

## Supporting Information

### High-performance alkaline hydrogen evolution electrocatalyzed by Ni<sub>3</sub>N-CeO<sub>2</sub> nanohybrid

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## Experimental section

*Materials:*  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{F}$ ,  $\text{KOH}$  and urea were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (10 wt% Pt) was provided by Alfa Aesar (China) Chemicals Co. Ltd. Titanium mesh was provided by Phychemi Hong Kong Company Limited. All reagents were used without further treatment. Deionized water used throughout all experiments was purified through a Millipore system.

*Preparation of  $\text{Ni}_3\text{N-CeO}_2/\text{TM}$ ,  $\text{Ni}_3\text{N}/\text{TM}$  and  $\text{CeO}_2/\text{TM}$ :* 2.8 mmol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 1.4 mmol  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 8.1 mmol  $\text{NH}_4\text{F}$ , and 14.0 mmol urea were dispersed into 40 mL deionized water with moderately stirring. The homogeneous mixture and a piece of clean TM (2 cm×3 cm) were heated and held at 120 °C for 6 h in a sealed Teflon-lined stainless-steel autoclave. The TM with corresponding precursor was thoroughly rinsed with deionized water and ethanol several times, and then vacuum-dried at 60 °C for 6 h. After annealing at 350 °C for 2 h in air atmosphere,  $\text{NiO-CeO}_2/\text{TM}$  was then obtained. The precursor  $\text{NiO-CeO}_2/\text{TM}$  was transferred into a porcelain boat and heat treated at 420 °C for 3 h under a flowing gas of  $\text{NH}_3$  in a tube furnace. Finally, the system naturally cooled down to room temperature still keeping the atmosphere of  $\text{NH}_3$ .

$\text{Ni}_3\text{N}/\text{TM}$  and  $\text{CeO}_2/\text{TM}$  were also fabricated for comparison by the same procedure, except no cerium or nickel salts was added during hydrothermal reaction, respectively.

*Characterization:* X-ray powder diffraction (XRD) measurements were performed with a diffractometer (Cu K $\alpha$   $\lambda$  = 1.5418 Å, RigakuD/MAX 2550). Hitachi S-4800 field emission scanning electron microscope (SEM) was utilized to obtain SEM images. High-resolution transmission electron microscopy (HRTEM) images were received with a Hitachi H-8100 electron microscopy. X-ray photoelectron spectrometer (ESCALABMK II) was utilized to record the X-ray photoelectron spectra (XPS) data with Mg as the exciting source.

*Electrochemical measurements:* Electrochemical experiments were carried out in a conventional three-electrode electrochemical system using a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai). Ni<sub>3</sub>N-CeO<sub>2</sub>/TM was performed as the working electrode with an Hg/HgO reference electrode and a graphite plate counter electrode. All the potentials were calibrated against the reversible hydrogen electrode (RHE) following the equation: E (RHE) = [E (Hg/HgO) + (0.098 + 0.059 pH)] V. Linear sweep voltammetry measurements were carried out in 1.0 M KOH electrolyte with a scan rate of 5 mV s<sup>-1</sup>. And *iR* correction was applied to all polarization curves unless specified. Electrochemical impedance spectroscopy data were obtained in the frequency ranging from 0.01 Hz to 100 kHz. All experiments were performed at 25 °C.

*Faradaic efficiency (FE) determination:* The gas generated in electrolysis process was verified by gas chromatography (GC-2014C, Shimadzu Co.) and

quantified by a calibrated pressure sensor (CEM DT-8890). The FE was obtained by contrasting the amount of experimentally produced hydrogen with that of theoretically calculated hydrogen.

*Calculation of double-layer capacitance ( $C_{dl}$ ), roughness factor ( $R_f$ ), and specific current density ( $j_s$ ):* The current density differences ( $\Delta j = j_a - j_c$ ) against sweep rates are plotted to yield a linear line, the slope of which is equivalent to twice the value of  $C_{dl}$ :

$$C_{dl} = \Delta j / 2 \cdot v = (j_a - j_c) / 2 \cdot v$$

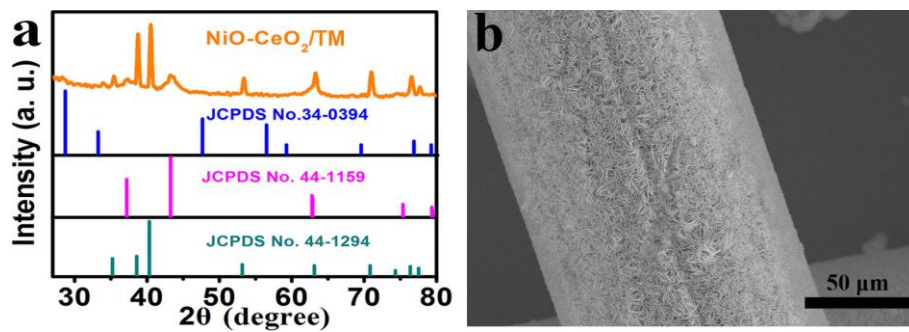
in which  $j_a$  and  $j_c$  represent the anodic and cathodic current density at a potential of + 0.736 V vs. RHE, respectively and  $v$  is the sweep rate. The  $C_{dl}$  of an ideal plane electrode is  $40 \mu\text{F cm}^{-2}$ , and  $R_f$  can be acquired by the equation:

$$R_f = C_{dl} / 40$$

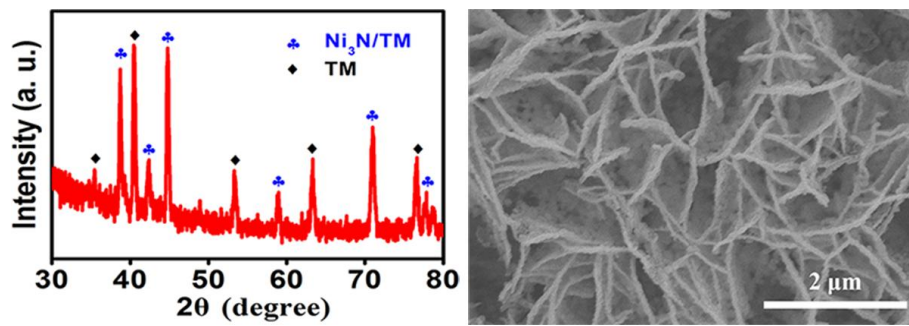
$j_s$  can be obtained following the equation:

$$j_s = j / R_f$$

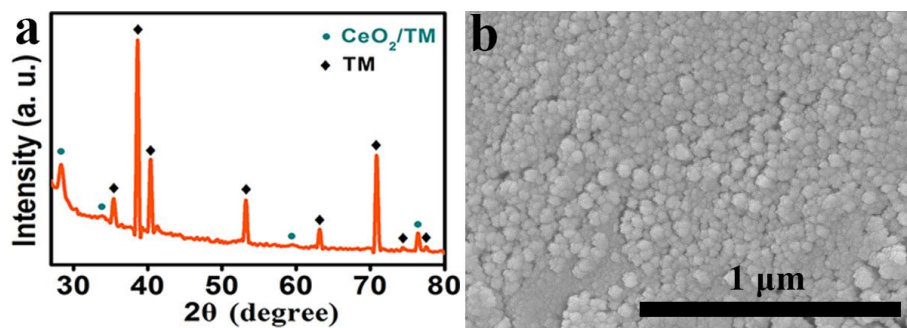
In which  $j$  is the HER current density at a potential of - 0.1 V vs. RHE.



**Fig. S1.** (a) XRD pattern and (b) SEM image of NiO-CeO<sub>2</sub>/TM.



**Fig. S2.** (a) XRD pattern and (b) SEM image of  $\text{Ni}_3\text{N}/\text{TM}$ .



**Fig. S3.** (a) XRD pattern and (b) SEM image of  $\text{CeO}_2/\text{TM}$ .

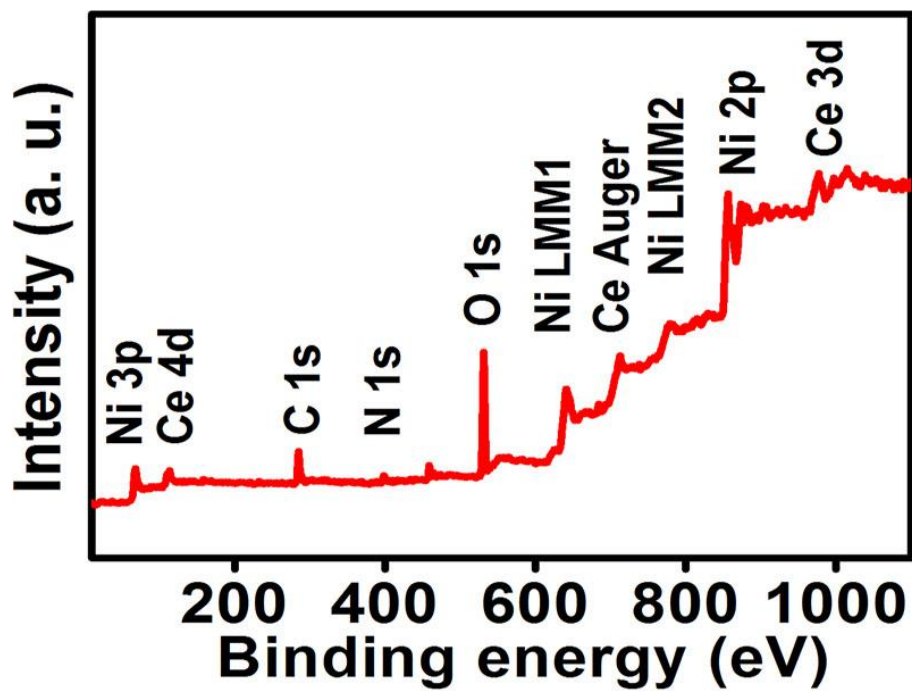
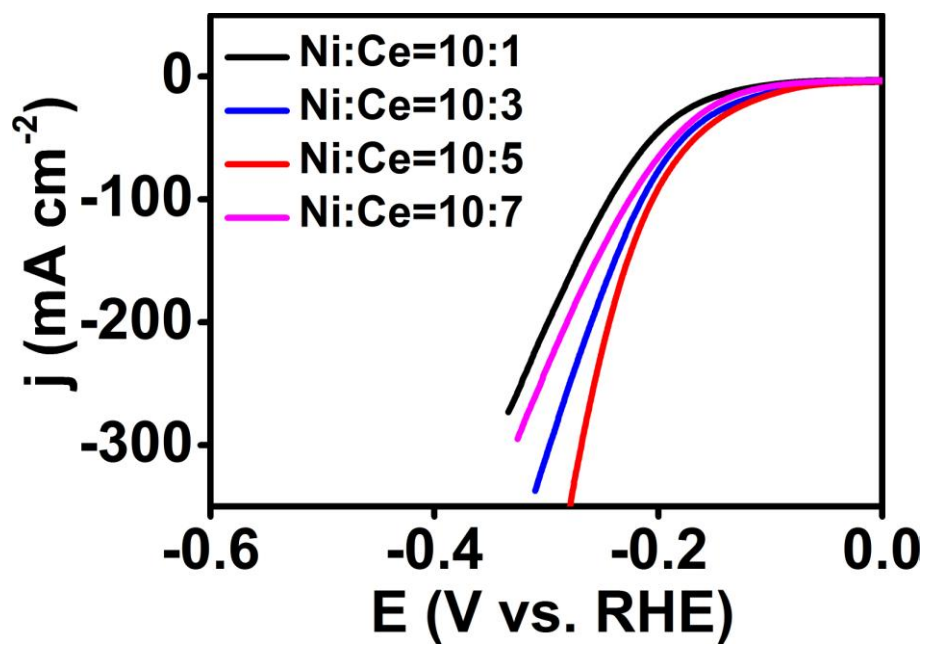
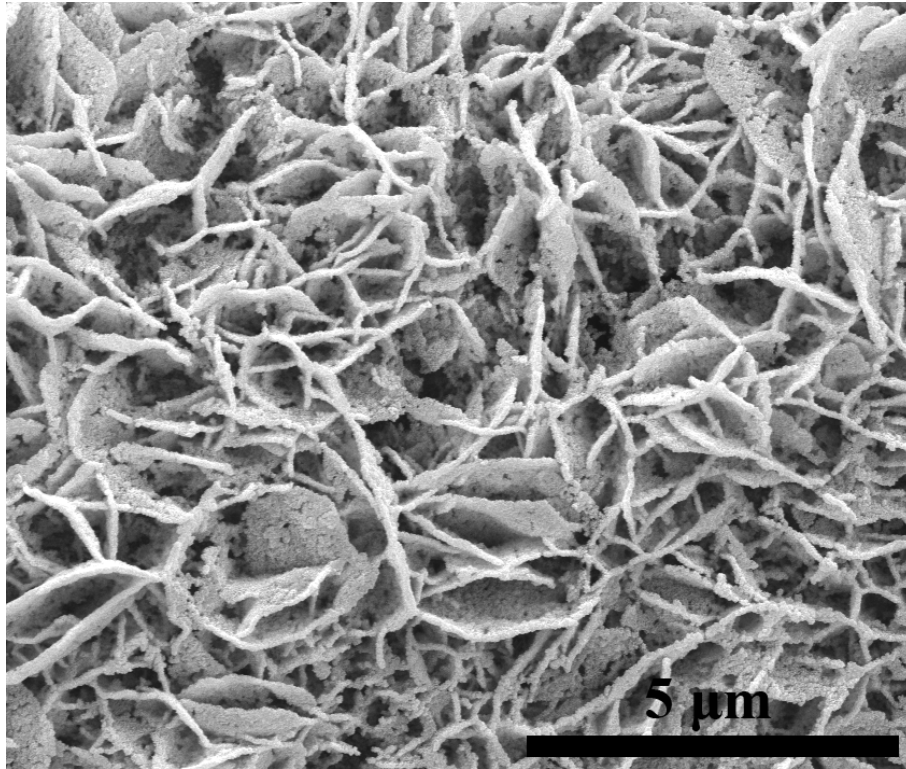


Fig. S4. X-ray photoelectron spectroscopy for Ni<sub>3</sub>N-CeO<sub>2</sub>.

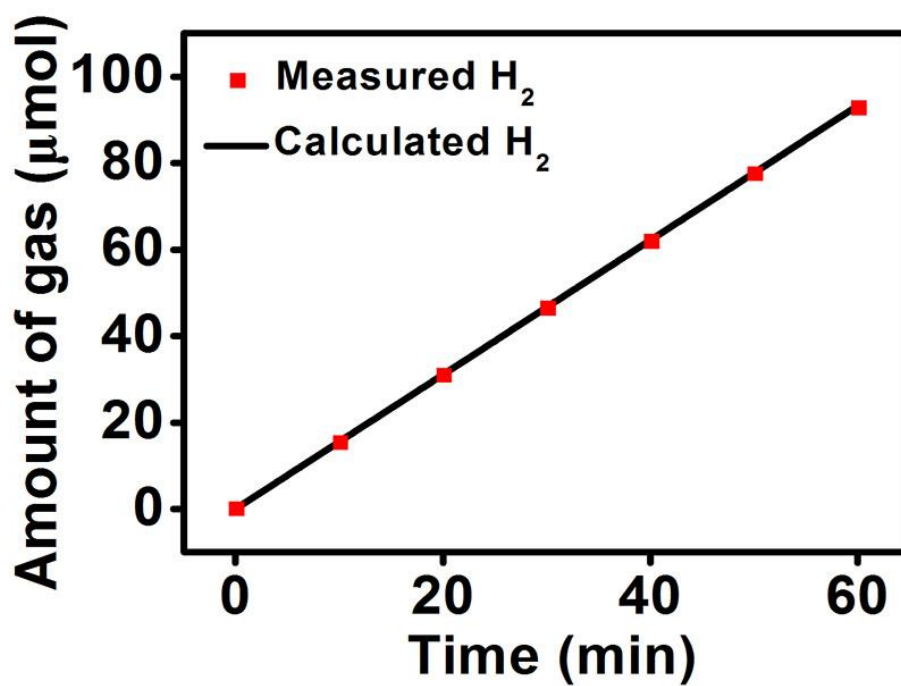




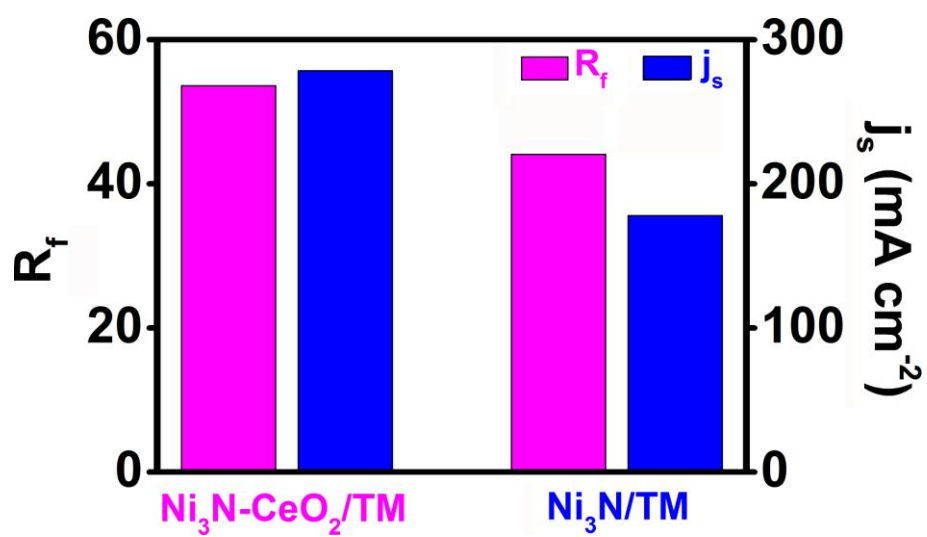
**Fig. S5.** Polarization curves of Ni<sub>3</sub>N-CeO<sub>2</sub>/TM catalysts with various atomic ratios of Ni/Ce.



**Fig. S6.** SEM image of  $\text{Ni}_3\text{N-CeO}_2/\text{TM}$  after long-term electrolysis.



**Fig. S7.** The hydrogen amount of experimentally produced and theoretically calculated versus time for Ni<sub>3</sub>N-CeO<sub>2</sub>/TM.



**Fig. S8.** Comparison of  $R_f$  and  $j_s$  for  $\text{Ni}_3\text{N-CeO}_2/\text{TM}$  and  $\text{Ni}_3\text{N}/\text{TM}$ .

**Table S1.** Comparison of HER performance of Ni<sub>3</sub>N-CeO<sub>2</sub>/TM with other Ni-based electrocatalysts in 1.0 M KOH.

Catalyst	j (mA cm <sup>-2</sup> )	$\eta$ (mV)	Electrolyte	Ref.
Ni <sub>3</sub> N-CeO <sub>2</sub> /TM	10	80	1.0 M KOH	This work
Ni/ceria-rGO (1,3)	10	208	1.0 M KOH	[1]
Ni/ceria-rGO (1,1)		111		
Ni/ceria-rGO (3,1)		485		
Ni/ceria		588		
Ni/rGO		289		
NiMoN-550	10	89	1.0 M KOH	[2]
Ni <sub>3</sub> FeN-NPs	10	158	1.0 M KOH	[3]
Ni/NiP	10	130	1.0 M KOH	[4]
Ni/NiS		230		
FeNi-N/CFC	10	106	1.0 M KOH	[5]
Ni <sub>3</sub> FeN-NPs	10	238	1.0 M KOH	[6]
Ni <sub>3</sub> N NA/CC	10	136	1.0 M KOH	[7]
NiMoN	10	109	1.0 M KOH	[8]

$\text{Fe}_2\text{Ni}_2\text{N}$	10	180	1.0 M KOH	[9]
$\text{NiCo}_2\text{N/NF}$	10	180	1.0 M KOH	[10]
$\text{Ni}_3\text{N/CMFs/Ni}_3\text{N}$	10	115	1.0 M KOH	[11]
$\text{NiO NRsm-Ov}$	10	110	1.0 M KOH	[12]
$\text{NiFeO}_x\text{/CFP}$	10	88	1.0 M KOH	[13]

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