CoTe₂-NiTe₂ heterojunction directly grown on CoNi alloy foam for

efficient oxygen evolution reaction

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Experimental section

Reagents

Sodium tellurite (Na₂TeO₃), hydrazine hydrate (N₂H₄·H₂O), Potassium hydroxide (KOH), and CoNi alloy foam (Co:Ni = 24:1, at%) with a thickness of 1 mm were employed. All chemicals used are of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. Ultrapure deionized (DI) water was used throughout this study.

Hydrothermal synthesis of CoTe₂-NiTe₂ heterojuction on CoNi alloy foam (CNT/CNF)

In general, in order to remove the contaminants on the surface of CoNi alloy foam and to increase its hydrophilicity, a piece of CoNi foam (i. e. 3.0×4.0 cm²) was cleaned by ultrasonication in 1.0 M HCl for 30 min to remove the surface oxide layer, and successively washed in water and alcohol, and finally dried at 60 °C in vacuum for 30 min. In a typical hydrothermal experiment, 0.443 g sodium tellurite (Na₂TeO₃) was dissolved in 65 mL of deionized (DI) water to form a homogeneous solution by continuous magnetic stirring for 30 min. Then different amounts of hydrazine hydrate (N₂H₄·H₂O, 4.0 ml, 3.0 ml, 2.0 ml and 1.0 ml) used as reducing agent were added into the above solution. The precursor mixture was stirred for another 30 minutes at room temperature until a homogeneous suspension was formed, and then the solution was loaded into a 100 mL Teflon-lined autoclave reactor where a piece of cleaned CoNi foam was placed against the wall. Subsequently, the autoclave reactor was sealed, heated to 200 °C (denoted as 4CNT/CNF-200C, 3CNT/CNF-200C, 2CNT/CNF-200C and 1CNT/CNF-200C) and maintained 20 hours for hydrothermal reaction. Finally, the reactor was naturally cooled down to room temperature. After the hydrothermal processing, the color of CoNi foam turned to dark black from light grey, suggesting the formation of CoTe₂-NiTe₂ heterojuction on the foam surface. The resultant sample was then rinsed successively with DI water and ethanol, and dried at 50 °C for 1 hour. We used the same procedure to prepare $CoTe_2$ at 240 °C on the Co foam, which is denoted as 3CT/CF-240C. We further change the hydrothermal reaction temperature to 180 °C, 220 °C and 240 °C comparative study (denoted as 3CNT/CNF-180C, 3CNT/CNF-220C and 3CNT/CNF-240C).

Structural characterization

The morphology, microstructure, and chemical composition of bare CoNi foam (denoted as bare CNF), 3CT/CF-240C and 3CNT/CNF-240C electrodes were examined by field-emission scanning electron microscopy (FESEM, FEG Quanta 450) and transmission electron microscopy (TEM, JEOL JEM-2100 operating at 200 keV) equipped with energy-dispersive X-ray spectroscopy (EDX). The crystalline structure of samples was studied by X-ray diffractometry (XRD, PANalytical X'Pert PRO) using Cu Ka radiation ($\lambda = 1.540598$ Å) and a PIXcel detector. The surface chemical states of bare CNF, 3CT/CF-240C and 3CNT/CNF-240C were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250 Xi), and the C (1s) line (at 284.80 eV) corresponding to the surface adventitious carbon (C–C line bond) has been used as the reference binding energy.

Electrochemical measurements

The OER performance was evaluated by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) in a three-electrode configuration in 1.0 M KOH (pH = 13.5) using a CS2350H electrochemical workstation (Wuhan Corrtest Instruments Corp., China). A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The as-fabricated CoTe₂-NiTe₂ heterojuction working electrode (3CNT/CNF-240C) was directly used as the working electrode, and the active electrode area was kept to $1.0 \times 1.0 \text{ cm}^2$. Cyclic voltammetric (CV) scans were recorded between 1.05 and 1.80 V vs. reversible hydrogen electrode (RHE) at the scan rate of 5 mV s⁻¹. The electrochemical double-layer capacitance (Cdl) of each sample was measured given that Cdl is positively proportional to the effective surface areas (ESA).

 C_{dl} can be extracted through CV scans at different rates (from 10 to 100 mV s⁻¹) in the non-faradaic potential window of -0.05 - 0.05 V vs. SCE. All current density values were normalized with respect to the geometrical surface area of the working electrode. For comparison, the electrocatalytic performance of a bare CNF and 3CT/CF-240C was also measured. All CV curves presented in this work are iR-corrected (85%), and the correction was done according to the following equation:

 $E_{\rm c} = E_{\rm m} - iR_{\rm s}$

where E_c is the *iR*-corrected potential, E_m experimentally measured potential, and R_s the equivalent series resistance extracted from the electrochemical impedance spectroscopy (EIS) measurements. Unless otherwise specified, all potentials are reported versus reversible hydrogen electrode (RHE) by converting the potentials measured vs. SCE according to the following formula:

E (RHE) = E (SCE) + 0.241 + 0.059 pH

The EIS measurements were performed in the frequency range of 10 mHz - 100 kHzunder a constant potential of 1.60 V vs. RHE.



Supplementary figures:

Fig. S1. SEM images (a-b) and EDS-EDX results (c-e) of the bare CNF.



Fig. S2. SEM images (a-b, 3CNT/CNF-240C; c-d, 3CT/CF-240C) of different samples.



Fig. S3. XRD pattern of CNT/CNF-200C sample with different N_2H_4 · H_2O addition, the standard powder diffraction patterns of Co, Ni, CoTe₂, and NiTe₂ are given for reference.



Fig. S4. (a-d) SEM images of 1CNT/CNF-200C; 2CNT/CNF-200C; 3CNT/CNF-200C and 4CNT/CNF-200C samples.



Fig. S5. CV curves (a), the overpotentials needed to achieve anodic current density at 10 mA cm⁻² (b), Tafel plots (c) and Nyquist plots (d) of the 1CNT/CNF-200C, 2CNT/CNF-200C, 3CNT/CNF-200C and 4CNT/CNF-200C samples.



Fig. S6. XRD pattern of CNT/CNF-200C sample with different reaction temperature. The standard powder diffraction patterns of Co, Ni, CoTe₂, and NiTe₂ are given for reference.



Fig. S7. (a-c) SEM images of 3CNT/CNF-180C; 3CNT/CNF-200C; 3CNT/CNF-220C and 3CNT/CNF-240C samples.



Fig. S8. CV curves (a), the overpotentials needed to achieve anodic current density at 10 mA cm⁻² (b), Tafel plots (c) and Nyquist plots (d) of the 3CNT/CNF-180C; 3CNT/CNF-200C; 3CNT/CNF-220C and 3CNT/CNF-240C samples.



Fig. S9. Equivalent circuit models of bare CNF, CT/CF and CNT/CNF samples used for EIS fitting.



Fig. S10. CV curves (a–c) of the bare CNF, 3CT/CF-240 and 3CNT/CNF-240 electrodes measured in 1 M KOH in the non-faradaic region at different scan rates ranging from 10 to 100 mV s⁻¹. J_a and J_c represent the anodic and cathodic current densities recorded at 0 V vs. SCE, respectively



Fig. S11. XRD patterns of the 3CNT/CNF-240 electrode before and after the long-term stability test for 18 hours under OER conditions.

Table S1. Comparison of electrocatalytic parameters of 3CNT/CNF-240C electrodes toward OER

Catalysts	Electrolyte	Tafel	Jgeo(Current density	Reference				
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		slope (mV dec ⁻ ¹)	in mA cm ⁻² @overpotential in mV)		
3CNT/CNF-240C		19.4	10@η=280	This work	
3CT/CF-240C	1.0 M KOH	39.6	10@η=390		
Co@CoTe ₂	1.0 M KOH	42	10@η=286	Inorg. Chem. Front. 7 (2020), 2523-2532.	
Co@0.2gNiCoTe ₂ - 240	1.0 M KOH	34	10@η=280	Inorg. Chem. Front. DOI:10.1039/D1QI00693B.	
NiCo-NiCoO ₂ nano- heterostructure	1.0 M KOH	-	10@η=327	<i>Int. J. Hydrogen Energ.</i> 46 (2021), 18936-18948	
Ni ₂ P-Co ₂ P	1.0 M KOH	58.3	10@η=340	Appl. Catal. B-Environ. 272 (2020), 118951	
NiCo- LDH/NiCo ₂ S₄/CC	1.0 M KOH	48	50@η=254	Electro. Acta. 367 (2021), 137534	
Ni ₂ P-Fe ₂ P/rNF	1.0 M KOH	-	10@η=218	J. Alloy compd. 847 (2020), 156363	
Ni ₃ Te ₂ -CoTe/CC	1.0 M KOH	68	100@η=390	Appl. Surf. Sci. 490 (2019), 516-521	
NiCo/Ni/CuO/CF	1.0 M KOH	37.9	10@η=246	<i>Int. J. Hydrogen Energ.</i> 45 (2020), 21354-21363	
Co ₈ FeS ₈ /CoS@CNT	1.0 M KOH	49	10@η=278	J. Power sources. 449 (2020), 227561	
Ni-Co ₃ SeO ₄ /rGo	1.0 M KOH	71	10@η=284	<i>Nanoscale,</i> 3 (2021), 3698-3708.	
CoNiTe ₂ /NF	1.0 M KOH	44	10@η=181	Renewable Energy, 162 (2020), 2190-2196.	
Ni _{0.4} Fe _{0.6} Te ₂ /NF		26	10@η=190		
Ni _{0.2} Fe _{0.8} Te ₂ /NF	1.0 M KOH	71	10@η=340	<i>Electrochimica Acta,</i> 371 (2021), 137830.	
Ni _{0.8} Fe _{0.2} Te ₂ /NF		53	10@η=320		

Catalysts	Ni (at%)	Co (at%)	Te (at%)	O (at%)
3CNT/CNF-240C	1.60	16.49	32.92	48.43
3CNT/CNF-240C-OER	4.39	34.48	10.5	63.99

 Table S2. Estimated compositions in 3CNT/CNF-240C catalysts obtained from EDX results.