We developed Al$_2$O$_3$/W heterogeneous nanopore arrays for field effect modulated nanofluidic diodes. They are fabricated by transferring self-organized nanopores of anodic aluminium oxide into a W thin film. The nanopores are ~20 nm in diameter and 400 nm in length. After mild oxidation, approximately 10 nm WO$_3$ grows on the surface of W, forming a conformal and dense dielectric layer. It allows the application of an electrical field through the surrounding W electrode to modulate the ionic transport across the entire membrane. Our experimental findings have potential applications in high throughput controlled delivery and electrostatic sorting of biomolecules.

A nanofluidic diode possesses the unique property of creating ionic current rectification in nanochannels. It is a basic element for directional control of ionic and molecular transport mimicking biological ion channels. Various approaches have been developed to achieve asymmetric transport in a nanochannel. A typical nanofluidic diode consists of heterogeneous surface charges along a nanochannel by using surface functionalization or different native oxides. Alternatively, for a mono-charged nanochannel, the breaking of symmetry is possible through geometry, gradient in ion concentration or liquid viscosity, and external chemical stimuli such as pH and binding of polyvalent cations. However, the property of the diode cannot be modified once it is made without changing its chemical environment.

Tuning the rectifying property of a nanofluidic diode in situ through an external electrode is important for controlled delivery, electrostatic sorting, and detection in biochemical processes. A gate electrode can be used to modulate the potential and charge density of the electrical double layer near the channel walls in electrolytes. Several types of planar nanofluidic diodes were fabricated based on conventional “etching followed by bonding” technique. In such a configuration a top gate electrode is used to modulate ionic transport through the nanochannels for nanofluidic transistors. However, planar nanochannels are generally long with small cross section and therefore have very small throughput of ionic current.

We present here a membrane approach for field effect modulated nanofluidic diodes based on nanopore arrays. The obvious advantage of a membrane is that it presents a high number of parallel short nanopores within a small area. Figure 1(a) shows the schematic geometry of the membrane. The nanopore is composed of heterogeneous Al$_2$O$_3$ and W layers. The surface of the W metal is passivated by WO$_3$ dielectric thin film via thermal oxidation. Figure 1(b) illustrates the working principle of a field effect reconfigurable nanofluidic diode. It is a three-terminal device. A pair of Ag/AgCl electrodes is used to apply bias and measure ionic conductance across the membrane. The gate potential is applied on the W layer. The current through drain (I$_D$) and gate (I$_G$) are monitored simultaneously. The gate potential regulates the charge polarity and density of the electrical double layer both inside the nanochannel and on the surface of the membrane at the W side. Consequently, the rectification property of the membrane can be modulated by the gate potential.

We have developed a strategy to fabricate heterostructured nanopore membranes based on pattern transfer of anodic aluminium oxide (AAO). The process is described in Figure S1 of the supplemental material. Briefly, 200 nm W was deposited on a freestanding low stress SiN membrane followed by an annealing process (Figure S2 in the supplemental material). Afterwards, 150 nm Al was deposited and...
anodized to create self-organized alumina nanopores. By re-active ion etching of W through AAO, some of the top nano-pores penetrate into the bottom W layer. Finally, the membrane was released by selective etching of the supporting SiN layer. The nanopores are thus composed of Al2O3 layer and W layer with natively positive and negative surface charges, respectively. A conformal dielectric layer is formed at W surface by mild oxidation.

The SEM sample characterizations are shown in Figure 2. Figure 2(a) reveals typical dense alumina nanopore pattern generated by anodization of a thin Al film. It shows a distribution in pore size and shape. The pore size of the top alumina layer is 26 ± 7 nm. The openings in the W layer (Figure 2(b)) are smaller (<20 nm) and mostly located at grain boundaries. The pore density of ~20 pores μm⁻² in the W bottom is relatively low, compared to ~200 pores μm⁻² of top AAO layer. This means that only 10% of AAO pores are fully transferred through W. The profile of the hetero-structured nanopore is shown in the FIB-SEM cross section image Figure 2(c). The pore density of 20 pores μm⁻² of top AAO layer. W etching process through top alumina creates nanocavities with nanochannels open through the membrane.

Tungsten oxide has high-
The response of regulation on electrical double layer properties through a gate potential for WO$_3$ can be interpreted by a metal-dielectric-electrolyte electrochemical model. Considering a flat gate electrode in electrolyte as depicted by a metal-dielectric-electrolyte electrochemical capacitors of gate dielectric ($C_{\text{Dielectric}}$) and Stern layer properties through a gate potential for WO$_3$ can be intertions. The overall effect on rectifying factor taken between related to the short ionic channels as suggested by simulations. The overall effect on rectifying factor taken between |$I_D$| at 0.4 V and −0.4 V can be modulated from 2 to 11.

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gate potential. As for the situations of $\Gamma = 0.5$ and $5$, $\sigma_{DL}$ is much lower at positive gate potentials due to the buffering effect of the dissociated negative surface charges.

The modulation of the gate potential on the ionic transport through the membrane can be qualitatively understood by the COMSOL simulation in Figure 5 using the Poisson-Nernst-Planck equations. The model considers a heterogeneous nanopore connected by two reservoirs of 1 mM KCl solution with bias $V_{bias}$. The nanopore is axisymmetric with diameter of 20 nm and total height of 400 nm. It is composed of a positively charged top side with $\sigma_1 = +3 \text{ mC m}^{-2}$ and down side with $\sigma_2$ varying from $-5$ to $+1 \text{ mC m}^{-2}$. $\sigma_2 = \sigma_{DL}$ is obtained in Figure 4 at different gate potentials. The same charge polarity and density are also applied to the entrance of corresponding side of nanopores as indicated in the schematic. When the gate potential changes from $-0.4 \text{ V}$ to $+0.4 \text{ V}$, the IV curves deviate from ideal rectifying behaviour with lower forward current and higher reverse current. The simulation is qualitatively consistent with the experimental observations shown in Figure 4. The experimental conductance value is about 4 orders of magnitude higher than that of the simulated value for a single pore of 20 nm in diameter, which corresponds to the summed throughput of a pore density of ~20 pores $\mu \text{m}^{-2}$ and a membrane area of $10^4 \mu \text{m}^2$.

In conclusion, we have demonstrated field effect reconfigurable nanofluidic diode membranes composed of alumina/tungsten (Al$_2$O$_3$/W) heterogeneous nanopore arrays. Typical membrane size is $100 \times 100 \mu \text{m}^2$ with $10^5$ pores in total. The fabrication process is scalable, based on pattern transfer of self-organized nanopores of anodic aluminium oxide into a W layer. We have provided a simple method to fabricate efficient gate dielectric by thermal oxidation of W at relatively low temperature. The ionic current rectifying behavior through the membrane can be efficiently modulated by an external electrical potential through the W electrode. Our experimental findings have potential applications in controllable molecular separation, chemical processing and biosensing.

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25See supplementary material at http://dx.doi.org/10.1063/1.4807781 for Figure S1: fabrication process flow of Al$_2$O$_3$/W hetero-structured nanopore membranes; Figure S2: stress releasing of a W film on a LS SiN membrane; and Figure S3: ionic transport properties of native diode membranes.