*Supporting information*

**High-rate decoupled water electrolysis system integrated with α-MoO3 as a redox mediator with fast anhydrous proton kinetics**

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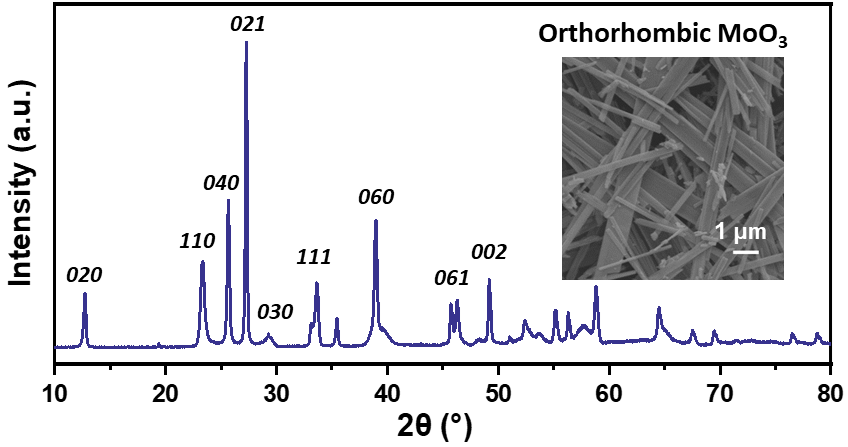
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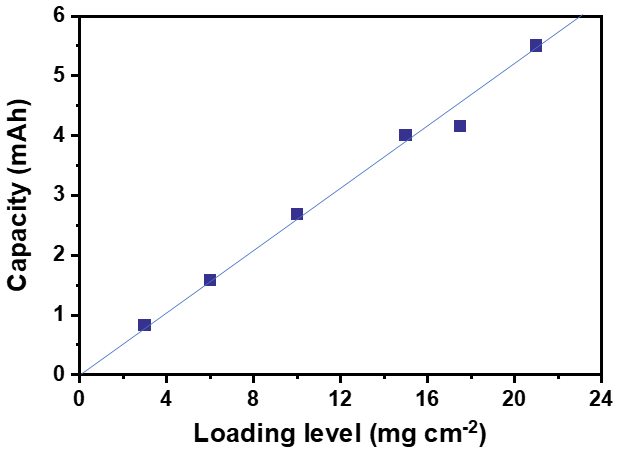
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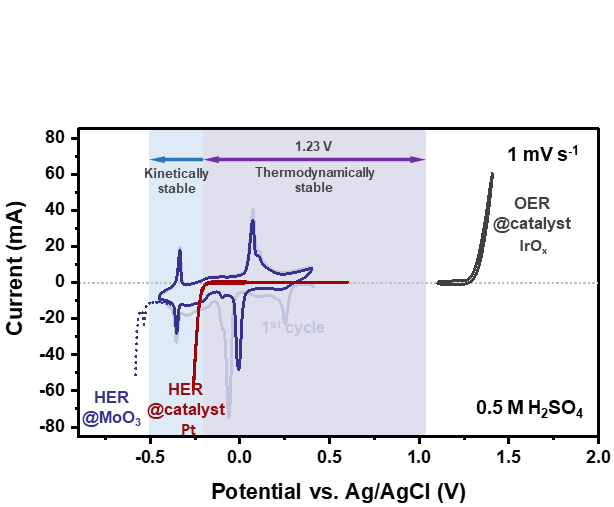
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**Figure S1.** X-ray diffraction pattern of the as synthesized MoO3. Inset: scanning electron microscopy image of as-synthesize MoO3**.**



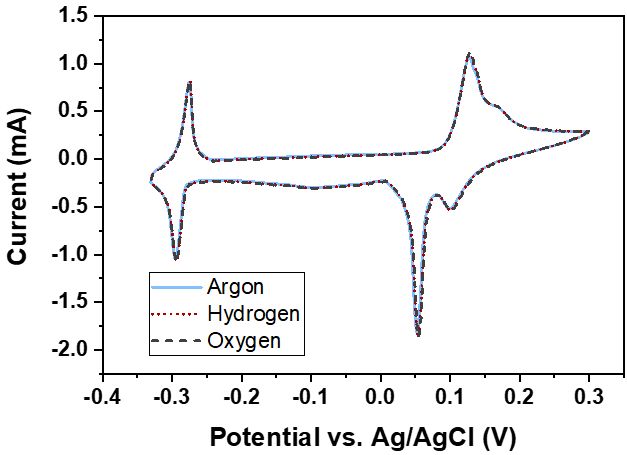
**Figure S2. loading level optimization of MoO3 in a 10 M H3PO4 aqueous electrolyte.** The capacity of the MoO3 electrode is almost linear to the loading level when the loading is < 20 mg cm-2, we chose a loading level of 10 mg cm-2 to match the maximum current output of the electrochemical workstation (1 A) to enable a maximum current density of 100 A g-1 with an electrode of 1 cm2.



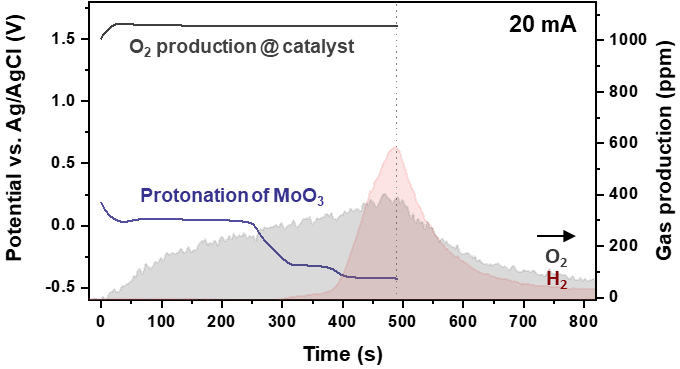
**Figure S3.** Electrochemical characterization of MoO3. Cyclic voltammograms (CVs) over MoO3 supported on the carbon cloth, Pt platinized Pt mesh, and IrOx/Ti felt were recorded at a scan rate of 1 mV s–1 and a temperature of 25 °C in 0.5 M H2SO4 aqueous solution.



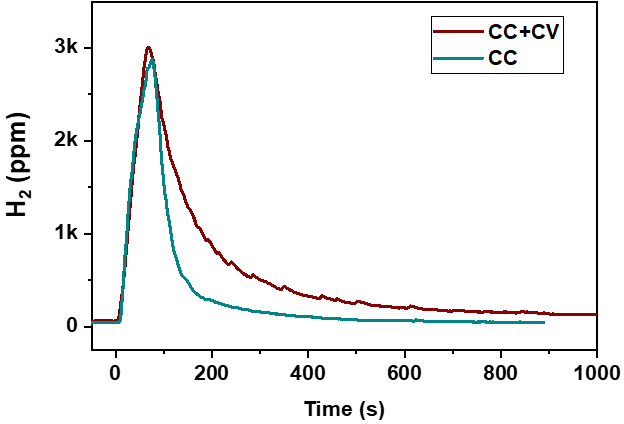
**Figure S4.** **Constant current- constant voltage (CC-CV) deprotonation of MoO3 in 10 M H3PO4 aqueous solution.** With a constant current (CC) deprotonation mode, only part of the proton inserted could be extracted. When a constant voltage (CV) at 0.5 V *vs.* Ag/AgCl of 3 h is applied after constant current deprotonation (CC-CV mode), almost all inserted proton can be extracted. This phenomena can be explained by the deceleration of proton kinetics at the end of CC deprotonation.



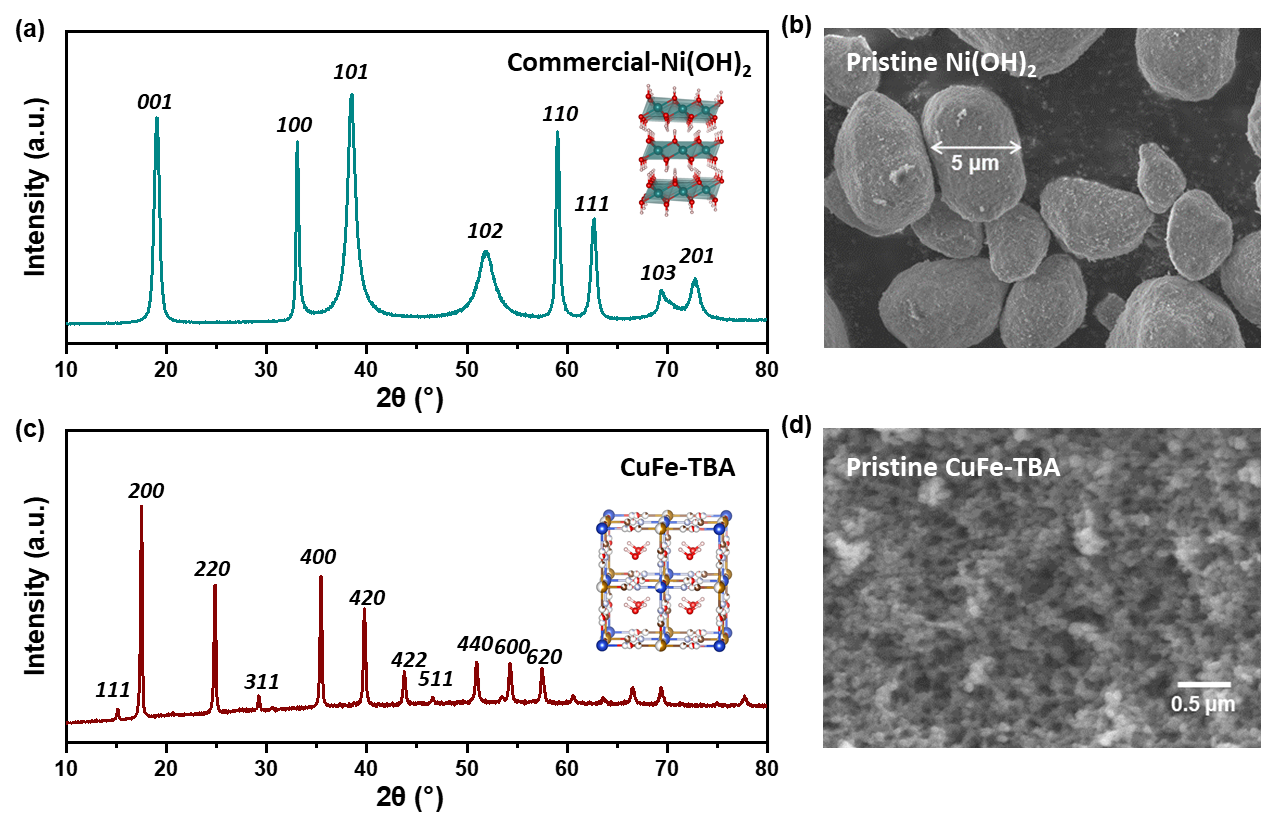
**Figure S5.** **Electrochemical characterization of MoO3 in different atmospheres.** Cyclic voltammograms (CVs) over MoO3 supported on the carbon cloth were recorded at a scan rate of 1 mV s–1 and a temperature of 25 °C in Ar, H2, and O2 saturated 0.5 M H2SO4 aqueous solution, respectively. The MoO3 electrode was cycled under each atmosphere for 5 cycles and the last cycle for each is shown.



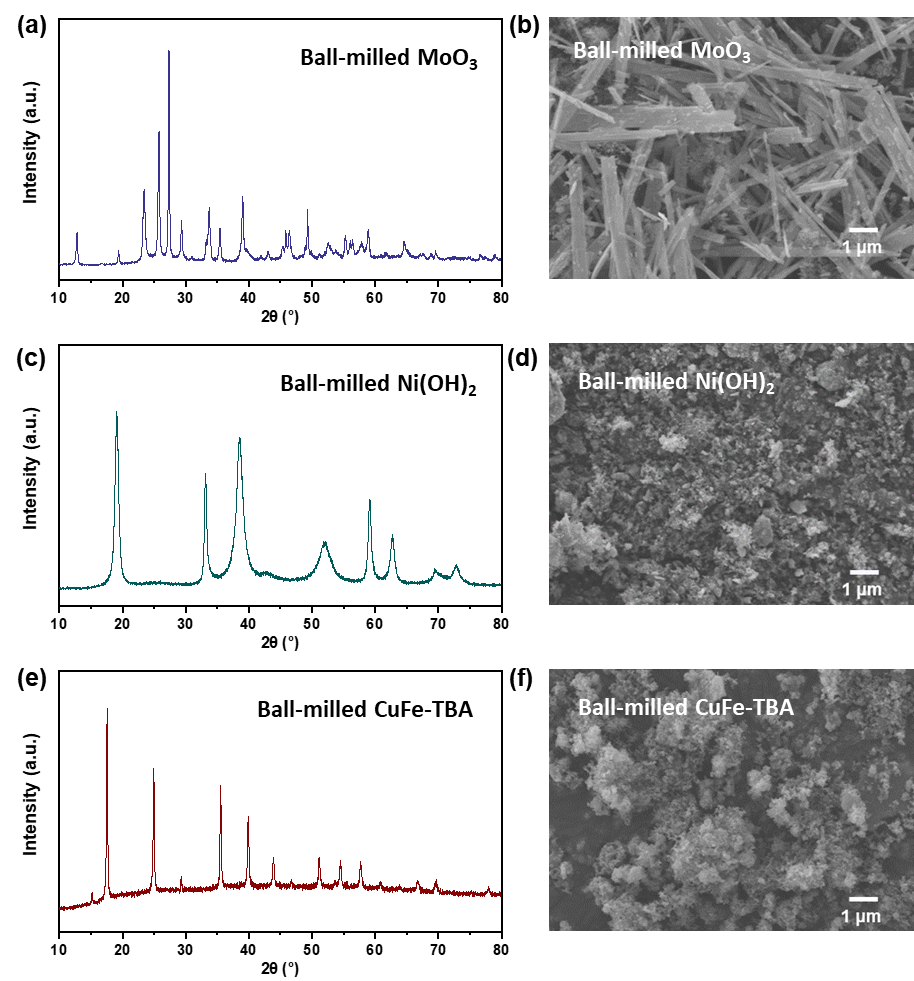
**Figure S6.** Parasitic hydrogen evolution reaction (HER) of MoO3 upon over protonation in 10 M H3PO4 aqueous solution**.** According to theoretical calculation, MoO3 can only accommodate 2.5 H+ to form H2.5MoO3. The over protonation would lead to structural decomposition and parasitic hydrogen evolution at low potential.



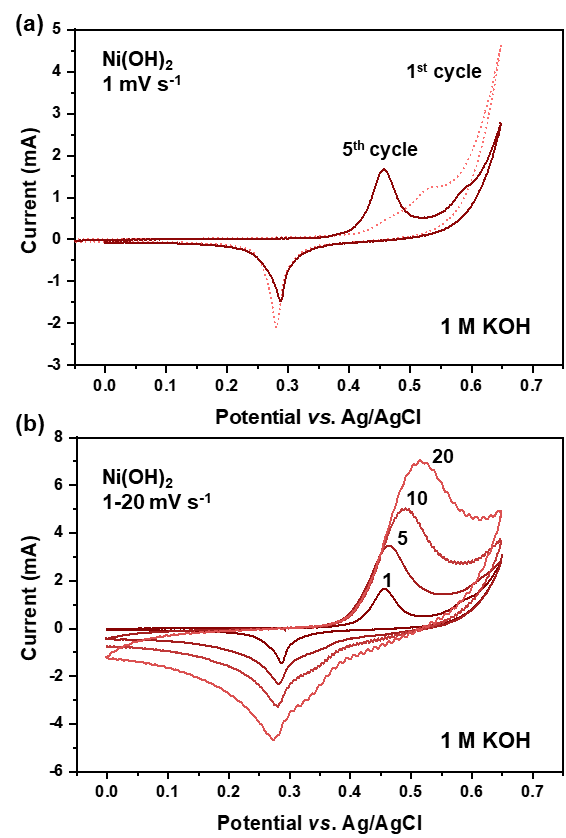
**Figure S7.** The additional hydrogen production using a constant current- constant voltage (CC-CV) deprotonation mode of MoO3 in 10 M H3PO4 aqueous solution. When a constant voltage (CV) at 0.5 V *vs.* Ag/AgCl is applied after constant current deprotonation (CC-CV mode), additional ~50% of hydrogen can be produced, indicting the “trapped” proton in MoO3 was releasaed.



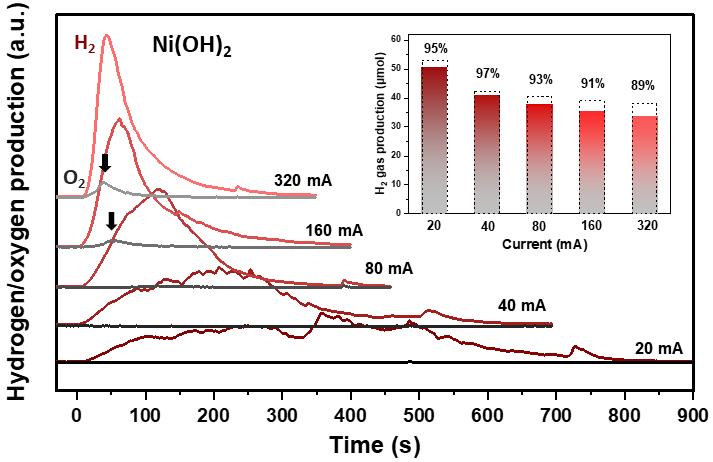
**Figure S8.** The X-ray diffraction p patterns and scanning electron microscopy images of commercial (a, c) Ni(OH)2 and (b, d) CuFe-TBA.

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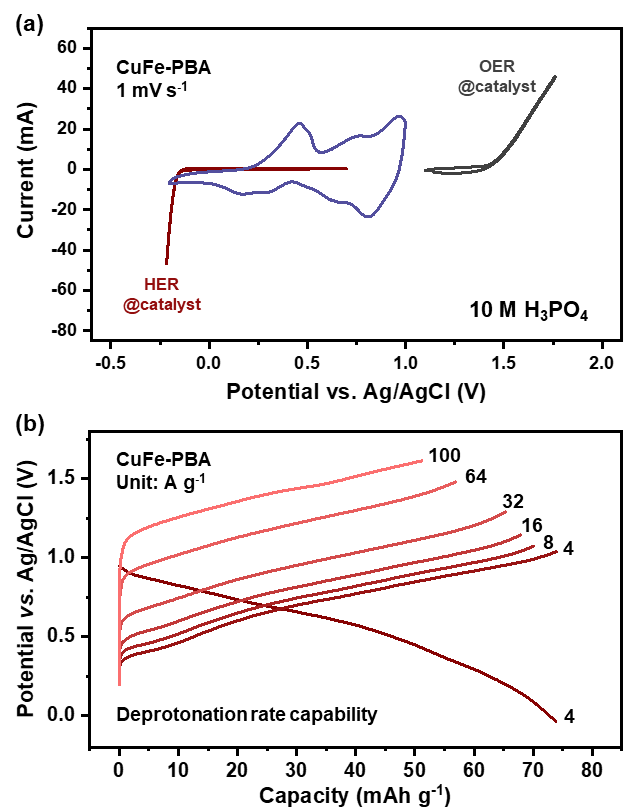
**Figure S9.** The X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images of ball-milled MoO3, Ni(OH)2 and CuFe-TBA. XRD patterns of samples ball-milled with 20 wt% carbon addictives for 30 min: (a) MoO3, (c) Ni(OH)2 and (e) CuFe-TBA and the corresponding SEM images (b) MoO3, (d) Ni(OH)2 and (f) CuFe-TBA.



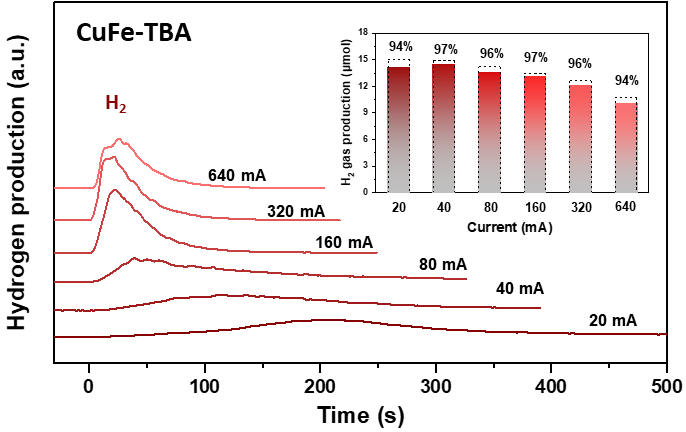
**Figure S10. Electrochemical characterization of Ni(OH)2.** Cyclic voltammograms (CVs) over Ni(OH)2 supported on the carbon cloth were recorded at various scan rates and a temperature of 25 °C in Ar saturated 1 M KOH aqueous solution, respectively: (a) the first and fifth CV cycles and (b) the CV cycles with different scan rates of Ni(OH)2 in a 1 M KOH aqueous electrolyte.



**Figure S11. Gas production using Ni(OH)2 as a redox mediator.** The qualification of generated H2 and O2 gas using mass spectroscopy. Inset: theoretical H2 gas amount (red solid bars) and detected gas amount (dash squares), the corresponding Faradic efficiency was marked at the top of each bar.Remarkable parasitic oxygen evolution can be observed at current rates of > 160 mA (marked with black arrows).



**Figure S12. Proton storage properties of CuFe-TBA as a redox mediator.** (a) Cyclic voltammograms (CVs) over CuFe-TBA supported on the carbon cloth, Pt platinized Pt mesh, and IrOx/Ti felt were recorded at a scan rate of 1 mV s–1 and a temperature of 25 °C in 10 M H3PO4 aqueous solution**.**. (b) The potential curves of CuFe-TBA upon deprotonation at rates from 4 A g-1 to 100 A g-1.



**Figure S13. Gas production using CuFe-TBA as a redox mediator.**  The qualification of generated H2 gas using mass spectroscopy. Inset: theoretical hydrogen gas amount (red solid bars) and detected gas amount (dash squares), the corresponding Faradic efficiency was marked at the top of each bar.