Supplementary information

A nitrogen-doped nano carbon dodecahedron with $Co@Co_3O_4$ implants as bifunctional electrocatalyst for efficient overall water splitting

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Experimental Section

Synthesis

Synthesis of ZIF-67. 4 mmol of $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 50 mL of methanol, which was subsequently poured into 50mL of methanol containing 16 mmol of 2-methylimidazole (MeIM). The solution was incubated at room temperature for 24h after thorough mixing. Obtained precipitates were collected by centrifugation, washed with methanol for many times and dried in an oven at 80 ºC for 12 h, resulting in the purple ZIF-67 crystals.

Synthesis of Co-NC composites. 0.5g ZIF-67 crystals were carbonized under a N_2 atmosphere at 700 ºC for 3 h, with a heating rate of 5 ºC·min^{-1}, Co-NC was obtained after cooled down to room temperature naturally.

Synthesis of Co@Co_3O_4-NC composites. 60 mg Co-NC heat treated in air at 200 ºC for 3 h to form Co@Co_3O_4-NC.

Synthesis of Co_3O_4-NC composites. 60 mg Co-NC was heat treated in air at 200 ºC for 48 h to form Co_3O_4-NC.

Characterization

X-ray diffraction (XRD) measurements were performed by using a Rigaku Ultima IV instrument using Cu Kα radiation (λ=1.5418 Å). Raman spectra were obtained using a XploRA Raman microscope with an excitation wavelength of 785 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5300 ESCA spectrometer (PerkinElmer) with an energy analyzer working in the pass energy mode at 35.75 eV. An Al Kα line was used as the X-ray source. The morphologies were characterized by a scanning electron microscopy (Hitachi S-4800) and transmission electron microscopy (FEI Tecnai F30). The electro-performance was evaluated by an electrochemical workstation (CHI 760E) equipped with a rotation electrode equipment (PINE). Over all water splitting tests were conducted in a home-made device.

Electrocatalytic performance analysis

The HER and OER polarization curves of all the catalysts was measured in 1 M KOH aqueous electrolyte using a rotating disk electrode (RDE) at room temperature (~25 ºC). Catalyst loading is 0.4 mg cm^{-2}. 4 mg of catalyst powder was dispersed in 400 μL of solution (5% Nafion solution: isopropyl alcohol: DI water = 1: 19: 19 in volume) and under ultrasonicated for least 40 min to form a homogeneous ink. 8 μL catalysts ink was dropped on a polished RDE (0.196 cm^{-2}). Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were recorded in a three-electrode electrolytic cell, RDE coating with catalysts as working electrode, a graphite rod as a counter electrode, and Hg/HgO as a reference electrode. All the measured potentials were converted to potentials versus to reversible hydrogen electrode (RHE), and the counter electrode was calibrated with a homemade RHE in hydrogen saturated 1 M KOH solution.

$$E_{RHE} = E + 0.0592pH + E^{\theta}(Hg/HgO)$$

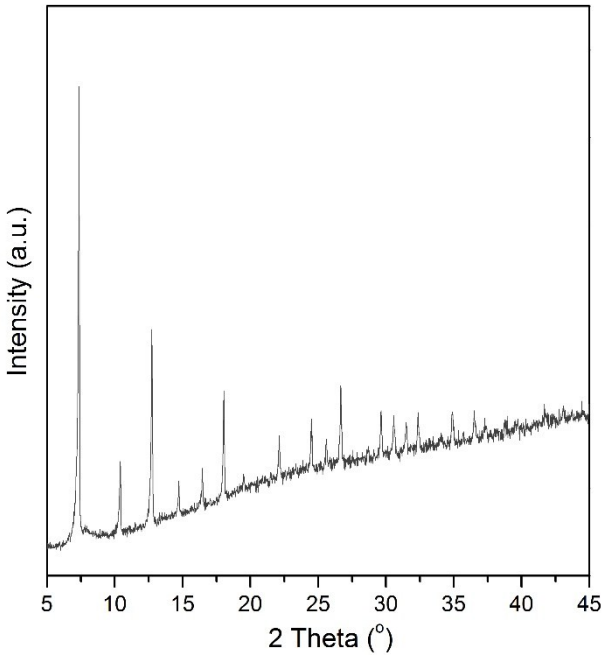

Fig. S1. The XRD petterns of ZIF-67.

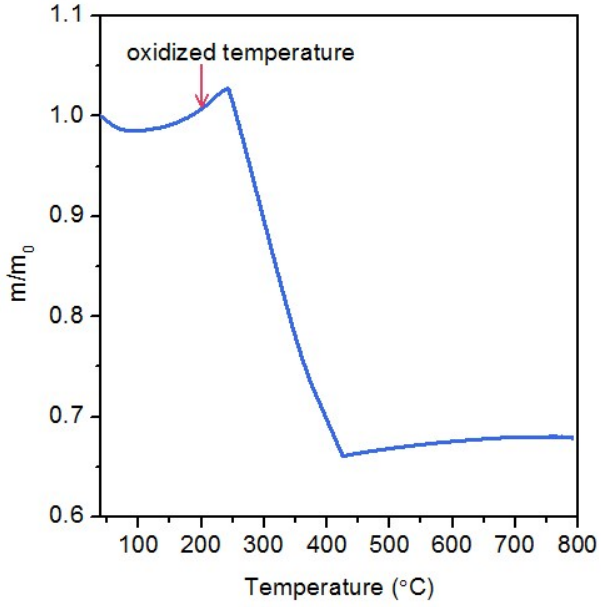

Fig. S2. The TG curve of Co-NC in air.

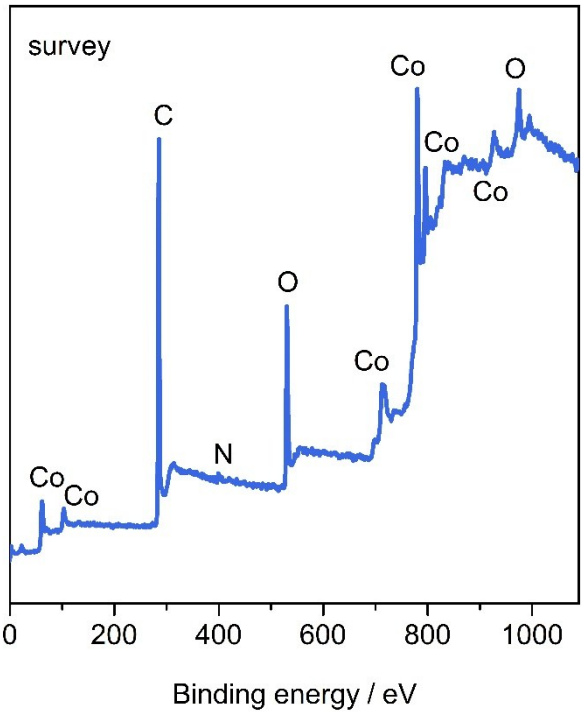

Fig. S3. The XPS survey of Co@Co_3O_4-NC.

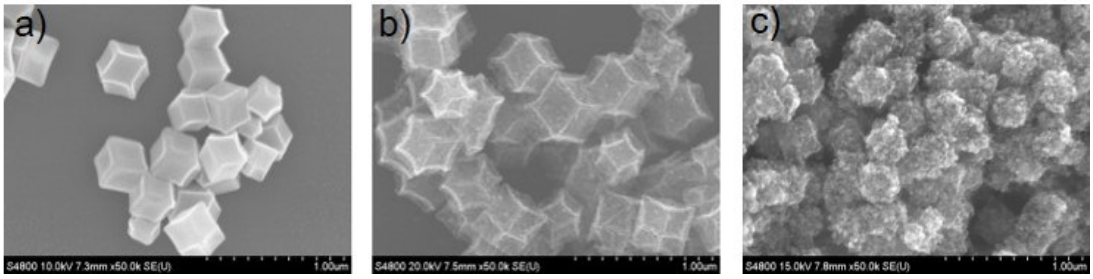

Fig. S4. SEM images of **a)** ZIF-67, **b)** Co-NC and **c)** Co_3O_4-NC.

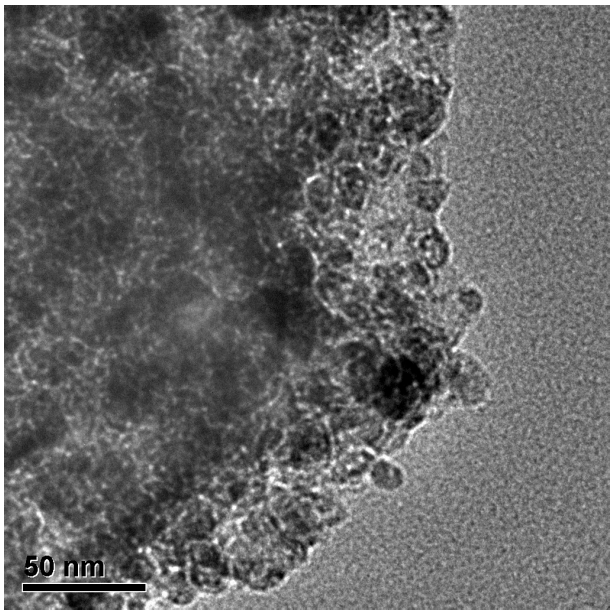

Fig. S5. The HRTEM image of $Co@Co_3O_4$-NC.

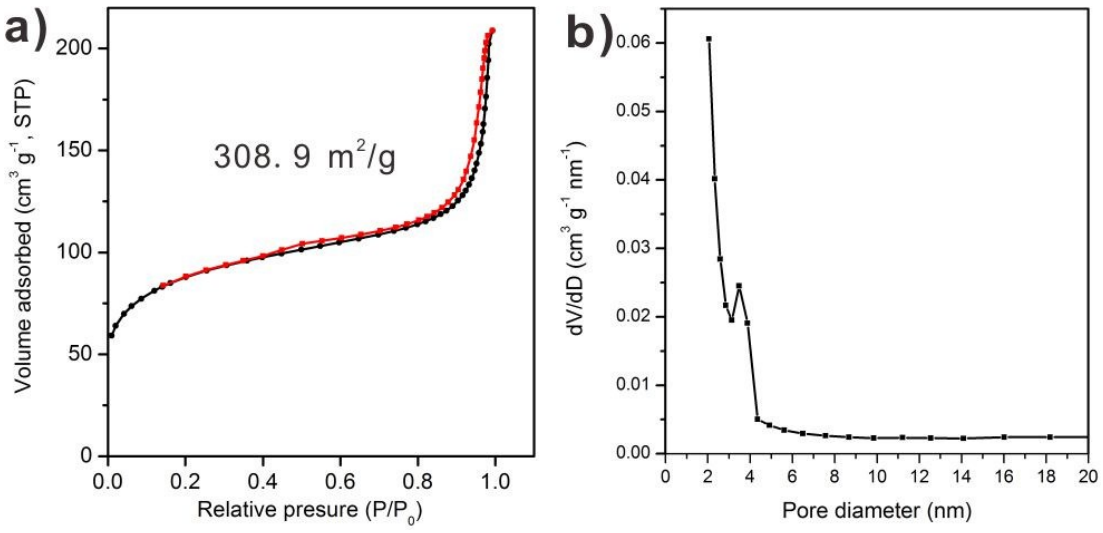

Fig. S6. a) N_2 adsorption–desorption isotherms and **b)** pore size distribution curve of $Co@Co_3O_4$-NC.

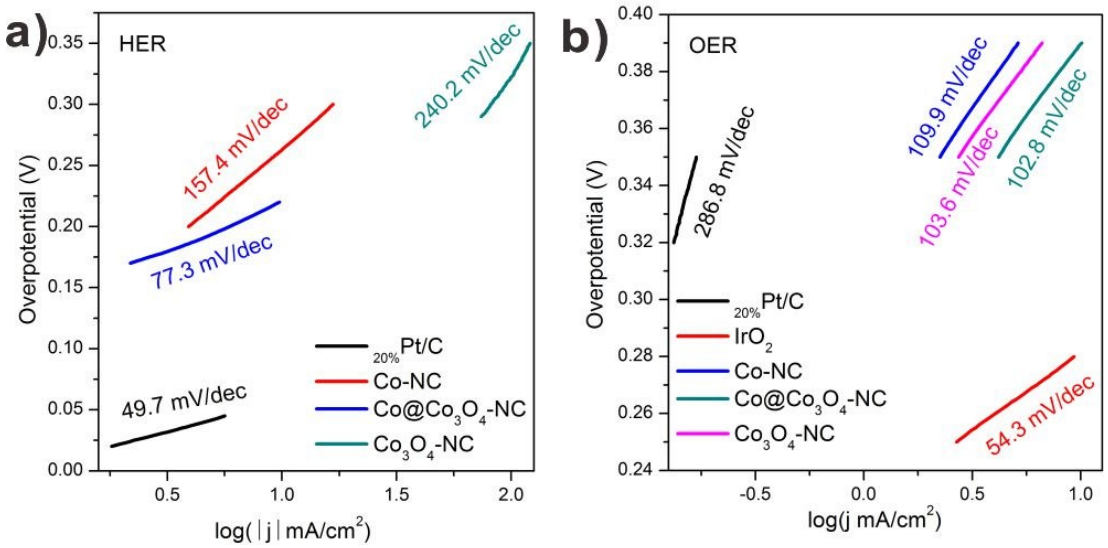

Fig. S7. a) HER, **b)** OER Tafel plots of different catalysts.

Table S1. Comparison of $Co@Co_3O_4$-NC with the reported various HER catalysts in alkaline electrolyte.

Catalysts	**Overpotential at 10 mA/cm^{-2}**	**Reference**
$Co@Co_3O_4$-NC	221	In this work
NiFe-LDH	210 mV	Science, ***2014,*** 345, 1593.
N, O, P-Carbon	450	*Energy Environ. Sci.* ***2016****, 9*, 1210.
$Ni_{2.5}Co_{0.5}Fe$	275 mV	*J. Mater. Chem. A,* ***2016****, 4*, 72450.
MoO_2	124 mV	*Adv. Mater.,* ***2016****, 28*, 3785.
CoO*x*@N-carbon	243 mV	*J. Am. Chem. Soc.* ***2015****, 137*, 2688.
N, P-Carbon	470 mV	*Angew. Chem.* ***2016****, 128, 2270.*
g-C_3N_4@N-graphene	>600 mV	*Nat. Commun.* ***2014****, 5, 3783*

Table S2. Comparison of $Co@Co_3O_4$-NC with the reported various OER catalysts in alkaline electrolyte.

Catalysts	**Overpotential at 10 mA/cm^{-2}**	**Reference**
$Co@Co_3O_4$-NC	391 mV	*In this work*
NiFe-LDH	302 mV	*Nat. Commun.* ***2016,*** *7, 11981.*
α-MnO_2	490 mV	*J. Am. Chem. Soc.* ***2014,*** *136, 11452.*
N, S-graphene	420 mV	*Nano Energy* ***2016****, 19, 373.*
$NiCo_2O_4$	290 mV	*Angew. Chem. Int. Ed.* ***2016,*** *55, 1.*
g-C_3N_4-graphene	580 mV	*ChemSusChem* ***2014****, 7, 2125.*
N-CNTs-CVD	400 mV	*Small,* ***2014****, 10, 2251.*
B-CNTs-CVD	600 mV	*Electrochim.Acta* ***2014****, 143, 291.*