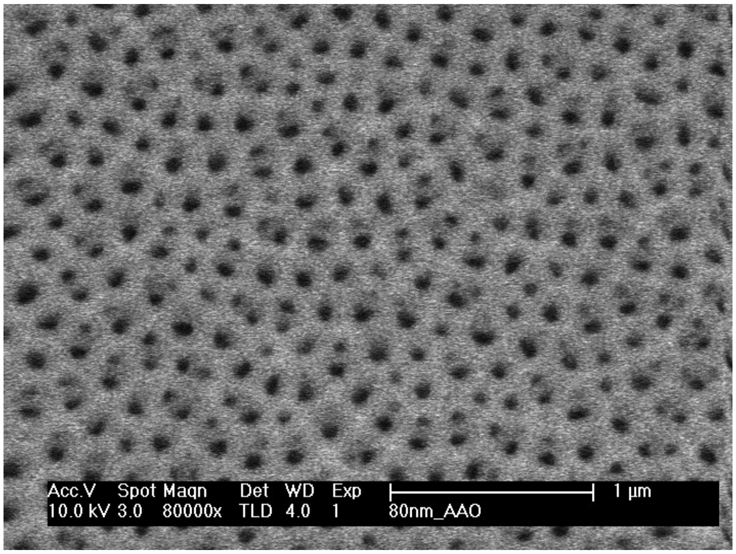

Figure 3 SEM image of the bare AAO membrane

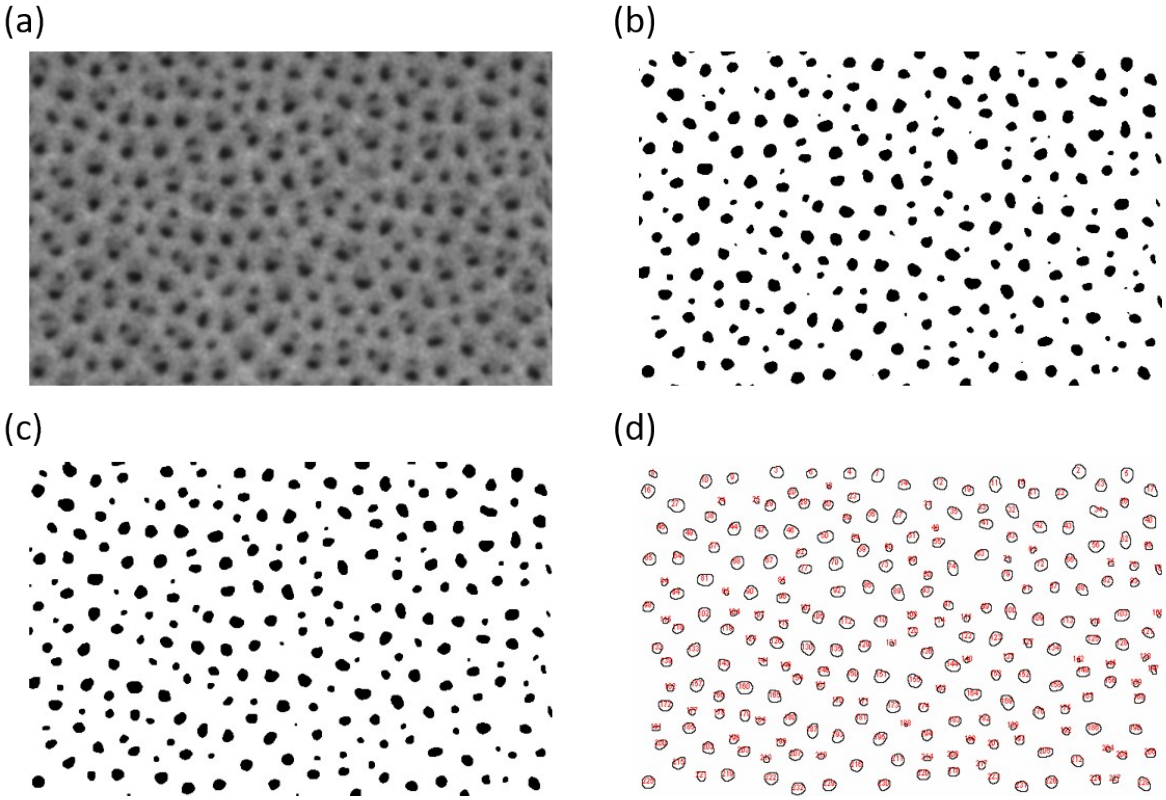

Figure 4 Image processing for the characterization of the nanoporous membrane. All processes were done with ImageJ. (a) Gaussian blurred image for the noise reduction (b) Converted to black and white image by setting the threshold value (c) Image after the smoothing process with erode and dilate (d) Particle analysis result

We also characterized the sputter deposited membrane with FEI Quanta-600 scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS). The result is shown in Figure 5.

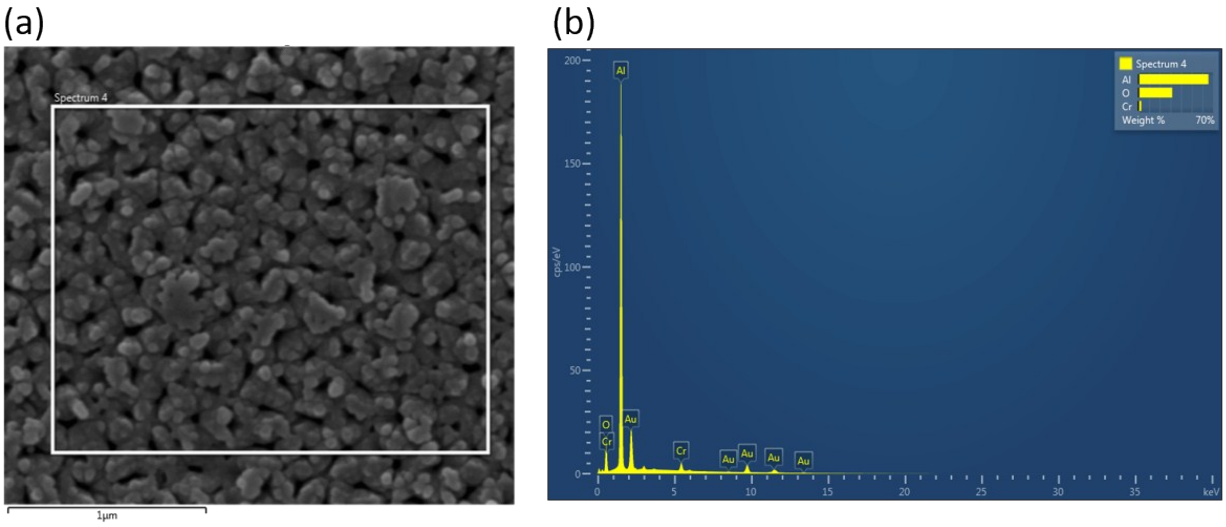

Figure 5. Surface characterization with energy-dispersive spectroscopy (EDS). (a) SEM image of the surface acquired with a FEI Quanta-600 scanning electron microscope. Surface marked with the white square was analyzed (b) EDS spectrum acquired with EDS. Al, O, Cr, Au peaks are observed.

3. Surface charge modification and measurement

It is known that we can determine the surface charge of the nanochannel by measuring the electrical conductance through the channel in KCl solution.[2] Conductance plateau on a log-log scale plot is observed when we measure the conductance through the nanochannel as shown in Figure 6. In cylindrical nanochannel with low concentration, the surface charge density must be balanced by counterions accumulated in the nanochannel because of the electroneutrality as shown in eq (1).

$$2\pi r l \sigma = \pi r^2 l F C_e \qquad (1)$$

We can calculate the surface charge density σ by measuring the transition KCl concentration, C_t. A conductance plateau $G_p$is reached, where C_t corresponds to 0.5 times the excess mobile counterion concentration C_e. When the bulk salt concentration is lower than C_e, the nanochannel attracts the counterion. Since the conductance of the nanochannel is determined by the number of ions accumulated in the nanochannel, the conductance plateau appears below certain background ion concentration, C_e. Hence, we can calculate the surface charge density σ as shown in eq (2).

$$\sigma = \frac{F C_e r}{2} = F C_t r \qquad (2)$$

Here, F is a Faraday constant, $F = 9.65 \times 10^4\ C/mol$ and r is a radius of the nanochannel. In our experiment, r = 80nm.

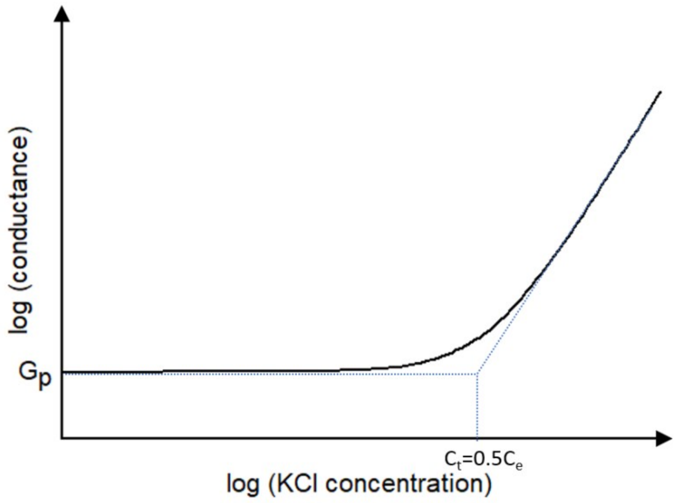

Figure 6 Schematic behavior of the nanochannel conductance as a function of the KCl concentration.

We measured the conductance of the bare AAO membrane, the AAO membrane treated with a 2% solution of 3-glycidoxypropyl trimethoxysilane(GPS) for 1 hour, and the AAO membrane with 1 hour GPS treatment followed by treating in the 50mM ethanolamine in DI water for 30 minutes. (GPT-E treatment) The results are shown in Figure 7. The calculated transition concentration and surface charge value are shown in Table 2. The GPS treatment did not decrease the surface charge density. The following ethanolamine treatment attaches ethanolamine to the covalent bonded GPS and reduced the surface charge.

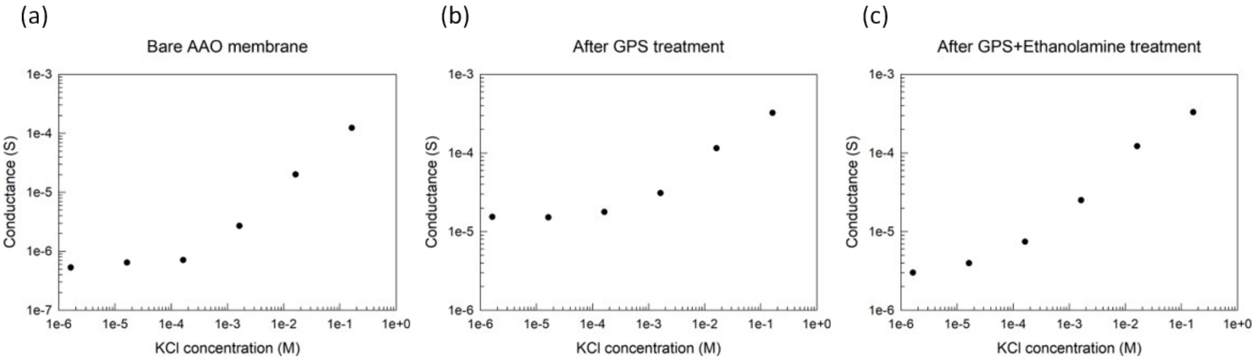

Figure 7 Measured conductance through the nanoporous membrane. (a) Bare membrane (b) After treating the membrane with a 2% solution of 3-glycidoxypropyl trimethoxysilane(GPS) in ethanol for 1 hour (c) After treating the membrane with a 2% solution of GPS in ethanol for 1 hour followed by 50mM ethanolamine in DI water for 30 minutes. Note that the active area of each membrane was different.

Table 2. Measured transition KCl concentration C_t and calculated surface charge

	Bare AAO	After GPS treatment	After GPS-E treatment
C_t (mol/m^3)	0.279	0.377	0.032
σ(mC/m^2)	1.08	1.45	0.12

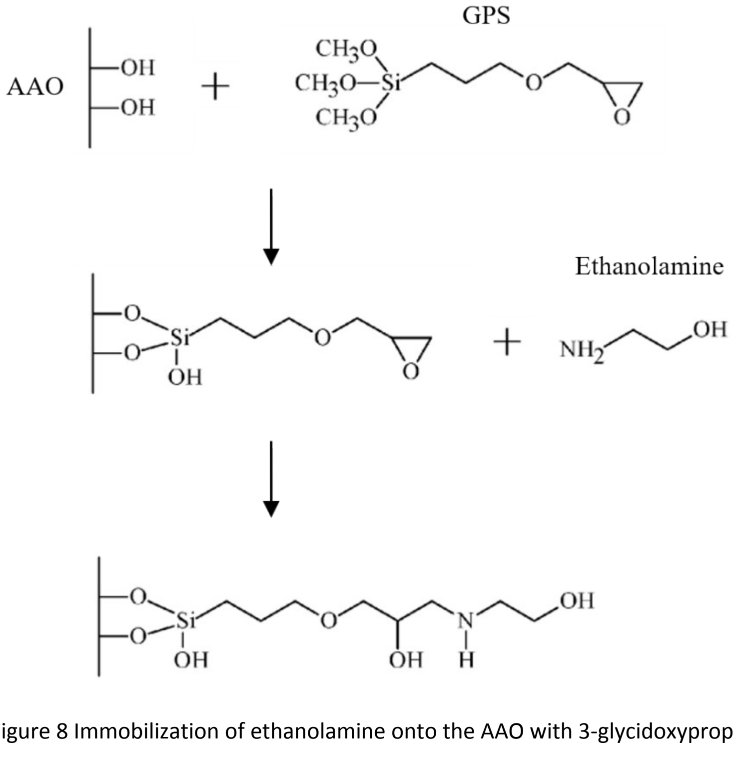

Figure 8 Immobilization of ethanolamine onto the AAO with 3-glycidoxypropyl-trimethoxysilane (GPS)

The intrinsic surface charge of the native AAO membrane was 1.08mC/m^2. The 1 hr GPS treatment in 2% solution in ethanol increased surface charge to 1.45 mC/m^2. After the final ethanolamine bonding for 30 minutes, the surface charge is reduced to 0.12 mC/m^2. The surface modification is done with the process depicted in Figure 8. GPS covalently bonded to the AAO surface with hydroxyl (-OH) groups on the AAO surfaces with silane coupling.[3] And the following ethanolamine treatment immobilizes the ethanolamine molecules onto the AAO surface.[4]

4. Surface charge modification and measurement

We can define the diffusion flux of the drug molecule J as,

$$J = -D_{eff}\frac{\partial C_{drug}}{\partial x}$$

where $C_{drug}$is a concentration of the drug molecule, D_{eff} is the effective diffusion coefficient of the fabricated membrane.

Since the change of the drug molecule concentration of the donor and acceptor chamber is relatively small, we can assume that the concentration gradient is linear. If we assume linear concentration gradient and the concentration difference between two chambers are constant,

$$\frac{\partial C_{drug}}{\partial x} = -\frac{C_{drug}}{l}$$

where l is a thickness of the AAO membrane. Here $l = 50\mu m$. The D_{eff} value can represent how well the membrane can diffuse the molecule through the membrane.

	ETHACRYNIC ACID		**TIMOLOL MALEATE**	
V_G	Bare	GPS-E	Bare	GPS-E
-2V	1.18E-02	1.23E-02	2.61E-03	3.32E-03
0V	2.44E-02	2.61E-02	2.25E-03	2.55E-03
2V	8.20E-02	6.89E-02	1.92E-03	1.67E-03

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