Supplementary Materials

Experimental Section

Regents and materials

Sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2\ 6H_2O$), chloroplatinic acid hexahydrate ($H_2PtCl_6\ 6H_2O$), ethylene glycol ($C_2H_6O_2$) and PVP (MW=55000 g/mol) were purchased from Aladdin Reagent Co., Ltd, Shanghai. Polytetrafluoroethylene emulsion (PTFE, 60 wt%) and DuPont Nafion(5 wt%) were purchased from Hesen electric Co., Ltd, Shanghai. Carbon black (Black Pearl 1000) was obtained from Cabot Corporation, Tianjing. High purity water (18.25 MΩ cm) was used in all experiments.

Preparation of catalyst and electrode

The commerical carbon (BP1000) was firstly treated by HNO_3 in order to introduce oxygen-functional group on surface. BP1000 (2 g) was added into 100 ml 7 M HNO_3 solution and refluxed at 120 ℃ for 16 h. The resulting product was filtered and washed with deionized water until the pH was approximately 7, then dried in a vacuum oven at 60℃for 12 h.

Pt/C electrocatalysts were synthesized by an ethylene glycol reduction method, that was similar to previous work [1]. 120 mg oxidized powder was dispersed in ethylene glycol by ultrasonic treatment for 20 min. Then 50 mg of $H_2PtCl_6\ 6H_2O$ and 3 mg PVP were added to the above mixture with ultrasonic treatment for 20min. The mixture solution was heated to 140 ℃ and maintain 3 h under vigorous stirring. After cooling down, the produced nanoparticles were filtered, washed with ethanol to remove PVP, and dried in a vacuum oven at 60 ℃ to obtain the home-made Pt/C.

5 mg Pt/C were dispersed in 500 μL isopropanol and Nafion under ultrasonic treatment. 8 μL of the electrocatalyst ink deposited on the surface of a glass carbon (GC) rotating disk electrode (RDE, Pine Instrument, geometric area: 0.196 cm^2) to form a thin catalyst film.

Preparation of Pt/C-HOR anode. The Pt/C-HOR anode was a sandwich structure electrode, which consisted of Pt/C catalyst layer (CL), gas diffusion layer (DL) and nickel foam current collector. The DL thick membrane was prepared by the roll-in method that was similar to our previous work [2]. The CL was

prepared by coating the catalyst ink onto the DL. 100 mg Pt/C or Pd/C catalyst and 100 mg PTFE emulsion were dissolved in 20 mL solution of H_2O:C_2H_5OH (V/V=1:1) to form solid-liquid catalyst ink. Then the catalyst ink was evenly coated on the surface of DL for several times to form the CL. The total loadings of Pt/C were controlled at 1 mg cm^{-2}. After that, the CL-DL was thermal-treated at 150 ℃ under flowing. The CL-DL and a nickel foam were pressed at 20 MPa into HOA with a sandwich structure.

The NiMo/$NiMoO_4$ electrode for HER was prepared according to the reported paper [3]

Structural characterizations

Transmission electron microscope (TEM) analysis of home-made Pt/C was carried out on a JEM-3010 operated at 200kV. Morphology structure of the NiMo/$NiMoO_4$ cathode were studied by a scanning electron microscopy (SEM，Zeiss SUPRA 55) operated at 20 kV.

Electrochemical polarization tests

The cathodic and anodic polarization tests, including LSV, CV and constant current test, were carried out with an Electrochemistry Workstation (PARSTAT 2273) in a conventional three-electrode system. The prepared Pt/C-HOR anode or NiMo/$NiMoO_4$ HER cathode was used as the working electrode, a platinum foil as auxiliary electrode and SCE as reference electrode. RDE tests of HOR on Pt/C/GC at the scan rate from 400 rpm to 2500 rpm were conducted at 25 ℃ in 6 M NaOH, 1.5 M Na_2CO_3 and 1 M $NaHCO_3$, respectively. The HOR on hydrogen diffusion anode in 1.5 M Na_2CO_3 and HER on NiMo/$NiMoO_4$ cathode in 6 M NaOH were both conducted at 70 ℃.

Electrolysis tests

The electrolysis test using OER-HER, OER-ORR and HOR-HOR were carried out in a two-compartment cell separated by ion-exchange membrane (F6801, Asahi Kasei Chemicals Corporation) at 70℃. OER Anode for OER and HOR was commerical RuO_2/Ti mesh (Northwest Institute for Nonferrous Metal Research, China) and home-made Pt/C-HOR electrode, respectively. Cathode for ORR and HER were Ag-ORC and NiMo/$NiMoO_4$, respectively. The effective areas of both the anode and cathode were 8 cm^2. 1.5 M Na_2CO_3 and 6 M NaOH solutions as the initial anolyte and catholyte were pumped into the anodic and cathodic chambers respectively. Hydrogen was fed into gas chamber at a steady flow rate of 20 ml min^{-1}. Electrolysis was carried out at a constant current of 800 mA for 8 h. Fresh electrolytes were pumped into the cathodic and anodic chambers after the previous electrolysis in order to identify whether the voltage is recovered.

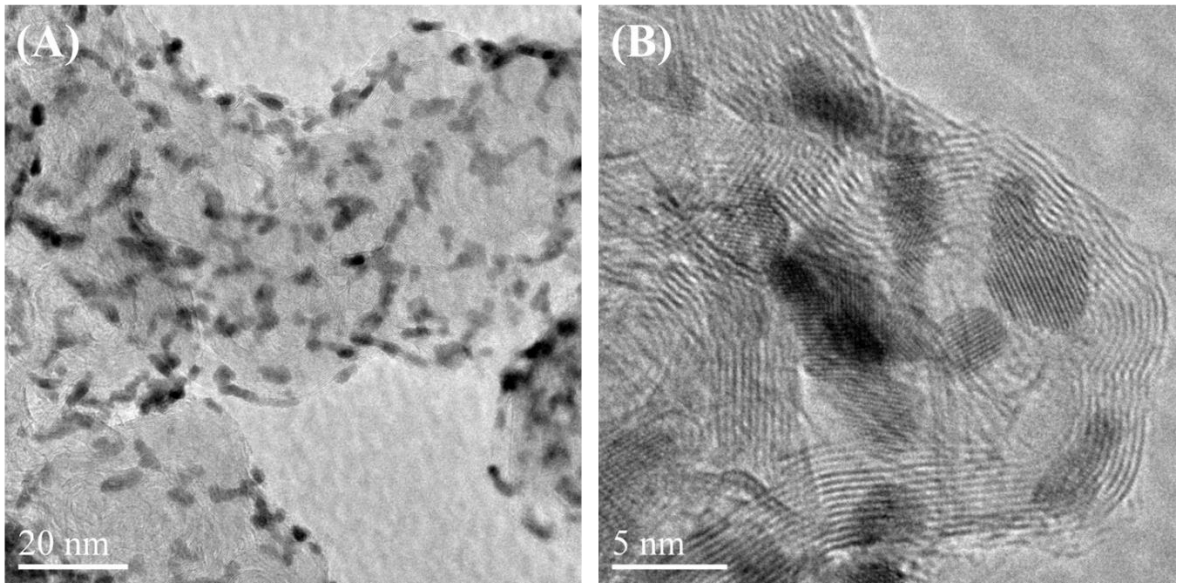

Fig.S1 (A) TEM and (B) HRTEM images of Pt/C electrocatalyst

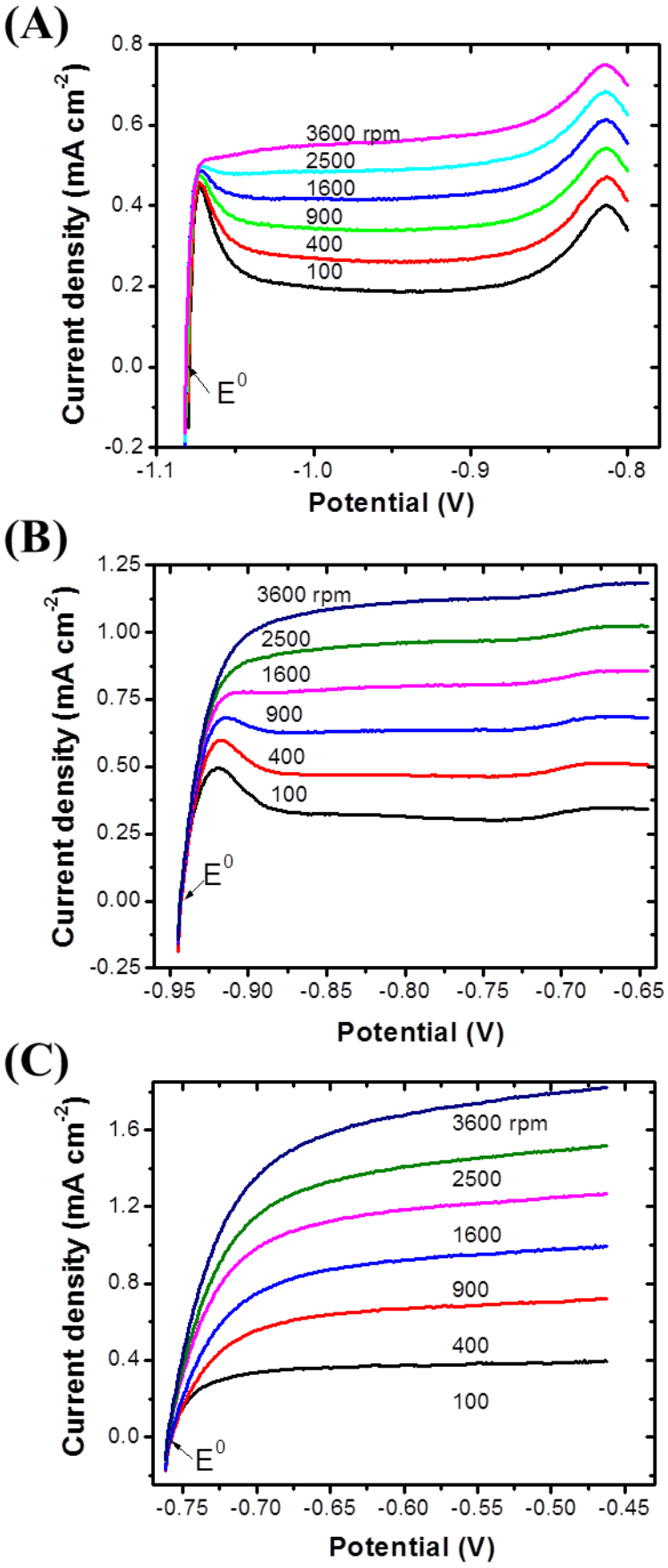

Fig. S2 The HOR LSV curves on Pt/C modified GC RDE in H_2-saturated NaOH (A), Na_2CO_3 (B) and $NaHCO_3$ (C) electrolyte at scan rate of 5 mV s-1. The rotation rate of RDE ranges from 100 to 3600 rpm.

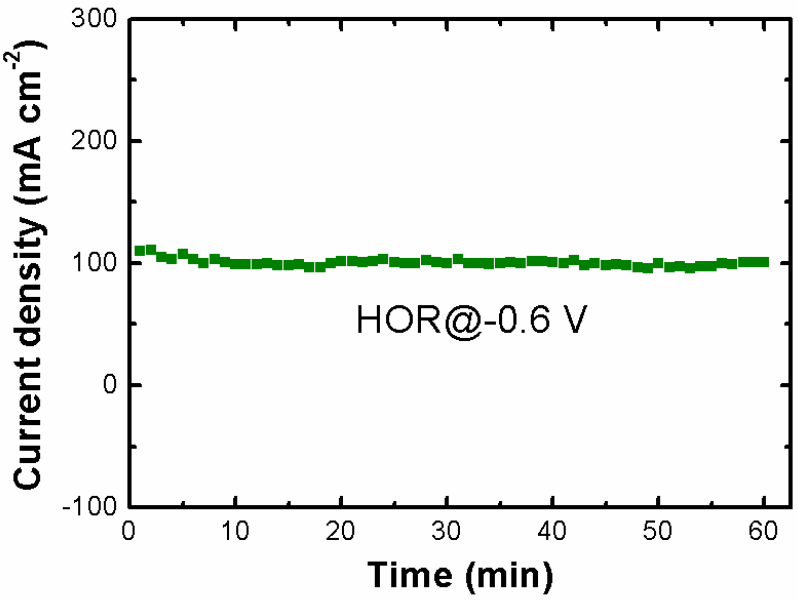

Fig. S3 The HOR current density on hydrogen diffusion anode at potential of -0.6 V in 1.5 M Na_2CO_3

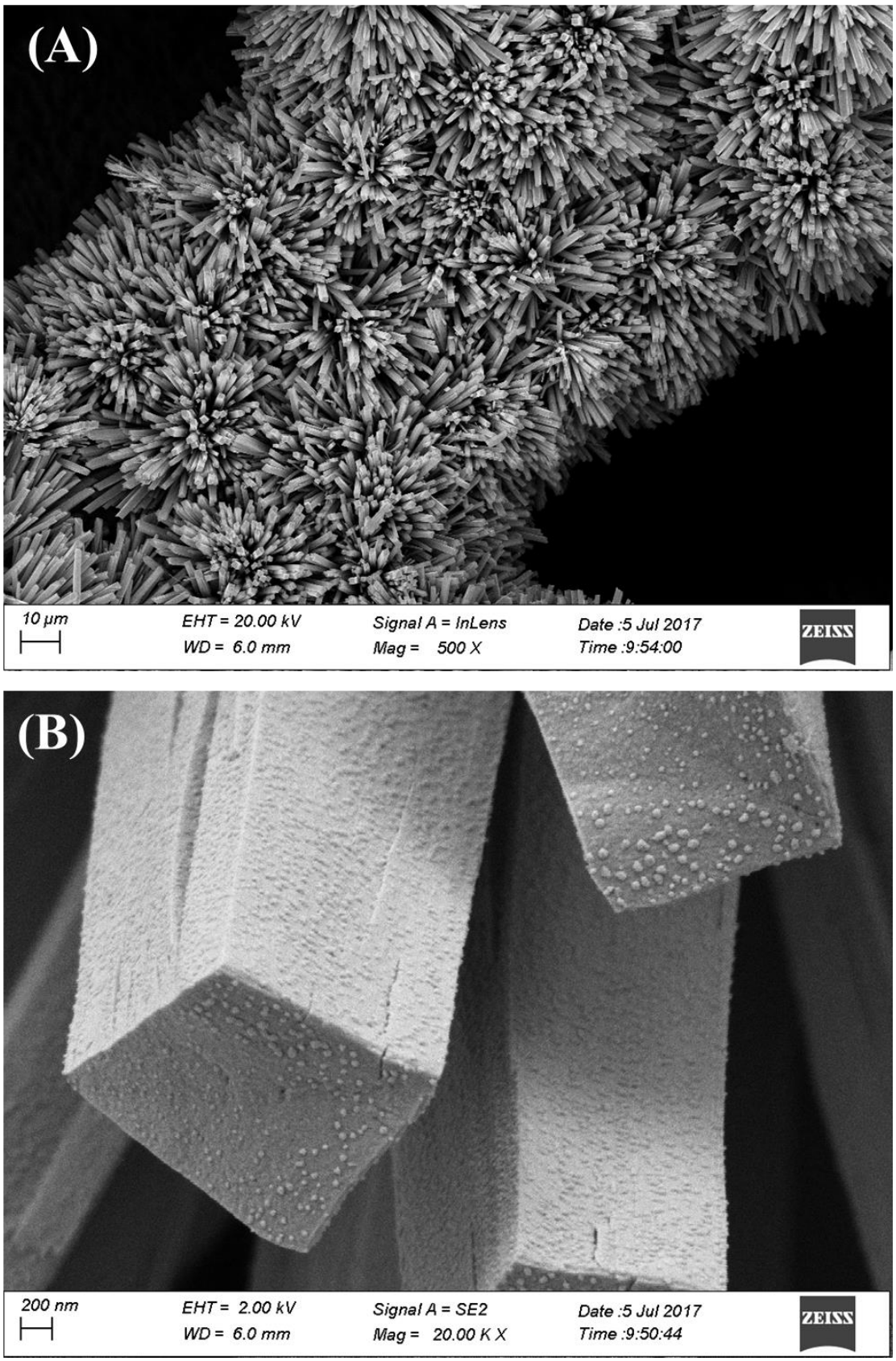

Fig. S4 The SEM (a) and high magnification SEM (b) images of NiMo/$NiMoO_4$ cathode

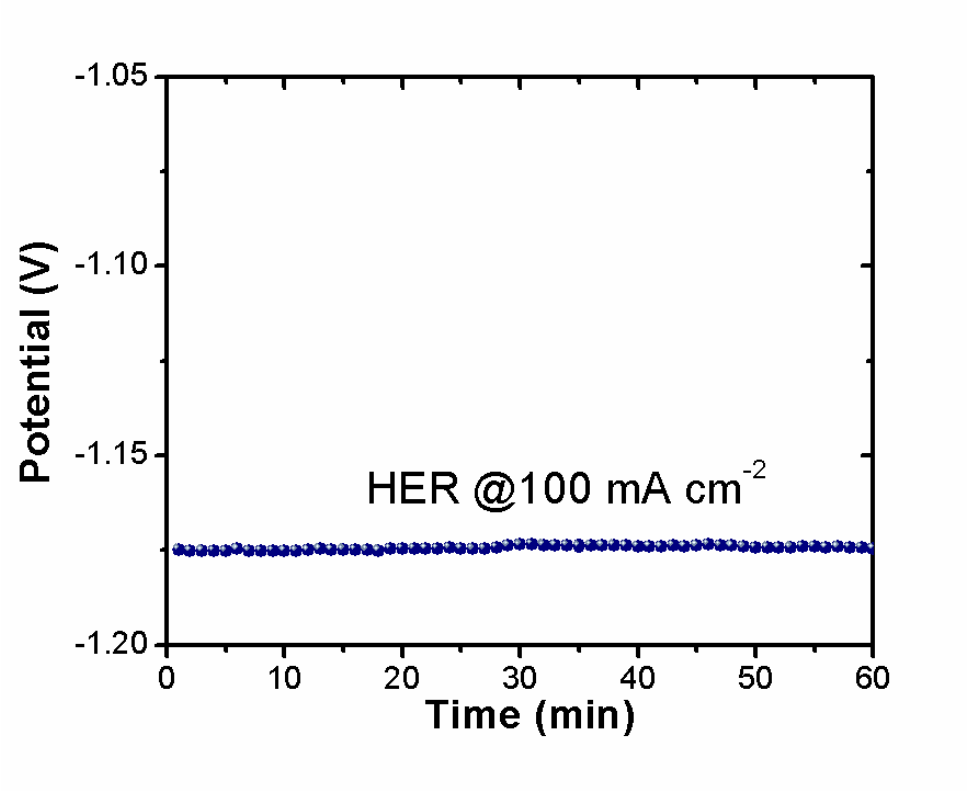

Fig. S5 Potential vs time for HER on NiMo/$NiMoO_4$ cathode at constant current density of 100 mA cm^{-2} in 6 M NaOH catholyte.

Tab. S1 Average cell voltage, CE and electrical energy consumption of different electrolysis methods

NO.	Anode	Cathode	Average cell voltage (V)*	CE_{NaOH} (%)	kWh/t_{NaOH}
1	HOA	HEC	0.88	90.3	653
2	OEA	ORC	1.51	91.2	1100
3	OEA	HEC	2.51	91.8	1832

Average cell voltage values were calculated according to the cell voltage during the 8 hours electrolysis at the same applied current density.

Reference

1. Rao, C. V.; Reddy, A. L. M.; Ishikawa, Y.; Ajayan, P. M., Synthesis and electrocatalytic oxygen reduction activity of graphene-supported Pt_3Co and Pt_3Cr alloy nanoparticles. *Carbon* **2011,** *49* (3), 931-936.

2. Tang, Y.; Li, Y.; Sun, Y.; Wang, J.; Chen, Y.; Yang, X.; Wan, P., Energy-saving electrolysis of sodium carbonate with a silver nanoparticles/carbon oxygen reduction cathode. *Electrochemistry Communications* **2013,** *27*, 108-111.

3. Zhang, J.; Wang, T.; Liu, P.; Liao, Z.; Liu, S.; Zhuang, X.; Chen, M.; Zschech, E.; Feng, X., Efficient hydrogen production on $MoNi_4$ electrocatalysts with fast water dissociation kinetics. *Nature Communications* **2017,** *8*, 15437.