

## Electronic Supplementary Information

### Redox-generated Biomimetic Membrane Potential across Polypyrrole Films

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## 1. Experimental Section

**Preparation of Oxidized Polypyrrole Films.** The oxidized polypyrrole films were prepared by an electrochemical polymerization of pyrrole on a gold minigrad with a diameter of 3 mm (2000 lines/inch, Gilder Grids) in 0.1 M pyrrole (J&K, China) aqueous solution containing 0.1 M KCl as a supporting electrolyte.<sup>1-3</sup> The electrochemical polymerization was performed using a three-electrode configuration. The gold minigrad acted as a working electrode and a platinum wire served as counter electrode. The reference electrode was an Ag/AgCl electrode in 3.5 M KCl aqueous solution. A CHI660D electrochemical workstation (Shanghai Chenhua Apparatus Co., Ltd., China) was used to provide a potential. The oxidized polypyrrole film was obtained by electropolymerization of pyrrole at a potential of +0.9 V for different times.

**Asymmetric Redox Reaction of Polypyrrole Films.** In order to introduce an asymmetric charge distribution, the polypyrrole film was subjected to an asymmetric redox reaction using a three-electrode configuration (Figure S4). The as-prepared oxidized polypyrrole film was mounted between the two chambers of a homemade electrochemical cell, which served as a working electrode. The Pt counter electrode and Ag/AgCl reference electrode were inserted into the two chambers of the electrochemical cells respectively, which were both filled with 1.0 mM KCl aqueous solution. An electrochemical potential provided by the CHI660D electrochemical workstation was used to initiate the asymmetric redox reaction of polypyrrole films. Because the Pt counter electrode was put into only one chamber of the electrochemical cell, the side of polypyrrole film that faced to the counter electrode would be oxidized or reduced preferentially.

**Characterization.** The morphology of polypyrrole films was observed using a Quanta FEG 250 environmental scanning electron microscope (FEI, USA). The UV-visible absorption spectra were investigated using Shimadzu UV-3600 spectrometer. The compositions of polypyrrole were characterized using a Thermo Nicolet 6700 Fourier transform infrared spectroscopy (FTIR) spectrometer and a Thermo Escalab 250Xi X-ray photoelectron spectroscopy (XPS). The energy dispersive X-Ray spectroscopy

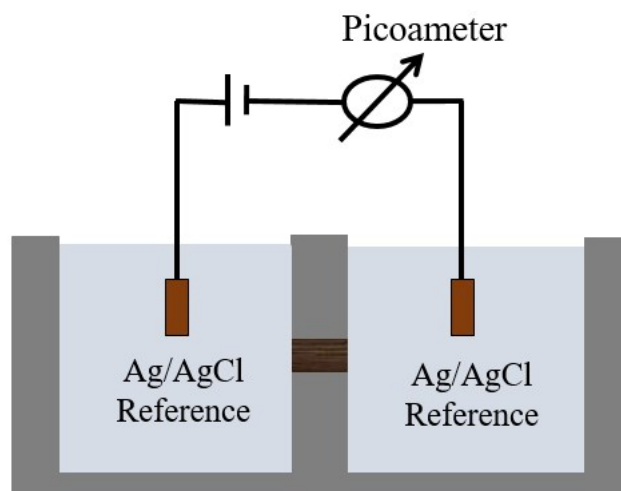
(EDS) was performed by a JSM-7500F field-emission scanning electron microscope (JEOL, Japan) coupled with an INCA Energy 250 energy spectrum analyzer.

**Measurements of Membrane Potential.** The membrane potential was studied by measuring the ion current-voltage (I-V) curves of polypyrrole films at scanned voltages from -0.2 V to +0.2 V. The ion conductance through the polypyrrole film in KCl electrolyte was calculated from the I-V curves. The polypyrrole film with an effective area of 0.8 mm<sup>2</sup> was mounted between two chambers of an electrochemical cell. The electrolyte was a KCl aqueous solution with a concentration of 1 mM. A pair of Ag/AgCl electrodes was used to apply a stable transmembrane voltage across the film. The ion current at scanned voltages was measured with a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH, USA) (Figure S1). The membrane potential was equal to the negative value of the applied voltage at zero current on the I-V curve.

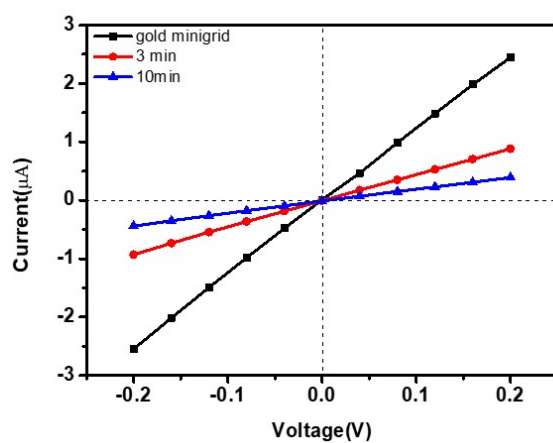
[1] P. Burgmayer, R. W. Murray, *J. Phys. Chem.* 1984, 88, 2515-2521.

[2] P. Burgmayer, R. W. Murray, *J. Am. Chem. Soc.* 1982, 104, 6139-6140.

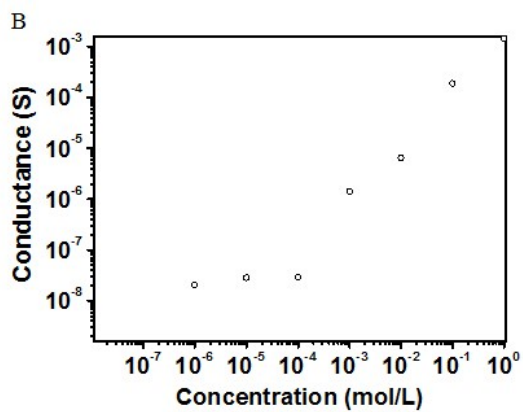
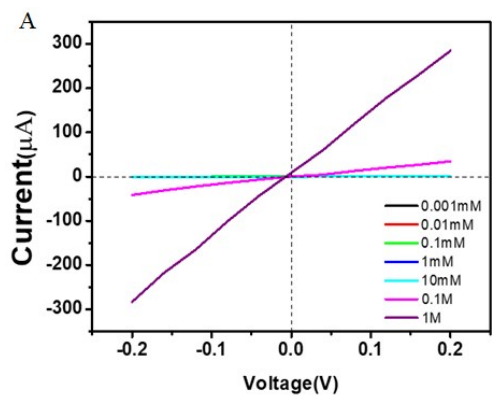
[3] Q. Zhang, J. Kang, Z. Xie, X. Diao, Z. Liu, J. Zhai, *Adv. Mater.* 2018, 30, 1703323.



**Figure S1.** Schematic setup for the measurement of ion current-voltage ( $I-V$ ) curves. The polypyrrole film was mounted between the two chambers of an electrochemical cell. A KCl aqueous solution with a concentration of 1 mM was chosen as an electrolyte. Two Ag/AgCl electrodes were used to apply a stable transmembrane voltage across the polypyrrole film to measure the ion current.

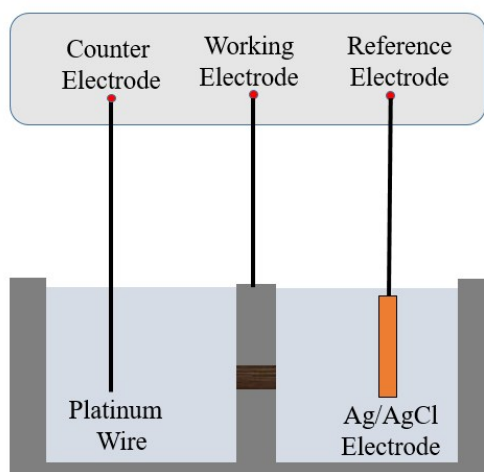


**Figure S2.** The ion current-voltage (I-V) curves of a blank gold minigrd and a polypyrrole film prepared by electrochemical polymerization for 3 min and 10 min. Following the increase of polypyrrole film thickness, the ion current and ion conductance decreased.

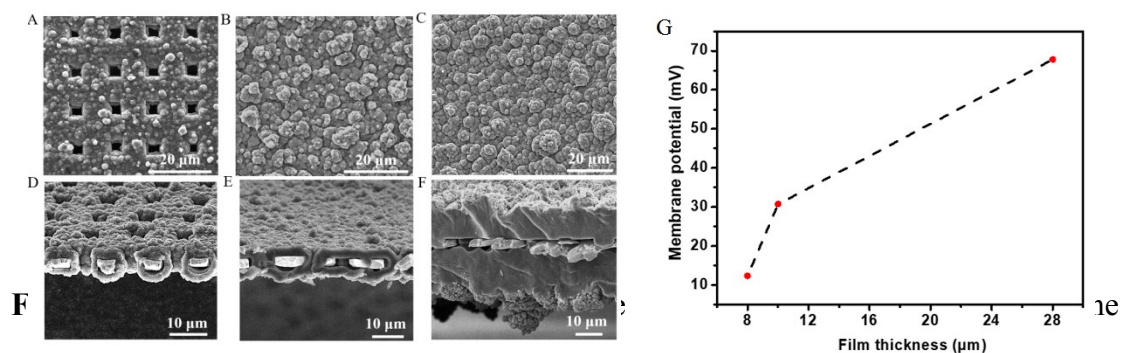


$10^{-3}$  M. (B) The function of ion conductance with the concentration of KCl electrolyte.

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**Figure S4.** Schematic setup for the asymmetric redox reaction of polypyrrole film in a three-electrode configuration. The polypyrrole film was mounted between the two chambers of an electrochemical cell. An electrochemical workstation was used to apply a potential to the polypyrrole film, which acted as a working electrode. A platinum wire was used as a counter electrode. The reference electrode was an Ag/AgCl in 3.5 M KCl solution. Because the Pt counter electrode was put into only one chamber of the electrochemical cell, the side of polypyrrole film that faced to the counter electrode would be oxidized or reduced preferentially.



corresponding membrane potential after applied with a reduction potential of  $-0.9$  V (vs. Ag/AgCl) for 100 s. (A-C) Top-viewed SEM images of polypyrrole films prepared by electrochemical polymerization for 3 min (A), 5 min (B) and 10 min (C). (D-F) The corresponding cross-sectional SEM images of the polypyrrole films, indicating the film thickness was 8, 10 and 28 μm. (G) The function of membrane potential with the thickness of polypyrrole films.