

Electronic Supplementary Information

Template-Assisted Synthesis of CoP Nanotubes to Efficiently Catalyze Hydrogen-Evolving Reaction

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Experimental Section

Chemicals and Materials: Al foil (purity: 99.99%, thickness: 0.3 mm) was purchased from Alfa Aesar. NaH_2PO_2 and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) was bought from Sigma-Aldrich. Other chemicals used were bought from Beijing Chemical Corporation. All the reagents were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of CoP NTs and CoP NPs: Porous AAO films were prepared according to reported method (H. Masuda, K. Fukuda, *Science*, 1995, **268**, 1466). As-synthesized AAO films (1 g) were soaked in 0.5 M cobalt chloride ethanol solution for 2 h, followed by drying in a vacuum oven at 80 °C. To impregnate the walls of the template with cobalt chloride completely, all the soaking process were assisted with sonication and repeated twice. The obtained pink films and NaH_2PO_2 were put at two separate positions in a porcelain boat with NaH_2PO_2 at the upstream side of the furnace, and then heated at 300°C for 2 h in a static Ar atmosphere. After that, the films were collected after cooling to ambient temperature under Ar. CoP NTs were obtained by etching AAO template with 5% HF solution and it was stable in the etching process. The CoP NPs were similarly prepared by direct phosphidation of cobalt chloride powder.

Characterizations: Powder XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical Test: All electrochemical measurements were performed at room temperature using a CHI660E potentiostat (CH Instruments, China) with a typical three-electrode setup. Glassy carbon electrode (GCE, $\Phi = 4 \text{ mm}$), graphite rod and saturated calomel electrode (SCE) were used as working, counter and reference electrode, respectively. Before each electrochemical measurement, SCE reference electrode was calibrated by a reversible hydrogen electrode (RHE) using a Pt foil immersed in 0.5 M H_2SO_4 saturated with high purity hydrogen (Y. Xu, M. Gao, Y. Zheng, J. Jiang and S. Yu, *Angew. Chem. Int. Ed.*, 2013, **52**, 8546), and all potentials in this work are reported versus RHE. A

solution of 0.5 M H₂SO₄ was used as electrolyte. Catalyst ink was prepared by dispersing 5 mg catalyst into 1 mL ethanol containing 20 μL 5 wt% Nafion and sonicated for 30 min. Then 5 μL of the catalyst ink was loaded onto a GCE with a loading of 0.2 mg/cm². Polarization curves were collected at a sweep rate of 2 mV/s over a range of -0.5 ~0.2 V. Corresponding Tafel curves were calculated from the LSV data. Durability were tested by CVs with a scan rate of 100 mV/s ranging from -0.2 to 0.2 V. The time-dependent current density curves were recorded under static overpotential of 150 mV. The number of active sites was examined by CVs at a scan rate of 50 mV/s ranging from -0.2 to 0.8 V in phosphate buffer (pH = 7). The FY was carried out under static overpotential of 250 mV, the pressure changes in cathodic compartment was monitored by a pressure sensor.

Table S1 Comparison of HER performance in acidic media for CoP NTs with other HER catalysts mentioned in the main text.

Catalyst	Loading (mg/cm ²)	Current density j (mA/cm ²)	Overpotential at the corresponding j (mV)	Ref.
CoP NTs	0.2	2	72	This work
		10	129	
double-gyroid MoS ₂	-	2	190	6c
metallic MoS ₂ nanosheets	-	10	195	6d
MoS ₃ particles	0.032	2	~190	6f
MoS ₂ /MoO ₃	-	10	~310	6h
Bulk Mo ₂ C	1.4	10	~210	6j
MoC nanocrystals	0.025	2	~200	6k
MoSe ₂ /RGO	0.16	10	~150	6l
NiMoN/C	0.25	2	~170	6o
Co _{0.6} Mo _{1.4} N ₂	0.24	10	200	6p
FeP nanosheets	-	10	~240	12c
TaCN nanoparticles	0.5	2	~280	15

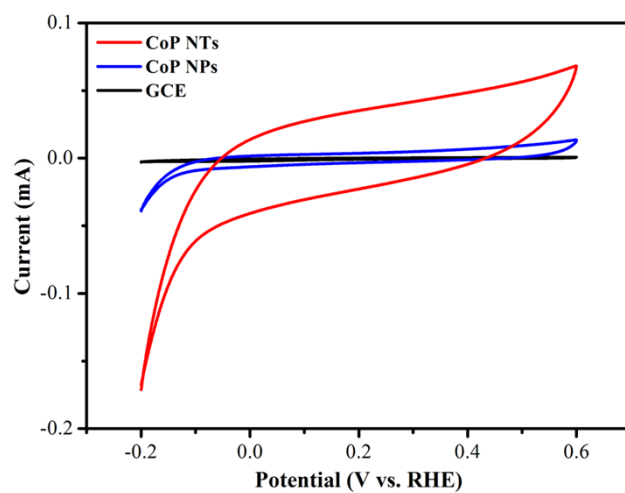


Fig. S1 CVs of CoP NTs, CoP NPs and bare GCE at a scan rate of 50 mV/s over a range of -0.2~0.8 V in phosphate buffer (pH = 7).

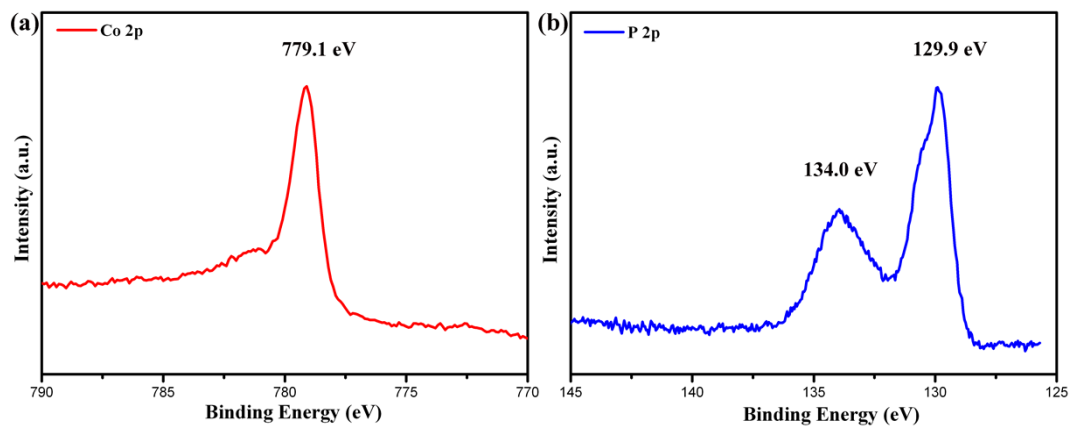


Fig. S2 XPS spectra in the (a) Co (2p) and (b) P (2p) regions of CoP NTs.