Advanced FeCoNi nitro-sulfide hierarchical structure from deep eutectic solvents for enhanced oxygen evolution reaction

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3. References

1. Experimental Procedures

1.1 Chemicals and Materials

Ferric trichloride hexahydrate (FeCl₃·6H₂O, \geq 99%), cobalt trichloride hexahydrate (CoCl₂·6H₂O, \geq 99%), nickel trichloride hexahydrate (NiCl₂·6H₂O, \geq 99%), potassium bromide (KBr, \geq 99%), potassium hydroxide (KOH, \geq 85%) were purchased from Sinopharm Chemical Reagent Co., Ltd. L-cyeteine (99%) was provided by Macklin Biochemical Technology Co., Ltd. All chemicals were used directly without further purification.

1.2 Synthesis Procedures

Formation of task-specific DESs: Trimetallic-based DES was synthesized by mixing of 3 hydrated metal salts consisting FeCl₃·6H₂O, CoCl₂·6H₂O, and NiCl₂·6H₂O with L-cysteine at molar ratio of 2:1 simultaneously; 3 bimetallic-based DESs were synthesized by mixing any 2 hydrated metal salts from FeCl₃·6H₂O, CoCl₂·6H₂O, and NiCl₂·6H₂O with L-cysteine at molar ratio of 2:1, respectively. 3 monometallic-based DESs were synthesized by simply mixing hydrated metal salts including FeCl₃·6H₂O, CoCl₂·6H₂O, and NiCl₂·6H₂O and L-cysteine at molar ratio of 2:1, respectively.

Synthesis of FeCoNi-based NSs: In a typical synthesis process, NSs were synthesized through one-step DES annealing process at 350 °C for twelve hours under N₂ atmosphere without any posttreatment. FeCoNi-NS was synthesized through the annealing of trimetallic-based DES. FeCo-NS, FeNi-NS, and NiCo-NS were obtained by the annealing of the related bimetallic-based DESs (FeCl₃·6H₂O-CoCl₂·6H₂O-L-cystenie, FeCl₃·6H₂O-NiCl₂·6H₂O-L-cystenie, and NiCl₂·6H₂O-CoCl₂·6H₂O-L-cystenie, respectively). Fe-NS, Co-NS, and Ni-NS were formed through the annealing of the corresponding monometallic-based DESs including FeCl₃·6H₂O-L-cystenie, CoCl₂·6H₂O-L-cystenie, and NiCl₂·6H₂O-L-cystenie, CoCl₂·6H₂O-L-cystenie, CoCl₂·6H₂O-L-cysteni

1.3 Characterization

Differential scanning calorimetry (DSC) was performed using a Q2000 DSC (TA Instruments-Waters LLC, USA) system at a heating rate of 10 °C·min⁻¹. The task-specific DESs were run in an aluminium pan in a sealed furnace from -80 °C (keep for 5 min) before heating up to 20 °C. The IR spectra were performed on the FTIR spectrometer (Prestige 21, Shimadzu, Japan, DTGS detector) in the range of 1000 to 4000 cm⁻¹. The concentration of Fe/Co/Ni in FeCoNi-NS was measured using a JY Ultima2 inductively coupled plasma-optical emission spectrometer (ICP-OES). Before measurement, the FeCoNi-NS was diluted with 0.1 M HNO₃. Each reported datum was the average value of three independent measurements.

The surface morphology and elemental composition of samples were analyzed by a field emission scanning electron microscopy (FESEM) (Hitachi SU8010, Hitachi High-technologies Corporation, Japan) equipped with an Oxford-Horiba Inca XMax50 energy dispersive X-ray spectroscopy (EDS) at an accelerating voltage of 5 keV and 15 keV, respectively. For SEM experiments, the samples were prepared by dispersing the products in ethanol and dropping the suspension on a silicon wafer. The detailed structural features were identified under transmission electron microscopy (TEM, Tecnal G2 F20, FEI) equipped with EDS mapping. And in the high-resolution TEM (HRTEM) images, obvious crystal stripes were obtained. For TEM and HRTEM experiments, the samples were prepared by dispersing the products in ethanol and dropping the suspension on a Cu microgrid.

X-ray powder diffraction (XRD) experiments of the FeCoNi-NS were performed with Y-2000 X-ray diffractometer (λ = 1.5406 Å) using Cu K radiation at a scanning rate of 0.5 °·s⁻¹. And the measuring data were fitted by the program TOPAS 3.0 using Rietveld analysis. The X-ray photoelectron spectroscopy (XPS) experiments were carried out on an XPS, ESCA Lab250

X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) with Al Kα source. All XPS data were aligned using C 1s line at 284.6 eV fitted according to the Gaussian fitting method.

 N_2 adsorption-desorption isotherms were obtained at 77 K on Belsorp-Mini II (BEL Japan Inc., Japan) after the sample was degassed in vacuum at 573 K for 4 h.

1.4 Modification of electrode

The FeCoNi-NS modified glassy carbon (GC) electrodes were prepared by dispersing 1mg FeCoNi-NS in 0.5 mL water and 0.5 mL ethanol with 10 μ L Nafion solutions (5%) to form homogeneous inks. Then, as prepared inks (5 μ L) was drop coating on GC electrode (3 mm) with a 0.07069 cm² area. This yielded a FeCoNi-NS powder loading weight of about 0.07 mg·cm⁻². The bare GC electrode was polished with 10 μ m Al₂O₃ powder, subsequently rinsed by water and sonicated in distilled water and ethyl alcohol. The Fe-NS, Co-NS, Ni-NS, FeCo-NS, NiCo-NS, and FeNi-NS modified GC electrodes were obtained in the same procedure.

1.5 Electrochemical measurements

The electrocatalytic activity of samples for OER was studied in 1 M KOH solution (pH = 13.7) and recorded on a CHI 660E electrochemical station at ambient temperature. All tests were performed in a three-electrode electrochemical cell with an Ag/AgCl electrode (3 M KCl) and a Pt wire as the reference electrode and counter electrode, respectively. For comparison, Fe-NS, Co-NS, Ni-NS, FeCo-NS, NiCo-NS, and FeNi-NS modified GC electrodes were used as the working electrodes to investigate their electrocatalytic activities toward OER. To enhance mass transport and remove generated gas bubbles on surface of the electrode, the electrolyte was stirred at a constant rate of 300 rpm. The potential was calibrated against the reversible hydrogen electrode (RHE) using E(RHE) = E(Ag/AgCl) + 0.198 V + 0.059 * 13.7. The related polarization curves shown in the article were calibrated after *iR* correction.

The linear sweep voltammogram (LSV) curves of FeCoNi-based NSs were performed with a scan rate of 5 mV·s⁻¹ for OER in 1 M KOH. The overpotential is defined as the potential at the current density of 10 mA·cm⁻² for OER. Electrochemical impedance spectroscopy (EIS) was performed in potentiostatic mode from 0.1 kHz to 1000 kHz. Cyclic voltammograms (CV) curves were conducted from 0.1 to 0.2 V (*vs.* Ag/AgCl, 3M KCl) at different scan rates. The FE was obtained during the chronoamperometry (CA) test. The experimental evolved O₂ gas amount was measured by gas chromatography analysis (Ar carrier, molecule sieve 5A column, TCD detector). Supposing that four electrons are needed to produce one O₂ molecular, the FE could be obtained as follows: $\eta = 4F^*n/(i^*t)$, where F is the Faraday constant (96485 s·A·mol⁻¹), n is the total amount of O₂, *i* is the current passed during the process, and t is the time.

2. Results and Discussion

Herein, we first develop a facile methodology based on the task-specific deep eutectic solvent annealing method for the synthesis of a series of FeCoNi-based NSs. The task-specific DESs were prepared by simply mixing of hydrated metal salts (FeCl₃·6H₂O, CoCl₂·6H₂O, and NiCl₂·6H₂O) and L-cysteine. As FeCl₃·6H₂O-L-cysteine system for example, the glass-transition temperatures (T_g) of them at different molar ratio were studied by DSC experiment and the results were shown in **Fig. S1**. It is apparent that a eutectic was formed at a composition of 67% FeCl₃·6H₂O which was in accordance with the eutectic reported for hydrated metal salt-urea system. While, the T_g of CoCl₂·6H₂O-L-cysteine and NiCl₂·6H₂O-L-cysteine was -51.1 °C, and -49.4 °C, respectively. So, the T_g of prepared DESs was lower than that of either of the constituents, which confirmed the formation of DESs¹.



Figure S1. (a) Differential scanning calorimetry (DSC) analysis of FeCl₃·6H₂O-L-cysteine at the molar ratio of 2:1; (b) The glass-transition temperatures (T_g) of FeCl₃·6H₂O with L-cysteine as function of composition.

The interaction between hydrated metal salts and L-cysteine were examined by IR analysis. As depicted in **Fig. S2**, the stretching characteristic absorption peaks of C=O were showed red shifts in the formed DESs, which further verified the intermolecular interaction between hydrated metal salts and the selected L-cysteine². And the stretching characteristic absorption peaks including –SH and –NH of L-cysteine were disappearing, which further proving the complex interaction between the metal ion and L-cysteine.



Figure S2. FTIR spectroscopy of trimetallic-based DES (orange) and L-cysteine (black).



Figure S3. SEM image of FeCoNi-NS at low (a) and high (b) magnification.



Figure S4. (a) HRTEM image and the corresponding lattice fringes of FeCoNi-NS; (b) EDS analysis of the element distribution of FeCoNi-NS.



Figure S5. SEM images of Fe-NS (a), Ni-NS (b), Co-NS (c), FeCo-NS (d) , NiCo-NS (e), and FeNi-NS (f).



Figure S6. XRD pattern of the prepared FeCoNi-NS, and XRD data were fitted by Rietveld analysis.



It could be conjectured that the unique morphology might lead to a high surface area and hierarchical structures owing to the hybrid of 1D and 2D nanostructures. As reported, the specific surface and pore size distribution of the materials markedly influence their electrocatalytic performance^{3, 4}. So it is essential to perform the BET experiments. N₂ adsorption-desorption isotherms and pore size distributions of FeCoNi-NS were shown in **Figure S8**. The specific surface area of FeCoNi-NS was about 142 m²·g⁻¹, which was higher than other prepared NSs (**Table 1**). This suggested that the introduction of Fe and Ni significantly enhanced the specific area of the FeCoNi-NS. The hierarchical porous structure of FeCoNi-NS was confirmed by the distribution of pore size (inset in **Figure S8**). The introduction of secondary and ternary metal ion was beneficial for the designable synthesis of hierarchically electrocatalyst, which were further favourable for the release of oxygen. The N₂ absorption-desorption isotherms of Fe-NS, Co-NS, Ni-NS, FeCo-NS, NiCo-NS, and FeNi-NS were depicted in **Figure S9-S14**. It was noticed that the BET area, the mean pore size and the distribution of metal ion.



Figure S8. Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of FeCoNi-NS.



Figure S9. Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of Fe-NS.



Figure S10. Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of Co-NS.



Figure S11. Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of Ni-NS.



Figure S12. Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of FeCo-NS.



Figure S13. Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of NiCo-NS.



Figure S14. Nitrogen adsorption and desorption isotherms and the inserted corresponding pore size distribution of FeNi-NS.

The electrochemically active surface area (EASA) was a parameter related to the practical active sites for catalysis. The value of electrochemical double-layer capacitance (C_{dl}) was positively related the value of EASA, namely $C_{dl} = C_s * EASA$ (for GC in 1 M KOH, $C_s = 0.04$ mF·cm⁻²). And the C_{dl} could be calculated from the CV curves in the potential of 0.1-0.2 V vs. Ag/AgCl (3 M KCl) electrode at different scans (ranging from 1 to 100 mV·s⁻¹) (**Figure S15**). As expected, the C_{dl} of FeCoNi-NS was remarkably high compared with other NSs (**Table 1**). That is to say, the FeCoNi-NS was predicated to provide more active sites to be exposed to the electrolyte, which was compatible with the BET results (**Fig. 2d**).



Figure S15. Cyclic voltammograms of FeCoNi-NS (a), Fe-NS (b), Co-NS (c), and Ni-NS (d) modified GC electrode ranging from 0.1-0.2V (*vs.* Ag/AgCl) at a class of scan rates of 1, 10, 30, 50, 70, and 100 mV·dec⁻¹; (e) Linear fitting of the oxidation currents of the catalysts at 0.15 V *vs.* Ag/AgCl (3 M KCl) versus scan rates; (f) Electrochemical double-layer capacitance (*C*_{dl}) values of Fe-NS (I), Co-NS (II), and Ni-NS (III), and FeCoNi-NS (IV) derived from e.



Figure S16. OER performance of the RuO_2 measured in 1 M KOH. (a) LSV curves (b) Tafel slopes of RuO_2 modified GC electrode.



Figure S17. OER performance of the synthesized bi-metal NSs measured in 1 M KOH. LSV curves (a) and Tafel polts (b) of FeCo-NS (black), NiCo-NS (red), and FeNi-NS (blue) modified GC electrode using Ag/AgCl (3 M KCl) and Pt wire as the reference and counter electrode, respectively.



Figure S18. SEM (a) and TEM (b) images of FeCoNi-NS after CA test.

Sample		HBDs		
	FeCl₃·6H ₂ O	CoCl ₂ ·6H ₂ O	NiCl ₂ .6H ₂ O	L-cystenie
Fe-NS	10 mmol			5 mmol
Co-NS		10 mmol		5 mmol
Ni-NS			10 mmol	5 mmol
FeCo-NS	10 mmol	10 mmol		10 mmol
NiCo-NS		10 mmol	10 mmol	10 mmol
FeNi-NS	10 mmol		10 mmol	10 mmol
FeCoNi-NS	10 mmol	10 mmol	10 mmol	15 mmol

 Table S1.
 Related HBDs and HBAs, different ratio of HBDs and HBAs of the as-prepared samples.

 Table S2. The main diffraction peaks and the corresponding plane of FeCoNi-NS.

20	(hkl)
29.7	(100)
31.1	(020)
44.3	(004)
47.4	(030)
49.9	(122)
51.9	(1-2-2)
54.7	(13-1)
55.3	(032)
73.0	(203)
54.7	(13-1)
55.3	(032)
73.0	(203)

Table S3. OER performance comparison between the synthesized catalysts and representative transition metal nitride and sulfide catalysts published in the literature. Fe₂Ni-BPTC ^a, Fe₂Ni clusters with biphenyl-3,4',5-tricarboxylic acid ligand; NCoM-Cb-Ar ^b, argon-annealed NaCo(PO₃)₃; Am-CFDH/NCNTs ^c, amorphous CoFe double hydroxides decorated with N-doped carbon nanotubes.

Sample	Overpotential (mV)	Tafel slope (mV·dec⁻¹)	Reference
FeCoNi-NS	251	58	Our work
FeCo-NS	289	72	Our work
NiCo-NS	333	99	Our work
FeNi-NS	278	81	Our work
RuO ₂	346	71	Our work
Fe ₃ O ₄ /Co ₃ S ₄	270	56	J. Mater. Chem. A 2017 , 5, 9210-9216⁵
CoTe ₂	357	32	Angew. Chem. Inter. Ed. 2017 , 56, 7769-7773 ⁶
Tannin-NiFe	290	28	Angew. Chem. Inter. Ed. 2019 , 58, 3769-3773 ⁷
Fe ₂ Ni-BPTC ^a	365	77	Angew. Chem. Inter. Ed. 2018 , 57, 9660-9664 ⁸
CoCuW oxide	313	162	Angew. Chem. Inter. Ed. 2019 , 58, 4189-4194 ⁹
NCoM-Cb-Ar ^b	340	76	Angew. Chem. Inter. Ed. 2019 , doi: 10.1002/anie.201901813 ¹⁰
LaFe _x Ni _{1-x} O ₃	302	50	Angew. Chem. Inter. Ed. 2019 , 58, 2316-2320 ¹¹
Fe-Ni ₃ S ₂ /FeNi	282	54	Small 2017 , <i>13</i> , 1604161 ¹²
CoFe ₂ O ₄ @N-CNF	349	80	<i>Adv. Sci.</i> 2017 , <i>4</i> , 1700226 ¹³
Am-CFDH/NCNTs ^c	270	57	ChemSusChem, 2019 , doi: 10.1002/cssc.201900754 ¹⁴

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