# Enhancement of Acidic Hydrogen Evolution Reaction Efficiency through Cu/Ni-doped MFI-type Protozeolite Layered Nanoclusters

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#Xiyuan Tong and Junyang Wang contributes equal to Xiaodi Zhang for this work

## Table caption

**Table S1.** Comparison of main element distribution ratio in EDS and XPS.

Element	Cu	Ni	Na	Al	Si
Method					
EDS (before electroreduction)	0.74%	1.47%	0.1%	0.82%	5.15%
EDS (after electroreduction)	0.2%	0.96%	0.19%	0.24%	18.73%
XPS (before electroreduction)	1.27%	6.66%		3.66%	16.9%
XPS (after electroreduction)	0.35%	4.42%		2.13%	22.76%

Table S1. Comparison of main element distribution ratio in EDS and XPS.

Note: Atom Conc %.

#### **Figure caption**

Figure S1. The EDS images for the catalyst (A), Al (B), Na (C), C (D), Si (E), O (F).

**Figure S2.** The XPS spectra of Al (A), Si (B), C (C) and O (D) in product before electroreduction and the XPS spectra of Al (E), Si (F), C (G) and O (H) in product after electroreduction.

**Figure S3.** CV of GC (A), MFI-PZ/GC (B), Ni/MFI-PZ/GC (C), Cu/MFI-PZ/GC (D) and Cu/Ni/MFI-PZ/GC (E) measured in a non-Faradaic region at scan rates from 60 to  $160 \text{ mV s}^{-1}$  in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (F) The linear relationship between scan rates and charging currents of Cu/Ni/MFI-PZ/GC (a), Cu/MFI-PZ/GC (b), Ni/MFI-PZ/GC (c), MFI-PZ/GC (d) and GC (e).

**Figure S4.** LSV of Cu/MFI-PZ/GC (A) and Ni/MFI-PZ/GC (B) were measured before and after A i-t C electroreduction at -1 V in 0.5 M  $H_2SO_4$  for the required time; (C) The relationship between activity time and overpotential of Cu/Ni/MFI-PZ/GC (a), Cu/MFI-PZ/GC (b) and Ni/MFI-PZ/GC (c); LSV plots of Ni/MFI-PZ/GC (D), Cu/MFI-PZ/GC (E) before and after stability test.



Figure S1. The EDS images for the catalyst (A), Al (B), Na (C), C (D), Si (E), O (F).



Figure S2. The XPS spectra of Al (A), Si (B), C (C) and O (D) in product before electroreduction. The XPS spectra of Al (E), Si (F), C (G) and O (H) in product after electroreduction.



Figure S3. CV of GC (A), MFI-PZ/GC (B), Ni/MFI-PZ/GC (C), Cu/MFI-PZ/GC (D) and Cu/Ni/MFI-PZ/GC (E) measured in a non-Faradaic region at scan rates from 60 to 160 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (F) The linear relationship between scan rates and charging currents of Cu/Ni/MFI-PZ/GC (a), Cu/MFI-PZ/GC (b), Ni/MFI-PZ/GC (c), MFI-PZ/GC (d) and GC (e).



Figure S4. LSV of Cu/MFI-PZ/GC (A) and Ni/MFI-PZ/GC (B) were measured before and after A i-t C electroreduction at -1 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> for the required time; (C) The relationship between activity time and overpotential of Cu/Ni/MFI-PZ/GC (a), Cu/MFI-PZ/GC (b) and Ni/MFI-PZ/GC (c); LSV plots of Ni/MFI-PZ/GC (D), Cu/MFI-PZ/GC (E) before and after stability test.