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Supporting Information

Ternary PtVCo Dendrites for Hydrogen Evolution Reaction, Oxygen Evolution Reaction, Overall Water Splitting and Rechargeable Zn–Air Batteries

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Zn-air battery measurements

The air-electrodes used for Zn-air battery were the composite catalysts loaded on carbon cloth. The catalyst ink was prepared as follows: 3 mg catalyst was first uniformly dispersed in 600 μ L absolute ethanol/nafion (0.5% nafion) to form a homogeneous solution. Then, the solution was dropwisely added onto the hydrophobic side of the carbon cloth (1 cm²), and dried naturally. A zinc flake with the thickness of 0.5 mm was utilized as the anode. Zn-air battery test installation was assembled like **Figure S5**. All Zn-air battery tests were accomplished by the CHI-440 electrochemical workstation (CH Instruments Inc.) in 6 M KOH containing 0.2 M ZnAc aqueous solution at ambient atmosphere. The discharge power density was acquired by linear sweep voltammograms (LSV) at a scan rate of 10 mV s⁻¹ and calculated by the **Equation S1**:

Power density $(mW \ cm^{-2}) = voltage (V) \times current density (mA \ cm^{-2})$ Equation S1

Galvanostatic charge–discharge curves were obtained by chronopotentiometry at current density of 10 mA cm⁻² with discharging 5 min and charging 5 min.

Table S1. The Pt calculated loading percentage and comparison of the electrochemical performance of different samples for OER

Sample	Pt (wt.%) ^a	E _{OER, 10} (V vs. RHE) ^b	E HER, 10 (V vs. RHE) ^c
PtVCo	20.5	1.59	-0.045
PtV	20.3	1.85	-0.092
PtCo	20.6	1.64	-0.058
IrO ₂	0	1.58	
Pt/C	20		-0.064

and HER (1 M KOH solution).

^a Calculated according to the initial addition quantities of Pt, V, Co precursors.

^b The E _{OER, 10} was the OER overpotential at a current density of 10 mA cm⁻¹.

^c The E _{HER, 10} was the HER overpotential at a current density of 10 mA cm⁻¹.

 Table S2. The comparison of the electrochemical performance of different catalysts for over-water splitting. (1 M KOH aqueous solution).

Sample	E _{OER, 10} (V vs. RHE) ^a	E _{HER, 10} (V vs. RHE) ^b	Gap (V) ^c
PtVCo	1.61	-0.031	1.641
PtV	1.88	-0.128	2.008
PtCo	1.65	-0.054	1.704
IrO ₂	1.57		
Pt/C	1.80	-0.067	1.867

^a The E _{OER, 10} was the OER part overpotential at a current density of 10 mA cm⁻¹ of the process combining HER and OER. ^b The E _{HER, 10} was the HER part overpotential at a current density of 10 mA cm⁻¹ of the process combining HER and OER. ^c Gap (V) = E _{OER, 10} (V vs. RHE) - E _{HER, 10} (V vs. RHE)



Figure S1 (a, b) The typical SEM images of the PtVCo sample.



Figure S2 The representative TEM images of (a) PtV and (b) PtCo alloys.



Figure S3 The XPS survey scan spectra of the PtVCo dendrites.



Figure S4 (a) CV curves of PtVCo, PtV, PtCo and commercial Pt/C under static condition in 0.1 M KOH solution at a scan rate of 10 mV s⁻¹. (b) LSV curves of PtVCo, PtV, PtCo and commercial Pt/C in a O₂-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm.



Figure S5 The self-assembled rechargeable Zn-air battery test installation: the cathode (red electrode clip) was the carbon cloth and nickel foam; the anode (black electrode clip) was the zinc flake conducted by the copper slice; the electrolyte was 6 M KOH aqueous solution containing 0.2 M ZnAc.