

**Ultrafine CoRu alloy nanoparticles *in situ* embedded in Co₄N porous nanosheets
as high-efficient hydrogen evolution electrocatalysts**

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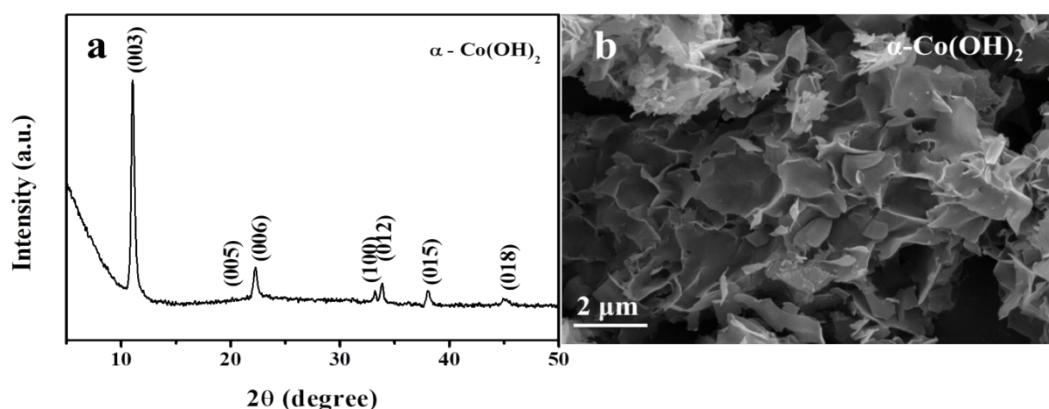


Fig. S1 XRD pattern and SEM image of α -Co(OH)₂.

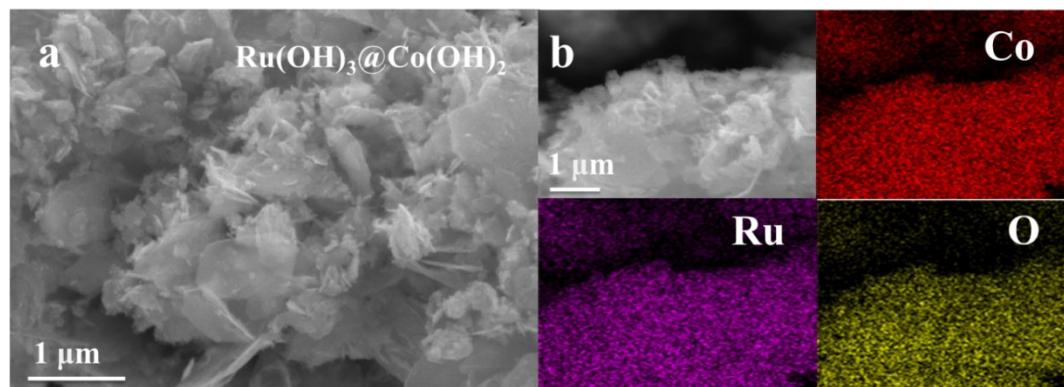


Fig. S2 (a) SEM image of Ru(OH)₃@Co(OH)₂ and corresponding (b) EDS mapping.

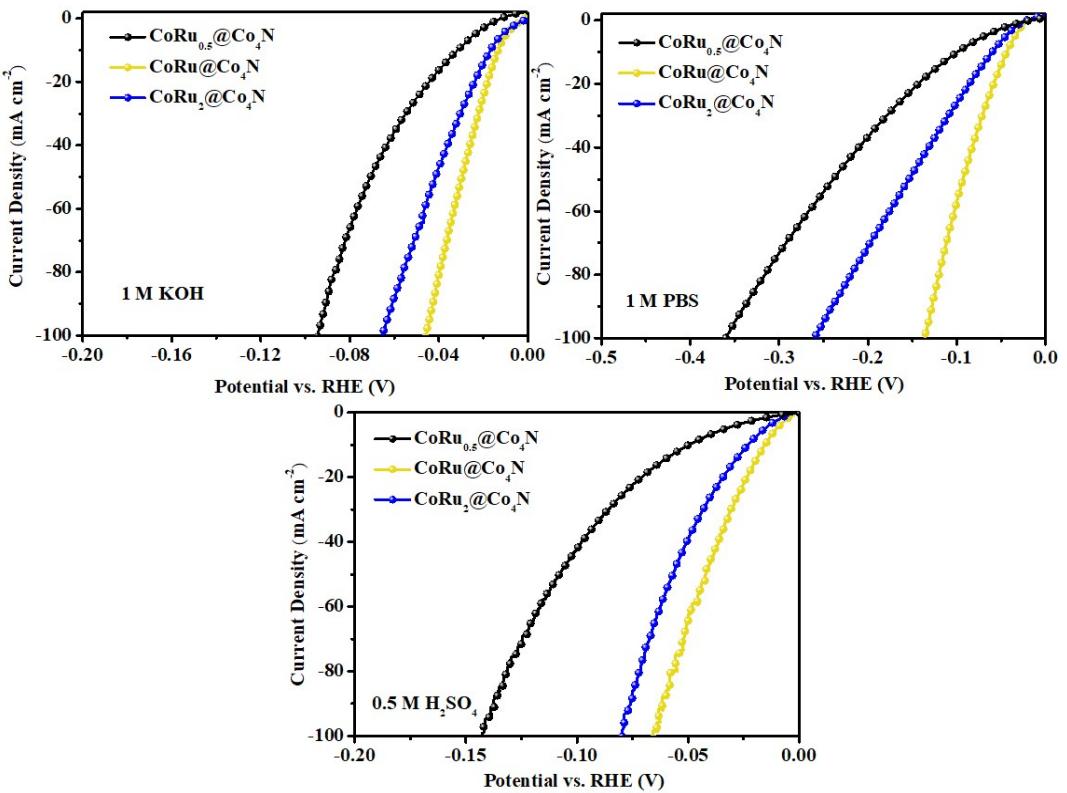


Fig. S3 LSV curves of $\text{CoRu}_{0.5}\text{@Co}_4\text{N}$, $\text{CoRu}\text{@Co}_4\text{N}$ and $\text{CoRu}_2\text{@Co}_4\text{N}$ tested in 1 M KOH, 1 M PBS and 0.5 M H_2SO_4 .

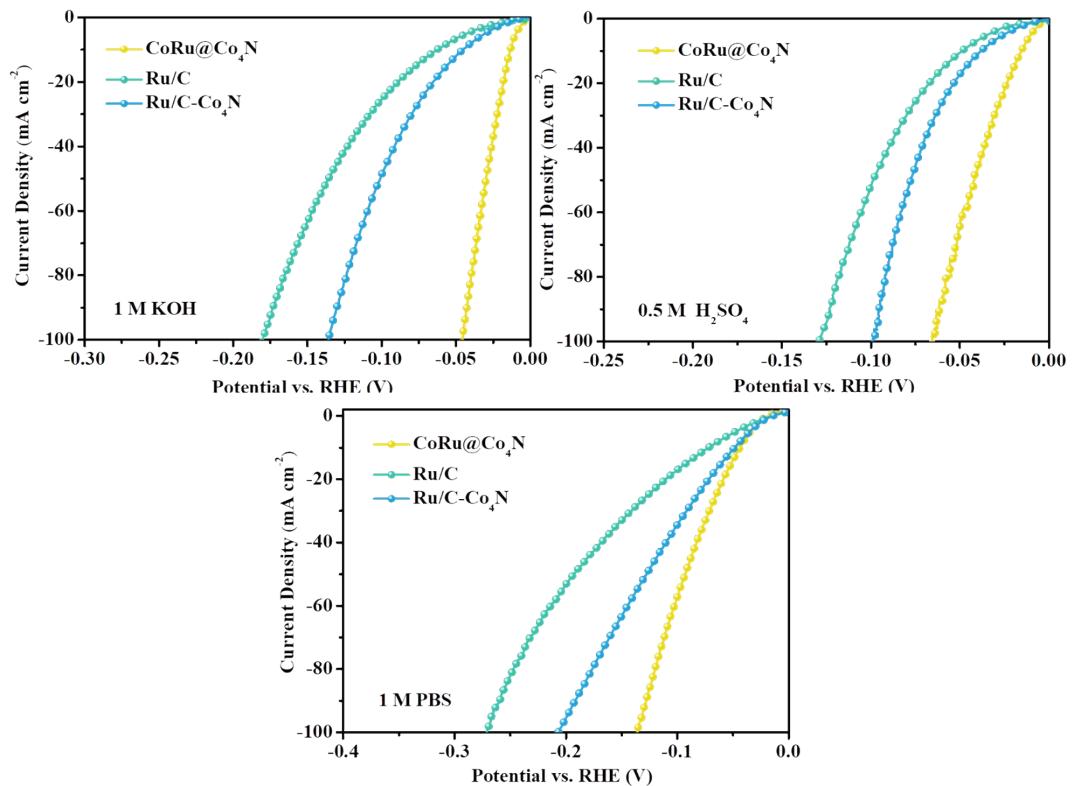


Fig. S4 LSV curves of $\text{CoRu}\text{@Co}_4\text{N}$, Ru/C and $\text{Ru/C-Co}_4\text{N}$ tested in 1 M KOH, 1 M PBS and 0.5 M H_2SO_4 .

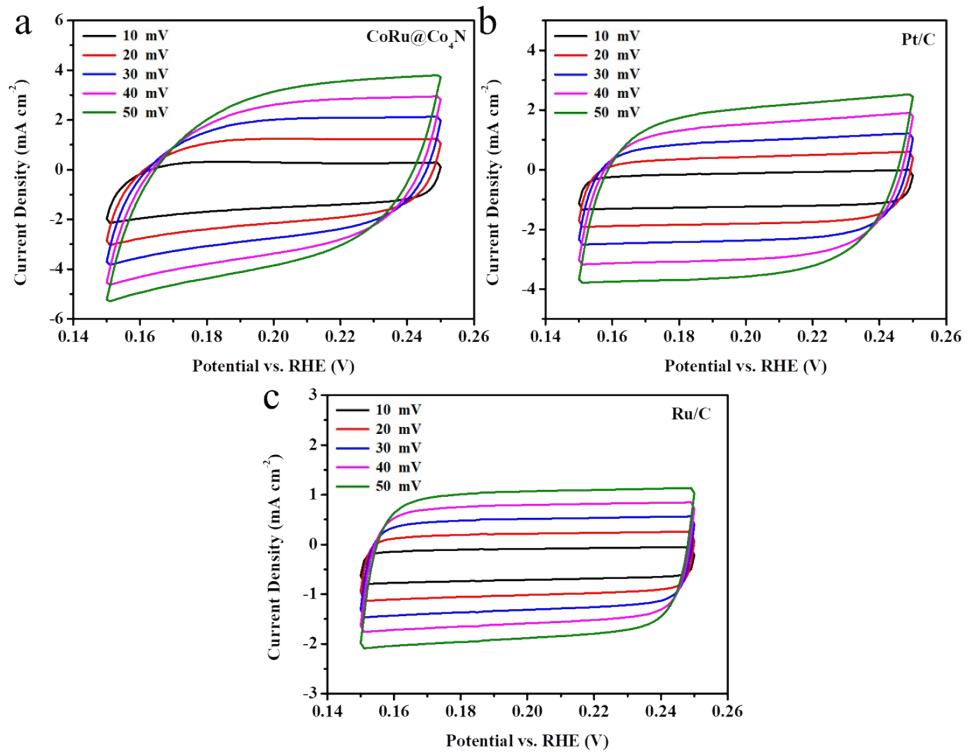


Fig. S5 CVs for HER in 1.0 M KOH.

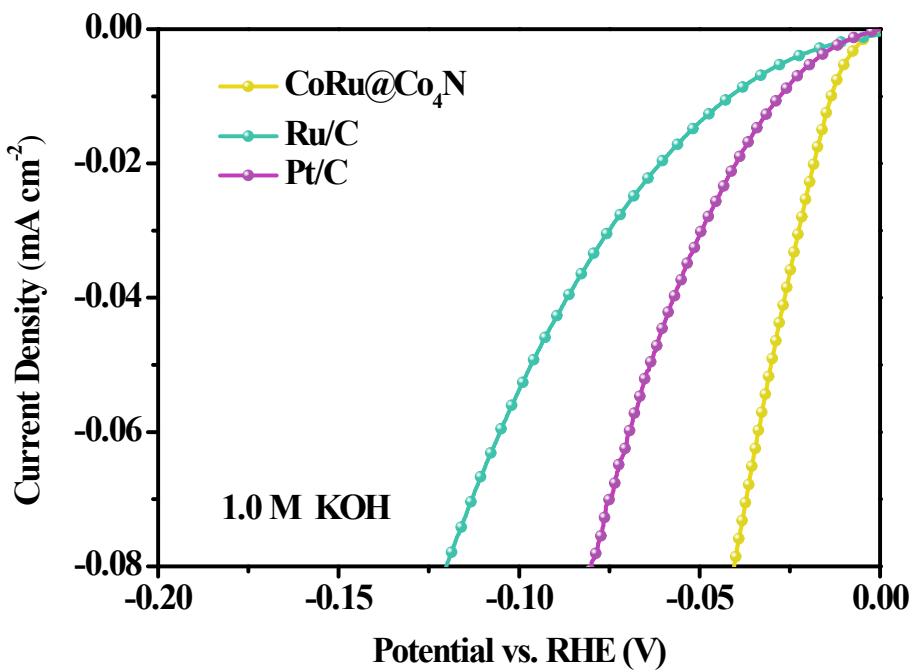


Fig. S6 ECSA-normalized LSV curves in 1.0 M KOH.

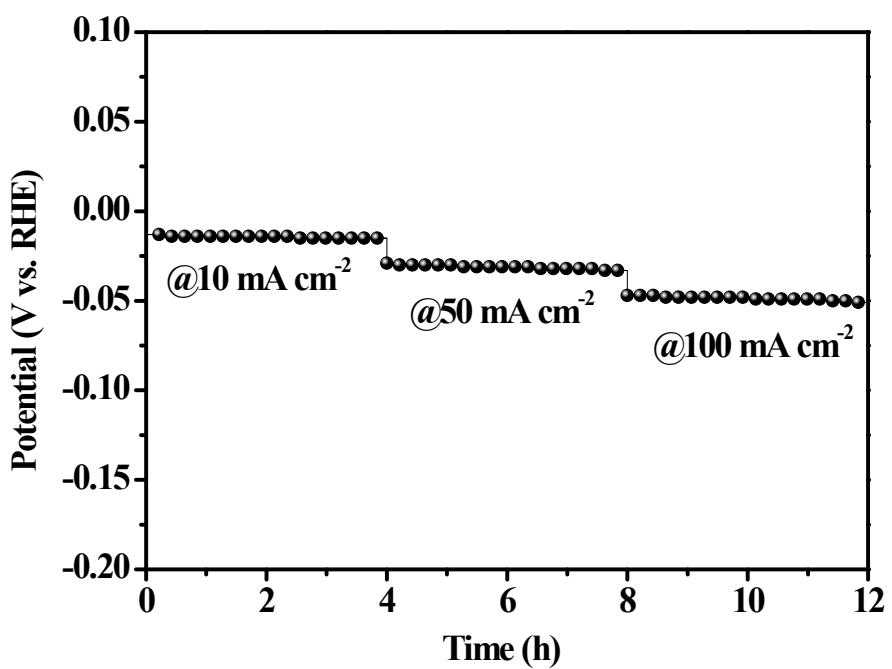


Fig. S7 Multi-current process of CoRu@Co₄N in 1.0 M KOH.

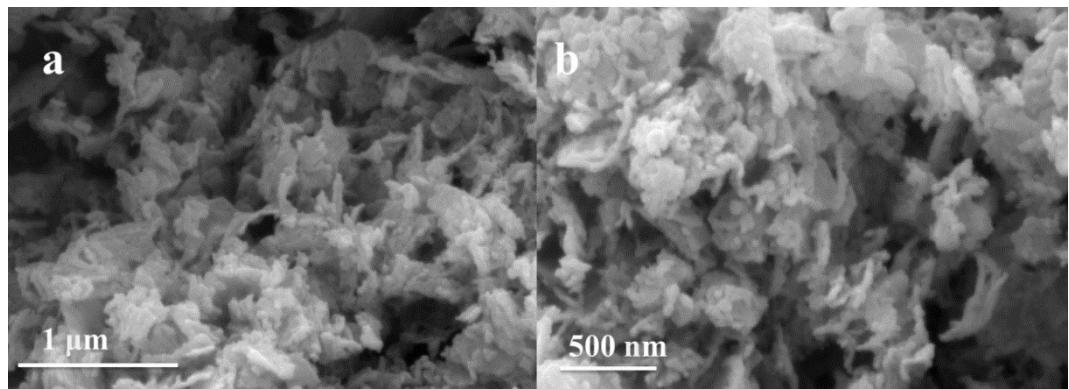


Fig. S8 SEM images of CoRu@Co₄N after stability test in 1.0 M KOH.

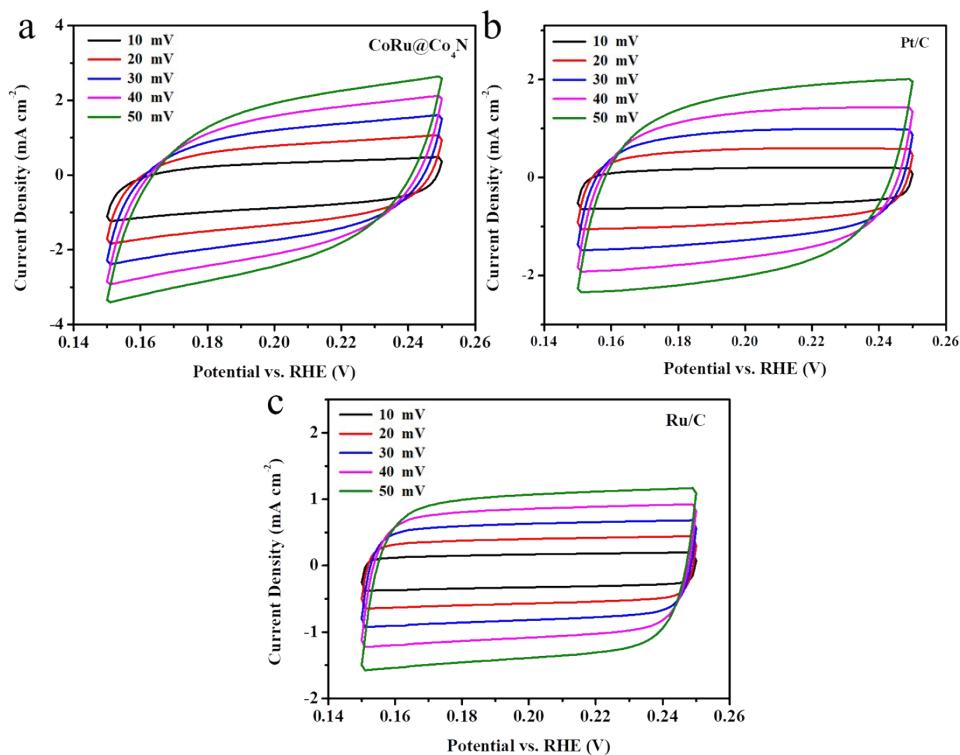


Fig. S9 CVs for HER in 1 M PBS.

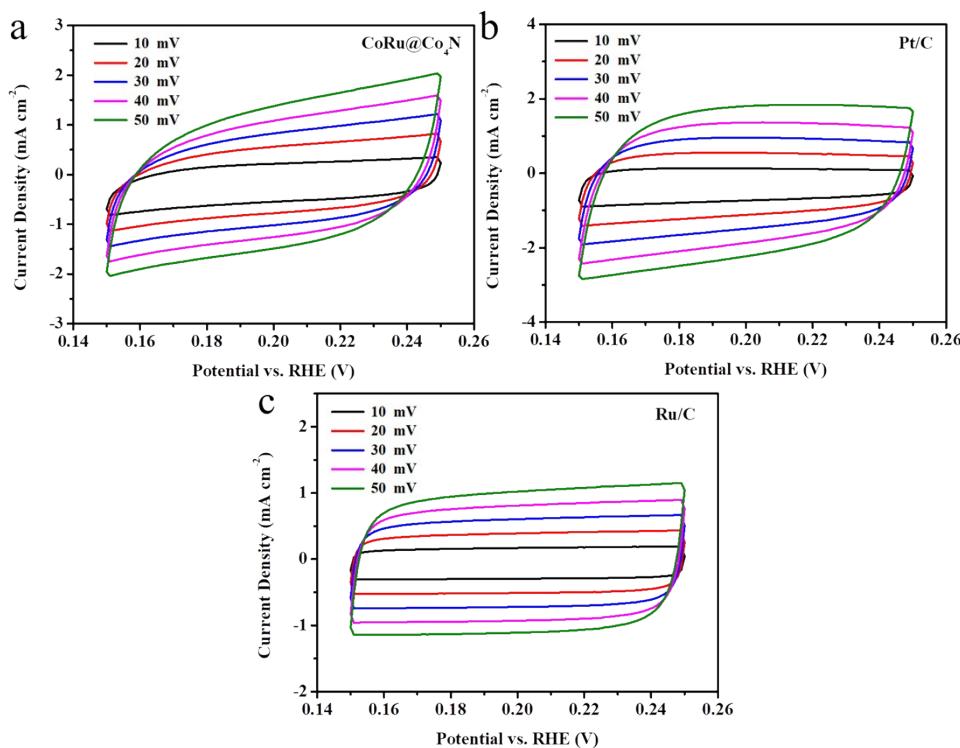


Fig. S10 CVs for HER in 0.5 M H_2SO_4 .

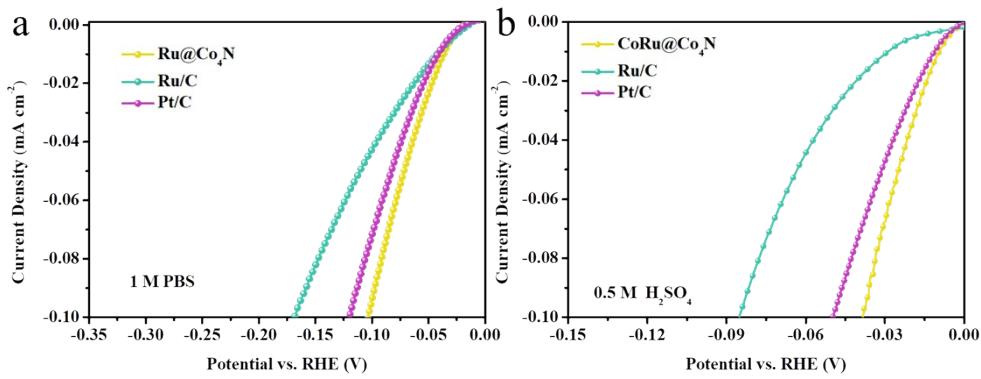


Fig. S11 ECSA-normalized LSV curves in 1M PBS and 0.5 M H_2SO_4 .

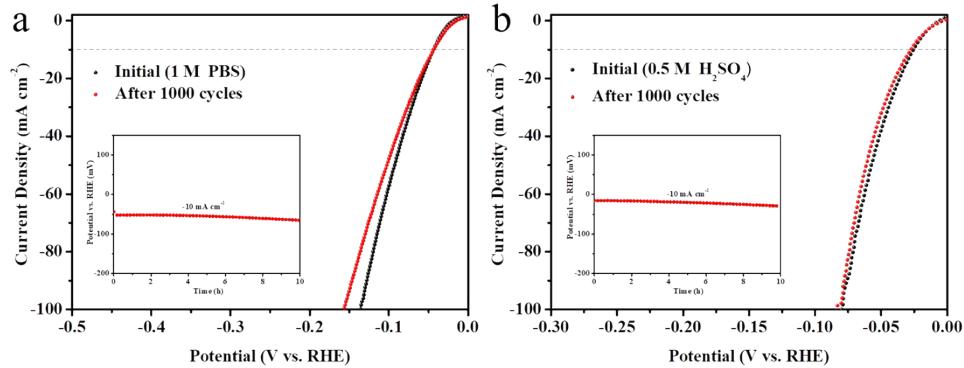


Fig. S12 ADT cyclic stability and time-dependent current density curve of CoRu@Co₄N in 1 M PBS and 0.5 M H_2SO_4 .

Table. S1 A performance comparison of CoRu@Co₄N to reported HER electrocatalysts recently.

| Catalyst | Electrolyte | η_{10} (mV) | Reference |
|-------------------------------------|--------------------------------------|------------------|--|
| CoRu@Co ₄ N | 1 M KOH | 13 | This work |
| | 0.5 M H ₂ SO ₄ | 15 | |
| | 1M PBS | 44 | |
| Ru@MWCNT | 0.5 M H ₂ SO ₄ | 13 | Nat. Commun., 2020, 11, 1278. |
| | 1 M KOH | 17 | |
| RuP ₂ @NPC | 1 M KOH | 52 | Angew. Chem. Int. Ed., 2017, 56, 11559-11564. |
| | 0.5 M H ₂ SO ₄ | 38 | |
| | 1M PBS | 57 | |
| Ru@C ₂ N | 1 M KOH | 17 | Nat. Nanotechnol., 2018, 12, 441-446. |
| | 0.5 M H ₂ SO ₄ | 13.5 | |
| Co ₁ /PCN | 0.5 M H ₂ SO ₄ | 151 | Nat. Catal., 2019, 2, 134-141. |
| | 1 M KOH | 89 | |
| L-Ag | 0.5 M H ₂ SO ₄ | 32 | Nat. Catal., 2019, 2, 1107-1114. |
| Ru-NC-700 | 0.5 M H ₂ SO ₄ | 29 | Nat. Commun., 2019, 10, 631. |
| | 1 M KOH | 12 | |
| Ru-MoO ₂ | 0.5 M H ₂ SO ₄ | 29 | J. Mater. Chem. A, 2017, 5, 5475-5485. |
| | 1 M KOH | 55 | |
| Pt-GT-1 | 0.5 M H ₂ SO ₄ | 18 | Nat. Energy, 2018, 3, 773-782. |
| Ni-FeP/C | 0.5 M H ₂ SO ₄ | 72 | Sci. Adv., 2019, 5, eaav6009. |
| | 1 M KOH | 95 | |
| Pt@PCM | 0.5 M H ₂ SO ₄ | 105 | Sci. Adv., 2018, 4, eaao6657. |
| | 1 M KOH | 139 | |
| Ru/GLC | 0.5 M H ₂ SO ₄ | 35 | ACS Appl. Mater. Interfaces, 2016, 8, 35132-35137. |
| Ru/C ₃ N ₄ /C | 0.5 M H ₂ SO ₄ | 70 | J. Am. Chem. Soc., 2016, 138, 16174-16181. |
| | 1 M KOH | 79 | |
| PtRu@RFCS | 0.5 M H ₂ SO ₄ | 20 | Energy Environ. Sci., 2018, 11, 1232-1239. |
| RuCoP | 0.5 M H ₂ SO ₄ | 11 | Energy Environ. Sci., 2018, 11, 1819-1827. |
| | 1 M KOH | 23 | |
| Ru@CN-0.16 | 0.5 M H ₂ SO ₄ | 126 | Energy Environ. Sci., 2018, 11, 800-806. |
| | 1 M KOH | 32 | |
| Ru-MoO ₂ | 0.5 M H ₂ SO ₄ | 29 | J. Mater. Chem. A, 2017, 5, 5475-5485. |
| | 1 M KOH | 55 | |
| L-RuP | 0.5 M H ₂ SO ₄ | 19 | Adv. Mater., 2018, 30, 1800047. |
| | 1 M KOH | 18 | |
| | 1 M PBS | 95 | |
| PtNi-O/C | 1 M KOH | 40 | J. Am. Chem. Soc., 2018, 140, 9046-9050. |
| Ni@Ni ₂ P-Ru | 0.5 M H ₂ SO ₄ | 51 | J. Am. Chem. Soc., 2018, 140, 2731-2734. |
| | 1 M KOH | 31 | |