

## Electronic Supporting Information

### In-Situ Synthesis of MOFs/PAA Hybrid with Ultrahigh Ionic Current Rectification

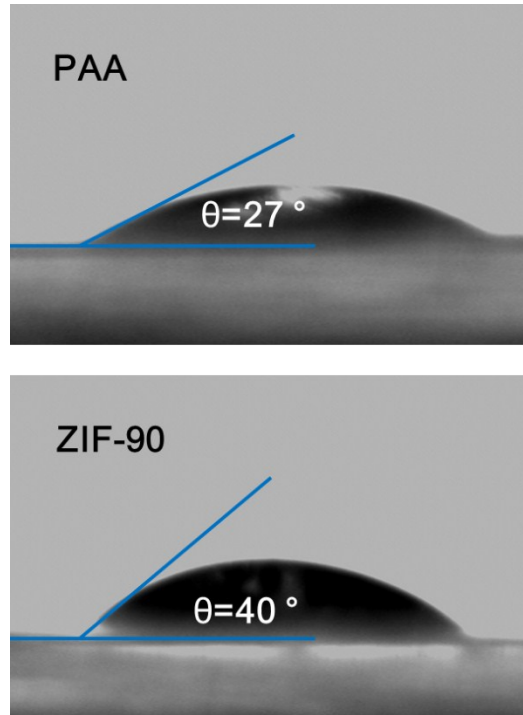
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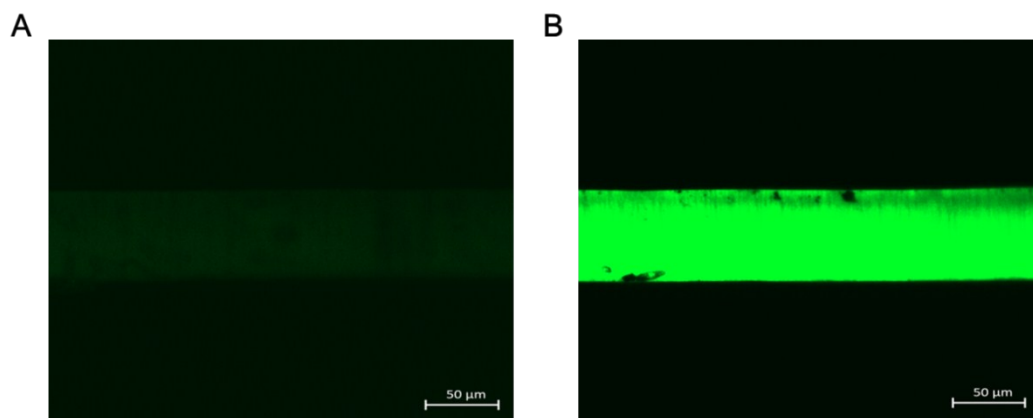
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100871, China

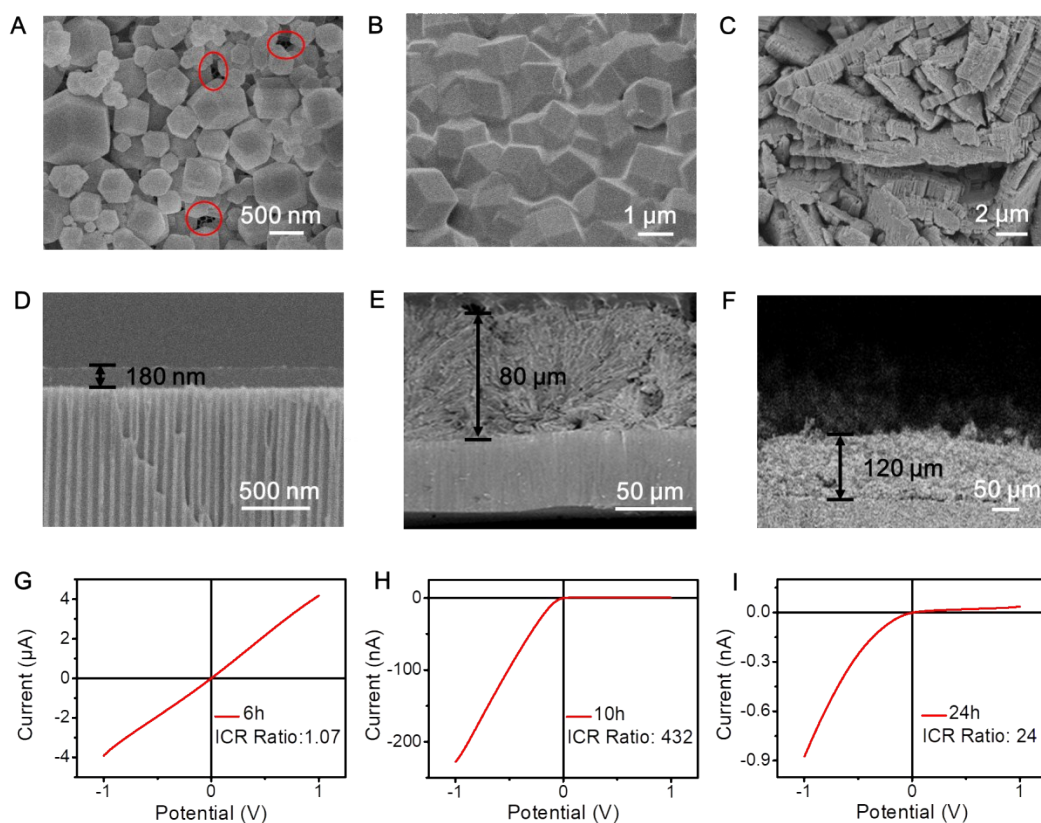
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Technology, Cambridge, MA 02139, USA



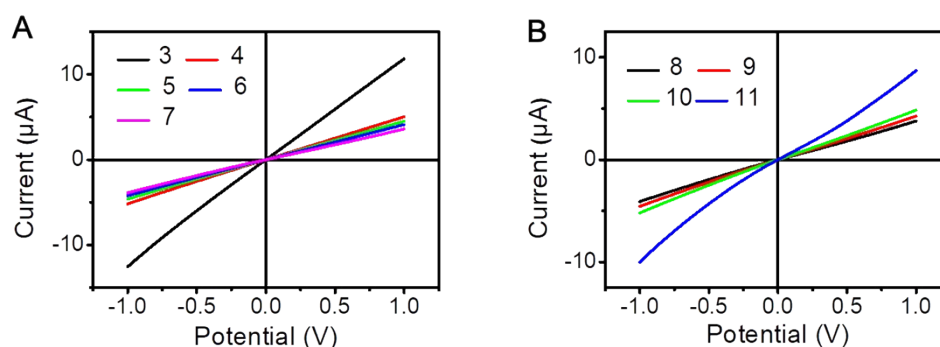
**Fig. S1** Surface contact angle measurements on MOFs/PAA hybrid. The upper is on the PAA side, and the bottom is on the ZIF-90 side.



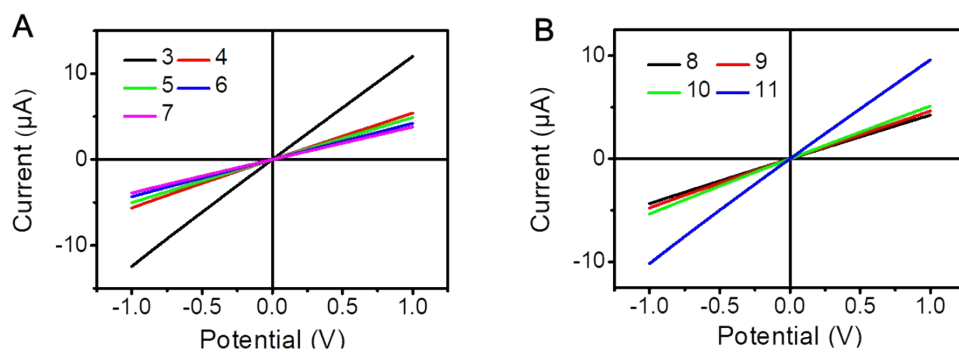
**Fig. S2** The LSCM cross-section of (A) pure PAA and (B) APTES-modified PAA.



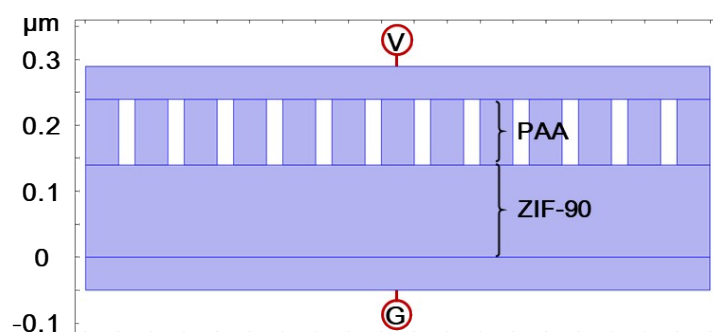
**Fig. S3** (A-C) SEM morphologies of the top surface with different reaction time, 6 h (A), 10 h (B), 24 h (C). (D-F) SEM morphologies of the cross section with different reaction time, 6 h (D), 10 h (E), 24 h (F). (G-I) *I*-*V* curves of the hybrid obtained at reaction time of 6 h (G), 10 h (H), 24 h (I), respectively, in 1 mM KCl at pH 11. 10 h was chosen due to the excellent ICR property of the fabricated hybrid.



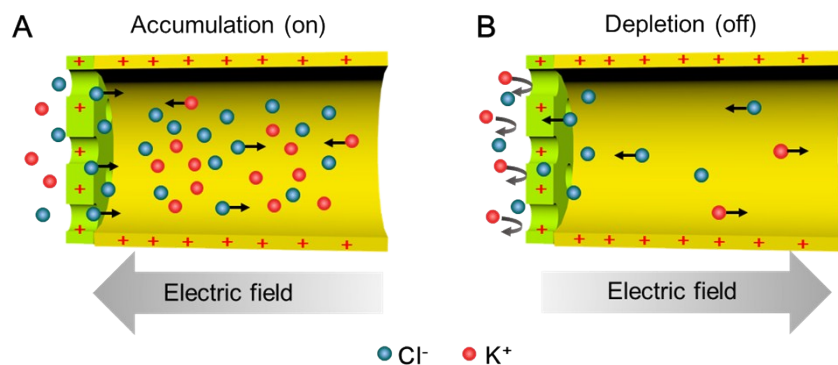
**Fig. S4** *I*-*V* curves of pure PAA membrane in 1 mM KCl solution at different pH values.



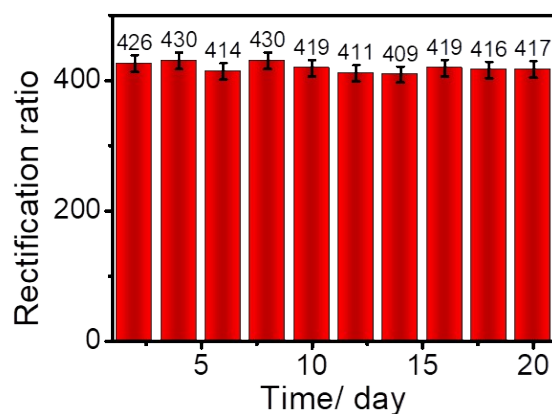
**Fig. S5**  $I$ - $V$  curves of APTES modified PAA membrane in 1 mM KCl solution at different pH values.



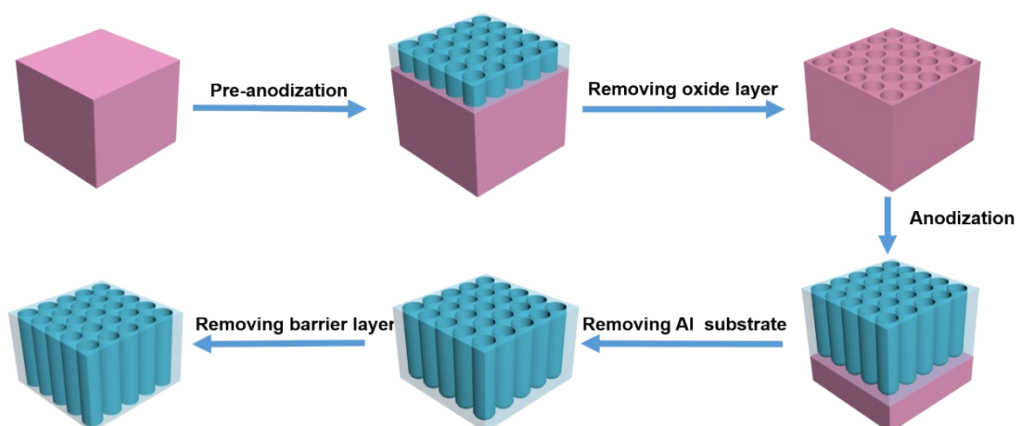
**Fig. S6** Simulation model. Thirteen nanochannels with length of 0.1  $\mu\text{m}$  and diameter of 50 nm are used to represent the nanochannels in PAA layer, while the ZIF-90 layer is modeled as an area of 0.95  $\mu\text{m}$  in width and 0.14  $\mu\text{m}$  in height.



**Fig. S7** Illustration of the ICR mechanism under acidic environment in 1 mM KCl (A: Accumulation (on), which comes from efficient ion concentration enrichment in the hybrid; B: Depletion (off), which results from remarkable ion concentration decrease in the hybrid).



**Fig. S8** The ion rectification ratios for nanochannel-ionchannel hybrid membrane in 1mM KCl at pH of 11 within 20 days.



**Fig. S9** Preparation of PAA membrane by two-step anodization method.