Electronic Supplementary Information

An ionic Diode Based on Spontaneously Formed Polypyrrole-modified Graphene Oxide Membrane

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Content:

1. Top-viewed and cross-sectional SEM images of polypyrrole-modified GO membrane.

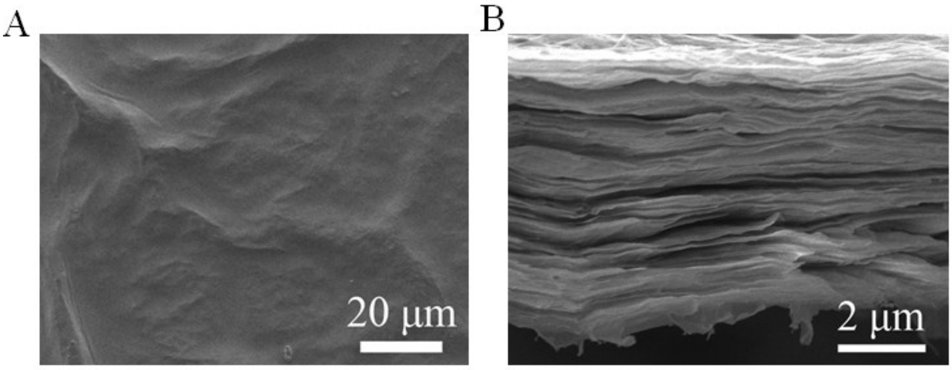

Figure S1. (A) Top-viewed and (B) cross-sectional SEM images of polypyrrole-modified GO membrane. After deposition of polypyrrole on GO membrane, the surface became slightly smooth, while the morphology of the cross-section remained almost unchanged.

2. Top-viewed SEM images of the two sides of GO membrane.

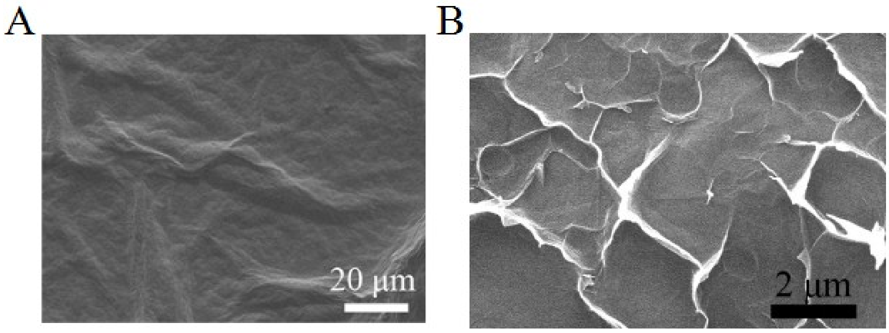

Figure S2. Top-viewed SEM images of the front (A) and back (B) side of GO membrane.

3. Ion current-voltage (I-V) curves of an ionic diode based on polypyrrole-modified GO membrane at a voltage range of -3~+3 V and -4~+4 V.

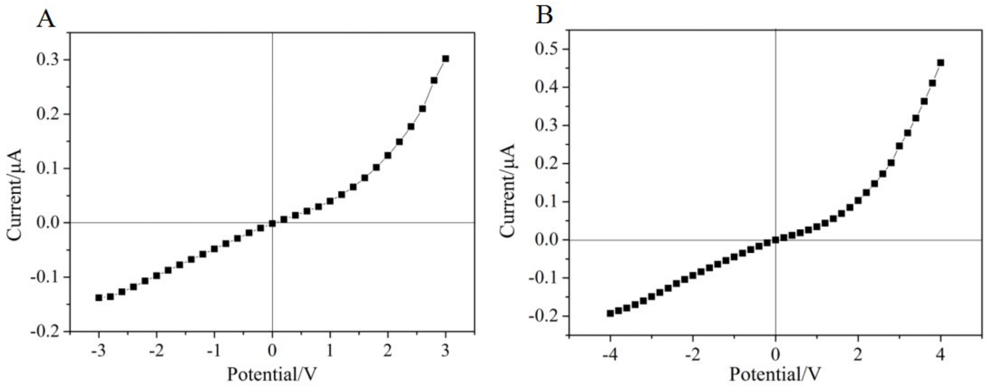

Figure S3. Ion current-voltage (I-V) curves of an ionic diode based on polypyrrole-modified GO membrane in 1 mM of KCl aqueous solution at a voltage range of -3~+3 V (A) and -4~+4 V (B).

4. A theoretical model of the polypyrrole-modified GO membrane.

The simplified model for calculating the ion concentrations and current-voltage curves of the polypyrrole-modified GO membrane was shown in Figure S3. To simplify the calculation, the polypyrrole-modified GO membrane was theoretically modeled as a cylindrical nanochannel. Figure S3 showed the axial section of the cylindrical nanochannel. The colored part represented the hollow interior of the nanochannels, while the white wide line represented the neutral polypyrrole in the nanochannel. The increase in the length of wide line implied the increase in the modification percentage of neutral polypyrrole.

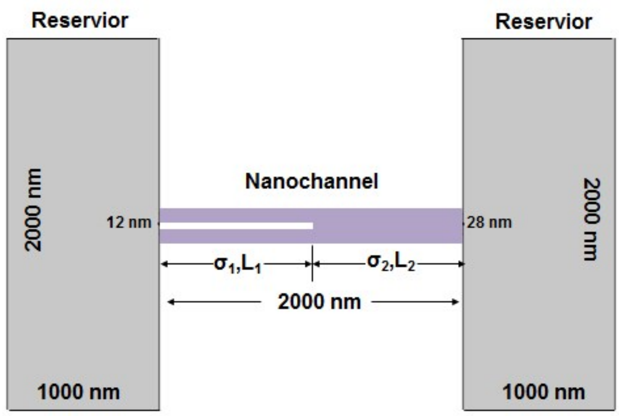

Figure S4. The simplified model of polypyrrole-modified GO membrane.

The total length of nanochannel was set to be 2000 nm. The modified percentage of polypyrrole was supposed to be 25%, 50%, 75% and 100% of the total length. The pore sizes of unmodified and modified nanochannel were set to be 28 nm and 12 nm respectively. The surface charge density was set as -0.001C/m^2.

The ion transport properties of the nanochannel were quantitatively calculated using “Electrostatics” and “Transport of Diluted Species” modules in COMSOL Multiphysics 5.4. σ_1 and L_1 are the surface charge density and the length of polypyrrole-modified GO segment. σ_2 and L_2 are those of unmodified GO membrane (σ_2=σ_1).

The calcualtion was carried out based on the Poisson-Nernst-Planck equations [1, 2]:

$$\nabla^2\phi = -\frac{F^2}{\varepsilon}\sum z_i c_i$$

$$J_i = -D_i(\nabla c_i + \frac{z_i F c_i}{RT}\nabla\phi)$$

$$\nabla J_i = 0$$

In these equations, φ, z_i, c_i, J_i and D_i denote electrical potential, the charge number, the ionic concentration, the ionic flux and the diffusion coefficient of each species i, respectively. ε is the dielectric constant of the solution. The boundary conditions of the nanochannel are as follows:

$$\vec{n}\cdot\nabla\phi = -\frac{\sigma}{\varepsilon}$$

$$\vec{n}\cdot J_i = 0$$

Where $\vec{n}$ and σ represent the unit normal vector and the surface charge density, respectively.

The ionic current of species i can be calculated by integrating the ionic flux along the cross section of the nanochannel:

$$I_i = \int_s J_i ds = -\int_s D_i(\nabla c_i + \frac{z_i F c_i}{RT}\nabla\phi)ds$$

5. References

[1] I. Vlassiouk, S. Smirnov, Z. Siwy, *ACS Nano* **2008**, *2*, 1589.

[2] H. Daiguji, Y. Oka, K. Shirono, *Nano Lett.* **2005**, *5*, 2274.