

Self-assembly of Bimetallic Polyoxometalates and Dicyandiamide to form Co/WC@NC for Efficiently Electrochemical Hydrogen generation

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Experimental Sections

Chemicals and Reagents.

Na₂WO₄•2H₂O, Na₂CO₃, NaCl and dicyandiamide (DCA) were purchased from Aladdin. NaClO₄, Co(NO₃)₂, KCl, 85% H₃PO₄ solution and HCl were purchased from Macklin. All chemicals were purchased from commercial sources and used as received without further purification. Nafion solution (5 wt.%) was purchased from Alfa Aesar. The water used throughout all experiments was purified through a Millipore system.

Characterization.

The powder X-ray diffraction (PXRD) pattern was collected using

Siemens D5005 diffractometer. At 293 K, the Cu-K α ($\lambda=1.54118$ Å) radiation range is $5^\circ \sim 80^\circ$ (2θ). A transmission electron microscope (TEM, JEOL-2100F) and an energy dispersive X-ray detector (EDX, SU8000 ESEM FEG) were used to analyze the microstructure. Raman spectra was obtained by JY Labram HR 800. Using Al K α as the X-ray source, X-ray photoelectron spectroscopy (XPS) measurements were performed on the PHI Quantera SXM (ULVAC-PHI). The N₂ adsorption test was carried out on an automatic volume adsorption device (Belsorp mini II).

Preparation of Co₄P₄W₃₀ precursor.

1) Co₄P₄W₃₀ was synthesized by the previously reported literature [S¹]. In detail, Na₂WO₄.2H₂O (100 g) was dissolved into 350 mL of water, and the solution was heated to boiling. When the temperature rose to 110 °C, 150 mL 85% H₃PO₄ was slowly dispersed to the boiling solution and the resulting yellow-green solution was refluxed for 5-13 hours. After cooling, 100 g solid KCl was added, and the precipitated product of P₂W₁₈ was collected.

2) P₂W₁₈ (20.0 g) was dissolved in 50 mL of H₂O and heated gently. After the solution was dropped to room temperature, 15 g of NaClO₄ was added. After stirring for one hour the precipitate was filtered out, Na₂CO₃ (1 M) was dropwise added to the filtrate, and the precipitate Na₁₂P₂W₁₅O₅₆ (abbreviated P₂W₁₅) was gathered by standing.

3) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.73 g, 2.5 mmol) was dissolved in 50 mL of sodium chloride solution. Solid P_2W_{15} (5.0 g, 1.25 mmol) was heated with stirring to dissolve, with concentrated hydrochloric acid to adjust $\text{pH}=3$, the original light pink solution turned to red-brown solution revealing a homogeneous green solution. The obtained solution was kept overnight at 5 °C to obtain the $\text{Co}_4\text{P}_4\text{W}_{30}$.

Preparation of Co/WC@NC.

0.1 g of $\text{Co}_4\text{P}_4\text{W}_{30}$, 0.7 g of DCA, and 0.2 g of cobalt nitrate were dissolved in 10 mL of water. After stirring for some time, the mingled solution was heated to a boil to remove the solvent. Next, the calcination process was carried out in two parts under a nitrogen atmosphere. In the first stage, the calcination temperature rised to 500 °C at a rate of 2 °C min^{-1} and kept for 30 minutes; in the second stage, the temperature went up to 700 °C at a rate of 5 °C min^{-1} and maintained for 2 hours. Finally, the catalyst **Co/WC@NC** was obtained by natural cooling to room temperature.

Preparation of WC@NC.

The synthesis process of **WC@NC** as comparison sample is basically the same as that of **Co/WC@NC** except the addition of cobalt nitrate correspond to 0.1 g $\text{Co}_4\text{P}_4\text{W}_{30}$ and 0.7 g DCA dissolved in 10 mL H_2O . In the first stage, the calcination temperature rised to 500 °C at a rate of 2 °C min^{-1} and kept for 30 minutes; in the second stage, the

temperature went up to 700 °C at a rate of 5 °C min⁻¹ and maintained for 2 hours.

Preparation of Co@NC.

Co@NC also as a comparison sample, the synthesis process is similar to that of Co/WC@NC except for the addition of Co₄P₄W₃₀.

Preparation of different calcination temperatures samples.

The synthesis process is basically the same as that of Co/WC@NC except the addition of cobalt nitrate. The calcination process is the same, but the calcination temperature is changed.

Preparation of different distinct ratios samples.

The synthesis process is basically the same as that of Co/WC@NC except the addition of cobalt nitrate. The ratio of Co₄P₄W₃₀ to dicyandiamide was changed as the contrast sample.

Preparation of different mass loadings samples.

The synthesis process is basically the same as that of Co/WC@NC. The quality of the samples decomposed during the preparation of the working electrode was different as contrast samples.

Preparation of work electrode.

4 mg of the catalyst material was dispersed in 200 μL of deionized water, 200 μL of ethanol solution and 30 μL of Nafion solution, and ultrasonicated for 30 minutes to form a homogeneous ink.

Electrochemical measurements.

All electrochemical experiments were carried out tests on **CHI660E** electrochemical workstation, using the three-electrode system for examination, the Ag/AgCl (saturated KCl solution) electrode as reference electrode, a platinum electrode for the counter electrode, with a diameter of 3 mm glassy carbon disk electrode as the working electrode. 4 mg composite material was dispersed into a mixed solution containing 200 μL deionized water, 200 μL of ethanol and 30 μL 0.5 wt% Nafion by ultrasonic wave. In this case, mass loading was 0.66 mg cm^{-2} . After evenly dispersed, 5 μL of the liquid was dropped on the surface of the working electrode with a pipette gun. Before electrochemical measurement, high purity Ar gas saturated 0.5 M H_2SO_4 solution 5 min, and the reference electrode used for the calibration. CV scan rate was 5 mV s^{-1} ; linear sweep voltammetry (LSV) was used to evaluate the catalytic performance of the catalyst, and the sweep rate was 5 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) measurement range was $0.01 \sim 10^5 \text{ Hz}$, and the amplitude was 0.01 V.

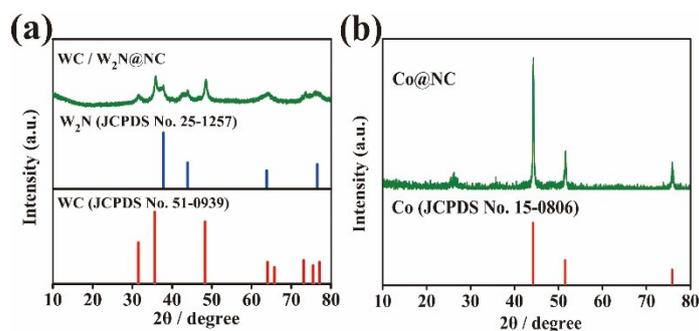


Figure S1. powder X-ray diffraction (PXRD) patterns of (a) WC/W₂N@NC and (b) Co@NC.

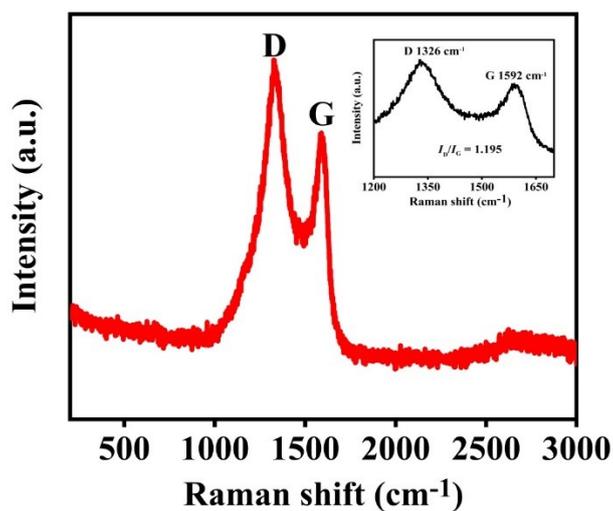


Figure S2. Raman spectrum of Co/WC@NC.

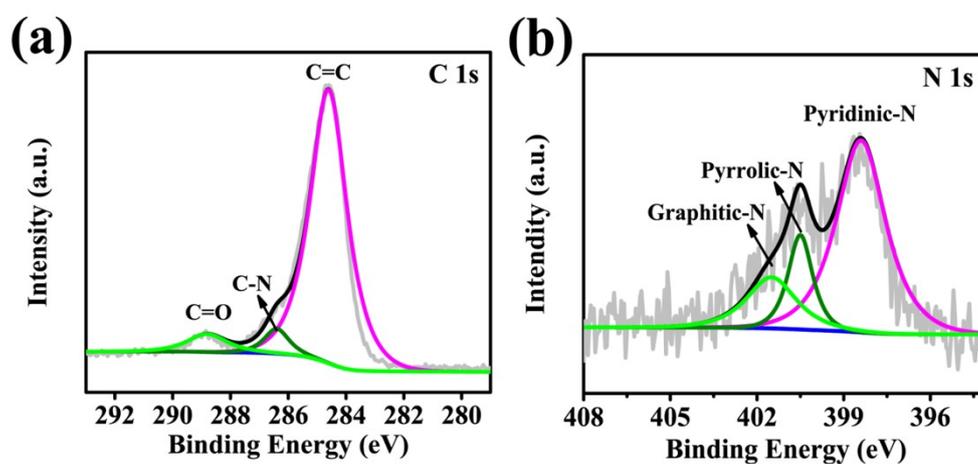


Figure S3. XPS spectra of (a) C and (b) N for Co/WC@NC.

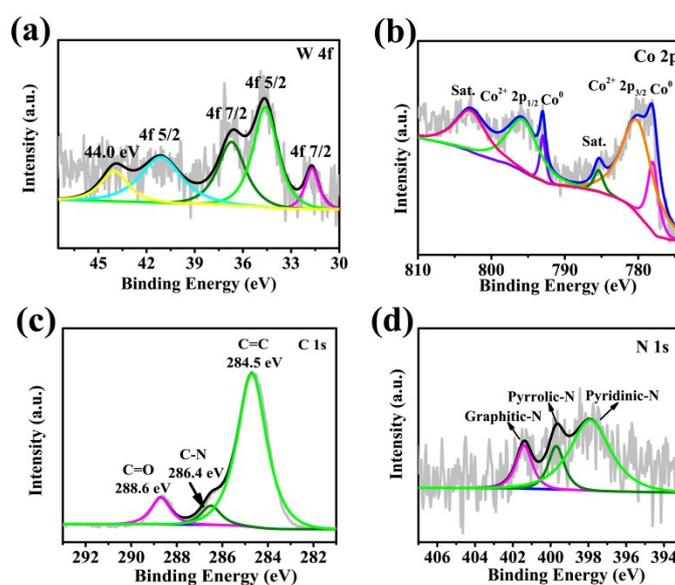


Figure S4. XPS spectra of (a) W, (b) Co, (c) C and (d) N for WC@NC.

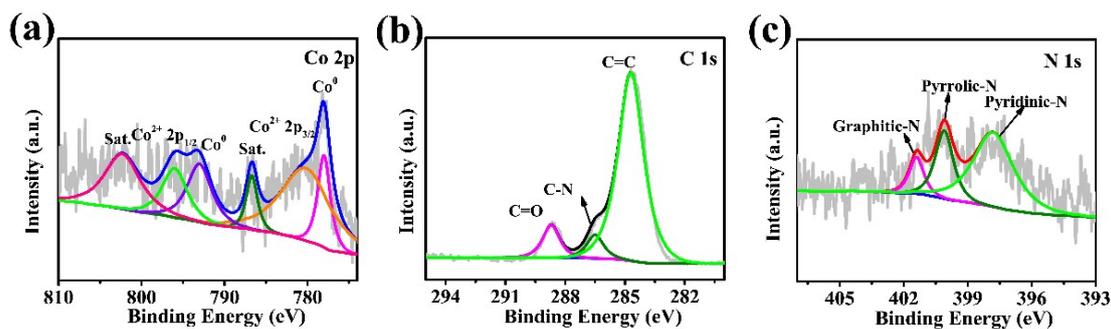


Figure S5. XPS spectra of (a) Co, (b) C, and (c) N for Co@NC.

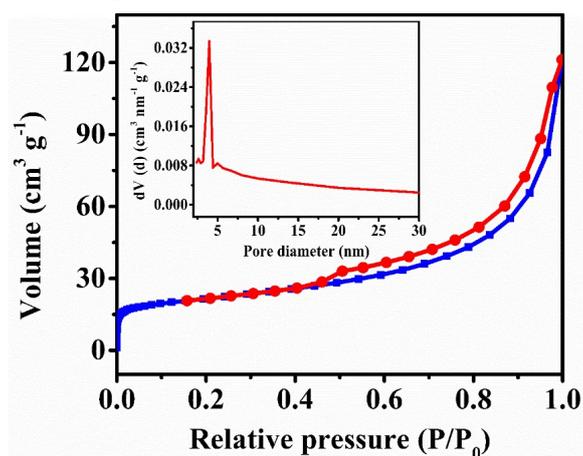


Figure S6. N₂ sorption isotherm of Co/WC@NC. Insets: pore size distribution by DFT method.

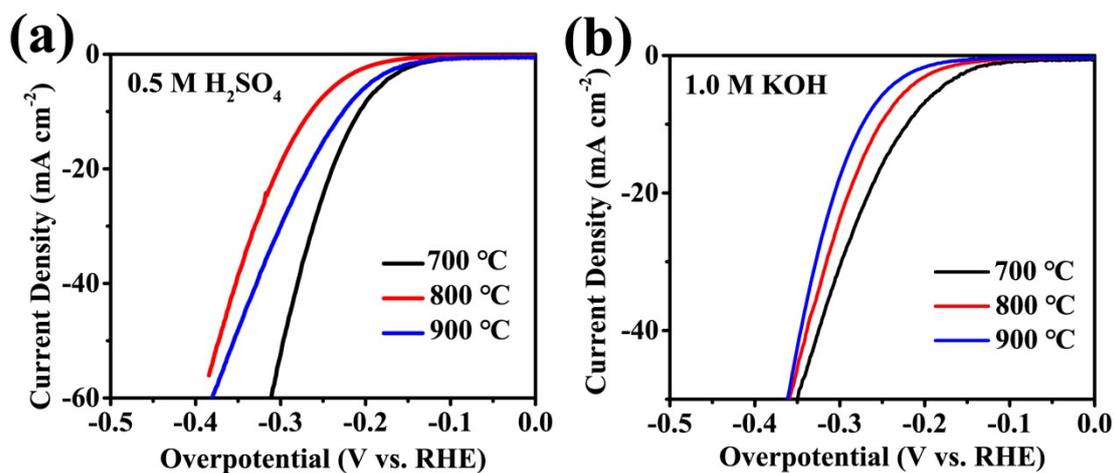


Figure S7. Polarization curves of the WC@NC catalyst at different temperature (700, 800, 900 °C).

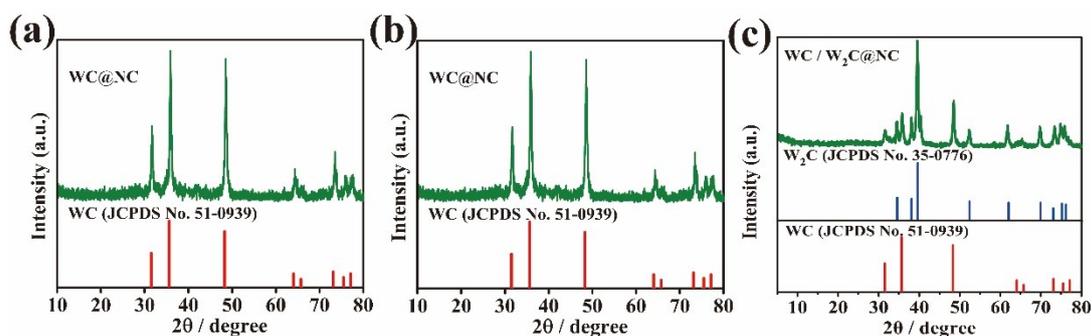


Figure S8. powder X-ray diffraction (PXRD) patterns of WC@NC with different temperature (700, 800, and 900 °C).

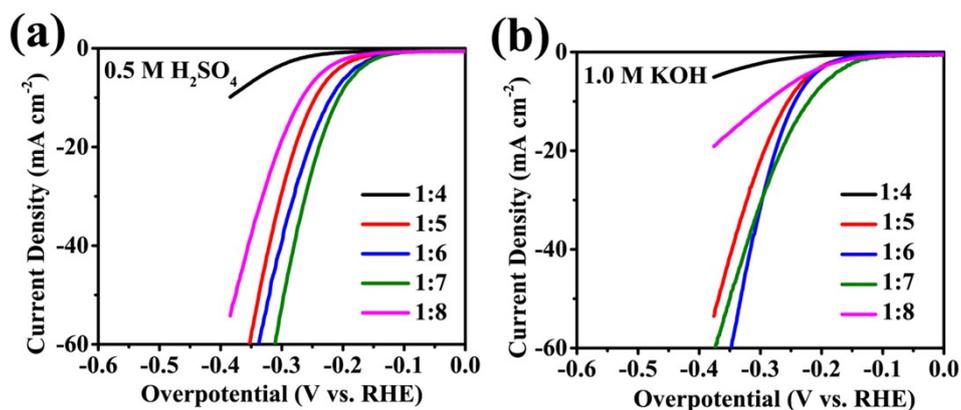


Figure S9. Polarization curves of the WC@NC catalyst with different ratio of polyoxometalate to dicyandiamide.

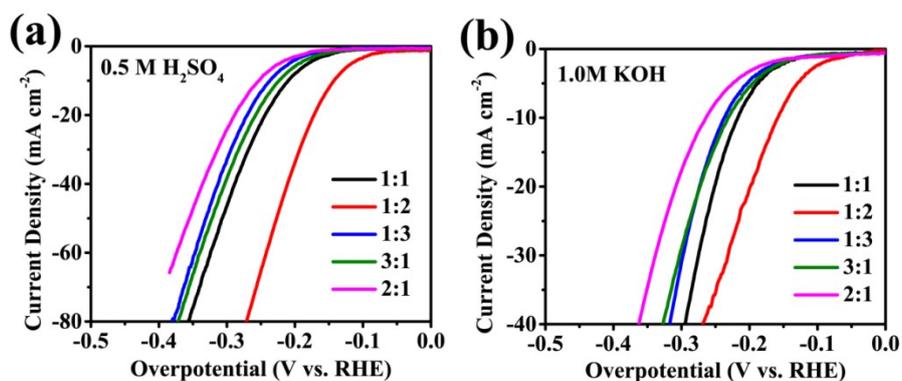


Figure S10. Polarization curves of the Co/WC@NC catalyst with different ratio of polyoxometalate to cobalt nitrate.

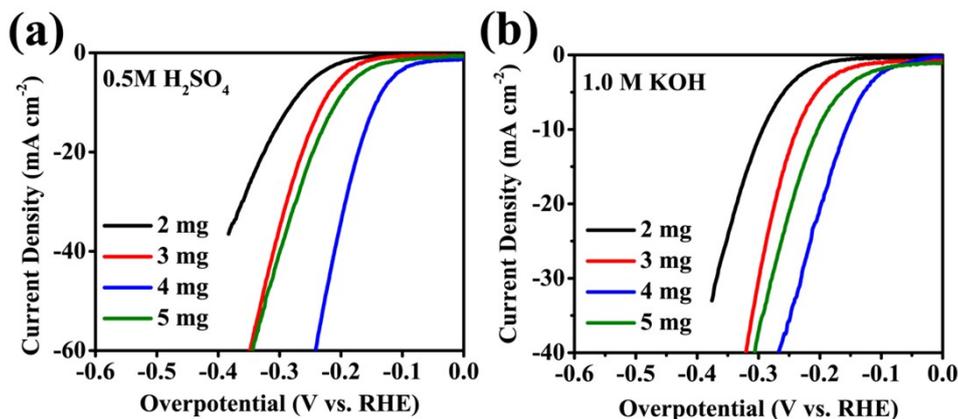


Figure S11. LSVs of Co/WC@NC with different quality load (0.33, 0.50, 0.66 and 0.83 mg cm⁻²).

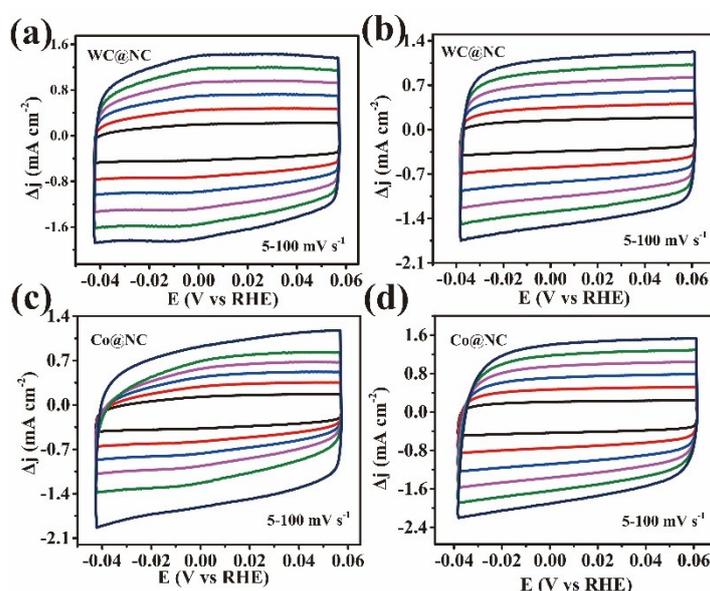


Figure S12. (a) (c) CV plots of WC@NC and Co@NC at a scan rate with ranging from 5, 10, 25, 50 and 100 mV s⁻¹ in 0.5 M H₂SO₄ solution and (b) (d) CV plots of WC@NC and Co@NC at a scan rate with ranging from 5, 10, 25, 50 and 100 mV s⁻¹ in 1.0 M KOH solution.

Table S1. Atomic percent of different catalysis by XPS measurement.

Catalysts	Elemental composition (at %)				
	C	N	Co	W	P
Co/WC@NC	93.21	4.45	0.7	1.31	0.33
WC@NC	98.47	1.11	0.37	0.04	--
Co@NC	98.74	1.08	0.17	--	--

Table S2. HER performance for transition metal-based carbide.

Catalyst	Electrolyte	Overpotential	Tafel slope (mV dec ⁻¹)	Stability	Ref.
		(mV) η ₁₀			
Co/WC@NC	0.5 M H ₂ SO ₄	142	93	24 h at 10 mA cm ⁻²	This

	1.0 M KOH	158	96	2000 cycles	work
Co ₆ W ₆ C@NC	0.5 M H ₂ SO ₄	59	45.39	50 h at 10 mA cm ⁻²	[S2]
Ni(OH) ₂ -WC/NF	1.0 M KOH	74	67	12 h at 10 mA cm ⁻²	[S3]
				3000 cycles	
W ₂ C/C NFs	1.0 M KOH	81	53.5	10 h at 10 mA cm ⁻²	[S4]
				3000 cycles	
W-Mo _x C/C	1.0 M KOH	178	54.3	12 h at 10 mA cm ⁻²	[S5]
				2000 cycles	
W ₂ C/W	0.5 M H ₂ SO ₄	132	84.9	10 h at 10 mA cm ⁻²	[S6]
Mo ₂ C/W ₂ C	0.5 M H ₂ SO ₄	140	51		
	1.0 M KOH	132	76	5000 cycles	[S7]
WC/NC	0.5 M H ₂ SO ₄	156	64	10 h at 10 mA cm ⁻²	[S8]
				1000 cycles	
Fe ₃ W ₃ C	0.5 M H ₂ SO ₄	226	91	10 h at 10 mA cm ⁻²	[S9]
				1000 cycles	
WC@rGO	0.5 M H ₂ SO ₄	199	80	2000 cycles	[S10]
W ₂ C/WS ₂	0.5 M H ₂ SO ₄	133	70		
	1.0 M KOH	105	84	20 h at 10 mA cm ⁻²	[S11]

Reference

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