Electronic Supplementary Material (ESI) for ChemComm.

Electronic supplementary information

Facile synthesis of CoNix nanoparticles embedded in nitrogen-carbon frameworks for highly efficient electrocatalytic oxygen evolution

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Chemicals and reagents

$Co(NO_3)_2·6H_2O$ (98%, Alfa), $Ni(NO_3)_2·6H_2O$ (98%, Alfa), $Zn(NO_3)_2·6H_2O$ (98%, Alfa), 2-methylimidazole (2MI, 99%, Acros), ethanol (99.8%, AR grade, Beijing Chemical Reagent Factory), Formaldehyde (99.8%, AR grade, Beijing Chemical Reagent Factory), Ammonium Hydroxide (25%-28%, AR grade, Beijing Chemical Reagent Factory), sodium dodecyl sulfate (SDS, 98%, Beijing Chemical Reagent Factory), resorcinol (98%, Beijing Chemical Reagent Factory), Ultrapure water (Millipore Milli-Q grade) with a resistivity of 18.2 MΩ was used in all the experiments. All of the chemicals used in this experiment were used as received without any further purification.

Synthesis process

Synthesis of $CoNi_{0.37}$-CN. First step, 1.0g SDS was dissolved in 100 ml ultrapure water. Then, 71.4 mg of $Co(NO_3)_2·6H_2O$, 28.6 mg $Ni(NO_3)_2·6H_2O$ and 113 mg of 2MI were mixed together under strongly stiring. After an hour reaction, the product was collected with centrifugation and washed with deionized water and ethanol for three times, respectively. Second step, the obtained product was dissolved in the mixture of 80 ml water and 16 ml ethanol. And 0.4 ml ammonium Hydroxide was quickly injected into the above solution and 0.1g resorcinol was added. After 12 h reaction, the phenol-formaldehyde resin (PF) was coated. The powder was collected following with centrifugation, washing and vacuum drying, respectively. The desired product was pyrolysis treated at 800 ^{o}C in nitrogen atmosphere for 3 h and then the catalyst of $CoNi_{0.37}$-CN was successfully prepared.

Synthesis of $CoNi_{0.81}$-CN, $CoNi_{1.42}$-CN and $CoNi_{1.86}$-CN. The synthesis method is the same as $CoNi_{0.37}$-CN. The adding amounts of $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ are 55.5 mg and 44.5 mg for $CoNi_{0.81}$-CN, 41.6 mg and 58.4 mg for $CoNi_{1.42}$-CN, 35.7 mg and 64.3 mg for $CoNi_{1.86}$-CN, respectively.

Synthesis of CoNix-CN without PF shell. The synthesis method is the same as the first step of CoNix-CN, and the product was pyrolysis treated at 800 °C in nitrogen atmosphere without the PF coating.

Synthesis of pure CN. First step, 1.0g SDS was dissolved in 100 ml ultrapure water. Then, 100 mg of $Zn(NO_3)_2 \cdot 6H_2O$ and 113 mg of 2MI were mixed together under strongly stiring. After an hour reaction, the product was collected with centrifugation and washed with deionized water and ethanol for three times, respectively. Second step, the obtained product was dissolved in the mixture of 80 ml water and 16 ml ethanol. And 0.4 ml ammonium Hydroxide was quickly injected into the above solution and 0.1g resorcinol was added. After 12 h reaction, the phenol-formaldehyde resin (PF) was coated. The powder was collected following with centrifugation, washing and vacuum drying, respectively. The desired product was pyrolysis treated at 800 °C in nitrogen atmosphere for 3 h and then the catalyst of pure CN was successfully prepared.

Characterization

Transmission electron microscopy (TEM) images were performed on a Hitachi H-800 transmission electron microscope. Dark field scanning transmission electron microscopy (DF-STEM) was performed on FEI Tecnai G2 F20 S-Twin highresolution transmission electron microscope operating at 200kV. The X-ray powder diffraction

(XRD) were obtained on a Rigaku RU-200b with Cu Kα radiation. The X-ray photoelectron spectroscopy (XPS) was measured by a PHI Quantera SXM system under $3.1*10^{-8}$ Pa using Al^+ radiation at room temperature. N2 adsorption measurements were performed with a Quantachrome Autosorb-1 instrument surface area analyzer at 77K. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area.

Electrochemical measurements

Linear sweep voltammetry (LSV) method was performed in 1.0 M KOH solution in a standard three-electrode system, in which a glassy carbon electrode (GCE) modified with samples, a Pt wire and a Ag/AgCl electrode were used as the working electrode, counter-electrode and reference electrode, respectively. The OER activity of the catalysts was measured by RDE (1200 rpm) with LSV in the potential from 0 to 1.0 V at a scan rate of 10 mV s^{-1}.

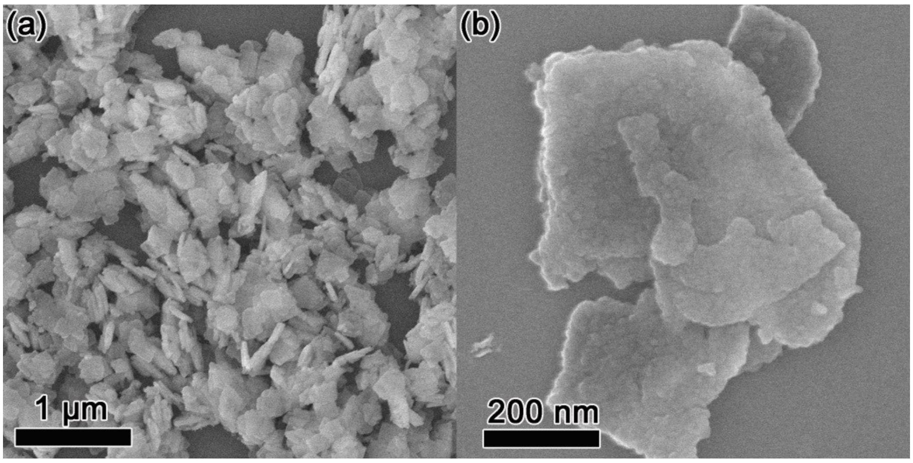

Figure S1. (a) Overall SEM of $CoNi_{0.37}$-CN, (b) locally amplified SEM image.

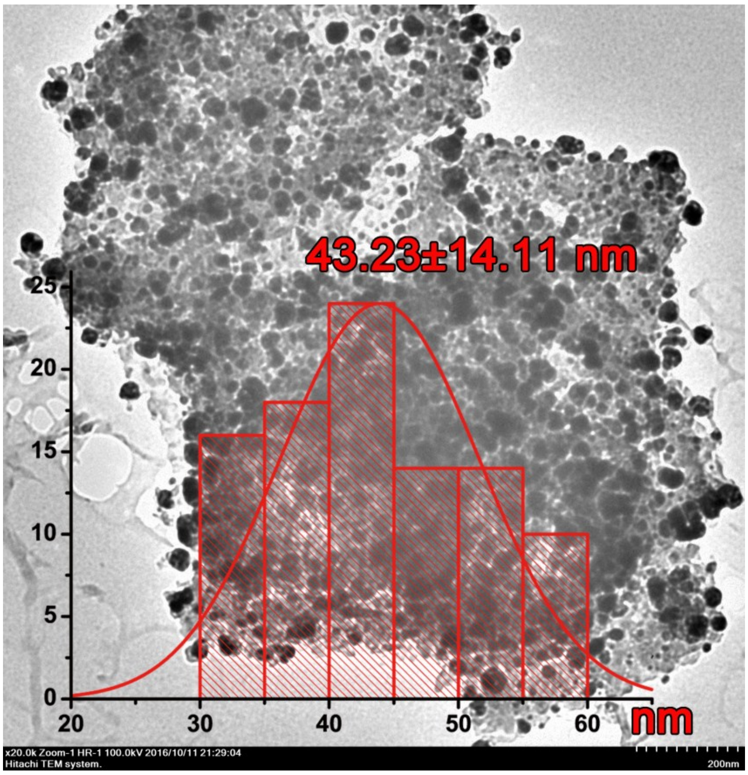

Figure S2. TEM image and diameter size distribution of CoNix-CN without PF shell.

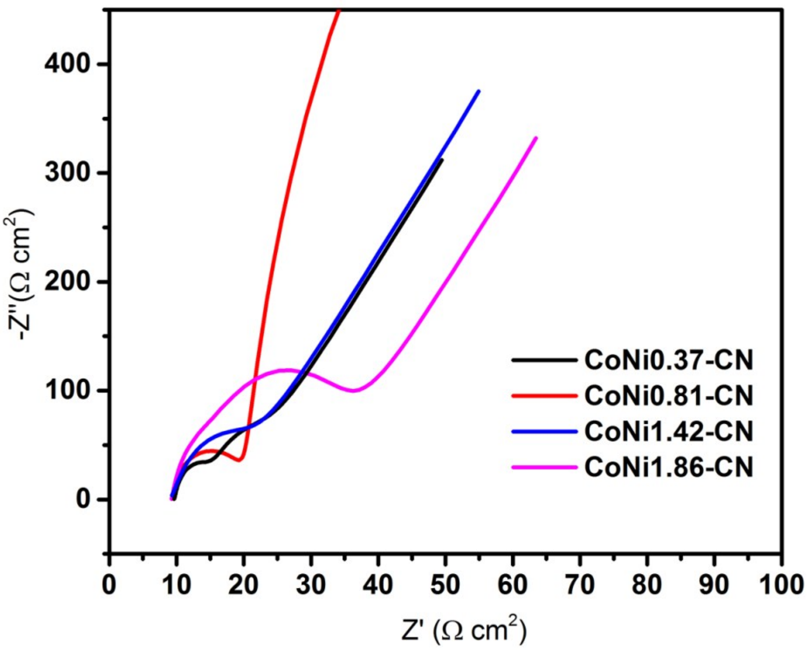

Figure S3. EIS measurement of CoNix-CN materials.

From **Figure S3**, the series resistance (*Rs*) is deduced by high frequency cut on the real axis (Z' axis), and *Rs* for the four CoNix-CNs are 9.62 ($CoNi_{0.37}$), 9.47 ($CoNi_{0.81}$), 9.30 ($CoNi_{1.42}$), and 9.25 Ωcm^2 ($CoNi_{1.86}$), which are almost same for all samples. Another important parameter can be read from **Figure S3** is the charge transfer resistance (*Rct*) at interface of catalyst/electrolyte. *Rct* is an important parameter that represents the electrocatalytic performance of the catalyst. *Rct* is derived from thr radius of high frequency semicircle on the real axis. Evidently, *Rct* is varied in the order of $CoNi_{0.37}$-CN (7.18 Ω cm^2) < $CoNi_{0.81}$-CN (11.8 Ω cm^2) < $CoNi_{1.42}$-CN (21.29 Ω cm^2) < $CoNi_{1.86}$-CN (36.65 Ω cm^2). The smallest *Rct* of $CoNi_{0.37}$-CN reveals that the facile charge transfer between electrolyte and electrode surface, leading to the best catalytic activity.

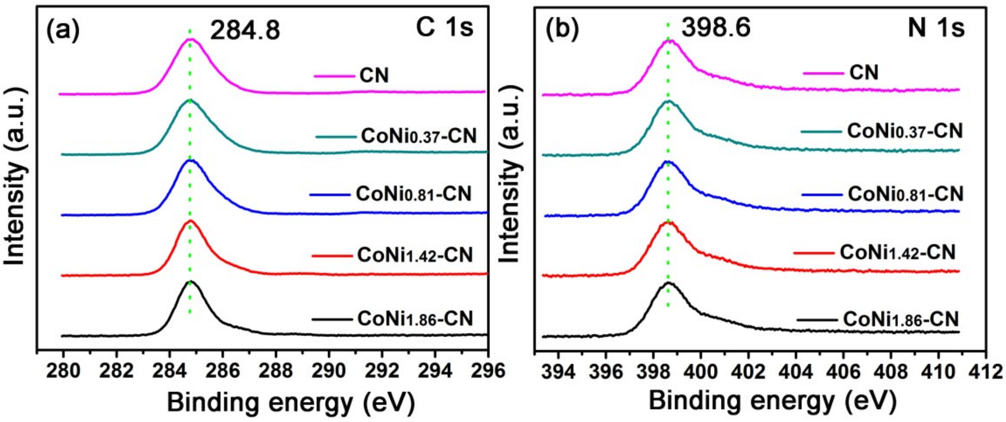

Figure S4. (a) C 1s XPS and (b) N 1s XPS spectra of CoNix-CNs and CN materials.

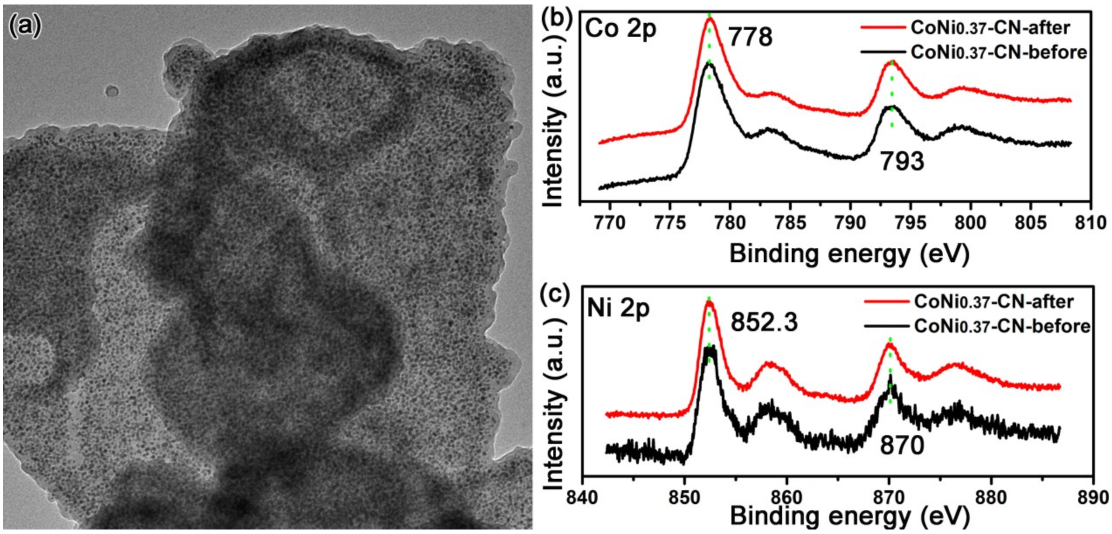

Figure S5. (a) TEM image of $CoNi_{0.37}$-CN after CA test, (b) Co 2p XPS and (c) Ni 2p XPS spectra of $CoNi_{0.37}$-CN before and after CA test.

From **Figure S5 (a)**, the morphology of $CoNi_{0.37}$-CN after CA test is not destroyed and there is not aggregation of $CoNi_{0.37}$ nanoparticles in the result. And Co 2p and Ni 2p XPS spectra were performed to discuss the surface change of $CoNi_{0.37}$ nanoparticles. Judged from **Figure S5 (b) and (c),** no valence change can be noticed. The surface of $CoNi_{0.37}$ nanoparticle can keep well stable in long term electrochemical reaction.

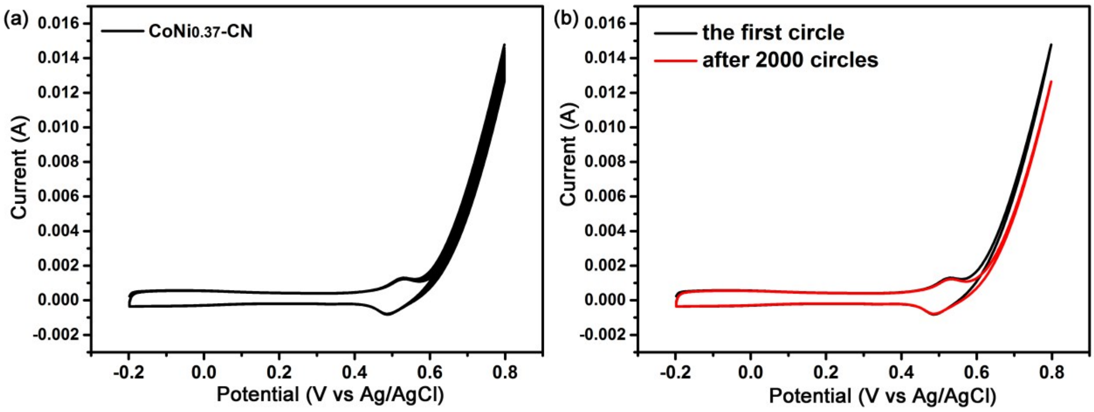

Figure S6. (a) Electrochemical CV stability test with 2000 circles, (b) CV spectra for the first circle and the 2000th circle.

CV method was performed in 1.0 M KOH solution in a standard three-electrode system, in which a glassy carbon electrode (GCE) modified with samples, a Pt wire and a Ag/AgCl electrode were used as the working electrode, counter-electrode and reference electrode, respectively. The electrochemical CV stability of the $CoNi_{0.37}$-CN was measured by RDE (1200 rpm) with CV in the potential from -0.2 to 0.8 V at a scan rate of 100 mV s^{-1} for 2000 circles. From **Figure S6 (a)**, the redox peaks of $CoNi_{0.37}$-CN are almost same after 2000 circles of CV. It can be more clearly observed from **Figure S6 (b)** that the redox peaks from the first circle and the 2000th circle coincide with each other. And the small difference in current over the potential of 0.6 V (V vs Ag/AgCl) can be found after 2000 circles. It can further illustrate the excellent long-term durability of $CoNi_{0.37}$-CN.