V doped hollow Co_3O_4 nanoprism with modulated electronic structure for high-performance oxygen evolution reaction

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1 Chemicals and materials

Cobalt acetate tetrahydrate, urea, sodium orthovanadate and silver nitrate with analytically pure were purchased from Shanghai Macklin Biochemical Technology Co. LTD, and used directly without further purification.

2. Characterization

The microstructure of the catalysts was observed using Scanning electron microscopy (SEM, Zeiss Ultra Plus, Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100F). The catalysts' crystallinity and purity were examined using X-ray diffractometer (XRD, Ultima IV, Rigaku). The surface elements and their chemical state of the catalysts were examined using X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi X-ray, Thermo Fisher Scientific).

3. Electrochemical measurement

Electrochemical measurements were performed in 1.0 M KOH using the standard threeelectrode system. Graphite rod, Ag/AgCl (KCl saturated) electrode, and electrocatalyst modified glassy carbon electrode (polished using α -Al₂O₃) are used as the counter electrode, reference electrode, and working electrode, respectively. The catalyst ink is prepared by dispersing 5 mg catalyst into a mixture of 480 µL H₂O, 480 µL ethanol and 40 µL Nafion. The 16 µL catalyst ink was dipped onto the glass carbon and dried naturally under room temperature. The linear sweep voltammetry (LSV) test is performed at a scan rate of 5 mVs⁻¹ with 85% IR compensation. Electrochemical impedance spectroscopy (EIS) was measured at a frequency of 0.01-10⁵ Hz at 0.5 V. The stability was evacuated at 10 mA cm⁻² using chronopotentiometry measurement. All the potentials were converted to the reversible hydrogen electrode via $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.0592 * pH$. To calculate the Faradic efficiency for overall water splitting, the current density was fixed at 50 mA cm⁻² using Ni-foam (1*1 cm²) loaded catalyst. The theoretical H₂ yield is calculated using V= V_m*It / (2Q_e*N_A), where V_m=22.4 L mol⁻¹, I=0.06 A, N_A= 6.02*10²³, Q_e=1.6*10⁻¹⁹ C.



Figure S1. SEM image of Co₃O₄.



Figure S2. SEM image of V-Co₃O₄-10.



Figure S3. SEM image of V-Co₃O₄-20.



Figure S4. N_2 ad-desorption isotherms and pore size distribution curves of V-Co₃O₄-5

and Co₃O₄.



Figure S5. XPS spectra of the catalysts.



Figure S6. EPR spectra of V-Co₃O₄-5 and Co₃O₄.



Figure S7. CV curves of the Co₃O₄, V-Co₃O₄-5, V-Co₃O₄-10 and V-Co₃O₄-20.



Figure S8. SEM image of V-Co₃O₄-5 after stability test.



Figure S9. XRD pattern of V-Co₃O₄-5 after stability test.

 Table S1 Comparison of the catalytic performance of recently reported Co₃O₄ based catalysts for OER

Catalyst	Overpotential @ 10mA cm ⁻²	Tafel	Stability	Ref
Mn-Co ₃ O ₄ /S	330 mV	68 mV dec^{-1}	20 h	1^{1}
F _{0.2} -V-Co ₃ O ₄ -350	320 mV	$75.9 \mathrm{mV} \mathrm{dec}^{-1}$	2000 cycles	2 ²
V-doped CoS ₂ NBs	290 mV	78.2 mV dec^{-1}	45 h	3 ³
P-Co ₃ O ₄ /NiO	283 mV	77 mV dec ⁻¹	20 h	44
N-Co ₃ O ₄ /N-CNs	354 mV	57.0 mV dec ⁻¹	1000 cycles	5 ⁵
Fe-doped Co ₃ O ₄	283 mV	79.08 mV dec ⁻¹	20 h	6 ⁶
V-doped CoP	340 mV	60.5 mV dec ⁻¹	10 h	77
P-Mo-Co ₃ O ₄ @CC	276 mV	53.9 mV dec ⁻¹	27 h	88
V-C03O4-5	288 mV	65.4 mV dec ⁻¹	91 h	This work

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