Supporting Information for *Acta Phys. -Chim. Sin.* doi: 10.3866/PKU.WHXB202107005

有机配体表面改性 $NiCo_2O_4$ 纳米线用于水全分解

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Surface Modification of $NiCo_2O_4$ Nanowires using Organic Ligands for Overall Water Splitting

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Chemical materials

Nickel nitrate hexahydrate (98.0%), cobalt (II) nitrate hexahydrate (99.0%), urea (99.0%), potassium hydroxide (90.0%), hydrochloric acid (37.0%), *N,N*-dimethylformamide (99.5%), absolutely ethyl alcohol (99.7%), Pt/C (20% (*w*)) and Ir/C (20% (*w*)) were purchased from Aladdin. Rod GCEs were from the Chenhua Co. Ltd. (Shanghai, China). The demonized (DI) water for solution preparation was from a Millipore Autopure system (18.2 MΩ, Millipore Ltd., USA). The 1.0 mol·L^{-1} KOH was employed as a supporting electrolyte in the electrochemical experiment. Ni foam was purchased from Fuel Cell Store. Nafion 117 (brand: Dupont) was purchased from Shanghai Hesen Electrical Co., Ltd. All the other Chemicals and reagents for electrochemical measurements were of analytical grade and used as received.

Material synthesis

Synthesis of Ni foam/$NiCo_2O_4$ nanowires

Ni foam (NF) is prepared by a modified method [1]. In the experimental, Ni foam is washed with 3 mol·L^{-1} hydrochloric acid first under ultrasonic conditions for 30 min, then washed with acetone under ultrasonic conditions for 15 min, finally absolute ethyl alcohol washed under ultrasonic conditions for 15 min.

Firstly, NF/$NiCo_2O_4$ NWs were prepared by a facile hydrothermal synthesis method [2]. Generally speaking, 0.3637 g $Co(NO_3)_2·6H_2O$, 0.1808 g $Ni(NO_3)_2·6H_2O$, and 0.15 g urea were dissolved in 50 mL DI water. After stirred for about 10 min, a transparent pink colored solution was obtained. Then the solution was transferred into an 80 mL Teflon-lined stainless-steel autoclave. One piece of Ni foam (NF) 3.5 cm × 4 cm vertically insert into the Teflon holder, subsequently soaked in the solution following by heated the solution to 120 °C in an electric drying oven, and kept at that temperature for 16 h. The as synthesized electrodes were then taken out, ultrasonically cleaned for 5 min in the DI water and rinsed with ethanol several times, dried at 80 °C over night, and annealed at 300 °C in air for 2 h to get the $NiCo_2O_4$ NWs on the Ni foam.

Preparation of Ni foam/$NiCo_2O_4$ NWs MOFs-74

Typically, 31 mg of 2,5-dihydroxyterephthalic acid was first dispersed in a mixed solvent of 20 mL of *N,N*-dimethylformamide, 1 mL absolute ethyl alcohol, and 1 mL of deionized water [3]. After 10 min of sonication, a homogeneous slurry was formed, then the solution was transferred into an 80 mL Teflon-lined stainless-steel autoclave. One piece of NF/$NiCo_2O_4$ NWs (3.5 cm × 4 cm) was immersed into the reaction solution and maintained at 130 °C for 1 h. After cooled down naturally, the sample was rinsed with ethanol three times then dried at 85 °C. The scheme is clear to understand. The as-obtained product was named as $NiCo_2O_4$ NWs-MOFA, while $NiCo_2O_4$ NWs-MOFB, $NiCo_2O_4$ NWs-MOFC, were prepared in a similar method, except changing the 2,5-dihydroxyterephthalic acid amount to 3.1mg and 0.31 mg.

Preparation of the Ni-MOF-74

Typically, 1.12 mmol 2,5-dihydroxyterephthalic acid and 3.7 mmol $Ni(NO_3)_2·6H_2O$ were dispersed in a mixed solvent of 25 mL of *N,N*-dimethylformamide, 25 mL absolutely ethyl alcohol, and 25 mL of deionized water [4]. After 30 min of sonication, a homogeneous slurry was formed, then solution was transferred into an 80 mL Teflon-lined stainless-steel autoclave. Following by heated the solution to 120 °C in an electric drying oven equipped with forced convection, and kept at that temperature for 24 h. After cooled down naturally, the sample was centrifuged five times with absolute ethyl alcohol under 1000 r·min^{-1}, then dried at 85 °C.

Preparation of the Co-MOF-74

The method of synthesis of Co-MOF-74 is similar to Ni-MOF-74, except instead of substituting $Co(NO_3)_2·6H_2O$ for $Ni(NO_3)_2·6H_2O$.

Structure characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a Tecnai G2 F30 Field Emission Transmission Electron Microscope. Powder XRD patterns were collected on a Rigaku D/Max-2400 diffractometer with Cu-K_α radiation ($\lambda = 0.154178$ nm). X-ray photoelectron spectroscopy (XPS) spectra were obtained on a PHI-5702 multifunctional spectrometer using Al K_α radiation. All XPS spectra were corrected using the C 1*s* line at 284.6 eV. Infrared Spectroscopy (IR) was recorded on a VERTEX70 Fourier Transform Infrared Spectrometer.

Electrochemical measurements

The HER and OER tests were performed with a CHI 760E electrochemical analyzer (CH Instruments). All electrochemical measurements were conducted in a standard three-electrode system with an Hg/HgO as the reference electrode, and the NF/$NiCo_2O_4$ NWs MOFs as the working electrode. In the OER process, Pt foil as the counter electrode, while in the HER process, carbon rod as the counter electrode. The electrolyte solution is 1.0 mol·L^{-1} KOH solution. Linear sweep voltammetry tests with a scan rate of 2 mV·s^{-1}, cyclic voltammetry tests with a scan rate of 100 mV·s^{-1}. The current density was normalized to the geometrical and the overpotentials are 83 mV at 10 mA·cm^{-2} for HER and of 280 mV at 10 mA·cm^{-2} for OER, the measured potentials versus Hg/HgO were converted to versus RHE (reversible hydrogen electrode) according to the Nernst equation ($E_{RHE} = E_{Hg/HgO} + 0.059pH + 0.098$). The Tafel slope was calculated according to the following formula $h = b\lg(j/j_0)$, where h is the overpotential, b is the Tafel slope, j is the current density, and j_0 is the exchange current density. Ir/C (20% (*w*)) and Pt/C (20% (*w*)) disperses in 1.47 mL of a DMF solution with 30 μL of a Nafion solution (5% (*w*), Sigma-Aldrich), then ultrasonic dispersed uniformly for 4 h. Finally, the catalyst ink was coated on NF (surface 2 cm × 0.5 cm, yielding a catalyst loading of 0.4 mg·cm^{-2}).

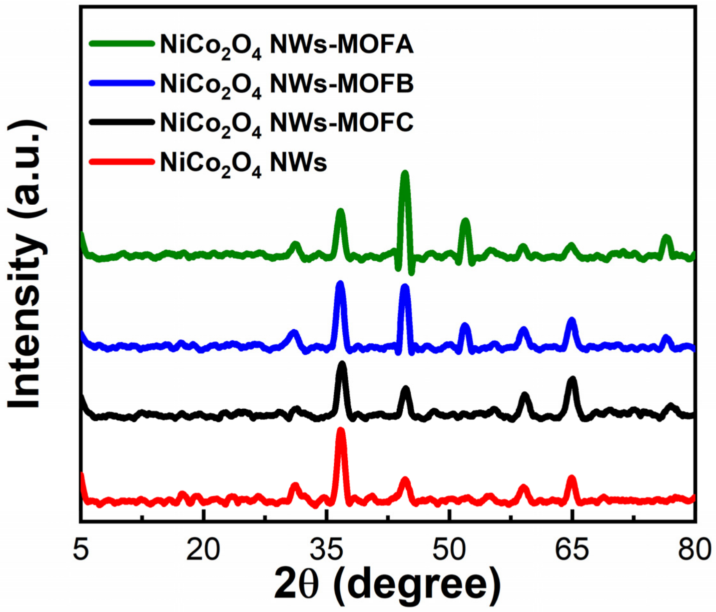

Fig. S1 XRD patterns of $NiCo_2O_4$ NWs-MOFA, $NiCo_2O_4$ NWs-MOFB, $NiCo_2O_4$ NWs-MOFC, and $NiCo_2O_4$ NWs.

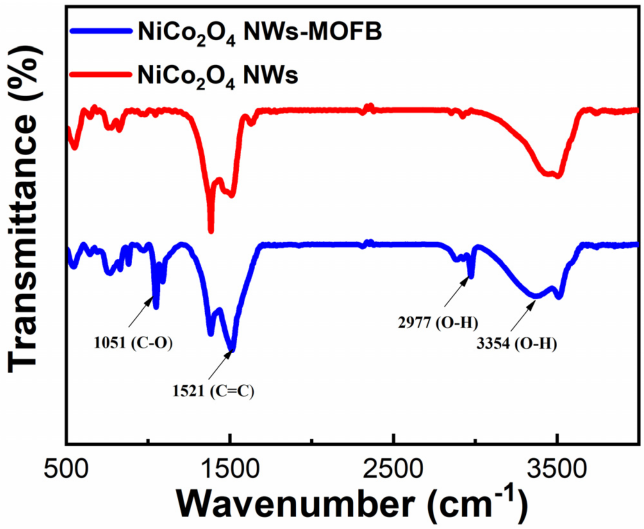

Fig S2 Confirmed by IR test that before and after MOFs grows. After growing MOFs, there are many characteristic peaks of organic functional group of the ligand.

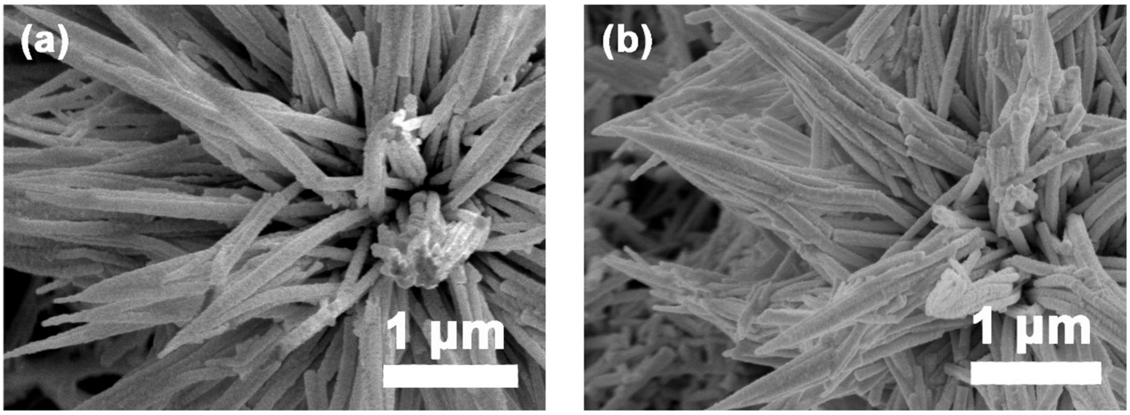

Fig. S3 (a) Morphology after OER stability test, (b) morphology after HER stability test.

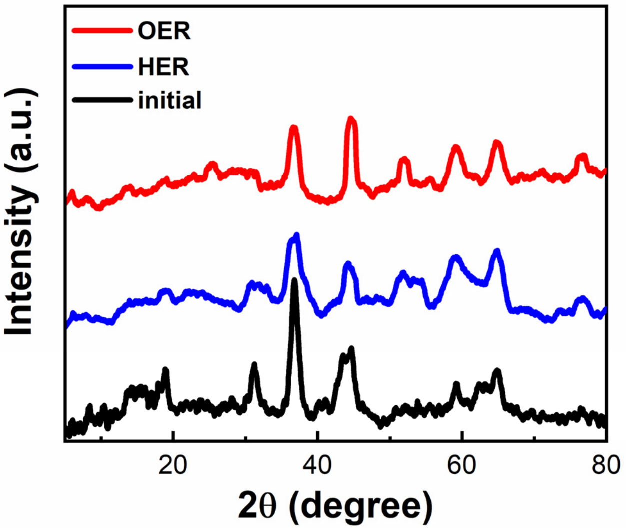

Fig. S4 XRD patterns of $NiCo_2O_4$ NWs-MOFB and after the stability test of OER and HER.

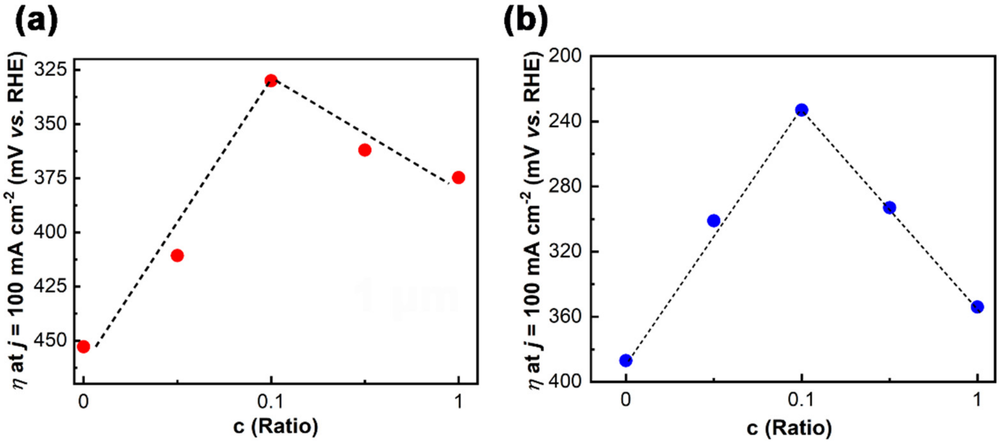

Fig. S5 Volcano plot (a) OER volcano plot (b) HER volcano plot.

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