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Reactive template-engaged synthesis of Ni-doped Co_3S_4 hollow and porous nanospheres with electronic modulation toward high-efficiency electrochemical oxygen evolution

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Experiment section

Reagents and Chemicals

Cobalt nitrate hexahydrate ($Co(NO_3)_2$ $6H_2O$) and Nickel nitrate hexahydrate ($Ni(NO_3)_2$ $6H_2O$) were purchased from Macklin. Glycerol, isopropanol and thioacetamide were purchased from Sigma-Aldrich. Commercial RuO_2 was purchased from Johnson Matthey Corporation. All the reagents were of analytical reagent grade and used without further purification.

Synthesis of Ni-Co-G spheres

In a typical preparation, 0.06 mmol of $Ni(NO_3)_2{\cdot}6H_2O$ and 0.14 mmol of $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in a mixture solution of 4 mL of glycerol and 20 mL of isopropanol under stirring for 30 min. Then, the solution was transferred into a 30 mL Teflon-lined stainless autoclave and heated at 180 °C for 6 h. The obtained product was collected by centrifugation, washed several times with anhydrous ethanol. For comparison, a series of reference samples were also synthesized under the above identical synthetic procedure except engineering the feeding amount of metal precursor. Specially, the pristine Co-G, Ni-Co-G-1, and Ni-Co-G-3 samples were synthesized by changing the amounts of $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ to be 0 and 0.2 mmol, 0.04 and 0.16 mmol, and 0.08 and 0.12 mmol, respectively.

Synthesis of Ni-Co_3S_4 hollow and porous spheres

For the synthesis of Ni-Co_3S_4 hollow and porous spheres, 10 mg of the as-prepared Ni-Co-G spheres and 20 mg of thioacetamide were dissolved in 15 mL ethanol under continuous stirring for 30 min. Subsequently, the above suspension was transferred into 30 mL Teflon-lined stainless autoclave and maintained at 180 °C for 15 h. After cooling down to room temperature, the harvested sample was washed by using water and anhydrous ethanol, eventually dried at 60 ^{o}C for 10 h.

Materials characterization

The X-ray powder diffraction (XRD) on a Rigaku D/max-RC diffractometer with a Cu Kα radiation (λ = 0.15406 nm) was employed to analyze the crystallinity of the samples. The surface chemistry of the products was determined by X-ray photoelectron spectroscopy (XPS) with a Thermo VG Scientific ESCALAB 250 spectrometer with an Al Kα light source. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) mapping images were detected on a JEOL JEM-2010F transmission electron microscope operated at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) measurements were carried out on a Hitachi S5500 scanning electron microscope.

Electrochemical measurements

All electrochemical tests were conducted on a CHI 760E electrochemical workstation at room temperature using a three-electrode configuration, in which a glassy carbon electrode (GCE), a saturated calomel electrode (SCE) and a graphite rod were served as the working electrode, the reference electrode and the counter electrode, respectively. For the preparation of catalyst ink, 5 mg of catalysts were dispersed in 0.75 mL of H_2O and 0.25 mL of ethanol under ultrasonication for 30 min. Subsequently, 20 μL of the catalyst ink was dropped on the surface of polished GCE and then dried at 40 ^{o}C. After that, 5 μL of Nafion (5 wt.%, Sigma-Aldrich) was dropped on the catalysts modified GCE surface and dried before electrochemical test. The OER measurement was estimated by linear sweep voltammetry (LSV) in O_2-saturated 1.0 M KOH solution at a scan rate of 5 mV s^{-1}. The EIS tests were conducted at 1.53 V by A.C. impedance within a frequency region (0.01 – 100000 Hz). The double-layer capacitance (C_{dl}) was determined by a series of CV tests (scan rate: 20 ~ 100 mV s^{-1}, potential region: 1.02 – 1.12 V). The *i-t* test was investigated by chronoamperometry at 1.53 V. All the potentials were referenced to reversible hydrogen electrode (RHE) in this work. The equation of potential conversion from SCE to RHE was described as follows: $E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.0591\ \mathrm{pH} + 0.242$.

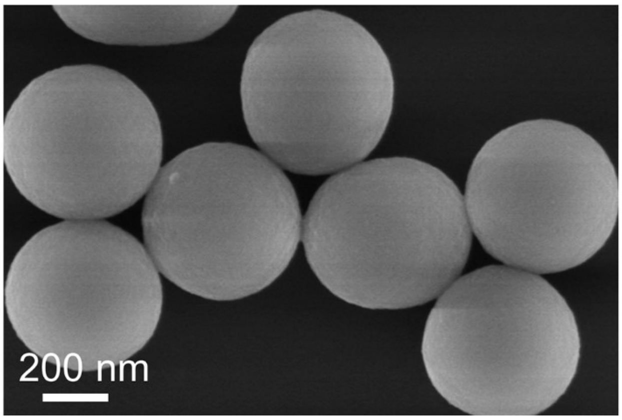

Figure S1 SEM image of Ni-Co-G spheres.

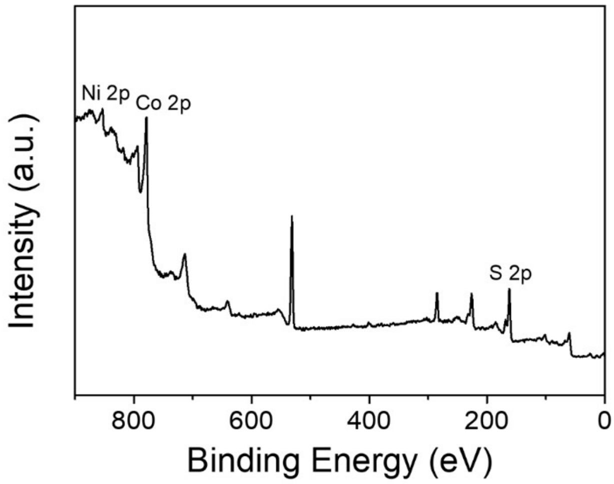

Figure S2 XPS survey of the obtained Ni-Co_3S_4-2 hollow and porous nanospheres.

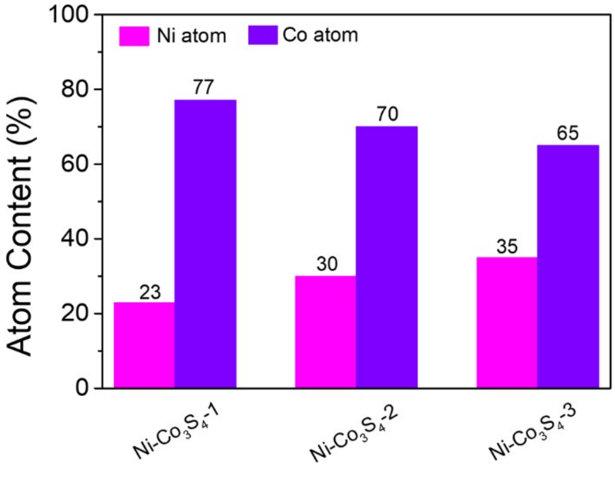

Figure S3 ICP results of the Ni-Co_3S_4 family samples.

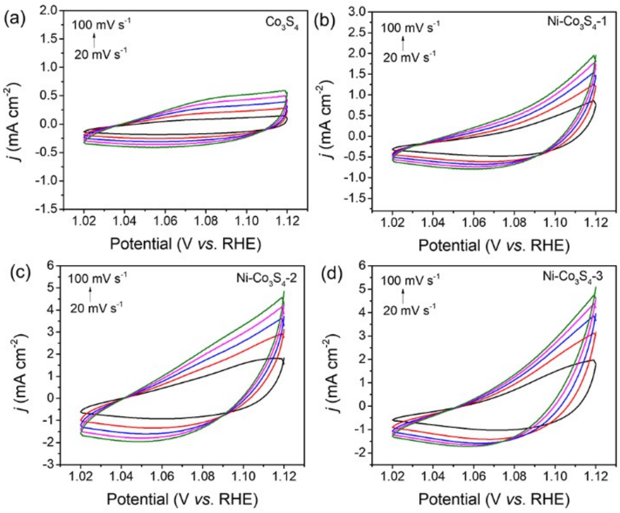

Figure S4 CV curves of the synthesized catalysts in the non-Faradaic region (1.02 – 1.12 V) obtained at different scanning rates. (a) Co_3S_4 hollow nanospheres, (b) Ni-Co_3S_4-1 hollow nanospheres, (c) Ni-Co_3S_4-2 hollow nanospheres and (d) Ni-Co_3S_4-3 hollow nanospheres.

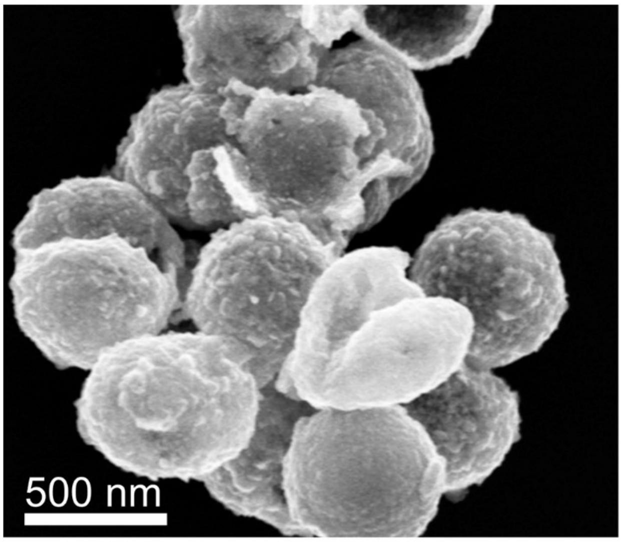

Figure S5 SEM image of the resultant Ni-Co_3S_4-2 hollow and porous nanospheres after OER stability test.

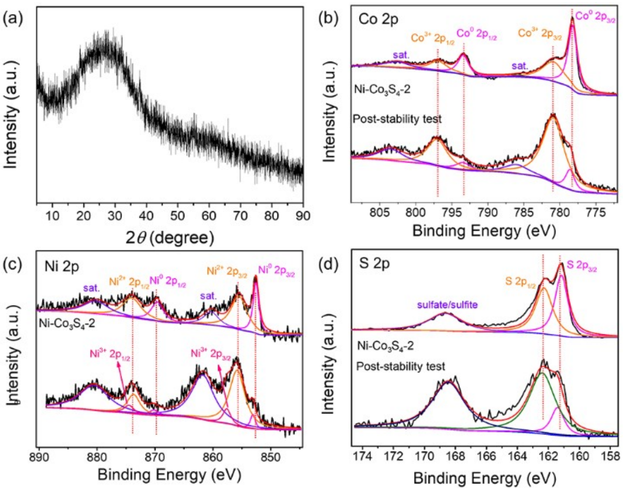

Figure S6 (a) XRD pattern and (b-d) XPS spectra of the Ni-Co_3S_4-2 after OER stability measurement.

Table S1. Comparison of the OER performance of Ni-Co_3S_4-2 hollow spheres with those of previously reported transition metal sulfide-based electrocatalysts in 1.0 M KOH.

Catalysts	η at 10 mA cm^{-2} (mV)	Tafel slope (mV·dec^{-1})	References
Ni-Co_3S_4-2	**298**	**90.5**	**This work**
$CoP_{0.5}S_{0.5}$	324	/	*ACS Catal.* **2019**, *9*, 2956
LSTL $NiPS_3$	300	88.0	*Small* **2019**, *15*, 1902427
MoS_2-NiS_2/NGF	370	/	*Appl. Catal. B -Environ.* **2019**, *254*, 15
H-CoMoS	315	74.0	*Nano Energy* **2020**, *75*, 104913
NiS/Ni interface	301	46	*J. Mater. Sci. Technol.* **2020**, *42*, 10
$Ni_8V_2(Mo_3S_4)_{11}$/Ni-Co foam	330	183	*ACS Sustainable Chem. Eng.* **2019**, *7*, 1622
N-CNTs/NiS_2@Mo_2C	320	77.5	*J. Power Sources* **2019**, *420*, 108
LMOS-4	300	45.37	*Chem. Eng. J.* **2022**, *428*, 131131
CoS_x@Cu_2MoS_4-MoS_2/NSG	351.4	61.5	*Adv. Energy Mater.* **2020**, *10*, 1903289
Ni_3S_2/NF	296	65.1	*J. Mater. Chem. A* **2019,** *7*, 18003
$CoFe_{0.2}S_x$	304	48.7	*ACS Catal.* **2020**, *10*, 1855
3D $CoS_{0.46}P_{0.54}$	302	67	*Small Methods* **2020**, *4*, 2000043