Electronic Supplementary Information

Experimental Section

Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) was purchased from Aladdin Ltd. in Shanghai. Ammonium fluoride (NH_4F), urea and nickel chloride ($NiCl_2$) were purchased from Beijing Chemical Works. Pt/C (20 wt% Pt on Vulcan XC-72R) and 5 wt% Nafion solution were purchased from Alfa Aesar (China) Chemicals Co. Ltd. Ti mesh was purchased from Phychemi Hong Kong Company Limited. The water use throughout all experiments was purified through a Millipore system. All the reagents were used as received without further purification.

Preparation of $Ni(OH)_2$/TM

In a typical procedure, 4.5 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 8 mmol NH_4F and 20 mmol urea were dissolved in 80 mL distilled water and stirred to form a clear solution. Then the aqueous solution and Ti mesh (TM) were transferred to a 50 ml Teflon-lined stainless-steel autoclave. It was heated at 120 ^oC for 6 h to achieve $Ni(OH)_2$/TM. After the autoclave cooled down naturally, the resulting TM was taken out and washed with distilled water and ethanol, followed by drying 2 h at 60 ^oC to obtain $Ni(OH)_2$/TM.

Preparation of Ni_3N/TM

To prepare Ni_3N/TM, $Ni(OH)_2$/TM was placed in a tube furnace, and heated at 380 ^oC for 3 h with a heating speed of 5 ^oC min^{-1} in NH_3 atmosphere, and then naturally cooled to room temperature under NH_3. Finally, the black Ni_3N/TM was collected for further characterization.

Preparation of $Ni(OH)_2$-Ni_3N/TM

In a typical synthesis, the electrodeposition of $Ni(OH)_2$ on Ni_3N/TM was carried out in a three-electrode cell (Ni_3N/TM as working electrode; a graphite plate as counter electrode; saturated calomel electrode (SCE) as reference electrode). The electrodeposition procedure was performed according to previous report. The electrolyte was an aqueous solution of 0.1 M $NiCl_2$. The electrodeposition experiments were all carried out at a constant cathodic potential of -1.0 V for 300 s. After the deposition, $Ni(OH)_2$-Ni_3N/TM was removed, rinsed with deionized water several times and dried at 60 ^oC in air. The loading for $Ni(OH)_2$ on Ni_3N/TM nanosheets was about 3.2 mg cm^{-2}.

Characterizations

The XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-

4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a conventional three electrode system, using $Ni(OH)_2$-Ni_3N/TM as working electrode, graphite plate as counter electrode and Hg/HgO electrode as reference electrode. All tests were carried out at room temperature.

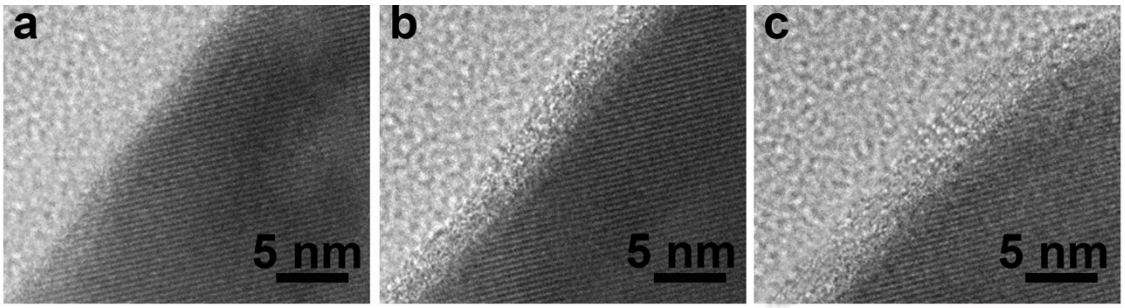

Fig. S1. HRTEM images taken from (a) Ni_3N , (b)$Ni(OH)_2$-Ni_3N/TM for 300s and (e) $Ni(OH)_2$-Ni_3N/TM for 540s.

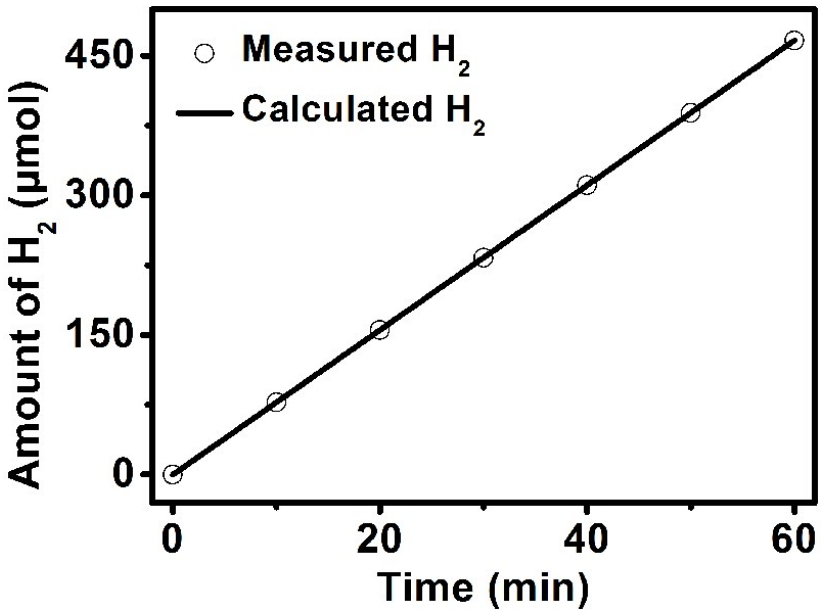

Fig. S2. The amount of H_2 theoretically calculated and experimentally measured versus time for HER of $Ni(OH)_2$-Ni_3N/TM in 1 M KOH.

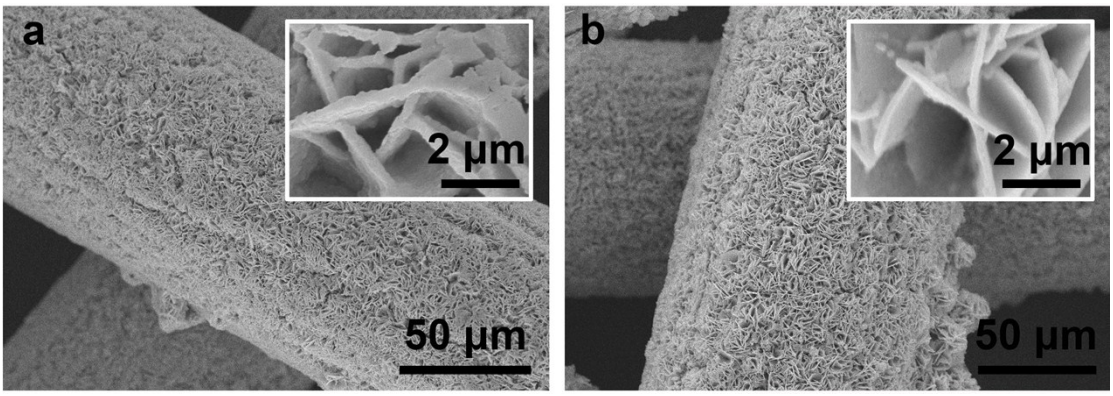

Fig. S3. SEM images of the $Ni(OH)_2$-Ni_3N/TM catalysts before (a) and after (b) reactions.

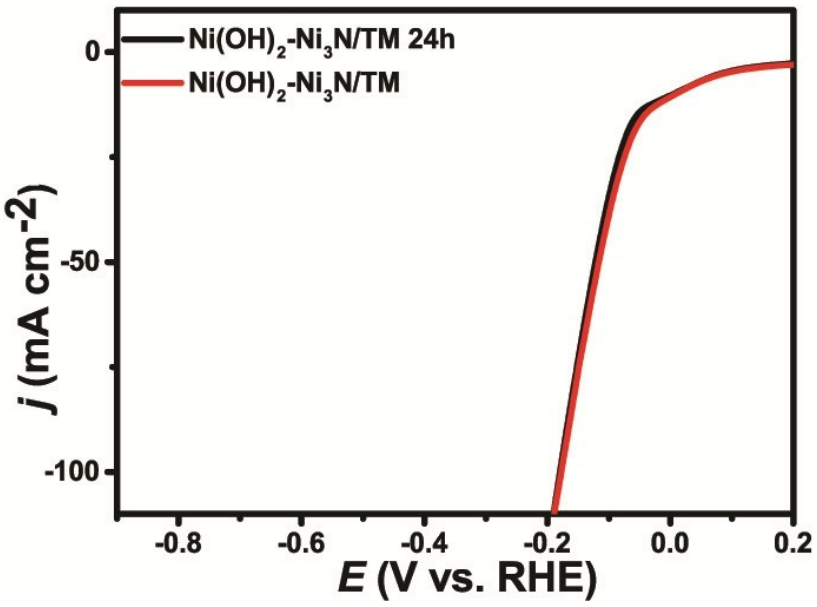

Fig. S4. LSV curves of the $Ni(OH)_2$-Ni_3N/TM and after reactions for 24h.

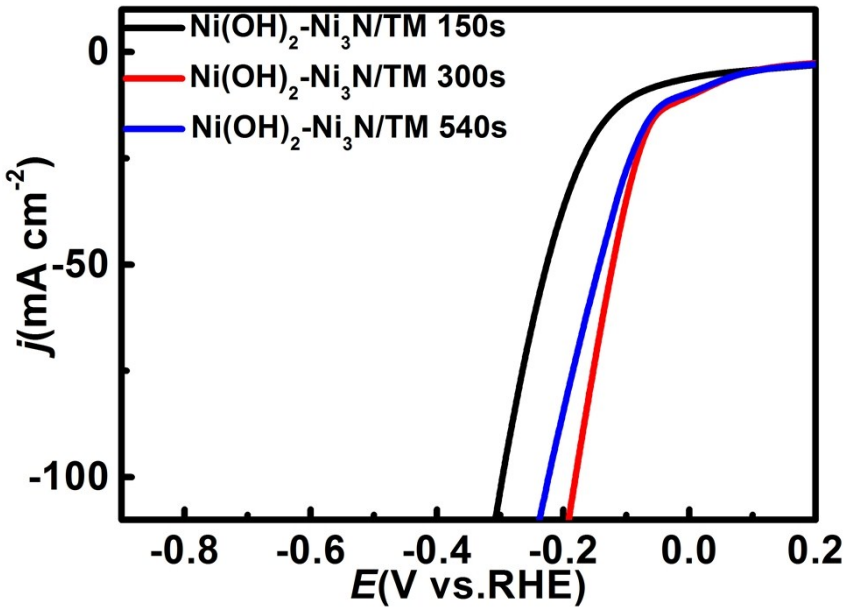

Fig. S5. LSV curves of the $Ni(OH)_2$-Ni_3N/TM with different electrodeposition time.

Table S1. Comparison of the HER activity for several recently reported catalysts.

Catalysts	Overpotential (mV vs. RHE)	Current density (mA cm^{-2})	Ref.
$Ni(OH)_2$-Ni_3N/TM	72	20	This work
	123	50	
	181	100	
Ni_3N/NF	177	20	1
TiN@Ni_3N	34	20	2
Ni_3N/Ni-foam	290	80	3
$NiCo_2S_4$ NA/CC arrays	228	20	4
NiS/Ni foam	220	80	5
Nickel phosphorus	150	80	6
Ni wire	350	10	7
Ni	83	50	8
Fe_2Ni_2N NPAs	110	10	9
NixPy-325	160	20	10
Ni-P film	110	20	11
Ni_2P/Ni	120	20	12
Ni@C-400 NSs	110	10	13
NiMo HNRs	92	10	14
NiSe NW	96	10	15

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