Electronic Supplementary Information (ESI)

Carbon-incorporated NiO/Co3O4 concave surface microcubes derived from a MOF precursor for overall water splitting

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Experimental details

Chemicals and reagents

All the chemicals and reagents used in the experiment were of analytical grade and used without further purification. The $Ni(NO_3)_2 \cdot 6H_2O$, $K_3[Co(CN)_6]$, KOH and $Na_3C_6H_5O_7 \cdot 2H_2O$ were all obtained from ShangHai Aladdin Biological Technology Co., Ltd.(ShangHai, China).

Synthesis process

Synthesis of $Ni_3[Co(CN)_6]_2$ precursors and carbon-incorporated NiO/Co_3O_4 microcubes (NCMC)

In a typical procedure, 1.3 g of sodium citrate and 0.8 g of nickel nitrate were dissolved in 20 mL of deionized water (DIW) to form solution A. 1.6 g of potassium hexacyanocobaltate (III) was dissolved in 20 mL of DIW to form solution B. Then, solutions A and B were mixed under magnetic stirring for 5 min. The obtained mixed solution was aged for 24 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 70^{o}C overnight. For the synthesis of carbon-incorporated NiO/Co_3O_4 microcubes, we directly annealed the as-obtained precursors at 300 ^{o}C for 1 h and 450 ^{o}C for 2 h in air at a heating rate of 2 ^{o}C min^{-1}.

Characterization

The morphologies of the samples were observed by field-emission scanning electron microscopy (FESEM, JSM-7800F) and transmission electron microscopy (TEM, JEOL-2100F). Energy dispersive spectrometer (EDS) mapping was used to further analyse the elemental compositions of the samples. The phases and crystal structures of the materials were characterized using the powder X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer, Co Kα radiation, λ=1.7902 Å). X-ray photoelectron spectroscopy (XPS) analyze was conducted on a VG ESCALAB MKII spectrometer using an Mg Kα X-ray source (1253.6 eV, 120 W) at a constant analyzer.

Electrochemical measurements

The relevant electrochemical measurements were performed on a CHI 660E Electrochemical Workstation (Shanghai CH660E Instruments, China). Linear sweep voltammetry (LSV) method was performed in 1.0 M KOH solution in a standard three-electrode system at a scan rate of 5 mV s^{-1} with a graphite rod and a Ag/AgCl (Sat. KCl) electrode served as the counter and reference electrodes, respectively. The working electrodes were prepared by mixing the 5 mg active material (NCMC, Pt/C and RuO_2), 0.44 mL of ethanol, 0.5 mL of DIW and 60 μL of 0.5 wt.% Nafion solution by ultrasonication for at least 0.5 h and 0.4 μL of the slurry was coated onto the surface of a carbon fiber paper electrode and then dried at ambient temperature. The mass loading of each electrode is around 0.28 mg cm^{-2} on the carbon fiber paper. Potentials were referenced to a reversible hydrogen electrode (RHE): E(RHE) = E(Ag/AgCl) + (0.2 + 0.059 pH)V. The long-term stability tests were performed by a continuous current density of 10 mA cm^{-2} was used. All the data presented were corrected for iR losses and carried out at ambient temperature.

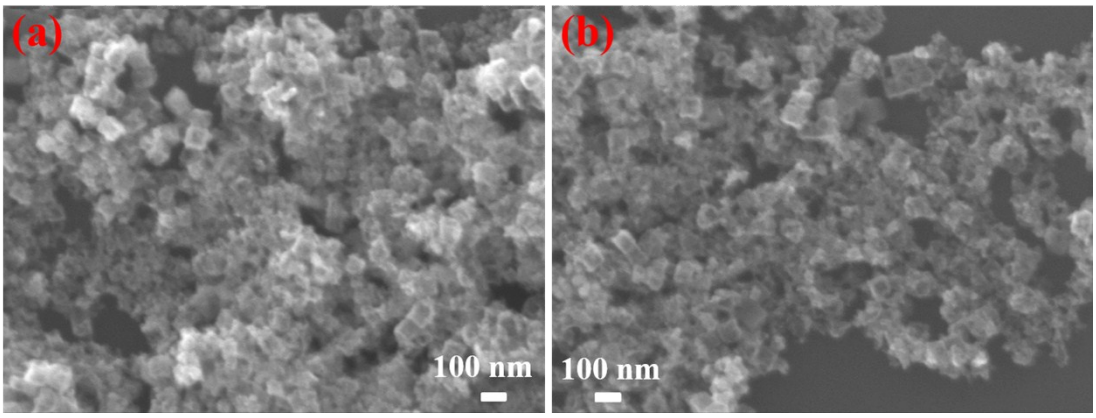

Figure S1. (a), (b) SEM images of the NCMC after stability test for OER and HER, respectively.

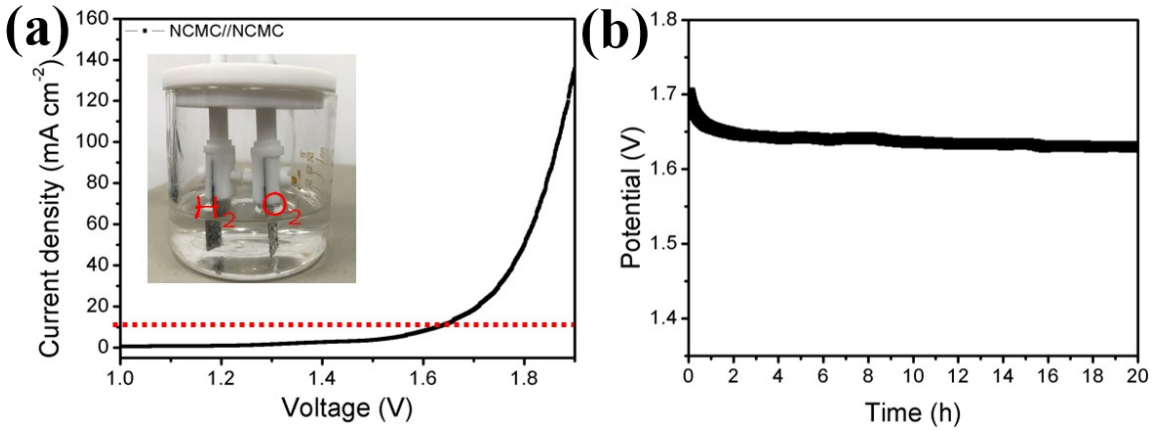

Figure S2. (a) Polarization curve of water electrolysis using NCMC as both OER and HER electrocatalysts in a two-electrode configuration. Inset: Optical photograph showing the generation of H_2 and O_2 bubbles on the NCMC. b) Chronopotentiometric curve of the NCMC for overall water splitting in a two-electrode configuration at 10 mA cm $^{-2}$ in 1 M KOH.

Table S1 Summary of various non-precious metal-based catalysts for OER.

Catalysts	**Overpotential (mV) at 10 mA cm^{-2}**	**Reference**
Fe_2O_3/CNT	410	Electrochimica Acta., **2016**, 222, 1316–1325
CoP/rGO hybrids	340	*Chem. Sci.* **2016**, *7*, 1690
γ-Fe_2O_3/CNTs	340	J. Mater. Chem. A, **2016**, 4, 5216
NiCoP/C nanoboxes	330	Angew. Chem. Int. Ed. **2017**, 56, 3897–3900
M-Co_3O_4/NPC	300	Nano-Micro Lett. **2018**, 10:15
Co_3O_4/$CoMoO_4$	318	J. Mater. Chem. A, **2018**, 6, 1639
Co_3O_4/Fe_2O_3	310	Chem. Eng. J. **2019**, 355, 336-340
NCMC	**290**	**This work**

Table S2 Summary of various non-precious metal-based catalysts for HER.

Catalysts	**Overpotential (mV) at -10 mA cm^{-2}**	**Reference**
Co_9S_8@MoS_2	430	Adv, Mater. **2015**, 27, 4752
Co-CoOx/CN	260	J. Am. Chem. Soc. **2015**, 137, 2688
$CoNi_2Se_4$	220	Chem. Commun. **2017**, 53, 5412
NCNT/Co-Fe-$CoFe_2O_4$	204	ACS Appl. Mater. Interfaces. DOI: 10.1021/acsami.8b15612
NS-MnO_2	197	Adv. Energy Mater. **2017**, 7, 1700005
$Ni_{0.9}Fe_{0.1}PS_3$@MXene	196	Adv. Energy Mater. **2018**, 1801127
CoO	191.5	ACS Nano. **2016**, 10, 8738-8745
NCMC	**169.5**	**This work**