

Electronic Supplementary Information

Facile synthesis of sponge-like Ni₃N/NC for electrocatalytic water oxidation

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General Methods and Materials.

All chemical reagents were purchased from commercial suppliers and were used without further purification. Milli-Q water of 18 M Ω cm was used in all experiments. XRD pattern of the sample was recorded on a X-ray diffractometer (Rigaku D/Max2550VB+/PC, Cu K α , $\lambda = 1.5406$ Å, 40 kV and 100 mA). XPS was performed on ThermoFisher ESCALab 250Xi using 200 W monochromated Al K α radiation. The base pressure in the analysis chamber was about 3×10^{-10} mbar. The C 1s peak at 284.8 eV from adventitious carbon is used for energy calibration. Raman spectra were recorded using a Horiba LabRam HR800 confocal Raman microscope with the wavelength at 638 nm, while the sample was prepared by crushing into a pellet. A Hitachi SU8020 cold-emission field emission scanning electron microscope (FE-SEM) was used to observe the morphology of the material with an accelerating voltage of 5 kV. TEM, HRTEM images and EDX analysis were obtained using FEI, Tecnai G2 F20 with an accelerating voltage of 200 kV. The specific surface area and pore size distribution were measured by BET on an ASAP 2020 of Micromeritics instrument corp. The amount of Ni in the as-prepared catalyst was confirmed by ICP-AES using VISTA-MPX ICP-AES.

Synthesis of Ni₃N/NC.

Ni₃N/NC was synthesized by dissolving Ni(OAc)₂ (1 mmol) and urea (4 mmol) in 1.0 mL of ethanol to generate a transparent green solution. The resulted solution was then placed in the center of a tube furnace. It is necessary to remove O₂ in the tube furnace by purging N₂ at least 30 min before heating. After that, the sample was

heated to 350 °C with a heating rate of 5 °C min⁻¹, and was stayed at this temperature for 3 h. The N₂ gas was stopped as soon as the heating began, while the tube furnace was protected under N₂ atmosphere throughout the synthesis. Black, shiny and sponge-like product was obtained after cooling the sample to room temperature.

Synthesis of NiO/NC.

The NiO/NC was synthesized in the same way as that for Ni₃N/NC except under the air condition.

Electrochemical Measurements.

All electrochemical experiments were carried out by using a CH Instruments (model CHI 660D Electrochemical Analyzer). In 15 mL of 1.0 M KOH electrolyte, we carried out the cyclic voltammogram (CV) and electrolysis with a conventional three-electrode configuration using GC, Ag/AgCl and Pt wire as the working electrode, reference electrode and counter electrode, respectively. Compensation for iR drop was used for all CVs. All potentials were reported versus reversible hydrogen electrode (RHE) based on the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + (0.197 + 0.059 \times \text{pH})$. The GC electrode was polished with α -Al₂O₃ powder of decreasing sizes (1.0 μm to 50 nm) and was ultrasonically washed with deionized water and absolute ethanol. Typically, 4 mg Ni₃N/NC was dispersed into the mixture of 750 μL water, 250 μL isopropanol and 40 μL Nafion. Then the turbid solution was subjected to ultrasonication for 30 min to get a homogeneous suspension. Then, 5 μL of the mixture was loaded onto the

polished GC electrode. The loading amount of the catalyst is about 0.28 mg cm^{-2} . The electrochemical impedance spectroscopy (EIS) was recorded under 0.58 V (vs Ag/AgCl) in a 1.0 M KOH solution over a frequency range from 0.1 Hz to 1 MHz at the amplitude of the sinusoidal voltage of 5 mV . The explicit Nyquist plots were thus obtained based on the EIS data. The produced O_2 during controlled potential electrolysis was analyzed by a calibrated Ocean Optics FOXY probe (Model NeoFox).

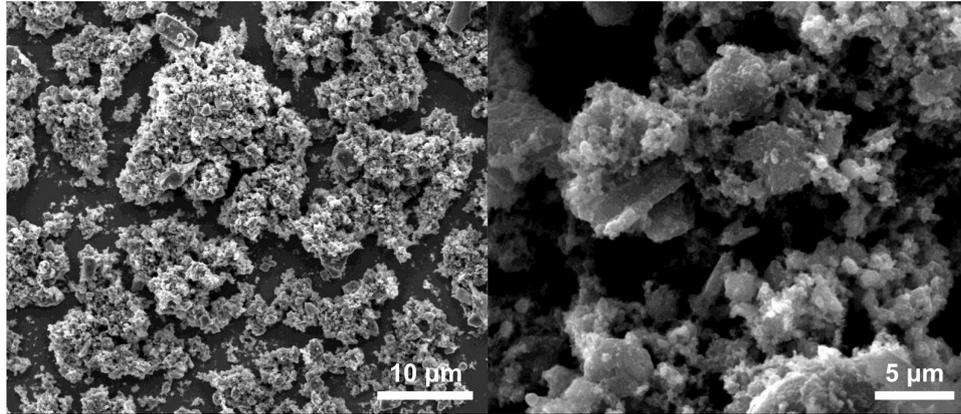


Fig. S1 SEM images of the NiO/NC material.

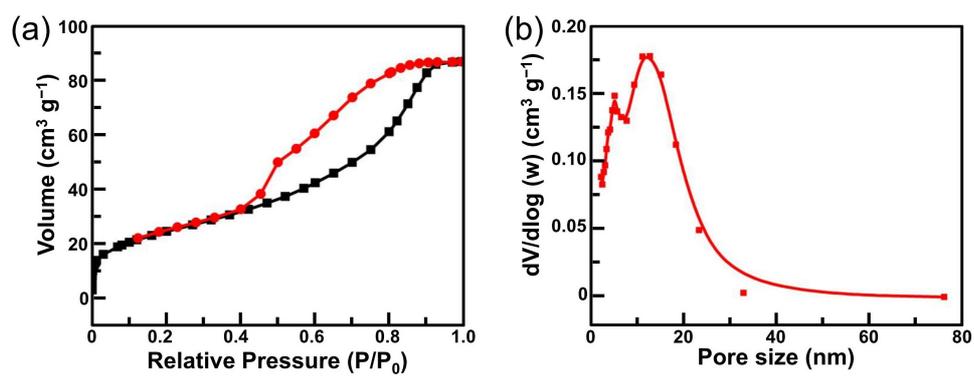


Fig. S2 (a) Adsorption-desorption isotherm and (b) pore size distribution of the Ni₃N/NC material.

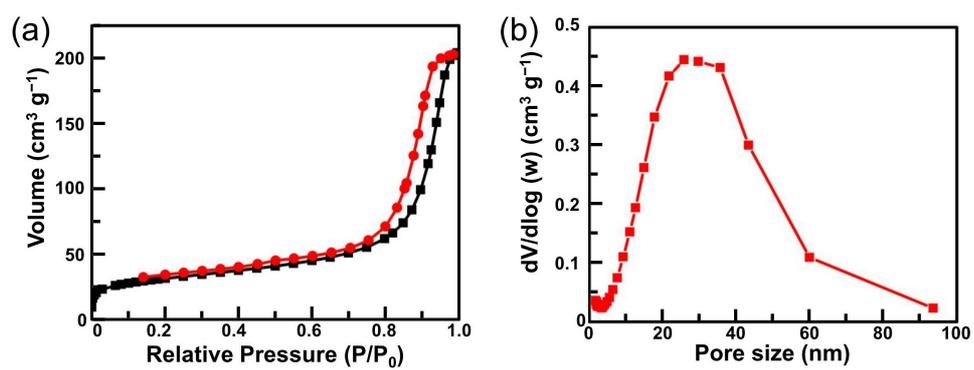


Fig. S3 (a) Adsorption-desorption isotherm and (b) pore size distribution of the NiO/NC material.

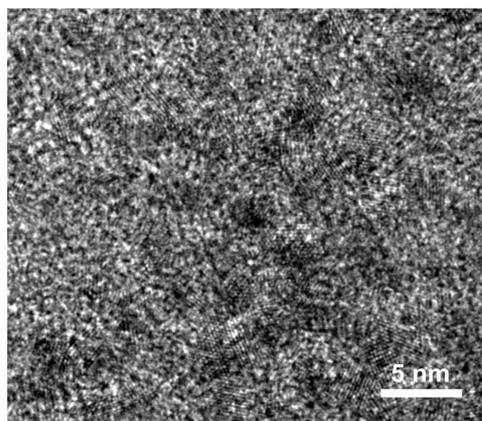


Fig. S4 The HRTEM image of Ni₃N/NC.

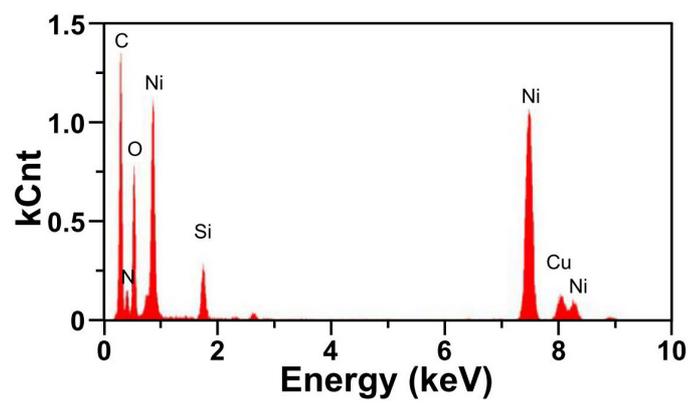


Fig. S5 The EDX spectrum of Ni₃N/NC.

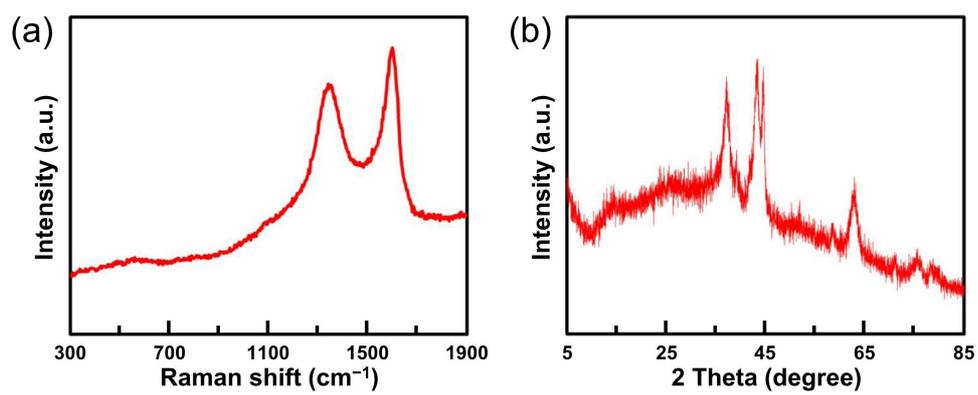


Fig. S6 (a) Raman spectrum and (b) XRD pattern of NiO/NC.

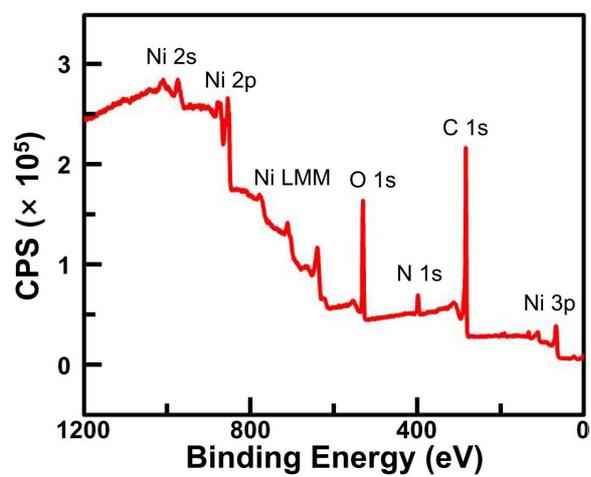


Fig. S7 The XPS survey spectrum of Ni₃N/NC.

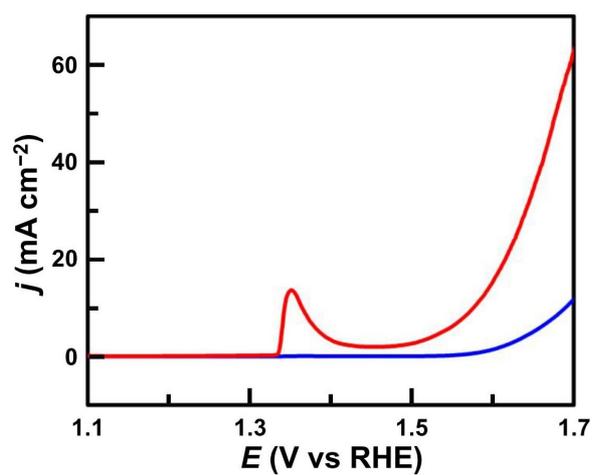


Fig. S8 The polarization data of GC electrodes with $\text{Ni}_3\text{N/NC}$ (red) or NiO/NC (blue)

at the scan rate of 1 mV s^{-1} .

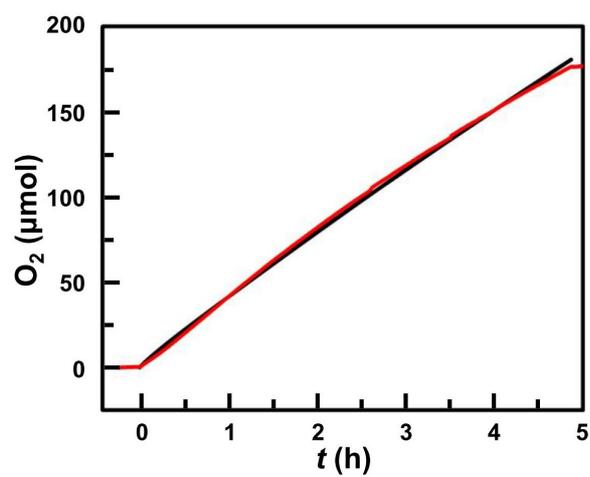


Fig. S9 Observed and theoretical amounts of O₂ evolved during 5-h controlled potential electrolysis with Ni₃N/NC.

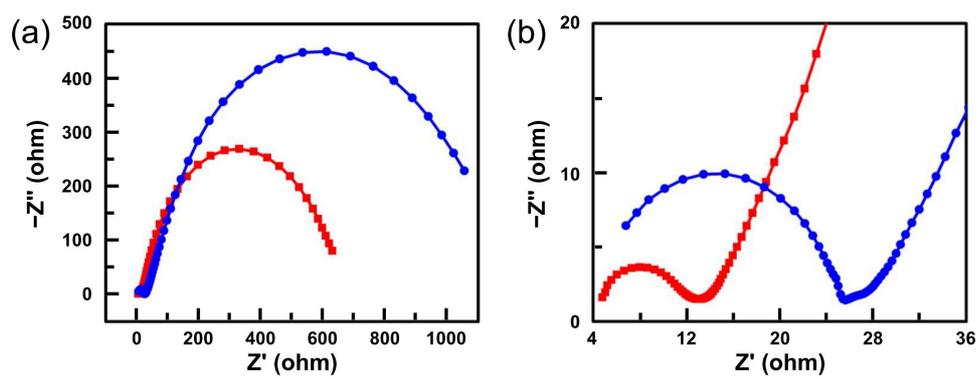


Fig. S10 (a) EIS Nyquist plots of Ni₃N/NC (red) and NiO/NC (blue) under 0.58 V (vs Ag/AgCl) and (b) the enlarged view.

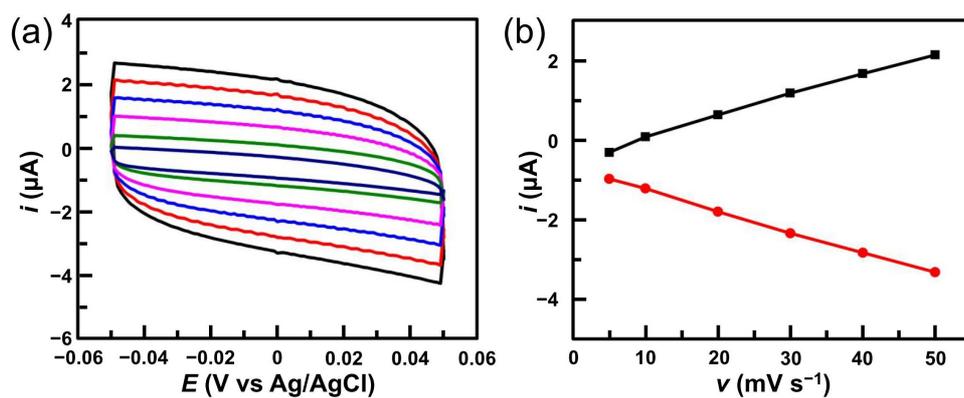


Fig. S11 (a) The charging currents of Ni₃N/NC recorded in the non-Faradaic potential region at different scan rates. (b) The anodic and cathodic charging currents at 0 V vs Ag/AgCl plotted against the scan rates.

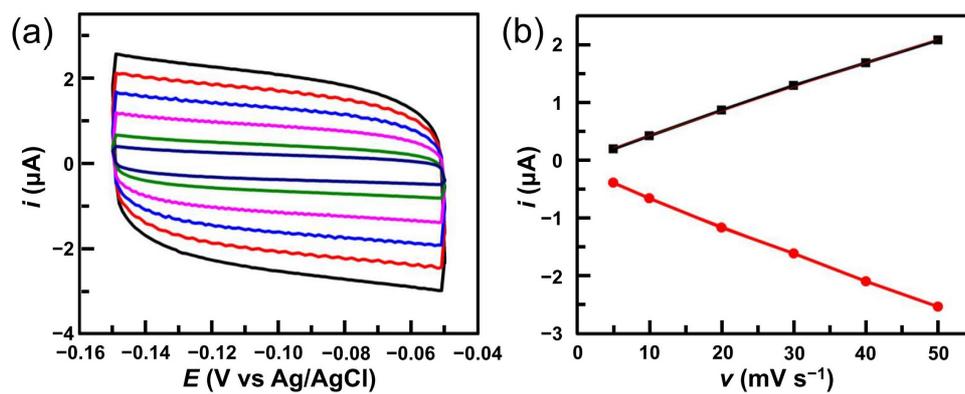


Fig. S12 (a) The charging currents of NiO/NC recorded in the non-Faradaic potential region at different scan rates. (b) The anodic and cathodic charging currents at -0.10 V vs Ag/AgCl plotted against the scan rates.

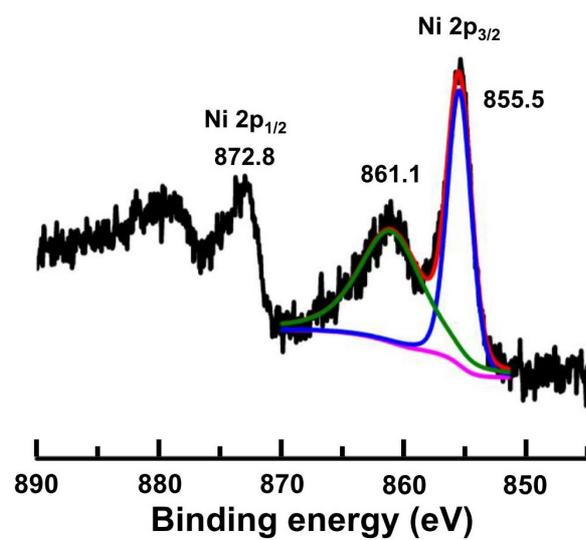


Fig. S13 The XPS spectrum of Ni 2p for Ni₃N/NC after controlled potential electrolysis.

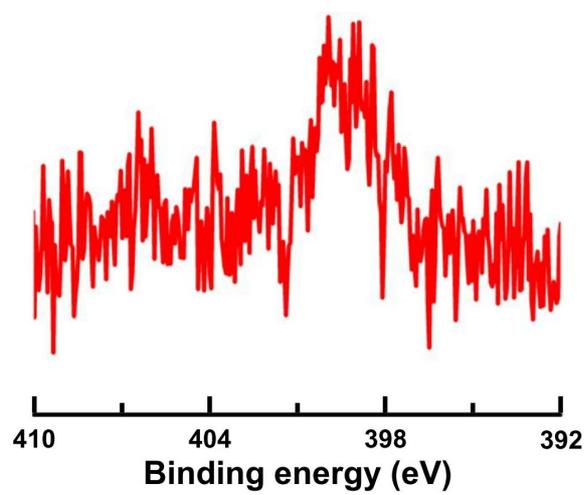


Fig. S14 The XPS spectrum of N 1s for Ni₃N/NC after controlled potential electrolysis.

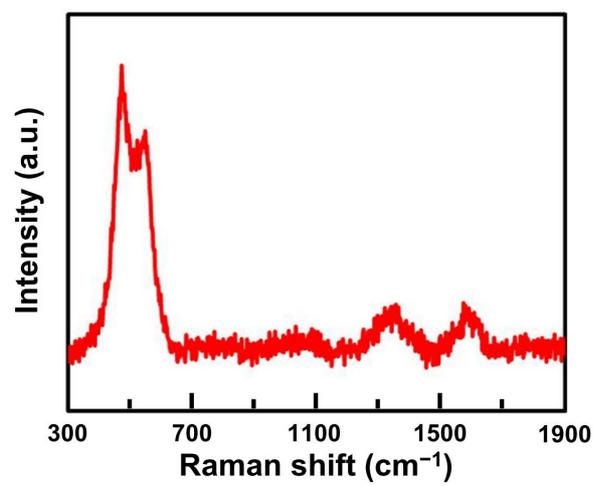


Fig. S15 The Raman spectrum of Ni₃N/NC after controlled potential electrolysis.

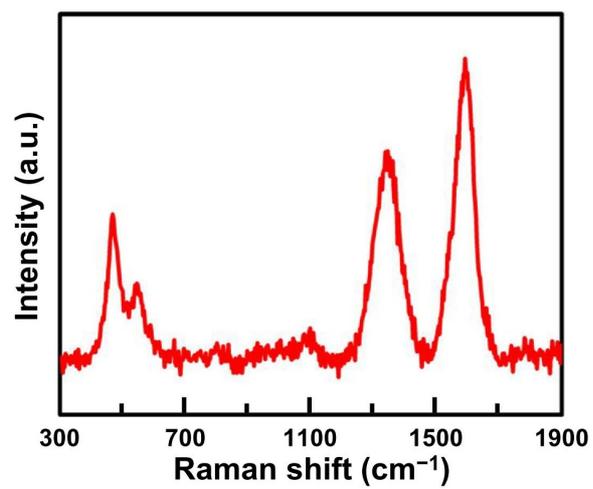


Fig. S16 The Raman spectrum of NiO/NC after controlled potential electrolysis.

Table S1. Comparison of Ni₃N/NC with catalyst materials reported in the literature for electrocatalytic OER in alkaline solutions.

Catalyst	Electrolyte (KOH)	Electrode	Loading (mg cm ⁻²)	η (mV) @ 10 mA cm ⁻²	Ref.
Ni ₃ N/NC	1 M	GC	0.28	310	<i>This work</i>
Ni(OH) ₂ /O-MWCNTs	1 M	GC	0.6	270	<i>Adv. Energy Mater.</i> 2016, 6 , 1600516
α -Ni(OH) ₂	0.1 M	CFP	0.2	331	<i>J. Am. Chem. Soc.</i> 2014, 136 , 7077
MWCNTs/Ni(OH) ₂	0.1 M	ITO	0.28	474	<i>J. Mater. Chem. A</i> 2014, 2 , 11799
25% NiO _x /PEI-CNTs	0.1 M	GC	0.1	350	<i>Int. J. Hydrogen Energy</i> 2014, 39 , 20662
ALD NiS _x	1 M	GC	–	353	<i>Chem. Mater.</i> 2016, 28 , 1155
amorphous Ni(OH) ₂	0.1 M	GE	0.15	344	<i>Cryst. Growth Des.</i> 2015, 15 , 4475
NiB _{0.45} -250	1 M	CF	1.4	296	<i>Nano Energy</i> 2017, 38 , 175
Ni ₂ P nanowires	1 M	FTO	0.1	400	<i>Chem. Commun.</i> 2015, 51 , 11626
Ni ₃ C/C	1 M	CFP	0.285	316	<i>Adv. Mater.</i> 2016, 28 , 3326
Ni-B _i @NB	1 M	GC	0.3	302	<i>Angew. Chem. Int. Ed.</i> 2017, 56 , 6572

O-MWCNTs: oxidized multiwall carbon nanotubes; PEI-CNTs: polyethylenimine functionalized carbon nanotubes; ALD: atomic layer deposition; NiB_{0.45}-250: NiB_{0.45} was annealed at 250 °C for 3 h under argon; Ni-B_i@NB: a Ni^{II}-B_i shell on a Ni boride (NB) nanoparticle core; GC: glass carbon electrode; GE: graphite electrode; CFP: carbon fiber paper; ITO: indium tin oxide electrode; FTO: fluorine doped tin oxide electrode; CF: Cu foil; η : overpotential; –: data not available.