

## Supporting Information

### Monocrystalline Platinum-Nickel Branched Nanocages with Enhanced Catalytic Performance towards Hydrogen Evolution Reaction

Zhenming Cao<sup>a</sup>, Huiqi Li<sup>a</sup>, Chenyang Zhan<sup>a</sup>, Jiawei Zhang<sup>a</sup>, Wei Wang<sup>c</sup>, Binbin Xu<sup>a</sup>, Fa Lu<sup>a</sup>, Yaqi Jiang<sup>a\*</sup>, Zhaoxiong Xie<sup>a,b\*</sup> and Lansun Zheng<sup>a</sup>

<sup>a</sup> State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

<sup>b</sup> Pen-Tung Sah Institute of Micro-Nano Science and Technology, Xiamen University, Xiamen 361005, China

<sup>c</sup> Research Institute for Biomimetics and Soft Matter, Department of Physics, Xiamen University, Xiamen 361005, China

E-mail: yqjiang@xmu.edu.cn, zxxie@xmu.edu.cn

**Chemicals and materials.** Platinum (II) 2,4-pentanedionate (Pt(acac)<sub>2</sub>), nickel (II) 2,4-pentanedionate (Ni(acac)<sub>2</sub>), oleic acid (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>, tech. 90%) and Pt/C (20 wt%) were purchased from Alfa Aesar. Formaldehyde solution (40%), isopropanol, acetic acid, and *n*-butylamine were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Oleylamine (C<sub>18</sub>H<sub>37</sub>N) was purchased from J&K Chemicals. All chemicals were analytical grade and used without further purification.

**Synthesis of Pt-Ni branched nanomultipods.** In a typical synthesis of Pt-Ni branched nanomultipods, 8.0 mg of Pt(acac)<sub>2</sub> and 15.7 mg of Ni(acac)<sub>2</sub> were dissolved in 9.00 mL of oleylamine and 1.00 mL of oleic acid under ultrasonic stirring. After the mixture became a clear solution, 800 μL of formaldehyde solution was injected successively. Then it was further stirred for 15 min, and transferred into a Teflon-lined stainless-steel autoclave with a capacity of 20 mL. The sealed vessel was heated from room temperature to 220°C in about 70 min and kept at this temperature for 12 h, then cooled to room temperature naturally. The products were collected by centrifugation (10000 rpm for 5 min) and then washed several times with hexane and ethanol to remove impurities.

**Synthesis of Pt-Ni branched nanocages.** 5 mg of the Pt-Ni branched nanomultipods prepared as above mentioned method were post-treated by the acetic acid (20 mL) at 70°C for 10 h. The products were collected by centrifugation (10000 rpm for 5 min) and then washed several times with ethanol to remove impurities.

**Structure and composition characterizations.** The morphology was observed by the scanning electron microscopy (SEM, Hitachi S4800). The crystal phase was determined by powder X-ray diffraction (XRD) using a Rigaku Ultima IV X-ray diffractometer with Cu K $\alpha$  radiation. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDS) were performed with a FEI TECNAI F30 microscope

operated at 300 kV. The precise composition of every element was determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, Baird PS-4). All samples for the transmission electron microscopic (TEM) analysis were prepared by depositing a drop of the diluted suspension in ethanol on carbon film coated copper grid.

### **Electrochemical measurement.**

**Synthesis of Pt-Ni branched nanocages supported on XC-72 (carbon support).** In a typical synthesis of Pt-Ni branched nanocages supported on XC-72, 16.0 mg of Pt(acac)<sub>2</sub>, 31.4 mg of Ni(acac)<sub>2</sub> and 8 mg of XC-72 were dissolved in 16.20 mL of oleylamine and 1.80 mL of oleic acid under ultrasonic stirring. Then, 1440  $\mu$ L of formaldehyde solution was injected successively, and kept stirring for 15 min. The well-mixed mixture was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL, which was heated from room temperature to 220 °C in about 70 min and kept at this temperature for 12 h, then cooled to room temperature naturally. The products were collected by centrifugation (11000 rpm for 10 min) and then washed several times with hexane and ethanol to remove impurities. The as-prepared Pt-Ni nanomultipods supported on XC-72 were further post-treated by acetic acid (30 mL) at 70 °C for 10 h to acquire the Pt-Ni branched nanocages supported on XC-72. The products were collected by centrifugation (11000 rpm for 10 min) and then washed several times with ethanol to remove impurities. Finally, the Pt-Ni branched nanocages supported on XC-72 were then post-treated in air at 150 °C for 6 h to remove the surfactant.

The carbon supported samples (3.0 mg) or commercial Pt/C (3.0 mg) were dispersed in 1.5 mL isopropanol respectively, and then 15  $\mu$ L of nafion (5%) was added in the ethanol by ultrasound in ice-water for 0.5 h. All the concentration of catalysts were 2.0 mg/mL. To prepare the catalyst supported electrode, the glassy carbon electrode (diameter = 5 mm, Pine Instrument) was firstly polished and washed carefully, and then the as-prepared catalyst suspension (3  $\mu$ L) was deposited on the pre-treated glassy carbon electrode (the actual amount of Pt on the electrode is 1.5  $\mu$ g through ICP-AES), which was used as the working electrode after the solvent was vaporized at room temperature.

All electrochemical measurements were carried out in a home-made three-electrode cell and the data were recorded using an electrochemical workstation (CHI 660E, Shanghai Chenhua Co., China). In a typical experiment, a graphite sheet and Hg/HgO (1 M KOH) were served as the counter electrode and the reference electrode, respectively. Before electrocatalytic experiments were performed, the electrolyte was bubbled by N<sub>2</sub> gas for 5 min to achieve the O<sub>2</sub>-free solution, and then the rotation-disk-electrode (RDE) loaded with the catalysts was electrochemically cleaned by continuous potential cycling between -0.90 V and 0.20 V (*vs* Hg/HgO) at 100 mV·s<sup>-1</sup> in a solution containing 0.1 M KOH (at 298 K). After that, H<sub>2</sub> gas was purged through the solution for 5 min to make the solution saturated with H<sub>2</sub>. Subsequently, the catalytic activity was measured by linear sweep voltammetry method with a scan rate of 10 mV·s<sup>-1</sup> (at 298±2 K) while

H<sub>2</sub> bubbling was continued during the HER activity measurement. The rotation rate of RDE was 1600 rpm in order to remove the H<sub>2</sub> bubble and all the polarization curves were *iR* corrected.

The ECSAs of the catalysts were determined by the area of the hydrogen desorption peaks in the cyclic voltammetry measurement performed in 0.1 M HClO<sub>4</sub> electrolyte with a scan rate of 100 mV·s<sup>-1</sup> (at 298 K). The ECSAs of the catalysts were calculated by the equation  $ECSA = Q/q_0$ , in which  $Q$  is the electric quantity calculated from hydrogen desorption peaks, and  $q_0$  is 210 μC·cm<sup>-2</sup>.

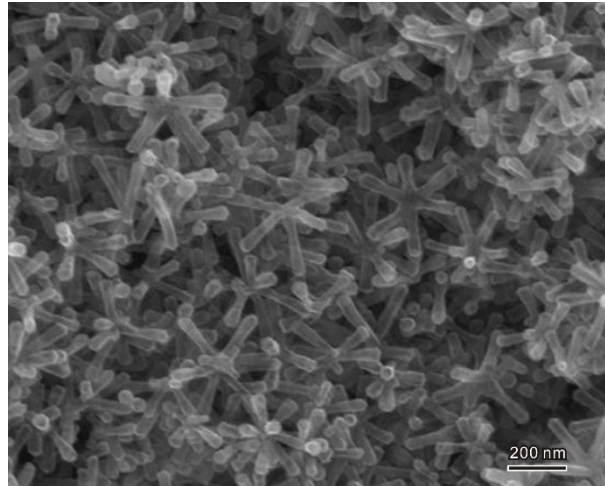


Figure S1. SEM image of the Pt-Ni branched nanocages at lower magnification.

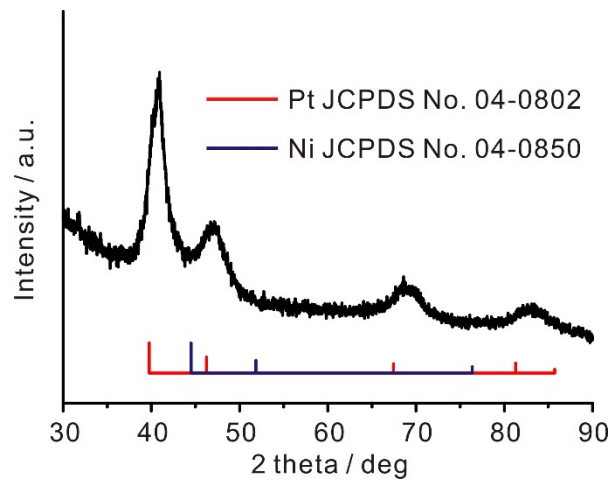


Figure S2. XRD pattern of the Pt-Ni branched nanocages.

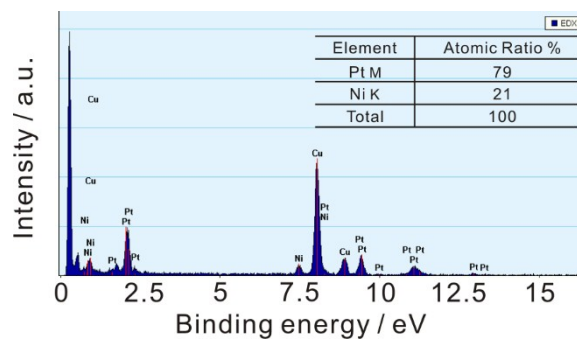


Figure S3. EDS analysis of the Pt-Ni branched nanocages.

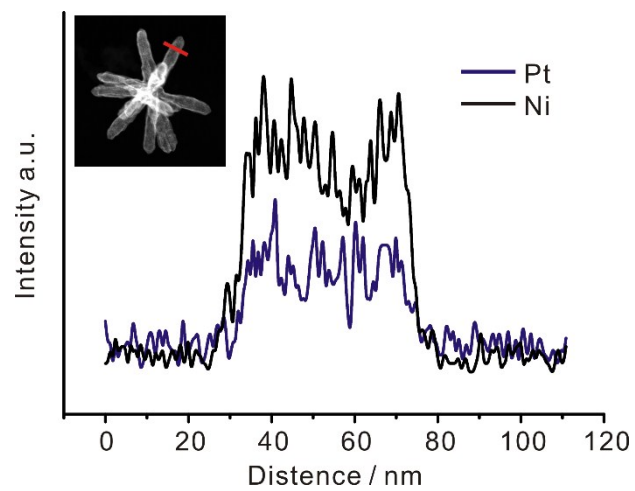


Figure S4. Cross sectional composition profile of the Pt-Ni branched nanocages.

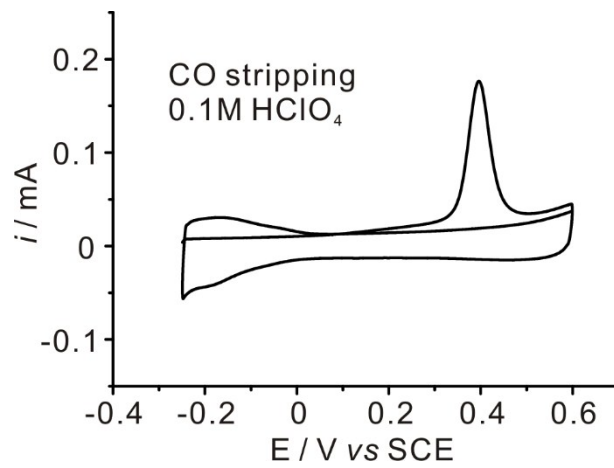


Figure S5. CO stripping curves of the Pt-Ni branched nanocages in 0.1 M HClO<sub>4</sub>. Scanning rate: 50 mV/s; Temperature: 298 K.

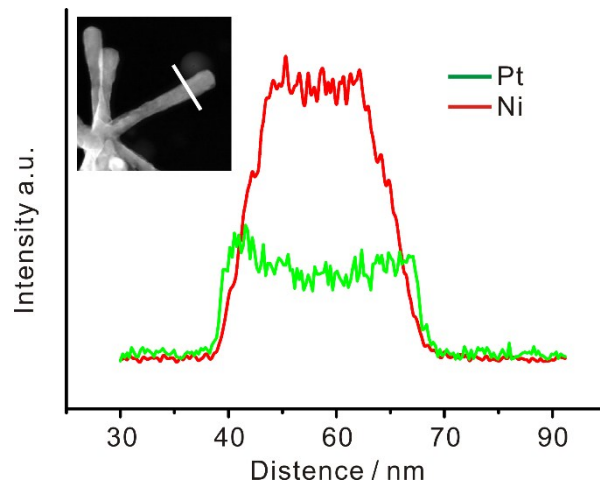


Figure S6. Cross sectional composition profile of the Pt-Ni branched nanomultipods.

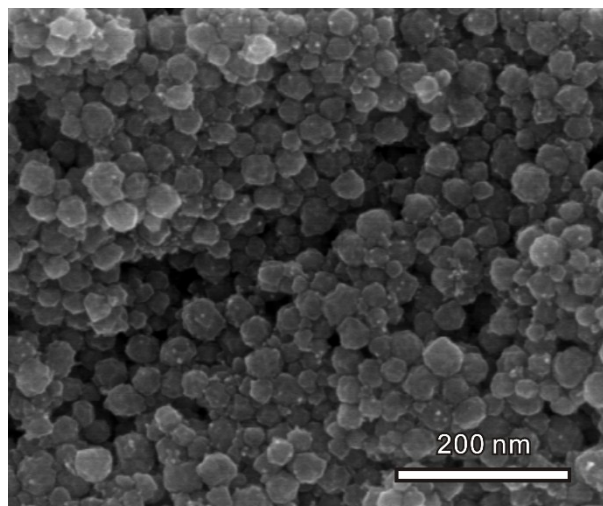


Figure S7. SEM image of the product synthesized in the absence of formaldehyde solution.

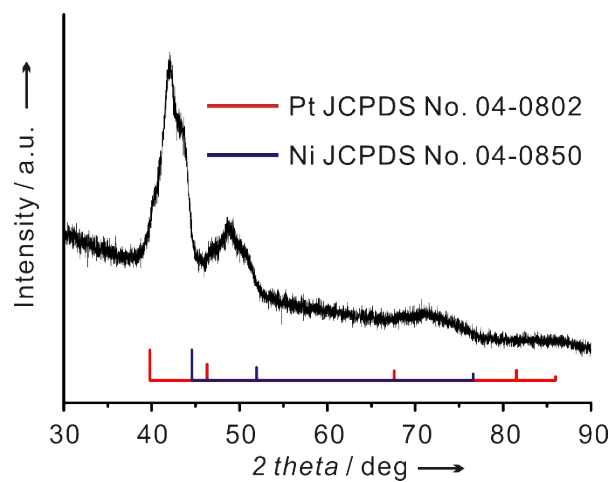


Figure S8. XRD pattern of the corresponding product synthesized in the absence of formaldehyde solution.

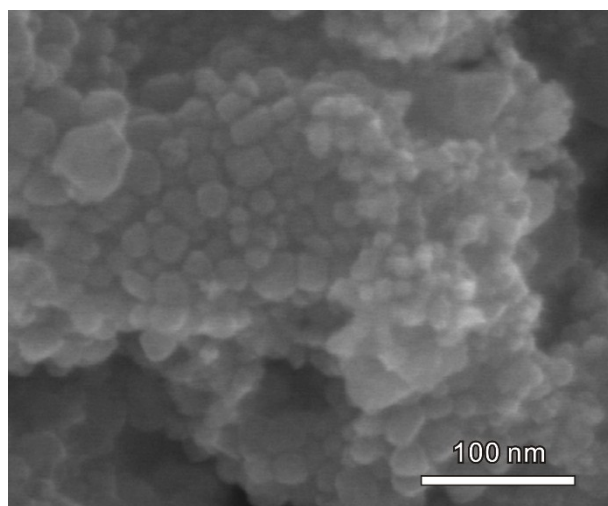


Figure S9. SEM image of the product synthesized in the absence of oleic acid.

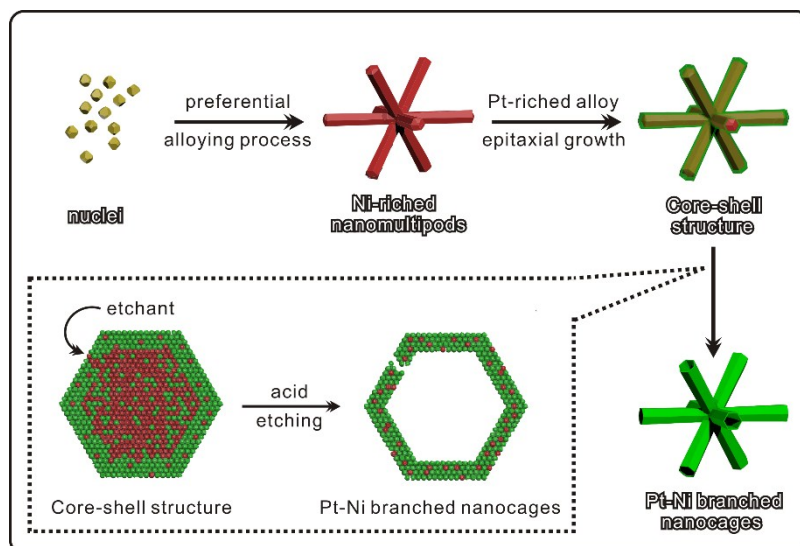


Figure S10. Schematic illustration for the formation of the Pt-Ni branched nanocages.

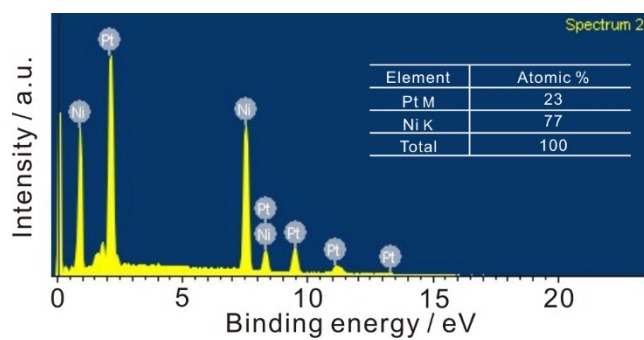


Figure S11. EDS analysis of the Pt-Ni branched nanomultipods.



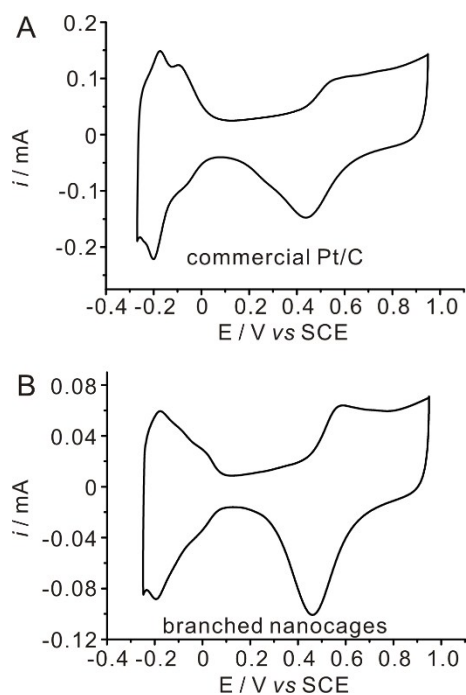


Figure S12. CV curves of the commercial Pt/C and Pt-Ni branched nanocages in 0.1 M HClO<sub>4</sub>. Scanning rate: 50 mV/s; Temperature: 298 K.

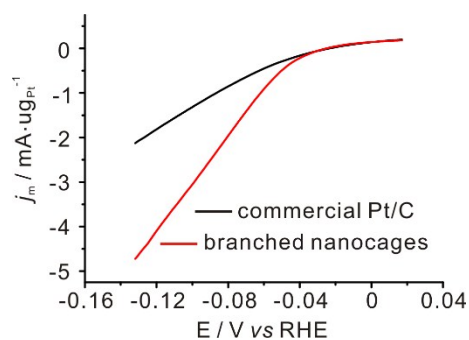


Figure S13. Linear sweep voltammetry (LSV) curves of commercial Pt/C and Pt-Ni branched nanocages normalized to the mass of Pt in 0.1 M KOH. Scanning rate: 10 mV/s; rotating rate: 1600 rpm; Temperature: 298 K.

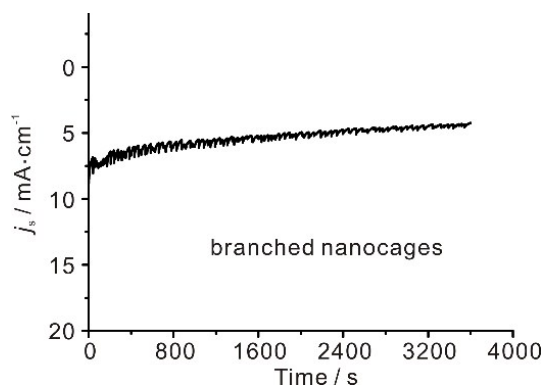


Figure S14. I-t curves of the Pt-Ni branched nanocages in 0.1 M KOH. Rotating rate: 1600 rpm; Temperature: 298 K.

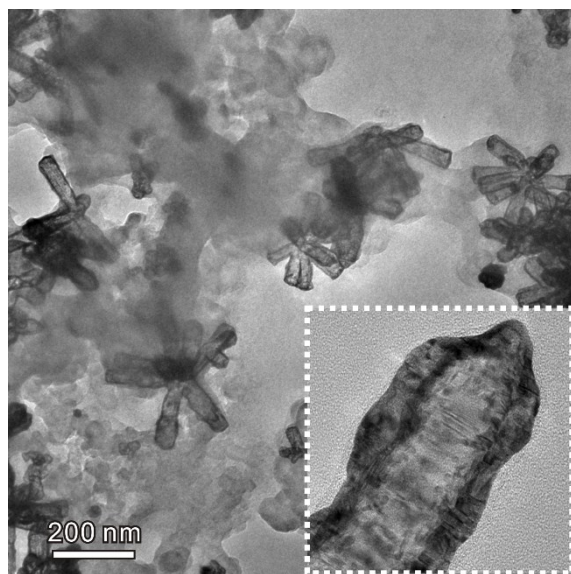


Figure S15. TEM image of the Pt-Ni branched nanocages after the stability test.

Table S1. Summary of the typical catalytic performances of different catalysts

sample	$m$	$j_o$	$j_s$	$j_m$	$\eta$	Ref
Pt (pc) electrode	N/A	0.7	2.3	N/A	N/A	1 <sup>1</sup>
Pt <sub>3</sub> Ni frames/C	N/A	N/A	2.3	N/A	84	2 <sup>2</sup>
Pt <sub>3</sub> Ni frames/Ni(OH) <sub>2</sub> /C	N/A	N/A	~6.0	N/A	~59	2 <sup>2</sup>
<i>hcp</i> -excavated Pt-Ni nano-multipods	7.65 $\mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$	1.65	11.1	3.03	38	3 <sup>3</sup>
Ni(OH) <sub>2</sub> /modified Ir surface	N/A	N/A	~5.4	N/A	~61	4 <sup>4</sup>
Ni(OH) <sub>2</sub> /modified Pt surface	N/A	N/A	~2.7	N/A	~95	4 <sup>4</sup>
Pt/C/20 wt% SL Ni(OH) <sub>2</sub> Li(OH)	1.13 $\mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$	N/A	2.28	N/A	106	5 <sup>5</sup>
Pt(111)/Co(OH) <sub>2</sub>	N/A	N/A	~0.5	N/A	159	5 <sup>6</sup>
Ni-Ag alloy	N/A	N/A	~0	N/A	~260	7 <sup>7</sup>
NiMo nanopowers	1000	N/A	N/A	N/A	N/A	8 <sup>8</sup>
Pt electrode	N/A	0.62	N/A	N/A	~70	9 <sup>9</sup>
Pt nanowires/SL-Ni(OH) <sub>2</sub>	16 $\mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$	N/A	6.31	1.59	57.8	10 <sup>10</sup>
Pt islands/Pt(111) surface	N/A	N/A	1.4	N/A	~140	11 <sup>11</sup>
Ni(OH) <sub>2</sub> /Pt islands/Pt(111) surface	N/A	N/A	~1.7	N/A	~110	11 <sup>11</sup>
Pt-Ni branched nanocages	7.65 $\mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$	1.21	4.5	1.5	67	This work

$m$  ( $\mu\text{g} \cdot \text{cm}^{-2}$ ): mass of the catalyst loading on the electrode.

$j_o$  ( $\text{mA} \cdot \text{cm}^{-2}$ ): exchange current density normalized to the ECSA.

$j_s$  ( $\text{mA} \cdot \text{cm}^{-2}$ ): current density normalized to the ECSA at  $\eta=70$  mV.

$j_m$  ( $\text{mA} \cdot \mu\text{g}_{\text{Pt}}^{-1}$ ): current normalized to the mass of Pt on the electrode at  $\eta=70$  mV.

$\eta$  (mV): overpotential at  $j_s=4$   $\text{mA} \cdot \text{cm}^{-2}$ .

## References

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