Efficient nanointerfaces hybridization in nickel/cobalt oxide nanorods bundle structure for urea electrolysis

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1. Experimental section

1.1 Materials

Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), urea, ethanol, and potassium hydroxide were obtained from Aladdin (Shanghai) Co. LTD, Nafion (5 wt%) was purchased from Sigma-Aldrich. XC-72R carbon black was obtained from Cabot USA Co. LTD. All chemicals used were of analytical grade and used without further purification in this study. All solutions were prepared with ultrapure water with a resistance of 18.2 MΩ (Thermo Fisher Scientific Co. LTD, USA).

1.2 Synthesis of Ni/Co oxide catalysts

The preparation process was described as followed: $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ with different molar ratios (0.3:1, 0.5:1 and 1:1) were added to a solution containing 75 mL high purity water, and 5 mmol urea was then added to the above solution with stirring. The solution was pink and transferred to a Teflon lined stainless steel autoclave for hydrothermal treatment at 120 ^{o}C for 6 h and then cooled down to room temperature under ambient condition. The product was filtrated and washed with high purity water and ethanol, respectively. Afterward, the sample was dried in a vacuum oven at 60 ^{o}C for 12 h. Finally, the samples were annealed at 400 ^{o}C for 3 h at the heating rate of 2 ^{o}C min^{-1} in the air to obtain the black powders. The final materials were obtained and named Ni/Co-1 (Ni/Co molar ratio is 0.3:1), Ni/Co-2 (Ni/Co molar ratio is 0.5:1) and Ni/Co-3 (Ni/Co molar ratio is 1:1).

1.3 Electrodes preparation

The glassy carbon electrode was polished separately by 1 micron and 50-nanometer alumina powder and then the electrode was sonicated in ultrapure water for a few seconds and dried in the air before use. The working electrode was prepared by coating the catalyst ink over the glassy carbon electrode (3.0 mm diameter). The catalyst ink was prepared as follows: 5 mg catalyst, 50 μL Nafion solution, 950 μL ethanol and 1 mg carbon black were mixture and sonicated for 30 min to form a well-distributed

suspension of the catalyst. Then, the working electrode was prepared by dropping 10 µL of the catalyst suspension on the glassy carbon disk electrode and dried at room temperature.

1.4 Materials characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer using a Cu Kα (λ = 1.5405 Å) radiation source operating at 40 kV and 40 mA at a scanning rate of 5° min⁻¹. The morphology and microstructure of the product was analyzed by scanning electron microscopy (FESEM, Hitachi, S-4800 II, Japan) and transmission electron microscopy (TEM, Philips, TECNAI 12, Holland). High-resolution transmission electron microscopy (HRTEM) was performed on a FEI Tecnai G2 F30 STWIN (USA) operating at 300 kV. Surface analysis of sample was studied by X-ray photoelectron spectroscopy (XPS, Thermo Science, ESCALAB 250Xi, USA).

Debye Scherrer equation:

The crystal size was calculated for the Ni/Co catalyst were evaluated using the full width at half maximum (FWHM) and the angular position ($2\theta_{max}$) of the Co_3O_4 (511) peak according to the following Debye Scherrer equation:

$$L = \frac{0.94\lambda_{K\alpha1}}{\beta_{(2\theta)}cos\theta_{max}}$$

where L denotes the average particle size, the value 0.94 comes from spherical crystallite geometry (Cubo octahedral shape), $\lambda_{K\alpha1}$ is the wavelength of X-ray radiation (0.15405 nm), θ_{max} is the angular position at the Co_3O_4 (511) peak maximum, and $\beta(2\theta)$ is the full width at half maximum (FWHM) of the peak broadening in radians [1].

1.5 Electrochemical analysis

The electrochemical measurements were conducted in a conventional three-electrode system and a saturated calomel electrode (SCE) and a graphite electrode were used as a reference electrode and a counter electrode, respectively. The potential was transferred to RHE scale for easy comparison, uncles otherwise noted. The catalytic performance of the catalysts for urea oxidation was examined by cyclic voltammetry (CV) with the potential from 1.04 V to 1.54 V vs. RHE at a scan rate of 10 mV s^{-1} in 1 M KOH with and without 0.33 M urea solution, respectively. Furthermore, the electrolytes were 1 M KOH with different concentrations of urea (0.01 M, 0.05 M, 0.1 M, 0.33 M, 0.66 M) were researched. The electrochemical impedance spectroscopy (EIS) was recorded in the above three-electrode cell with the frequency varies from 1 mHz to 15 kHz in alkaline solution containing urea. The chronoamperometry (CA) was measured in 1 M KOH with 0.33 M urea at the potential of 1.39 V for 3600 s. For the two-electrode electrolysis, the ink of Ni/Co-2 and commercial 20 wt.% Pt/C was dropped on a glassy carbon electrode with the catalysts loading about 0.4 mg cm^{-2} as the anode and cathode, respectively. The linear sweep voltammetry (LSV) was scanned at 5 mV s^{-1}. All the tests were measured at room temperature (about 25°C).
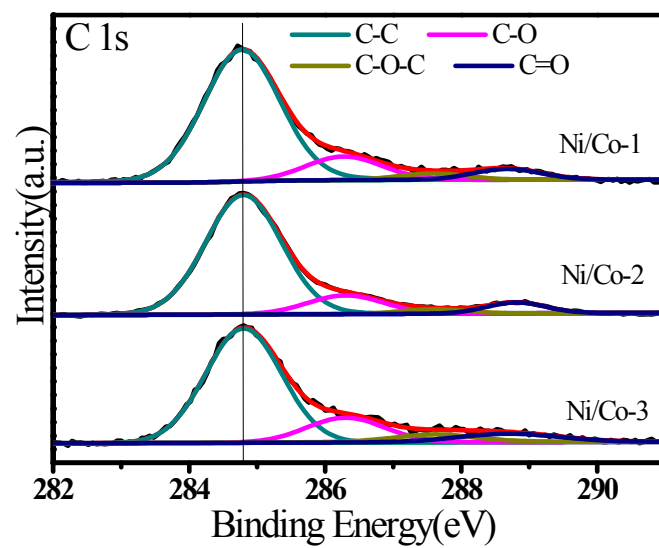
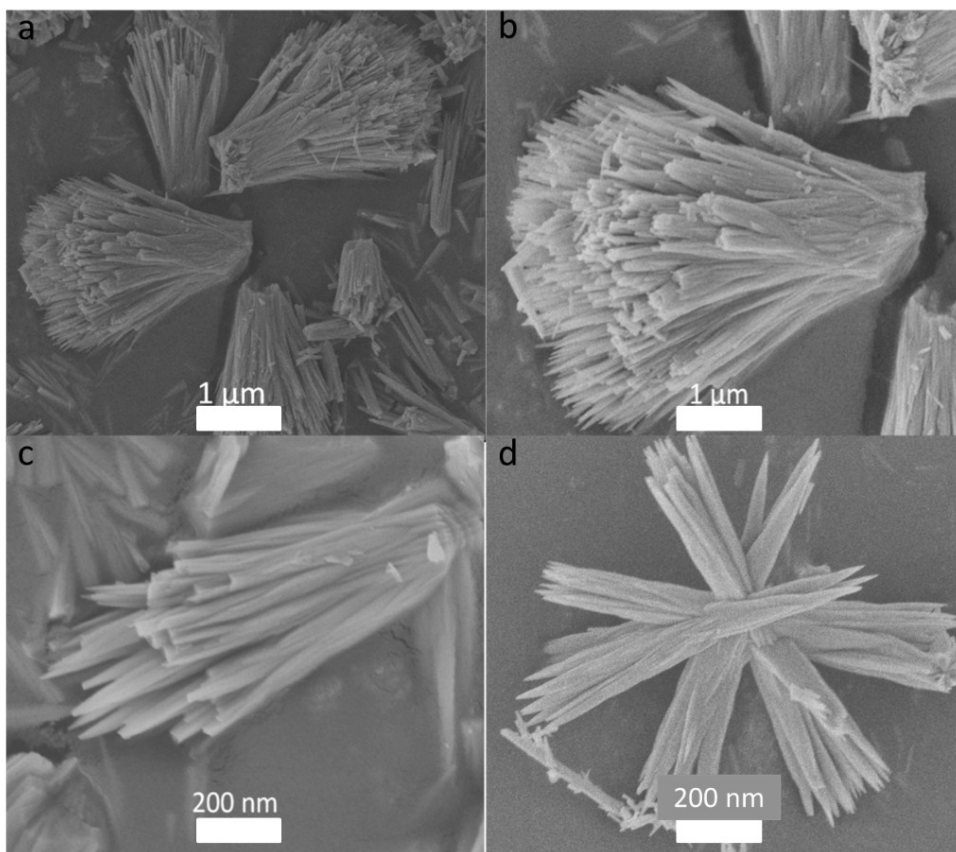**Figure S1.** XPS spectra of C 1s of different materials.

Figure S2. SEM images of the Ni/Co oxide-2 before thermal annealing (a-d).

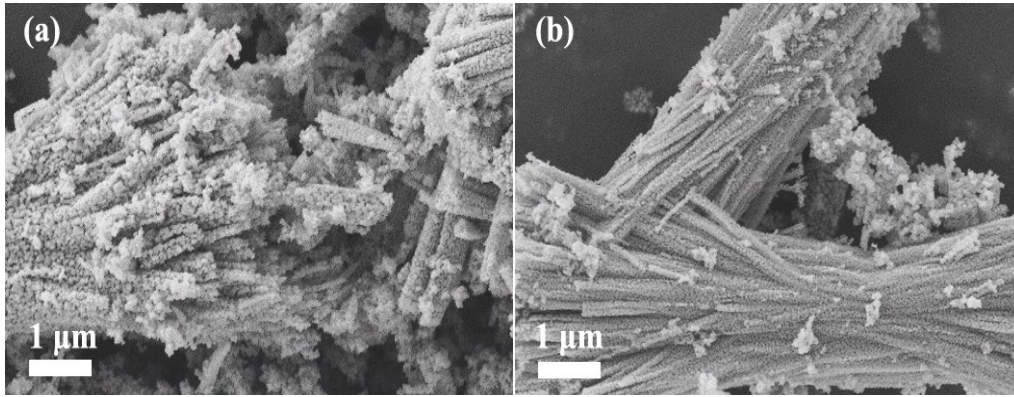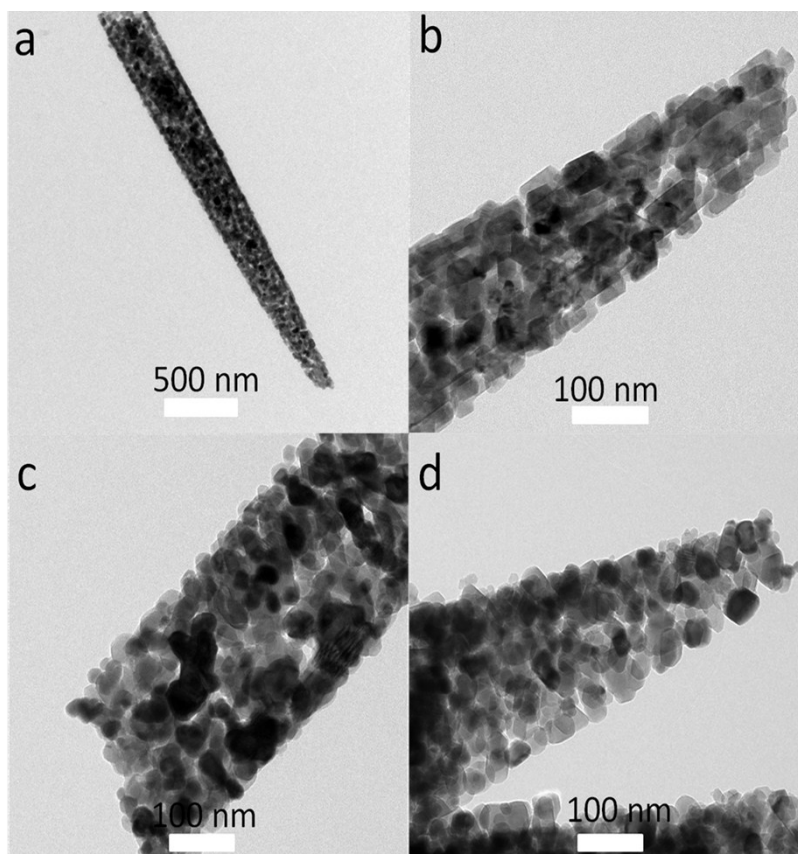**Figure S3.** SEM images of the of Ni/Co-1 (a) and Ni/Co-3 (b).

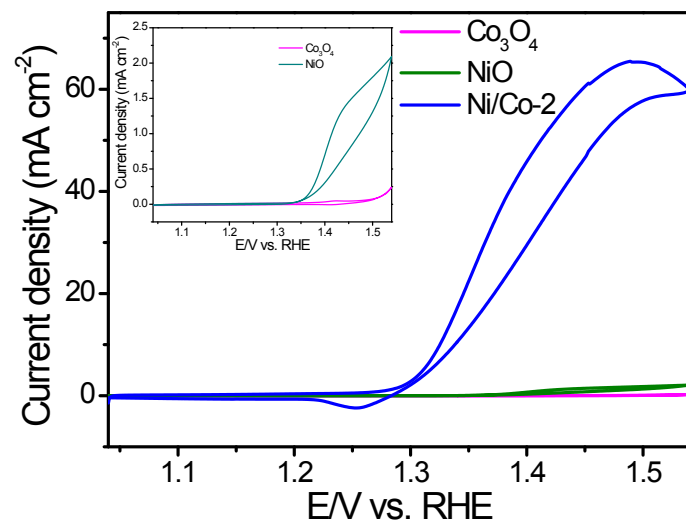**Figure S4.** TEM images (a-d) of Ni/Co-2.

Figure S5. CV curves of NiO, Co_3O_4 and Ni/Co-2 in 1 M KOH with 0.33 M urea at 10 mV s^{-1}.
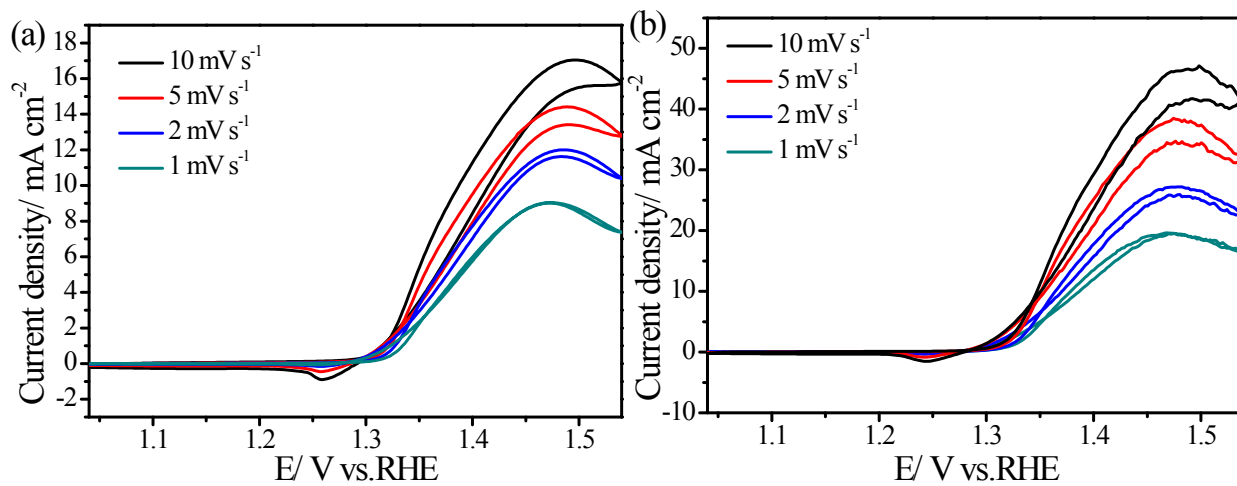
Figure S6. CV curves of (a) Ni/Co-1 and (b) Ni/Co-3 in 1 M KOH with 0.33 M urea at various scan rates.
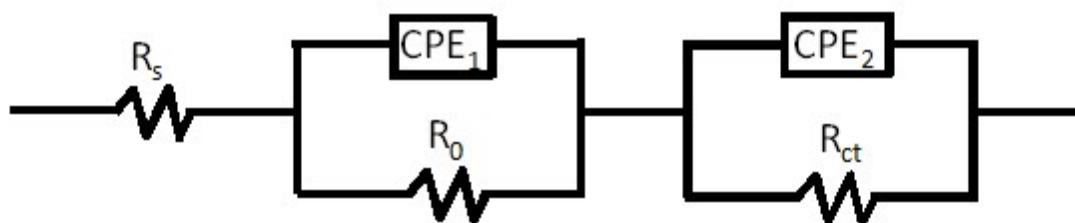
Figure S7. The electrical equivalent circuit model of Ni/Co-2 electrode in 1 M KOH with 0.33 M urea. R_s is a sign of the uncompensated solution resistance, R_{ct} is a charge transfer resistance arisen from urea oxidation, R_o is associated to the contact resistance between the catalyst material and the glassy carbon electrode and a constant phase element (CPE_1, CPE_2) for the double layer capacitance

Table S1. The high-resolution XPS analysis of Ni 2p for the Ni/Co-1, Ni/Co-2 and Ni/Co-3 catalysts.

Catalysts	Ni^{2+}	Ni^{3+}	Sat.	Ni^{2+}/Ni^{3+}
Ni/Co-3	12.09%	39.56%	48.35%	0.30
Ni/Co-2	12.36%	44.12%	43.52%	0.28
Ni/Co-1	6.64%	31.86%	61.50%	0.21

Table S2. The onset potential for different ratio of Ni/Co materials

Catalysts	Onset potential (V vs. RHE)
Ni/Co-1	1.315
Ni/Co-2	1.290
Ni/Co-3	1.307

Table S3. EIS fitting parameters of different electrode at a potential of 1.39 V vs. RHE.

Catalysts	R_s /Ω	CPE / S s^{-n}	n 0<n<1	R_{ct} /Ω	CPE /S s^{-n}	n / 0<n<1	R_o /Ω
Ni/Co-1	8.1	7.953E-004	0.8	260	6.920E-003	0.58	2.564E+002
Ni/Co-2	6.1	1.922E-001	0.8	79.8	1.288E-003	0.86	1.641E+002
Ni/Co-3	7.7	2.068E-001	0.9	96.7	6.614E-003	0.54	1.360E+002

References

1. J. H. Kim, S. M. Choi, S. H. Nam, M. H. Seo, S. H. Choi and W. B. Kim, *Appl. Catal., B*, 2008, **82**, 89-102.