

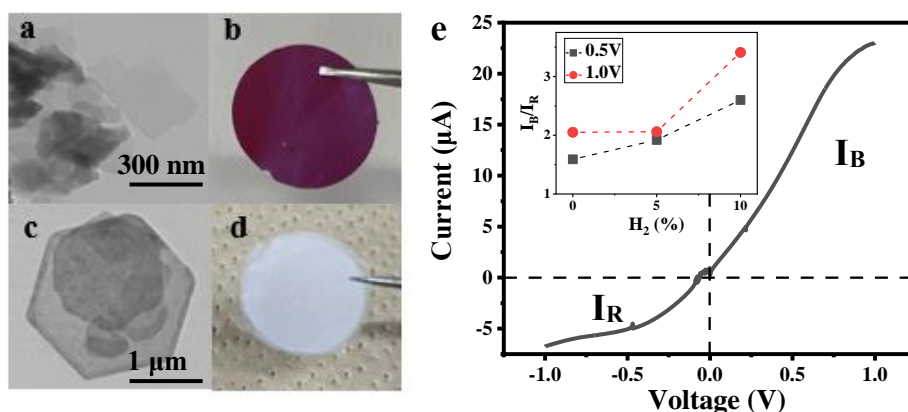
## Proton Rectification of Heterogeneous Membrane Base on Proton Conducting Metal-organic Framework and Hydroxy Conducting Layered Double Hydroxide

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Unidirectional proton transportation is a crucial phenomenon for the electrolytes in proton-exchange membrane fuel cells. However, implementing the asymmetric proton migration is not easy because a symmetry-breaking factor must be introduced into the proton pathway. In this study, we designed a heterogeneous  $H^+OH^-$  junction composed of  $H^+$ -type and  $OH^-$ -type membranes.  $Cu_2(CuTCPP)$  ( $CuTCPP^{4-}$ : copper tetrakis(4-carboxyphenyl)porphyrin)<sup>1</sup> and  $Mg-Al-LDH(NO_3^-)$  ( $LDH$ : layered double hydroxide)<sup>2</sup> nanosheets were selected as proton and hydroxy ion conductors, respectively, because their nanosheets are easy to form the free-standing membranes.

Both nanosheets were obtained by a solvothermal method. TEM images show that  $Cu_2(CuTCPP)$  nanosheets have an irregular shape (Figure 1a), whereas  $Mg-Al-LDH(NO_3^-)$  nanosheets have good hexagonal plate morphology (Figure 1c). After the exfoliation procedure, the  $Cu_2(CuTCPP)$  (Figure 1b) and  $Mg-Al-LDH(NO_3^-)$  (Figure 1d) free-standing membranes were obtained separately by a vacuum filtration method. Then the two kinds of membranes were sandwiched by the Pd electrodes to conduct the rectification experiments in different environments. Our preliminary measurements revealed that the rectification ratio reached 3.43 under 90% RH and 10% hydrogen atmosphere (Figure 1e).



**Figure 1.** (a) TEM image of Cu-TCPP nanosheets and (b) the free-standing membrane. (c) TEM image of  $Mg-Al-LDH(NO_3^-)$  and (d) the free-standing membrane. (e) Rectification ratio at different  $H_2$  atmospheres.

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