Constructing Bimetallic Conjugated Coordination Polymers as Efficient Electrocatalyst for Water Splitting

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Experimental

1. Materials

All the chemicals and solvents were of analytical grade and employed without further purification. Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), nickel chloride hexahydrate (NiCl_2 \cdot 6H_2O), 2,5-dihydroxycyclohex-2, 5-diene-1,4-dione (H₂DHBQ, 98%) were purchased from Aladdin Reagent Co., Ltd. Commercial Pt/C was purchased from Aldrich, RuO₂ (99.9+%)was purchased from Maclean Chemical Reagents Co., LTD. The 5% Nafion solution was purchased from Beijing InnoChem Science & Technology Co., Ltd.

2. Sample preparation

Synthesized of Co-DHBQ: 0.2 mmol $CoCl_2 \cdot 6H_2O$ was weighed and dissolved in the mixed solution of 8 mL water, denoted as solution A. 0.1 mmol H₂DHBQ was dissolved in a mixed solution of 8 mL water, denoted as solution B. The solution A was added to the solution B drop by drop under stirring, and the mixed solution was continued to stir for 30 min after the titration was finished and then left for 3 days. The obtained dark red product was filtered and washed with 20 mL distilled water for 3 times respectively.^[S1-S2]

Synthesized of Ni-DHBQ: the same method was applied for synthesizing Ni-DHBQ expect for a substitution from $CoCl_2 \cdot 6H_2O$ to $NiCl_2 \cdot 6H_2O$.

Synthesized of Co_xNi_{1-x} -DHBQs: For the synthesis of Co_xNi_{1-x} -DHBQs (x =0, 1/2, 1/3, 1/4, 1/5, 1), the same method was applied for synthesizing Co-DHBQ expect for different ratios between Co and Ni were controlled by adjusting the amounts of $CoCl_2 \cdot 6H_2O$ to $NiCl_2 \cdot 6H_2O$. The yield of

78%, 74%, 77%, 80%, 75% and 76% based on H₂DHBQ were determined for the Co-DHBQ, Co_{1/2}Ni_{1/2}-DHBQ, Co_{1/3}Ni_{2/3}-DHBQ, Co_{1/4}Ni_{3/4}-DHBQ, Co_{1/5}Ni_{4/5}-DHBQ, and Ni-DHBQ. And the Anal. Calcd for Co-DHBQ: (CoC6H10O6): C, 30.38%; H, 4.22%; O, 40.51%; found: C, 30.55%; H, 4.17%; O, 40.56%. Anal. Calcd for Co_{1/2}Ni_{1/2}-DHBQ: (Co_{1/2}Ni_{1/2}C6H10O6): C, 30.37%; H, 4.22%; O, 40.51%; found: C, 30.41%; H, 4.16%; O, 40.33%. Anal. Calcd for Co_{1/3}Ni_{2/3}-DHBQ: (Co_{1/3}Ni_{2/3}C6H10O6): C, 30.37%; H, 4.22%; O, 40.51%; found: C, 30.42%; H, 4.23%; O, 40.61%. Anal. Calcd for Co_{1/4}Ni_{3/4}-DHBQ (Co_{1/4}Ni_{3/4}C6H10O6): C, 30.37%; H, 4.22%; O, 40.51%; found: C, 30.52%; H, 4.33%; O, 40.42%. Anal. Calcd for Co_{1/5}Ni_{4/5}-DHBQ (Co_{1/5}Ni_{4/5}C6H10O6): C, 30.37%; H, 4.22%; O, 40.51%; found: C, 30.52%; H, 4.33%; O, 40.42%. Anal. Calcd for Ni-DHBQ: (NiC6H10O6): C, 30.42%; H, 4.22%; H, 4.22%; O, 40.51%; found: C, 30.52%; H, 4.33%; O, 40.56%; found: C, 30.63%; H, 4.18%; O, 40.34%.

3. Characterization

Powder X-ray diffraction (PXRD) data were recorded on a Rigaku MiniFlex600 diffractometer by Cu-Ka radiation at 5° min⁻¹ and the measurement range was from 5.0° to 60° (2 θ) with a step of 0.020° (2 θ). Thermal gravimetric analysis (TGA) data were conducted by a METILER TOLEDO TCA/DSC1 apparatus at a heating rate of 10 °C min⁻¹ from 40 to 800°C. Fourier transform infrared (FT-IR) spectra were conducted in the wavenumber of 400-4000 cm⁻¹ on a PerkinElmer Spectrum Two infrared spectrophotometer at room temperature under N₂ atmosphere. Scanning electron microscopy (SEM) images and EDS mapping images were obtained on a JEOL JSM-7900F scanning electron microscope. N₂ sorption analysis was performed on a SSA-4300 instrument with liquid nitrogen temperature (77 K). Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2F20 electron microscope. A Thermo Fisher K-alpha was employed to conduct X-ray photoelectron spectroscopy (XPS) and the binding energies were normalized by the C 1s peak at 284.6 eV with an Al Ka Xray source (hv = 1486.6 eV). The content of Co and Ni in $Co_x Ni_{1-x}$ -DHBQs was measured by an elementar Vario EL cube inductively coupled plasma-optical (ICP) emission spectrometer.

4. Electrochemical measurements

OER performance was defined using an electrochemical workstation (CHI 760E) with a standard three-electrode setup. The reference electrode was the Hg/HgO electrode, while the carbon rod was the counter electrode. The working electrode comprised carbon paper loaded with catalysts. The

measured potentials were converted versus RHE, $E_{RHE} = E_{Hg/HgO}$ $+0.098+0.0592 \times \text{pH}$. The inks for each electrocatalyst were prepared by dispersing 1 mg of therespective sample into 960 µL of DMF containing 40 µL of a 5 wt% Nafon solution, followed by ultrasonic treatment for 30 min. Subsequently, the resulting suspension was applied onto 1 cm \times 1 cm pieces of carbon cloth using a micropipette to achieve a catalyst loading of 1 mg cm⁻², and then dried at ambient temperature for subsequent use. The overpotential (η) for the OER was calculated using the equation: $\eta = E_{RHE}$ -1.23 V. The linear sweep voltammetry (LSV) curves were obtained at a scanning rate of 5 mV s⁻¹. The TS was derived by fitting the linear section following the Tafel equation: $\eta = b \log(i) + a$. The double layer capacitance was evaluated to determine the electrochemically active surface area (ECSA) through CV scans conducted within a nonFaradaic potential range using scan rates ranging from 10 to 100 mV s⁻¹. The double layer capacitance (C_{dl}) was calculated by plotting half of the diference in current density ($\Delta J=(J_{anodic}-J_{cathodic})/2$) at a potential of 1.16 V versus RHE against the scan rate, and this data was analyzed using linear regression fitting. The electrochemical impedance spectroscopy (EIS) for OER test was carried out at a potential of 0.5 V with respect to the Hg/HgO reference electrode, with an amplitude of 5.0 mV over a frequency spectrum ranging from 0.01 to 10^6 Hz. The EIS for HER test was carried out at a potential of -0.1 V with respect to the Hg/HgO reference electrode, with an amplitude of 5.0 mV over a frequency spectrum ranging from 0.01 to 10⁶ Hz. Turnover frequency (TOF) was calculated based on the equation of $TOF = J \times A / J$ $(z \times F \times n)$, where J is the measured current density at a certain potential, A is the electrode area, z is the number of electrons for the oxidation of one molecule (4 for OER, 2 for HER, F is the Faraday constant, and n is the moles of active sites on the electrode. TON = (the number of substrate)molecules transformed in the reaction)/(the number of active centers of the catalyst involved in the reaction)



Fig. S1 The PXRD patterns of the series $Co_x Ni_{1-x}$ -DHBQs.



Fig. S2 The one-dimensional chain structure and three-dimensional space structure of the series $Co_x Ni_{1-x}$ -DHBQs.



Fig. S3 The SEM images of (a) Co-DHBQ, (b) $Co_{1/2}Ni_{1/2}$ -DHBQ, (c) $Co_{1/3}Ni_{2/3}$ -DHBQ, (d) $Co_{1/4}Ni_{3/4}$ -DHBQ, (e) $Co_{1/5}Ni_{4/5}$ -DHBQ, and (f) Ni-DHBQ.



Fig. S4 The EDS-mapping of (a) Co-DHBQ, (b) $Co_{1/2}Ni_{1/2}$ -DHBQ, (c) $Co_{1/4}Ni_{3/4}$ -DHBQ, (d) $Co_{1/5}Ni_{4/5}$ -DHBQ, and (e) Ni-DHBQ.

ICP ICP **ICP** measured **EDS** measured measured measured molar ratio sample molar ratio (Co: Co content Ni content (Co: Ni) Ni) (wt%) (wt%) Co-DHBQ 25.73 --Co1/2Ni1/2-13.76 0.52: 0.48 12.35 0.49: 0.51 DHBQ $Co_{1/3}Ni_{2/3}$ -7.46 18.26 0.29: 0.71 0.33: 0.67 DHBQ Co_{1/4}Ni_{3/4}-5.92 19.81 0.23: 0.77 0.22: 0.8 DHBQ Co1/5Ni4/5-0.18: 0.82 4.63 21.10 0.17: 0.73 DHBQ 25.64 Ni-DHBQ

Table S1 ICP and EDS data of $Co_x Ni_{1-x}$ -DHBQs (x = 0, 1/2, 1/3, 1/4, 1/5, 1).





Fig. S6 N_2 adsorption/desorption isotherms of Co-DHBQ (a), $Co_{1/2}Ni_{1/2}$ -DHBQ (b), $Co_{1/3}Ni_{2/3}$ -DHBQ (c), $Co_{1/4}Ni_{3/4}$ -DHBQ (d), $Co_{1/5}Ni_{4/5}$ -DHBQ (e) and Ni-DHBQ (f).



Fig. S7 (a) Ultraviolet absorption spectra of solid materialsotherms of the series of Co_xNi_{1-x} -DHBQs; band gap of H₂DHBQ (b), Co-DHBQ (c),



Fig. S8 XPS survey spectra of Co-DHBQ, $Co_{1/3}Ni_{2/3}$ -DHBQ and Ni-DHBQ.



Fig. S9 CV curves of Co-DHBQ (a), $Co_{1/2}Ni_{1/2}$ -DHBQ (b), $Co_{1/3}Ni_{2/3}$ -DHBQ (c), $Co_{1/4}Ni_{3/4}$ -DHBQ (d), $Co_{1/5}Ni_{4/5}$ -DHBQ (e) and Ni-DHBQ (f) in OER.



Fig. S10 The chronoamperometry curve of $Co_{1/3}Ni_{2/3}$ -DHBQ at a current density of 50 mA cm⁻².



Fig. S11 1000 cycles curve of $Co_{1/3}Ni_{2/3}$ -DHBQ for OER.



Fig. S12 CV before and after chronoamperometric test and 1000 CV cycles of $Co_{1/3}Ni_{2/3}$ -DHBQ in OER.

Catalyst	η@10 mA	Tafel slope		D (
	cm ⁻² (mV)	$(mV dec^{-1})$	Solution	KeI.
Co _{1/3} Ni _{2/3} -DHBQ	270	62	1 M KOH	This work
$Co_{1/2}Ni_{1/2}$ -CA	349	110	1 M KOH	[S3]
[Co ₃ (HHTP) ₂] _n LB nanosheets	490	83	0.1 M KOH	[S4]
Co/Cu-MOF(3)	395	94	1 M KOH	[S5]
PDA-MOF-0.1	350	66.1	1.0 M KOH	[S6]
Co Tp 3:1(Ni)	371	53.6	1.0 M KOH	[S7]
MOF 2	389	108	1.0 M KOH	[S8]
Ni-MOFs	415	93	1.0 M KOH	[S9]
Ni(PyCHO)Cl ₂	356	79	1.0 M KOH	[S10]
CoIITP[Co ^{III} C] ₂ 3	412	63.6	1.0 M KOH	[S11]
Ni-BDC-1R	225	89	1.0 M KOH	[S12]
Ni-BDC-3R	332	132	1.0 M KOH	[S13]
CoCd-MOF	353	123	1.0 M KOH	[S14]
Co-MOF-C	342	119	1.0 M KOH	[S15]
Co _{1/2} Ni _{1/2} -HIPA	367	115	1.0 M KOH	[S16]

Table S2 Comparison of the OER performance of $Co_{1/3}Ni_{2/3}$ -DHBQ with other reported coordination polymers.

Co/Cu-MOF	395	94	1.0 M KOH	[S17]
Co-BDC	392	77.2	1.0 M KOH	[S18]
Co-BPDC	428	78.8	1.0 M KOH	[S18]
Co2/3Ni1/3-MOF	325	86	1.0 M KOH	[S19]
NiMn-MOFs	280	86	1.0 M KOH	[S20]
(Co1Ni1)2Fe(III)-MOF	309	97.04	1.0 M KOH	[S21]
β-Co(OH)2/Co-MOF	405	124	1.0 M KOH	[S22]
Ni0.8Fe0.2-MOF-B	301	62	1.0 M KOH	[S23]
ZIF-62-(Co)-Fe-CC	335	44.3	1.0 M KOH	[S24]
Co-BTC-IMI	360	88	1.0 M KOH	[S25]
2D CoZIF-9(III) sheets	380	55	1.0 M KOH	[S25]
2D-Co-NS	310	81	1.0 M KOH	[S26]
CoFe-MOF	355	49.05	1.0 M KOH	[S27]



Fig. S13 CV curves of Co-DHBQ (a), $Co_{1/2}Ni_{1/2}$ -DHBQ (b), $Co_{1/3}Ni_{2/3}$ -DHBQ (c), $Co_{1/4}Ni_{3/4}$ -DHBQ (d), $Co_{1/5}Ni_{4/5}$ -DHBQ (e) and Ni-DHBQ (f) in HER.



Fig. S14 LSV before and after chronoamperometric test of $Co_{1/3}Ni_{2/3}$ -DHBQ in HER.



Fig. S15 The chronoamperometry curve of Pt/C at a current density of 10 mA cm⁻² in HER.

Catalyst	η@10 mA cm ⁻² (mV)	Solution	Ref.
Co _{1/3} Ni _{2/3} -DHBQ	177	1 M KOH	This work
Ni-NKU-100	247	1 M KOH	[S28]
Co-BDC	529	1 M KOH	[S29]
Ni-MOF	177	0.1 M KOH	[S30]
bulk NiFe-MOF	196	1 M KOH	[S30]
Co-BTC/CC	437	1 M KOH	[S31]
Fe(OH)x@Cu-MOF	112	1.0 M KOH	[S32]
Fe2Zn-MOF	221	0.1 M KOH	[S33]

Table S3 Comparison of the HER performance of $Co_{1/3}Ni_{2/3}$ -DHBQ with
other reported coordination polymers.

Table S4 TOF of $Co_x Ni_{1-x}$ -DHBQs (x = 0, 1/2, 1/3, 1/4, 1/5, 1).

catalyst	TOF for OER	TOF for HER	TON for OER	TON for HER
Co-DHBQ	0.018	0.022	3465	3565
$Co_{1/2}Ni_{1/2}$ -DHBQ	0.025	0.032	4589	4770
Co _{1/3} Ni _{2/3} -DHBQ	0.039	0.053	8345	9560
Co _{1/4} Ni _{3/4} -DHBQ	0.032	0.047	7456	8765
Co _{1/5} Ni _{4/5} -DHBQ	0.028	0.039	6443	6985
Ni-DHBQ	0.014	0.016	2123	2556



Fig. S16 High-resolution XPS spectra of O 1s for $Co_{1/3}Ni_{2/3}$ -DHBQ after the OER and HER.



Fig. S17 FTIR spectra for $Co_{1/3}Ni_{2/3}$ -DHBQ after the OER and HER.

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