Supporting Information

Gas-Breathing Polymer Film for Constructing of Switchable Ionic Diodes

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FIGURE CAPTIONS

Figure S1 Schematic diagram of growth of polymer film via polymerization (SI-ATRP (surface initioated-atom transfer radical polymerization))[1-4] of monomer (PDEAEMA (2-(Diethylamino)ethyl methacrylate) on the channel embedded in PET membrane.

Figure S2 X-ray photoelectron spectroscopy (XPS) characterization of the modification process on the PET membrane. (A) Nitrogen XPS spectra before and after PEI adsorption on PET membrane. (B) Bromine XPS spectra before and after the initiator 2-BiB (2-Bromoisobutyryl bromide) modification (2-BiB) on PEI-adsorbed PET membrane.

Figure S3 ^{1}H NMR spectrum of polymer synthesized in solution via monomer DEAEMA (2-(Diethylamino)ethyl methacrylate).

Figure S4. SEM images of the nascent track-etched PET membrane (A) and the same membranes grafted with PDEAEMA after treated with different solutions including electrolyte solution purged with CO_2 (B), electrolyte solution purged with N_2 (C) and three buffering solutions (0.1 M KCL in 0.1 M PBS) at pH 5.0, 7.0 and 9.0 (D, E and F). Electrolyte solution at pH 7 contains 0.1 M KCL and 0.1 M PBS.

Figure S5. SEM images of the asymmetric channel in PET membranes (A and C) and the corresponding PET membrane covered by polymer film (B and D). (A) The base side of the channel membrane, (B) The polymer film-covered base side of the channel membrane, (C) The tip side of the channel membrane, (D) the polymer film-covered tip side of the channel membrane.

Figure S6. Switchable fluidic diode pairs (A and B) based on conical-shaped channel covered by gas-responsive polymer film. Each curve is divided into part I and part II. The corresponding cartoons illustrate the ion transport mechanisms under pH stimulation and voltage polarity. When the OH^- ions accumulate around the polymer film, this gate is shut down; when the OH^- ions decrease and H^+ dominate around the polymer film, the gate open up.

Figure S7 Challenging the conical-shaped channel with the asymmetric stimulation of pH pairs including (A) tip side pH 5.0||base side pH 7.0, (B) tip side pH 6.5||base side pH 7.0 and (C) tip side pH 6.5||base side pH 9.0. All the PBS (0.1 M) buffering solutions contain 0.1 M KCL.

Figure S8. SEM images of conical-shaped channels with tip diameter of 74 nm and base diameter of 222 nm before and after polymer film growth. The base side of the nascent asymmetric channel embedded in PET membrane before (A) and after (B) polymer film growth. The tip side of the nascent asymmetric channel embedded in PET membrane before (C) and after (D) polymer film growth. Cross-sections of the asymmetric channel before (E) and after (F) polymer film growth.

Figure S9. (A) I-V characterization of each modification step for the single conical-shaped channel with tip diameter of 200 nm and base diameter of 40 nm. a, b, c and d indicate the statuses for channels before modification, after PEI adsorption, after initiator modification and after polymer film growth, respectively. (B) “on” status with the stimulation of pH 5||pH 5 (a) and “off” status with the stimulation of pH 7||pH 7 (b). (C) (a) represents responsiveness of the conical-shaped channel to ambient pH 5|| pH 7 stimulation and (b) represents responsiveness of the conical-shaped channel to ambient pH 7||pH 5 stimulation.

Figure S1

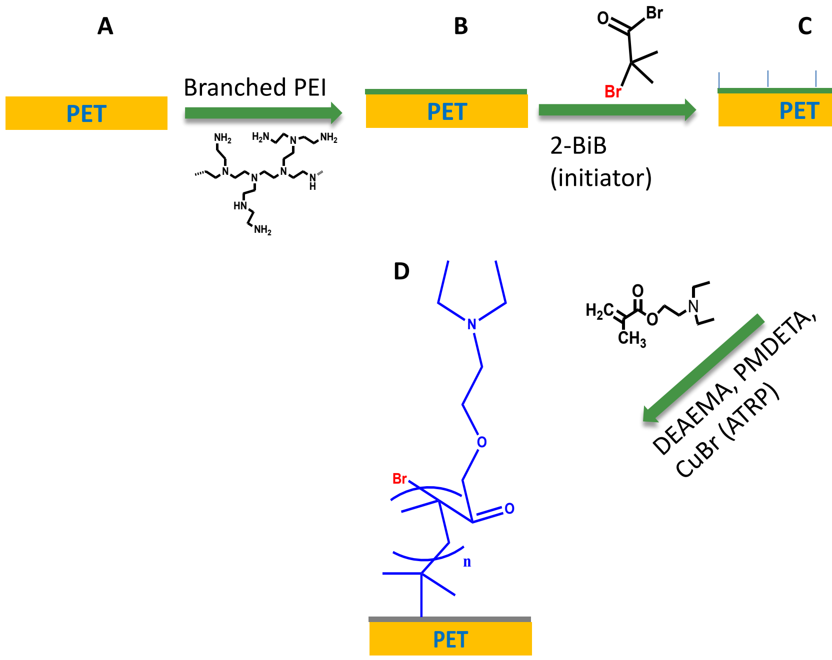


Figure S2

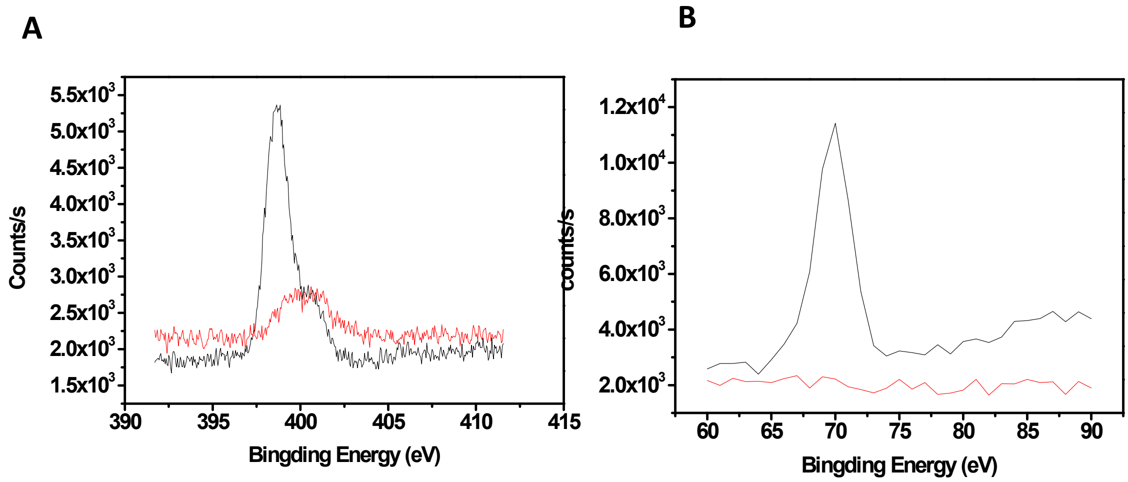


Figure S3

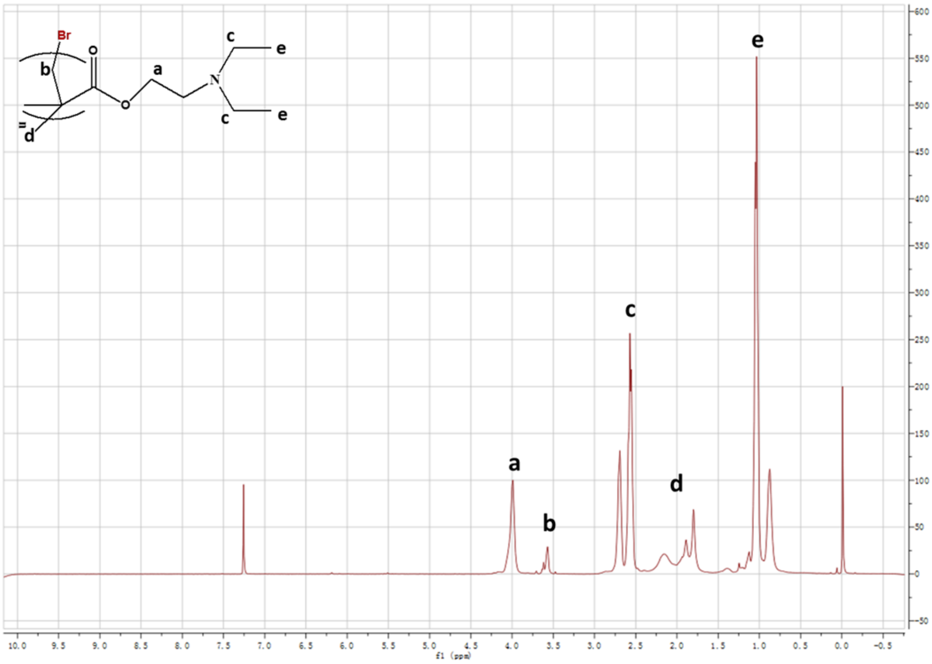
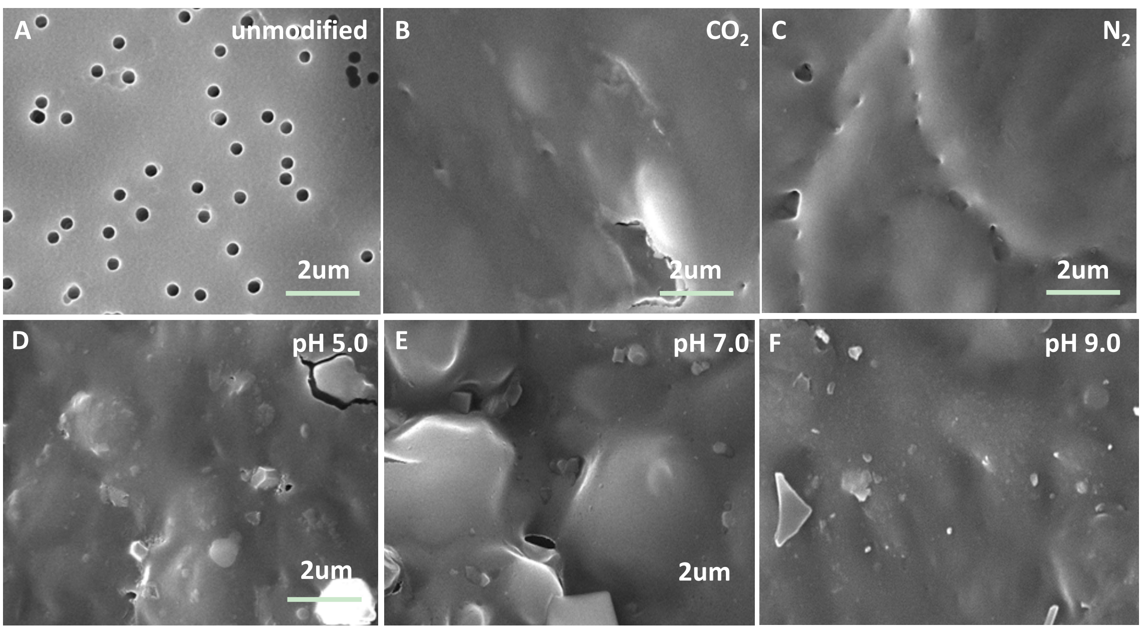


Figure S4



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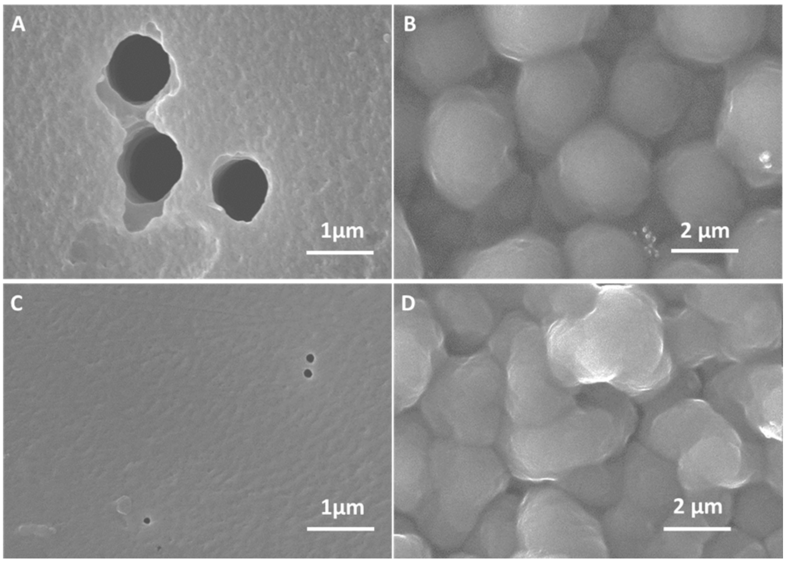


Figure S6

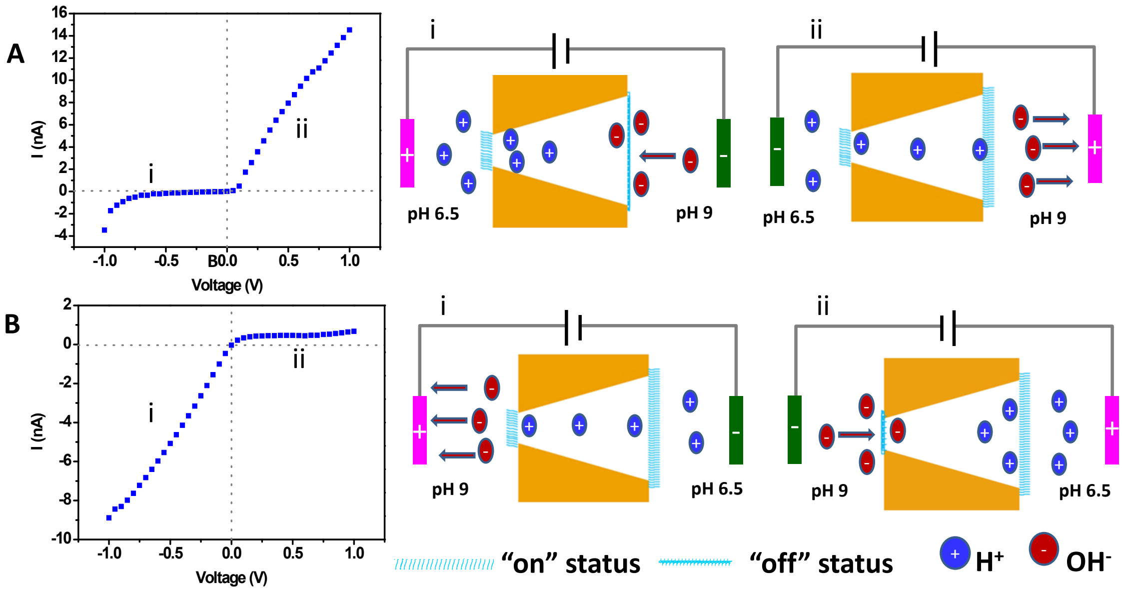


Figure S7

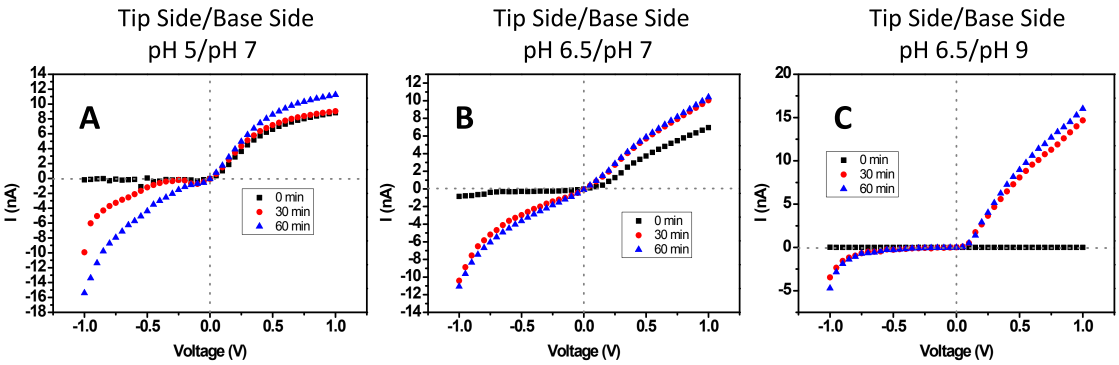


Figure S8

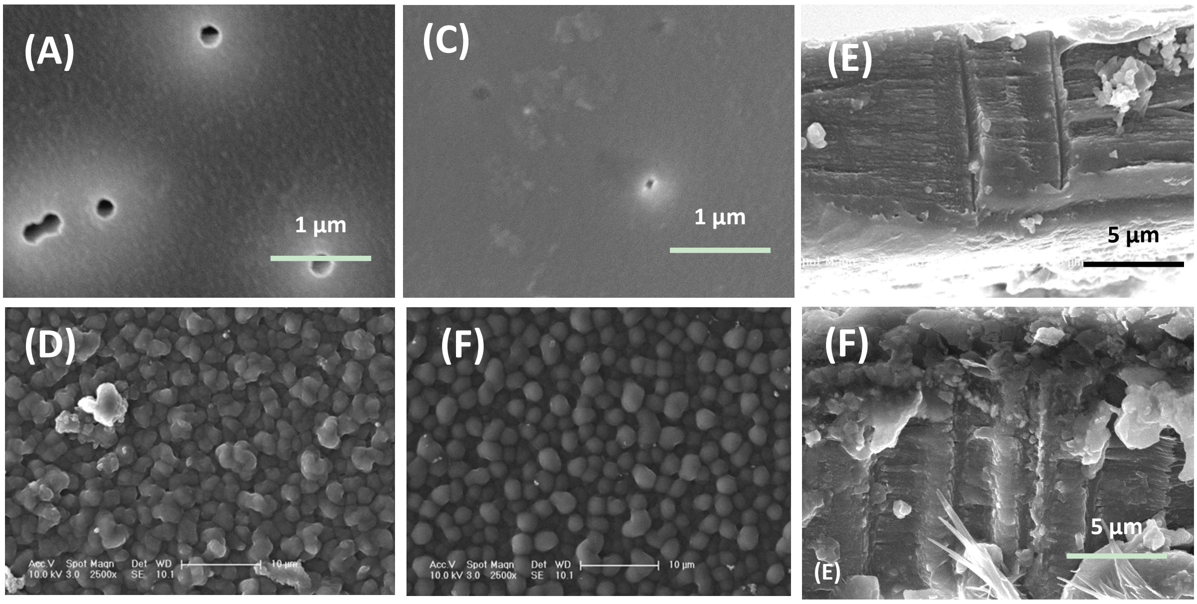
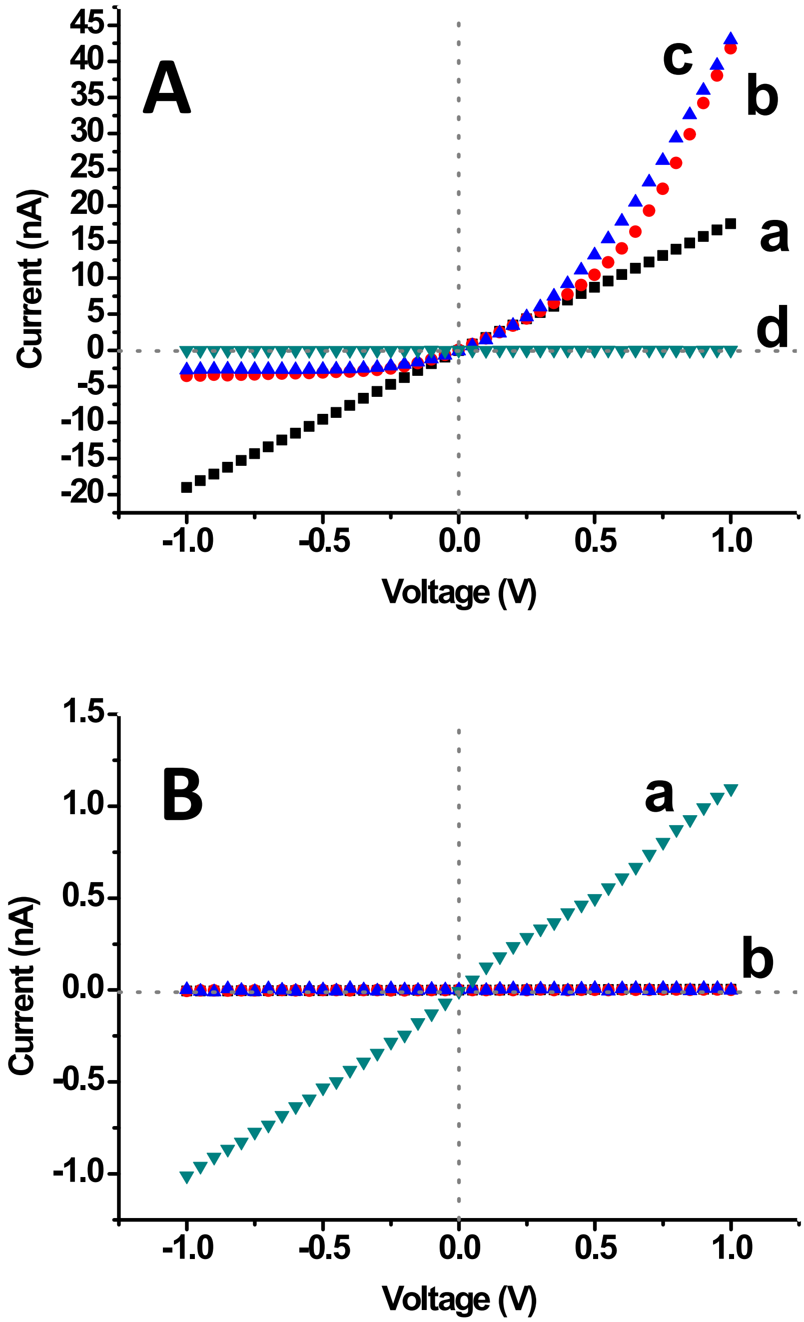
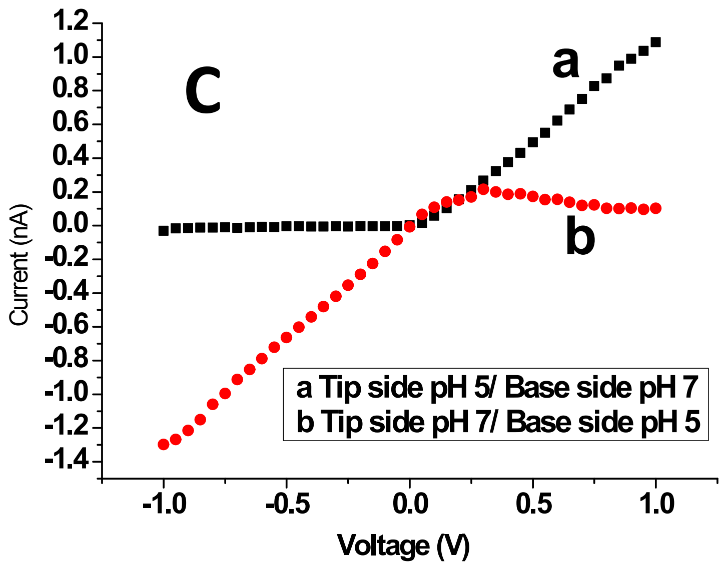


Figure S9


A
c
b
a
d
Current (nA)
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-1.0
-0.5
0.0
0.5
1.0
Voltage (V)
B
a
b
Current (nA)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.0
-0.5
0.0
0.5
1.0
Voltage (V)



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