Electronic Supplementary Information

Puzzle-inspired Carbon Dots Coupling Cobalt Phosphide for

Constructing High-effective Overall Water Splitting Interface

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This file includes Experimental Section, Figure S1-S14, and Table S1-S3.

Experimental Section

Materials

Ni foam was purchased from Shenzhen Green and Creative Environmental Science and Technology Co. Ltd., Co $(NO_3)_2$ 6H₂O, NH₄F and Urea were purchased from Aladdin Reagent (Shanghai, China). RuO₂ and Nafion were obtained from Alfa Aesar (Tianjin, China). 2, 2, 6, 6-tetramethylpiperidine-1-oxyl, TEMPO (Aldrich, 98%), Silk was from the State Key Laboratory of Cocoon Genetics (Southwest University). All the reagents in our experiment were used as received. The water used throughout all experiments was purified through a Millipore system.

Preparation of the carbon dots

The white cocoons were boiled in water and then washed with deionized water and dried in 60° C for several hours. Then 0.3 g obtained silk and 30 mL 0.1 mol L^{-1} NaOH aqueous solution were transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 180° C for 12 h. After above reaction completing, the autoclave was cooled down naturally. And then, it was washed through a dialysis membrane (100 MWCO) to detach residual NaOH. The concentration of the obtained carbon dots solution is about 1.06 mg/mL.

Preparation of the CDs/CoP/NF

A piece of Ni foam (1 cm × 3 cm) was washed with acetone, concentrated hydrochloric acid and deionized water, respectively, for ensuring that its surface was well cleaned before using. The CDs/Co (CO₃)_{0.5}(OH) ·0.11H₂O/NF was prepared as follows: First, 2 mmol Co (NO₃)₂·6H₂O, 5 mmol urea, and 2.5 mmol NH₄F were completely dissolved in 30 mL prepared carbon dots solution under magnetic stirring. Second, the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave with a piece of Ni foam. Third, the autoclave was sealed and maintained at 120 °C for 3 h. After the autoclave was cooled at room temperature, CDs/Co(CO₃)_{0.5}(OH)·0.11H₂O/NF was collected and washed with water and ethanol several times and then dried at 60 °C for several hours. Finally, CDs/Co (CO₃)_{0.5}(OH)·0.11H₂O/NF was placed in the hot center of a tube furnace, and an alumina boat containing approximately 1 g of sodium hypophosphite powder was placed at the farthest upstream location within the tube furnace, and then the tube furnace was heated from room temperature to 350 °C at 3 °C min⁻¹ under Ar and maintained at 350 °C for 120 min, followed by cooling to room temperature. CoP /NF were prepared in a same condition just replacing the carbon dots solution with deionized water. CDs/0.5-CoP/NF and CDs/2-CoP/NF were prepared in same condition just adjusting the amount of carbon dots to 0.53 mg/ml and 2.12 mg/ml, respectively. The concentration of the carbon dots solution was determined by the density method. We took a 5 mL carbon dots solution by finnpipette and weighed the mass of the carbon dots solution by high-precision analytical balance. This operation was repeated several times to calculate the density of the carbon dots solution. NiP foam used the same annealing method to phosphatize.

Preparation of Pt/C and RuO₂ loaded Ni foam electrodes

10 mg commercial Pt/C or RuO_2 and 5 μ L 5 wt% Nafion solution were dispersed in 2 mL 1:1 v water/ethanol solvent by 30 min sonication to form an ink. Then the catalyst ink was coated on Ni foam with the same loading with CDs/CoP/NF.

Characterizations

The crystal structures of the products were determined by powder X-ray diffraction (Shimadzu XRD-7000, Japan). The structures and morphologies of prepared catalysis were sequentially assessed using field-emission scanning electron microscopy (FESEM, JEOL-7800F, Japan Electron Optics Laboratory Co., Japan), energy-dispersive X-ray spectroscopy (EDX, INCA X-Max 250, Japan), and transmission electron microscope (TEM, JEM-2100, Japan). The surface properties of the samples were studied by X-ray photoelectron spectroscopy (XPS, Escalab 250 xi, Thermo Scientific). The functional group analysis of the carbon dots was carried out in a Fourier transform infrared (FTIR) spectrophotometer (Bruker Tensor 27) with an ATR accessory from 500 to 4000 cm⁻¹. X-band EPR was taken at room temperature using a Bruker ELEXSYS E500 EPR spectrometer with the following parameters: microwave frequency = 9.74 GHz; modulation amplitude = 8 G; modulation frequency = 100 kHz; time constant = 40.96 ms; conversion time = 40.96 ms; nonsaturating microwave power = 1.002 mW; 30 scans were added for each spectrum. \approx 5 mg of sample was loaded in a quartz EPR tube for each EPR measurement. Raman spectra were collected with a Renishaw 2000 model confocal microscopy Raman spectrometer with a CCD detector and a holographic notch filter (Renishaw Ltd., Gloucestershire, U.K.) at ambient conditions.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system in an aqueous KOH electrolyte (1.0 M) using CDs/CoP/NF as the working electrode, a graphite plate as the counter electrode and an Hg/HgO electrode as the reference electrode. The full electrolyzer configuration was assembled using two identical CDs/CoP/NF electrodes and measured in a two-electrode cell in 1 M KOH solution. The polarization curves were surveyed via the linear sweep voltammetry (LSV) at a scan rate of 2 mV s⁻¹, and the long-term durability was investigated using potentiostatic electrolysis at fixed potentials. The current density was calibrated corresponding to the geometric area of working electrode. The geometric area values of all the samples are 0.5 cm². The value of current density is calculated via dividing the current by geometric area. The onset overpotentials were ascertained up to the initiate of linear regime in Tafel plot. All potentials measured were calibrated to RHE using the following equation: E (RHE) = E (Hg/HgO) + (0.0591 pH+0.098) V. Electrochemical impedance spectroscopy (EIS) measurements were performed at different potentials between 10⁶ to 0.01 Hz with an amplitude of 5 mV. EIS data were analyzed and fitted by Zview software.



Figure S1 Fourier transformed infrared spectrum of the carbon dots.



Figure S2 Zeta potential test results for carbon dots at 25 degrees Celsius.



Figure S3 Photographs of bare Ni foam (left), CDs/Co (CO₃)_{0.5}(OH) +0.11H₂O/NF (middle) and CDs/CoP/NF (right).



Figure S4 (a, b) SEM images of CoP /NF at different magnifications. (c) TEM image of CoP. (d) HRTEM of CoP. (e) EDX elemental mapping images of Ni, Co, and P in CoP/NF.



Figure S5 XRD patterns of CDs/CoP/NF.



Figure S6 XPS spectra of carbon dots in the (a) C 1s, (b) N 1s regions.

Name	Start BE	Peak BE	End BE	Height CPS	FWHM e	e Area	(P)	Area (N	Atomic %	Peak	Type	SF ALTH	TXFN	Backgn	PP Heig	PP At.	Title
01s	538.58	530.97	526.08	27280.13	3.04	95395	. 69	0.1	22.08	Stand	lard	2.881	5682.58	Smart	31132	25.52	Survey
C1s	292.08	284.47	278.08	28927.34	3.44	11495	2.4	0.3	67.56	Stand	lard	1	5411.3	Smart	30825	64.17	Survey
N1s	404.58	399.28	391.08	7088.97	3. 38	27985	. 08	0.05	10.36	Stand	lard	1.676	5532.63	Smart	7860.9	10.31	Survey

Figure S7 Atomic percentage of nitrogen atoms on the surface of carbon dots.



Figure S8 Nyquist plots of EIS for CDs/CoP and CoP electrode at various HER overpotentials in 1 M KOH.



Figure S9 The charge transfer resistance Rct (a) and interfacial double layer capacitor of CDs/CoP and CoP electrode VS the HER overpotentials in 1 M

The Nyquist plots of the EIS response are shown in Figure S8 (Inset is the suggested equivalent circuit model for our studied system). Both the CDs/CoP and CoP electrodes exhibited two semicircles at various overpotentials (- η = 70, 80, 90, 100, 120, 150 mV). We use the Zview software to simulate and calculate the charge transfer resistance (R_{ct}) and interfacial capacitance (C_{dl}) derived from the second semicircles at all applied overpotential. The double layer capacitance C_{dl} was calculated from the following equations:

$$f(-Z_{img}^{\prime\prime}) = \frac{1}{(2\pi C_{dl}R_{ct})}$$

where $f(-Z''_{img})$ is the frequency at maximum imaginary component of the impedance and R_{ct} are the charge transfer resistances.



Figure S10 (a) LSV curves and (b) Tafel plots for CDs/1-CoP/NF, CDs/0.5-CoP/NF and CDs/2-CoP/NF. (c,d and e) CV curves of CDs/0.5-CoP/NF, CDs/1-CoP/NF and CDs/2-CoP/NF in the window of -0.95~-0.85V vs. Hg/HgO at various scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s⁻¹). (f) The current density against the different scan rates in the window of -0.95~-0.85 V vs. Hg/HgO of obtained samples after electrochemical activation.



Figure S11 (a) LSV curves and (b) Tafel plots for CDs/CoP/NF, CoP/NF, RuO₂/NF, NiP foam and bare Ni foam with a scan rate of 2 mV s⁻¹ for OER. The chronopotentiometric curves of CDs/CoP/NF from 10 to 100 and then back to 10 mA cm⁻² with an increment of 10 mA cm⁻² every 3600 s in (c) OER tests (without iR-correction).



Figure S12 CV curves of obtained samples in the window of 0.30-0.40 V vs. Hg/HgO at various scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100

mV s−1).



Figure S13 The current density against the different scan rates in the window of 0.30-0.40 V vs. Hg/HgO of obtained samples after electrochemical activation.



Figure S14 The photograph of the two-electrode cell setup for water splitting.

Table S1 Comparison of HER performances for CDs/CoP/NF with precious metal-free self-supporting electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential(mV)	Tafel slope	Ref.
			$(mV dec^{-1})$	
CDs/CoP	Ni foam	70.6 at 10 mA cm ⁻²	68.63	This work
Co-Ni ₃ N	Carbon cloth	194 at 10 mA cm ⁻²	156.0	<i>Adv.Mater.</i> 2018, 30 ,170
N-Ni ₃ S ₂	Ni foam	110 at 10 mA cm ⁻²	-	<i>Adv.Mater.</i> 2017, 29 ,170 1584
$\frac{SrCo_{0.85}Fe_{0.1}P_{0.05}}{O_{3-\delta} nanofilm}$	Ni foam	110 at 10 mA cm ⁻²	94	<i>Adv.Mater.</i> 2018, 30 ,180 4333
Fe-Ni@NC-CN Ts	Glassy carbon dish	202 at 10 mA cm ⁻²	113.7	Angew. Chem. 2018, 130 , 9059
NC/CuCo/CuCo Ox nanowires arrays	Ni foam	112 at 10 mA cm ⁻²	55	<i>Adv. Funct.</i> <i>Mater.</i> 2018, 28 ,170 4447
Partially oxidized Ni nanoparticles	Carbon nanofibers	262 at 10 mA cm ⁻²	97.42	Nano Energy 2018, 51 ,286
Mo-doped Ni ₃ S ₂ nano-rods	Ni foam	180 at 100 mA cm ⁻²	72.9	<i>J. Mater.</i> <i>Chem. A</i> 2017, 5 ,1595

Table S2 Comparison of OER performances for CDs/CoP/NF with precious metal-free self-supporting electrocatalysts in the alkaline media.

Electrocatalyst	Substrate	Overpotential(mV)	Tafel slope	Ref.
			$(mV dec^{-1})$	
CDs/CoP	Ni foam	320 at 50 mA cm ⁻²	68.63	This work

plasma-assisted synthesized	Ni foam	280 at 10 mA cm ⁻²	87	Nano Lett. 2016, 16 ,771 8.
NiCoP cone shaped nanowire	Ni foam	370 at 100 mA cm ⁻²	116	J. Mater. Chem. A 2017, 5 ,1482 8.
Ni ₃ S ₂ @MoS ₂ /F eOOH	Ni foam	260 at 10 mA cm ⁻²	49	Appl. Catal. B 2019, 244 , 1004.
CoS ₂ nanotube	Carbon cloth	276 at 10 mA cm ⁻²	81	Nanoscale Horiz. 2017, 2 ,342.
E-Mo-NiCoP	Carbon cloth	328 at 50 mA cm ⁻²	76.7	Nano-Micro Letters, 2019, 11 , 55.
CoN	Ni foam	290 at 10 mA cm ⁻²	70	Angew. Chem. Int. Ed., 2016, 55 ,867 0-8674
Co ₃ O ₄ NW	Carbon cloth	320 at 100 mA cm ⁻²	72	Angew. Chem., 2015, 127 ,14 923-14927

Table S3 Comparison of the bifunctional water splitting activity of the CDs/CoP/NF with precious metal-free self-supporting electrocatalysts in 1M

KOH solution.

Electrocatalyst	Substrate	Overpotential(mV)	Ref.
CDs/CoP	Ni foam	1.68 at 50 mA cm ⁻²	This work
Ni ₃ S ₂	Ni foam	1.76 at 13 mA cm ⁻²	Angew. Chem. Int.
			Ed., 2016, 55 ,
			6290-6294.
NiCo ₂ S ₄	Ni foam	1.63 at 10 mA cm ⁻²	Adv. Funct. Mater.
			2016, 26 , 4660-4660.
NiSe	Ni foam	1.63 at 10 mA cm ⁻²	Angew. Chem. Int.

			Ed., 2015, 54 ,
			9351-9355.
NiMoP ₂ nanowires	Carbon	1.67 V at 10 mA cm ⁻²	J. Mater. Chem. A
	cloth		2017, 5 , 7191.
Co5Mo1.0O//Co5Mo1.0P	Ni foam	1.68 V at 10 mA cm ⁻²	Nano Energy 2018, 45 ,
nanosheets			448.
NiCo ₂ P ₂ /graphene	Ti mesh	1.61 V at 10 mA cm ⁻²	Nano Energy 2018, 48 ,
quantum dot			284.
CoS ₂ nanotube	Carbon	1.67 V at 10 mA cm ⁻²	Nanoscale Horiz.
	cloth		2017, 2 , 342.

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