

Supporting Information for

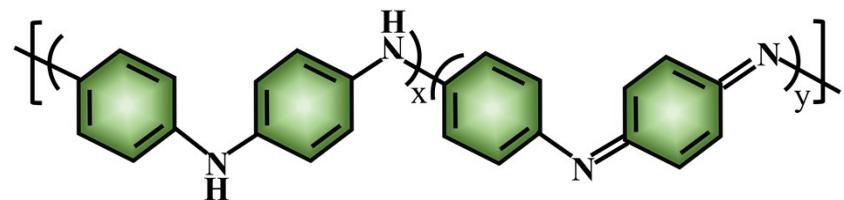
**Interface functionalization of mesoporous ruthenium film with polyaniline for enhanced hydrogen evolution electrocatalysis at all-pH value**

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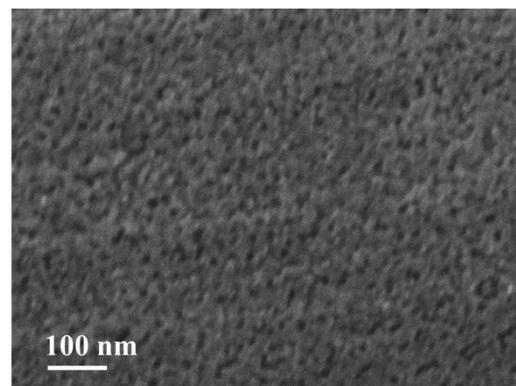
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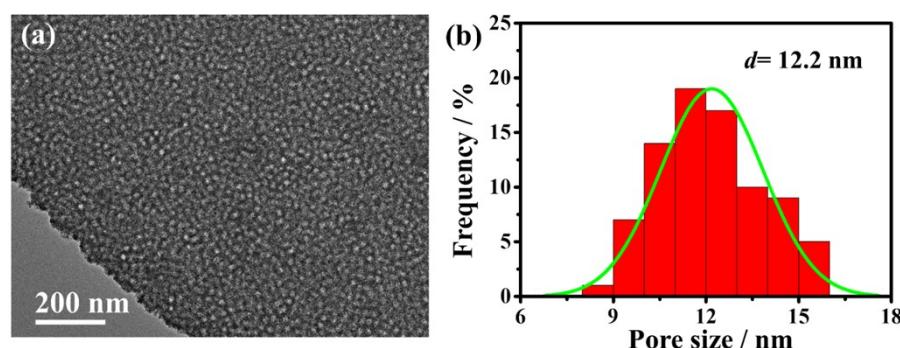
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**Scheme. S1** Molecular structure of PANI.



**Fig. S1** SEM image of the mRu film.



**Fig. S2** (a) TEM image and (b) corresponding pore size distribution of the mRu@PANI/CP. The inserted values indicate the average values.

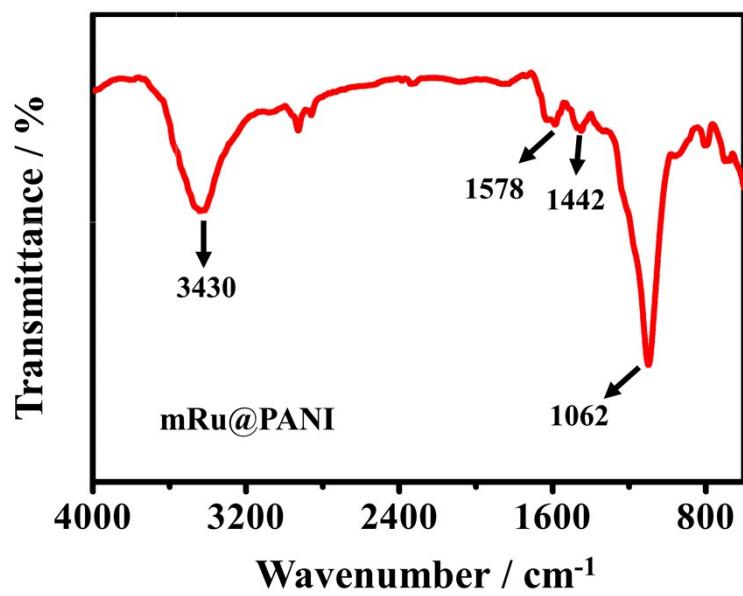


Fig. S3 FTIR spectra of mRu@PANI.

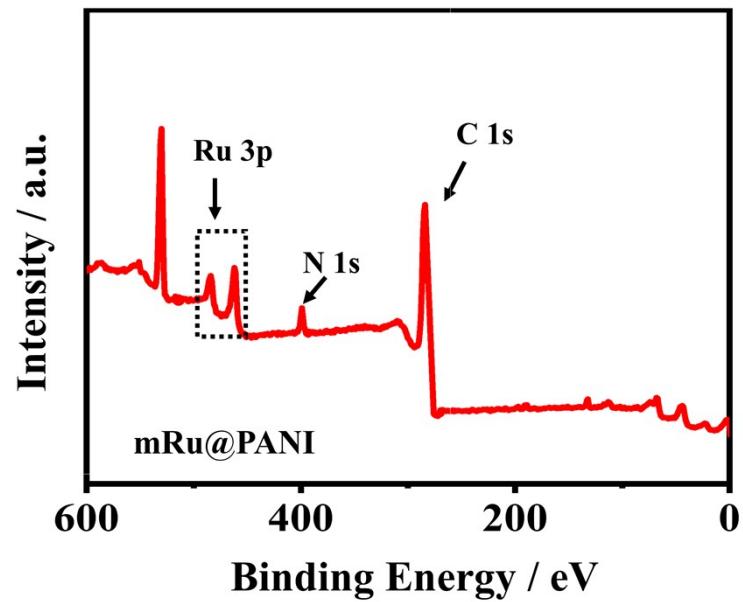
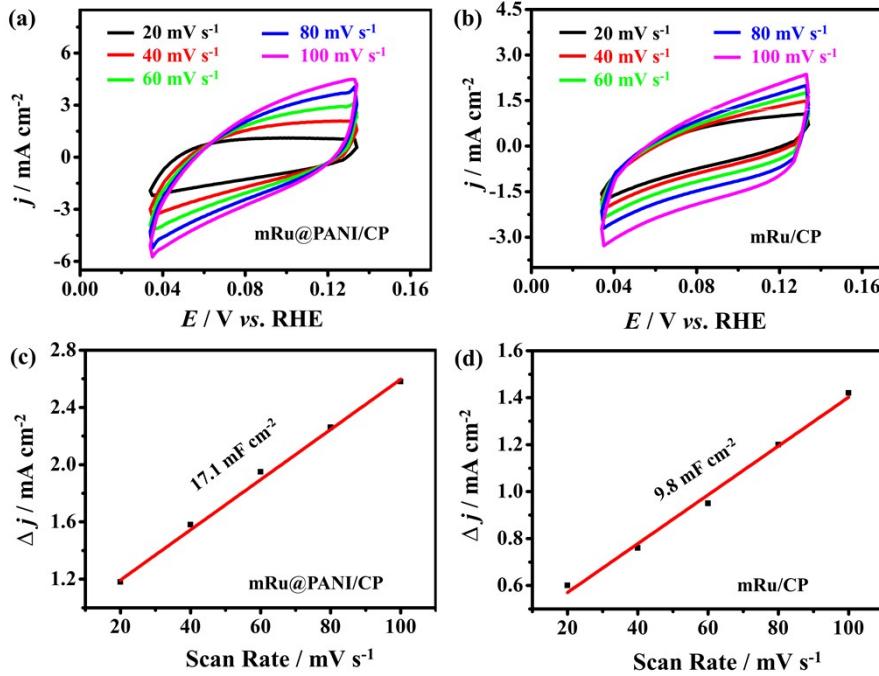
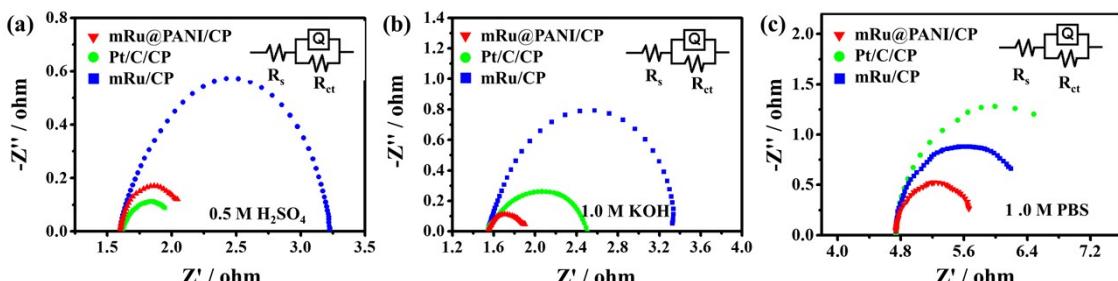


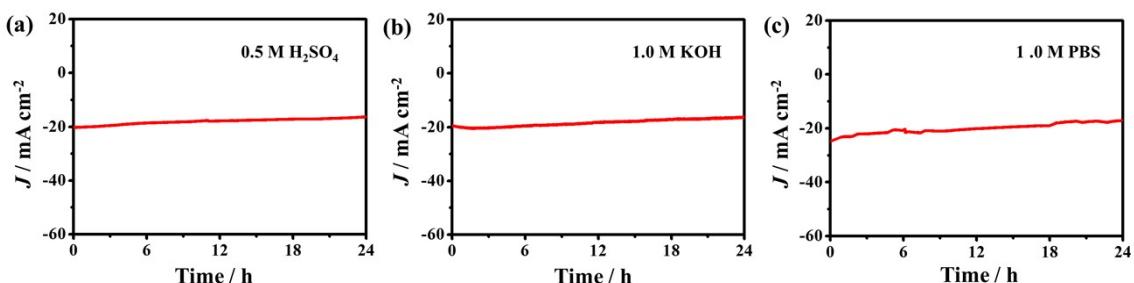
Fig. S4 XPS survey spectrum of mRu@PANI.



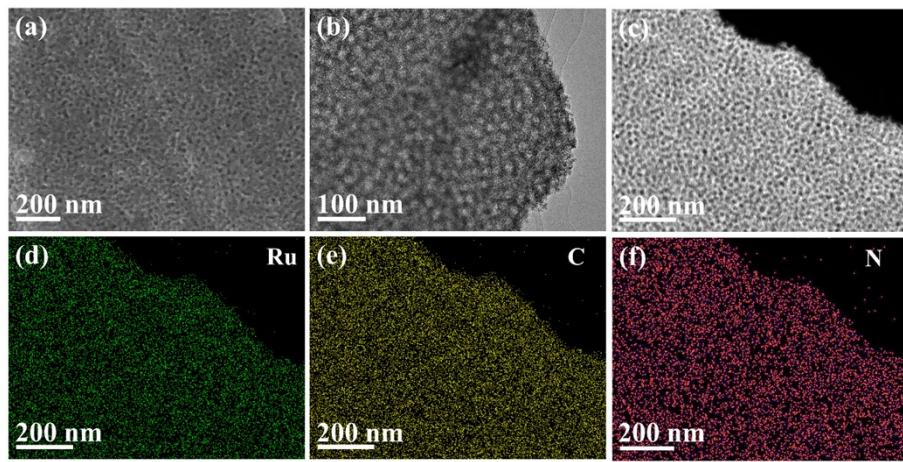
**Fig. S5** Cyclic voltammogram (CV) curves of (a) mRu@PANI/CP and (b) mRu with different scan rates in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The corresponding capacitive current densities of (c) mRu@PANI/CP and (d) mRu/CP.



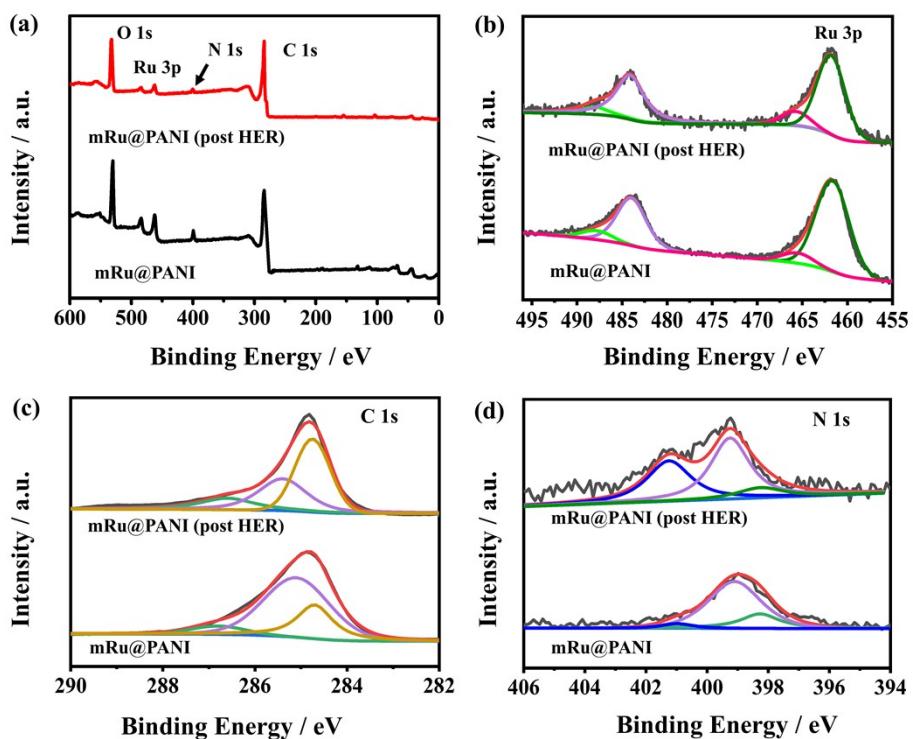
**Fig. S6** EIS spectra of various catalysts in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub>, (b) 1.0 M KOH and (c) 1.0 M PBS. The inserts show corresponding equivalent circuits.



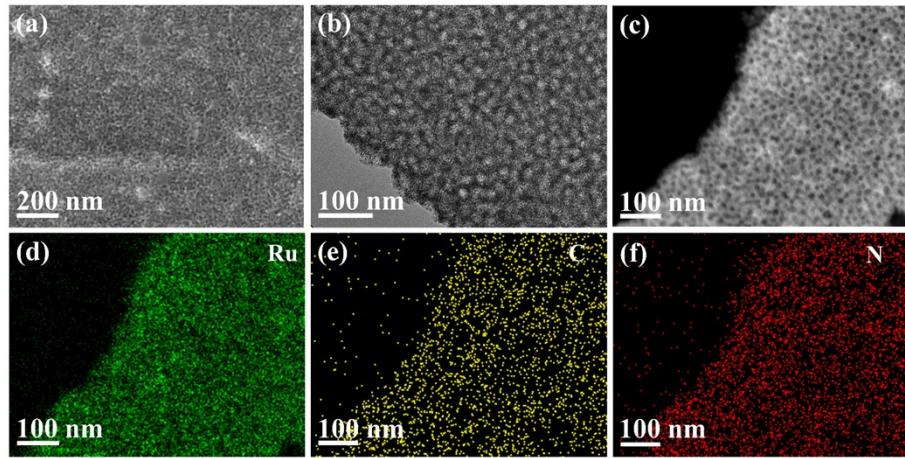
**Fig. S7** Chronoamperometry (i-t) curves of mRu@PANI/CP in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub>, (b) 1.0 M KOH and (c) 1.0 M PBS.



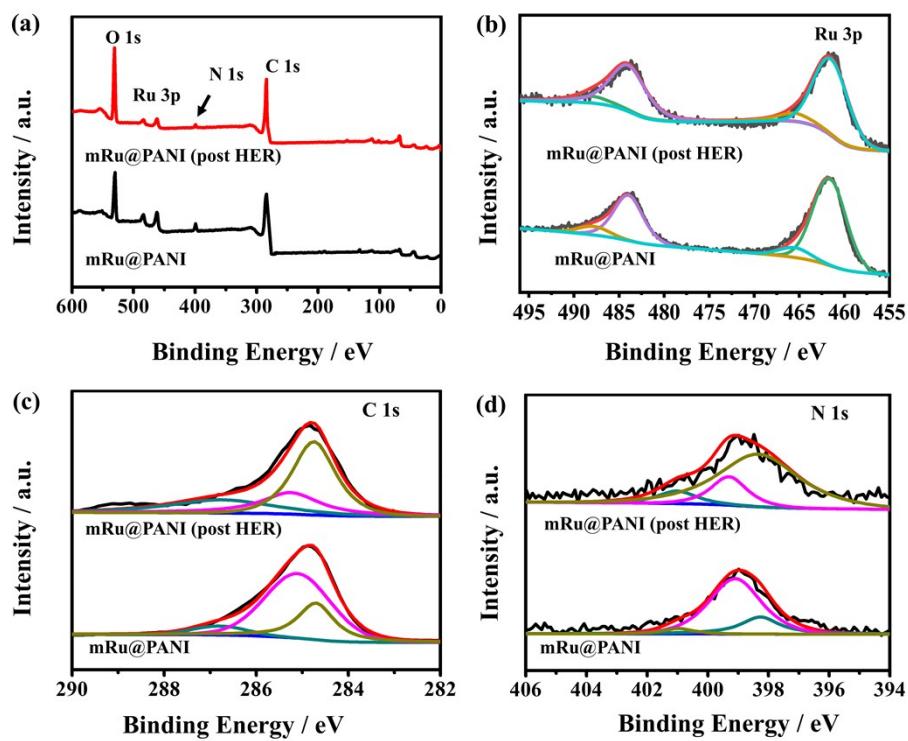
**Fig. S8** The (a) SEM, (b) TEM, (c) HAAD-STEM and (d) corresponding EDS mapping of mRu@PANI/CP after stability test in 0.5 M  $\text{H}_2\text{SO}_4$ .



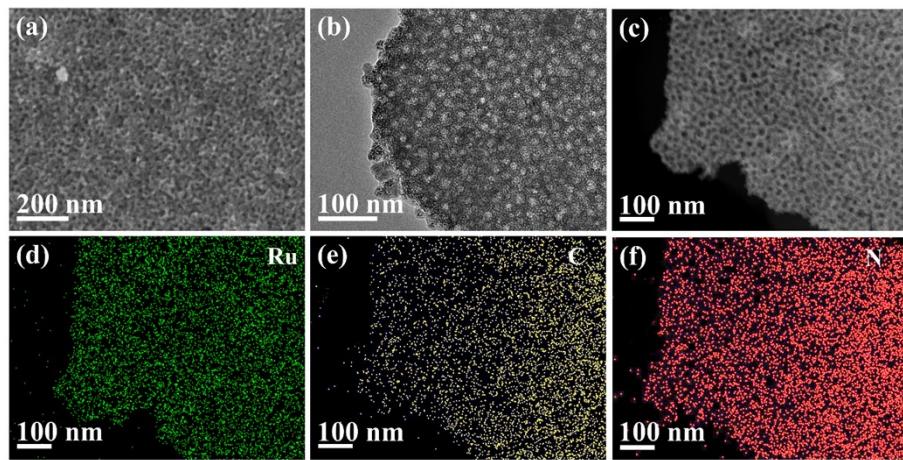
**Fig. S9** (a) XPS survey spectra, (b) Ru 3P, (c) C 1s, and (d) N 1s spectra of mRu@PANI before and after stability test in 0.5 M  $\text{H}_2\text{SO}_4$ .



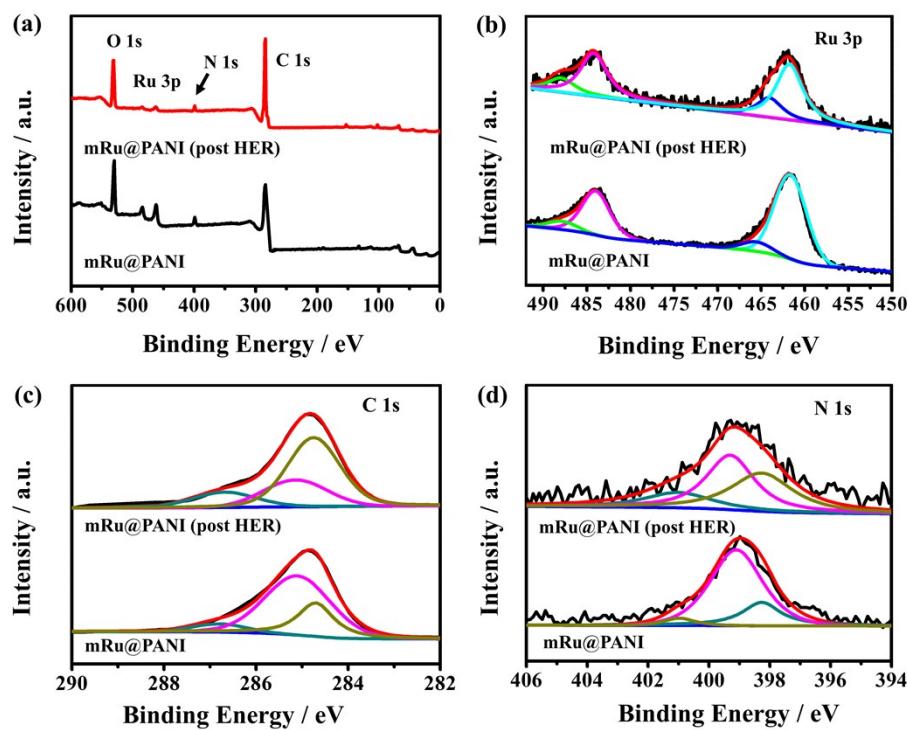
**Fig. S10** The (a) SEM, (b) TEM, (c) HAAD-STEM and (d) corresponding EDS mapping of mRu@PANI/CP after stability test in 1.0 M KOH.



**Fig. S11** (a) XPS survey spectra, (b) Ru 3P, (c) C 1s, and (d) N 1s spectra of mRu@PANI before and after stability test in 1.0 M KOH.



**Fig. S12** The (a) SEM, (b) TEM, (c) HAAD-STEM and (d) corresponding EDS mapping of mRu@PANI/CP after stability test in 1.0 M PBS.



**Fig. S13** (a) XPS survey spectra, (b) Ru 3P, (c) C 1s, and (d) N 1s spectra of mRu@PANI before and after stability test in 1.0 M PBS.

**Table S1.** HER performance comparison between the mRu@PANI/CP and some other reported Ru-based electrocatalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Catalyst	Electrolytes	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Ref.
mRu@PANI/CP	0.5 M H <sub>2</sub> SO <sub>4</sub>	30	This work
Ru <sub>x</sub> Fe <sub>y</sub> P-NCS/CNF	0.5 M H <sub>2</sub> SO <sub>4</sub>	66	1
RuNi NSs@PANI	0.5 M H <sub>2</sub> SO <sub>4</sub>	42	2
Ru <sub>x</sub> Se@MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	120	3
Rh <sub>2</sub> P	0.5 M H <sub>2</sub> SO <sub>4</sub>	55	4
Ru-MC	0.5 M H <sub>2</sub> SO <sub>4</sub>	40	5
Ru@N/S/TiO <sub>2</sub> /rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	60	6
Ni-Ru-P	0.5 M H <sub>2</sub> SO <sub>4</sub>	35	7
RuC	0.5 M H <sub>2</sub> SO <sub>4</sub>	35	8

**Table S2.** HER performance comparison between the mRu@PANI/CP and some other reported electrocatalysts in 1.0 M KOH.

Catalyst	Electrolytes	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Ref.
mRh@PANI/CP	1.0 M KOH	27	This work
Ru-MoS <sub>2</sub> /CC	1.0 M KOH	41	9
Ru–MoO <sub>2</sub>	1.0 M KOH	29	10
Ru@CN-0.16	1.0 M KOH	32	11
Ru/Cu <sub>2+1</sub> O NT/CuF	1.0 M KOH	44	12
Ru–Ru <sub>2</sub> P/PC	1.0 M KOH	43.4	13
RuCu NWs	1.0 M KOH	32	14
S-RuP@NPSC-900	1.0 M KOH	92	15
CuRu	1.0 M KOH	85	16

**Table S3.** HER performance comparison between the mRu@PANI/CP and some other reported electrocatalysts in 1.0 M PBS.

Catalyst	Electrolytes	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Ref.
mRh@PANI/CP	1.0 M PBS	24	This work
Ru@CN-0.16	1.0 M PBS	100	11
RuCu	0.1 M PBS	73	14
CuRu	1.0 M PBS	91	16
Ni-Ru	1.0 M PBS	80	17
Ni <sub>2</sub> P-Ru <sub>2</sub> P/CCG	1.0 M PBS	113	18
Ru-rGo	1.0 M PBS	72	19
RuSA-N-Ti <sub>3</sub> C <sub>2</sub> Tx	1.0 M PBS	81	20
Rh <sub>x</sub> Ru <sub>100-x</sub> @UiO-66-NH <sub>2</sub>	1.0 M PBS	114	21

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