

Electronic Supplementary Information

N-doped graphene-supported Co@CoO core-shell nanoparticles as high-performance bifunctional electrocatalysts for overall water splitting

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Experimental Section

Chemicals. Graphene sheets with a thickness of about 0.8 nm were purchased from Nanjing XFNANO Material Tech Co., Ltd. (Nanjing City, China). Other regants were purchased without further treatment.

Preparation of catalysts. The graphene sheets were treated at 700°C for 3 h under an NH₃ flow and then NG was obtained. 36 mg of NG was dispersed into 72 mL ethanol, and 200 mg of cobalt acetate was added. After sonication for 10 min, 3.6 mL distilled water and 2 mL ammonia were then added. The mixture above was sealed in a flask and kept at 80°C for 10 h under stirring. The precipitates were washed with distilled water and dried through a freeze-drying process. The obtained powder was thermally treated at 325°C for 2 h under an Ar/H₂ flow, and then was further treated in a furnace at 100°C for 30 min. under air atmosphere and then Co@CoO/NG composite was obtained. The Co@CoO/G composite was synthesized under the similar conditions except that NG was replaced with the pristine graphene. Co@CoO particles were fabricated without addition of any substrate.

Electrochemical measurements. Electrochemical measurements were carried out with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using Co-based catalysts on carbon paper as the working electrode, a graphite rod as the counter electrode and an Ag/AgCl electrode as the reference electrode.

Carbon paper electrode: The preparation of the working electrode was described below: the catalysts were dispersed in N-methyl-2-pyrrolidone solvent containing 7.5 wt% PVDF under sonication, in which the weight ratio of the catalyst to PVDF is 8:1. Then the slurry was coated onto a piece of carbon paper. The loading density of the catalyst was around 2 mg cm⁻².

Electrochemical measurements of the catalysts were measured in 1 M KOH solution after purging the electrolyte with N₂ gas for 30 min. Polarization curves were obtained using Linear sweep voltammetry (LSV). The long-term stability test was

carried out using chronopotentiometric measurements. All potentials measured were calibrated to RHE using the following Equation: $E_{(\text{RHE})} = E_{(\text{Ag/AgCl})} + 0.21 \text{ V} + 0.059 \times \text{pH}$. All current densities presented are corrected against ohmic potential drop.

TOF calculations.

$$\text{TOF (s}^{-1}\text{)} = I/2nF \text{ (HER)}$$

$$\text{TOF (s}^{-1}\text{)} = I/4nF \text{ (OER)}$$

where I (A) is the current of the polarization curve obtained by LSV measurements, F is Faraday constant and n is the mole number of the Co on the electrodes.

Structure characterizations. XRD data were performed on a X'Pert Pro diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418\text{\AA}$). TEM measurements were carried out on a transmission electron microscope (FEI Tecnai-F20) with an accelerating voltage of 200 kV. XPS data were accuired on a X-ray photoelectron spectrometer (ESCALAB 250, Thermofisher Co.)with Mg $K\alpha$ radiation. The binding energy was calibrated with the C 1s position of contaminant carbon in the vacuum chamber of the XPS instrument (284.6 eV).

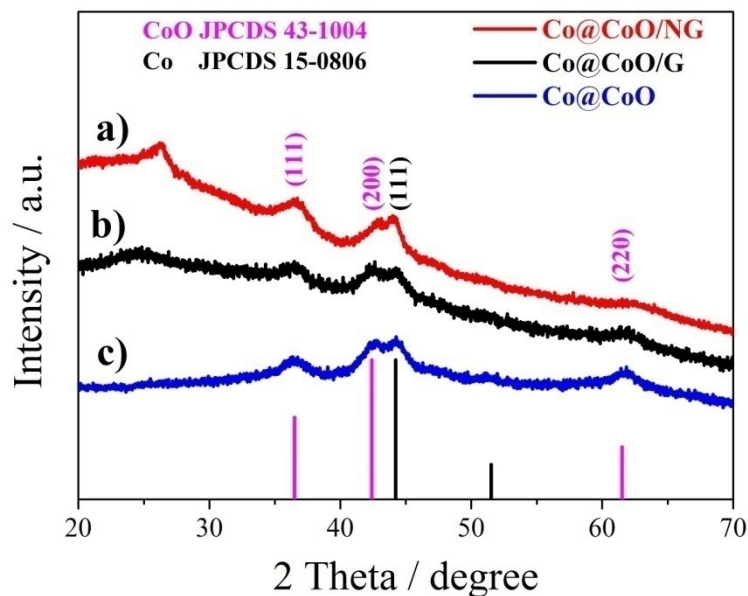


Figure S1 XRD patterns of samples. a) Co@CoO/NG, b) Co@CoO/G and c) Co@CoO

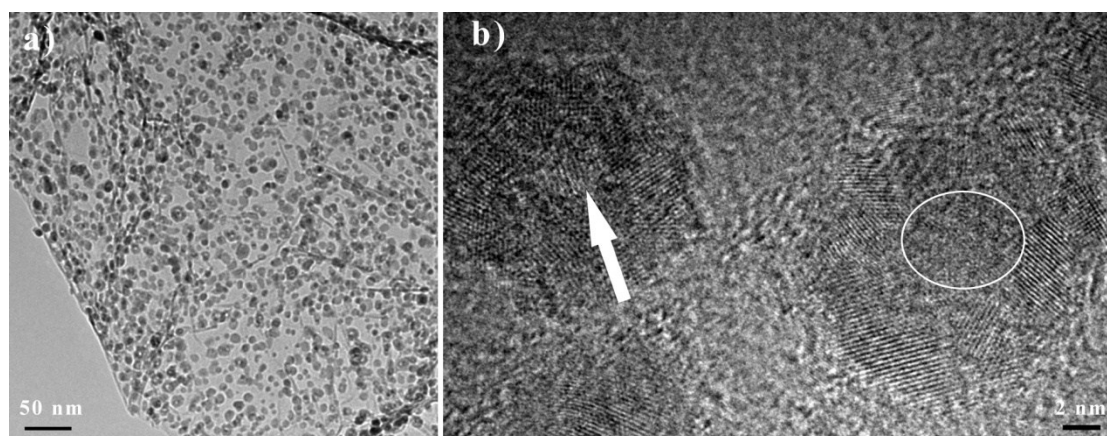


Figure S2 TEM image of Co@CoO/G. a) Low-magnification TEM and b) HRTEM images.

The TEM image shows that some particles in the Co@CoO/G composite have void space (Figure S2a)), and some particles have larger CoO shell thickness (4 to 6 nm, Figure S2b)). The hollow void space of one particle were indicated by a white arrow, and the metal Co and CoO regions for another particle were indicated by a white circle.

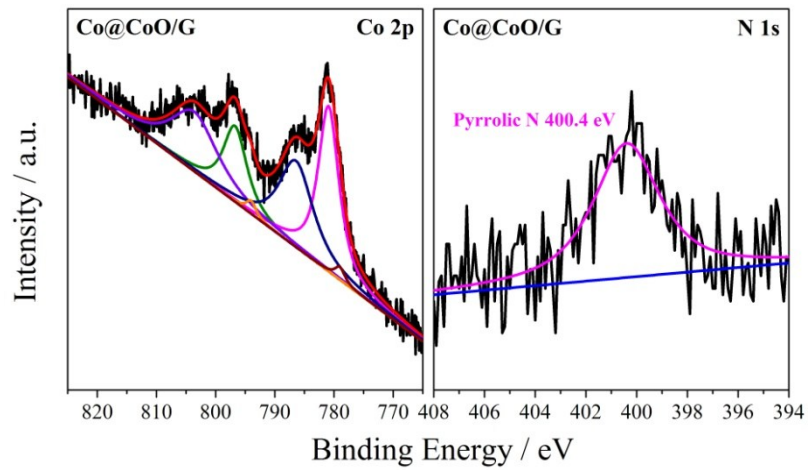


Figure S3 XPS spectra of Co@CoO/G composite.

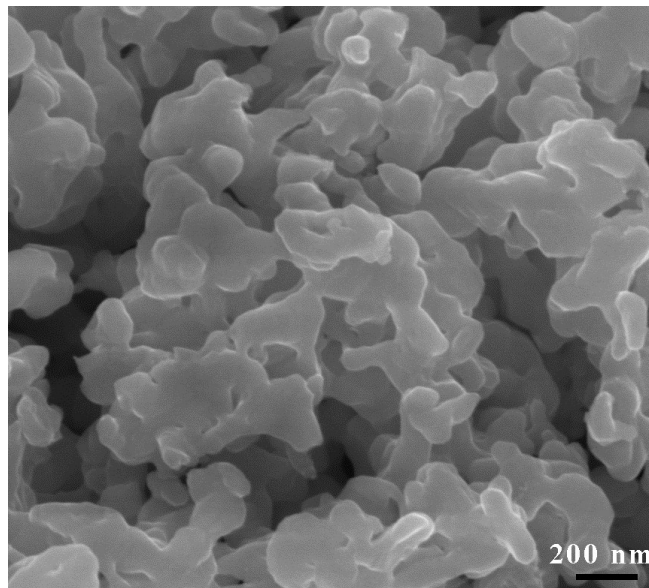


Figure S4 SEM image of Co@CoO catalysts.

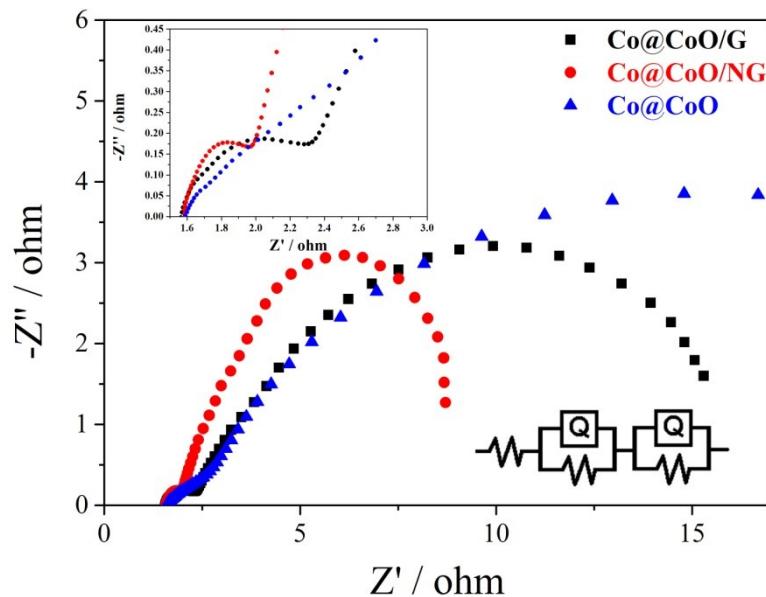


Figure S5 Nyquist plots of Co@CoO/NG, Co@CoO/G and Co@CoO. The upper and bottom insets show the magnified plots in high frequency and the equivalent circuit, respectively.

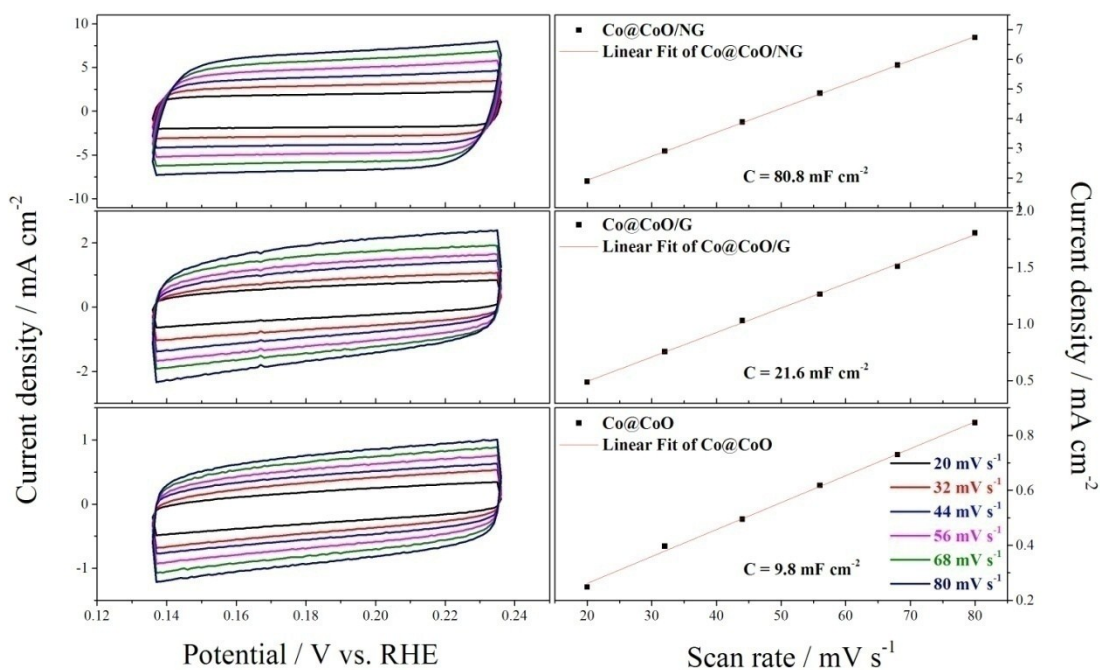


Figure S6 Cyclic voltammographs for Co@CoO/NG, Co@CoO/G and Co@CoO in the region of 0.136-0.236 V vs. RHE in 1M KOH. The differences in current density ($\Delta J = J_a - J_c$) at 0.19 V vs. RHE plotted against scan rate fitted to a linear regression allows for the estimation of C_{dl} .

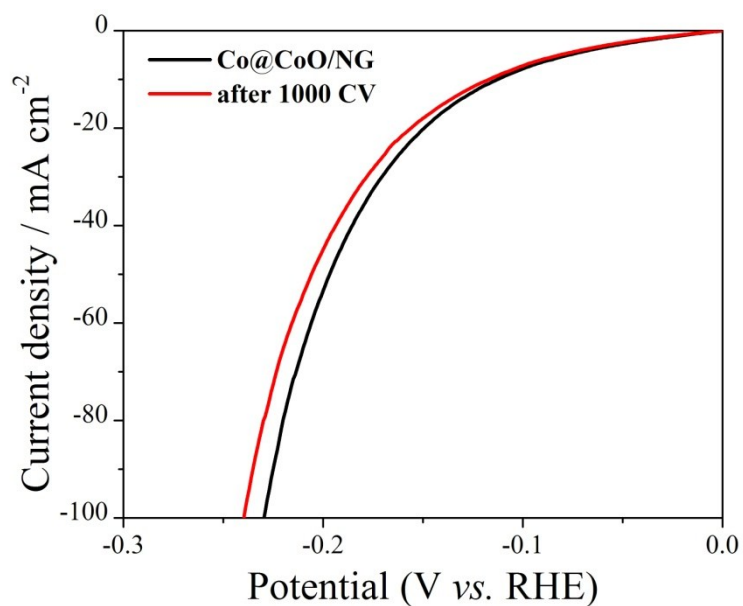


Figure S7 Stability test for the Co@CoO/NG by CV scanning for 1000 cycles in 1.0 M KOH solution at a scan rate of 50 mV s⁻¹.

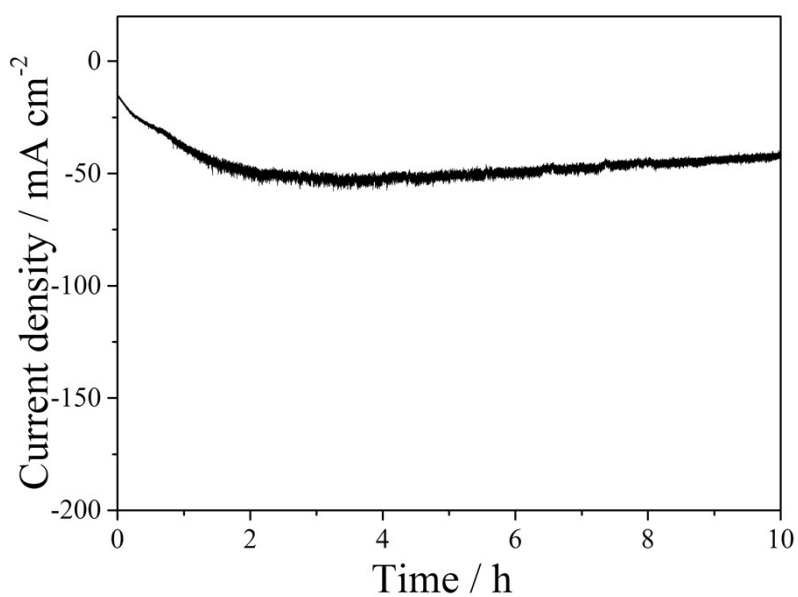


Figure S8 Time-dependent current density curve for the Co@CoO/NG under a static overpotential of 200 mV over 10 h.

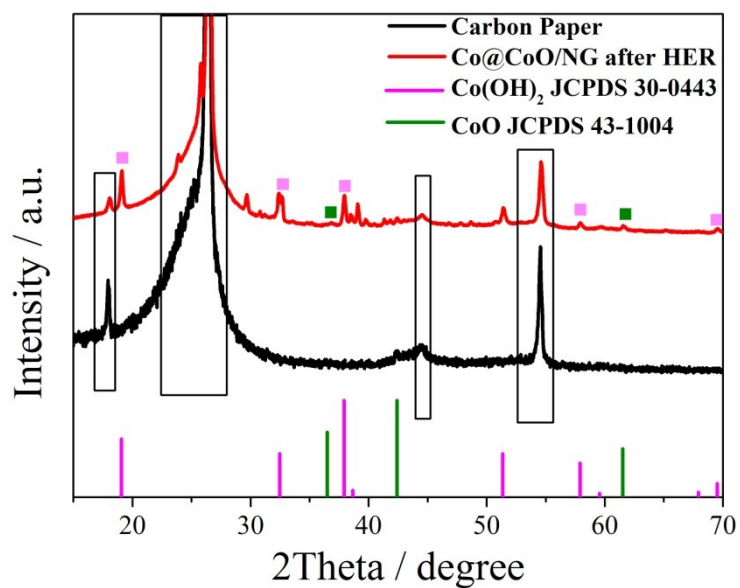


Figure S9 Comparison of XRD patterns of Co@CoO/NG before and after HER. The peaks indicated by square line come from carbon paper electrode.

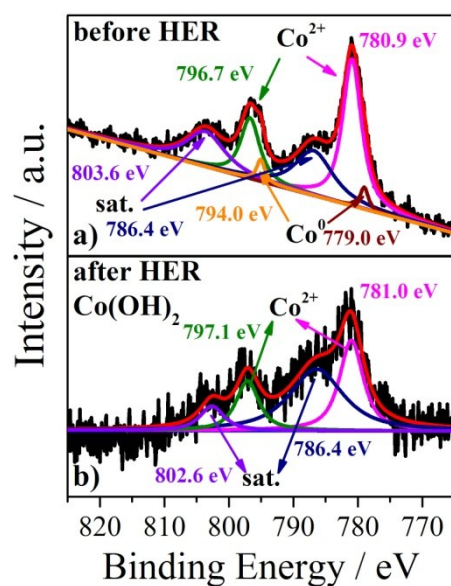


Figure S10 Comparison of XPS spectra of Co 2p core level of Co@CoO/NG before (a) and after HER (b).

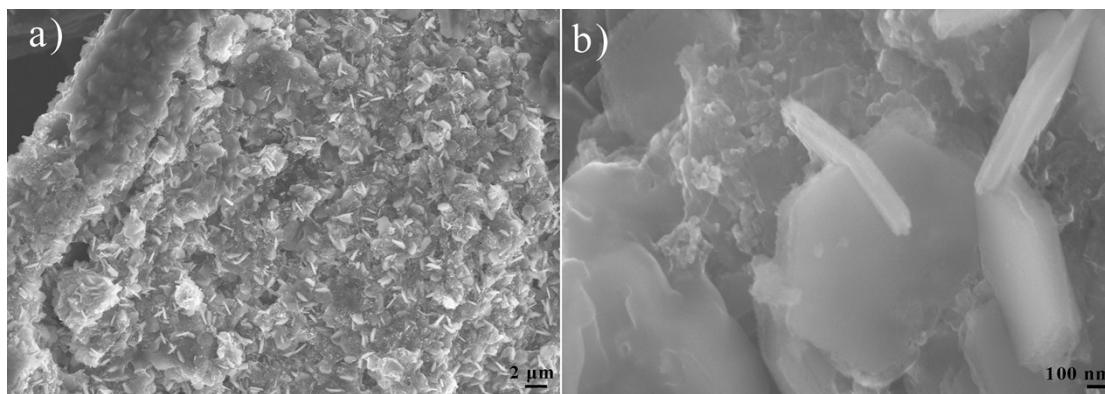


Figure S11 SEM images of Co@CoO/NG after HER.

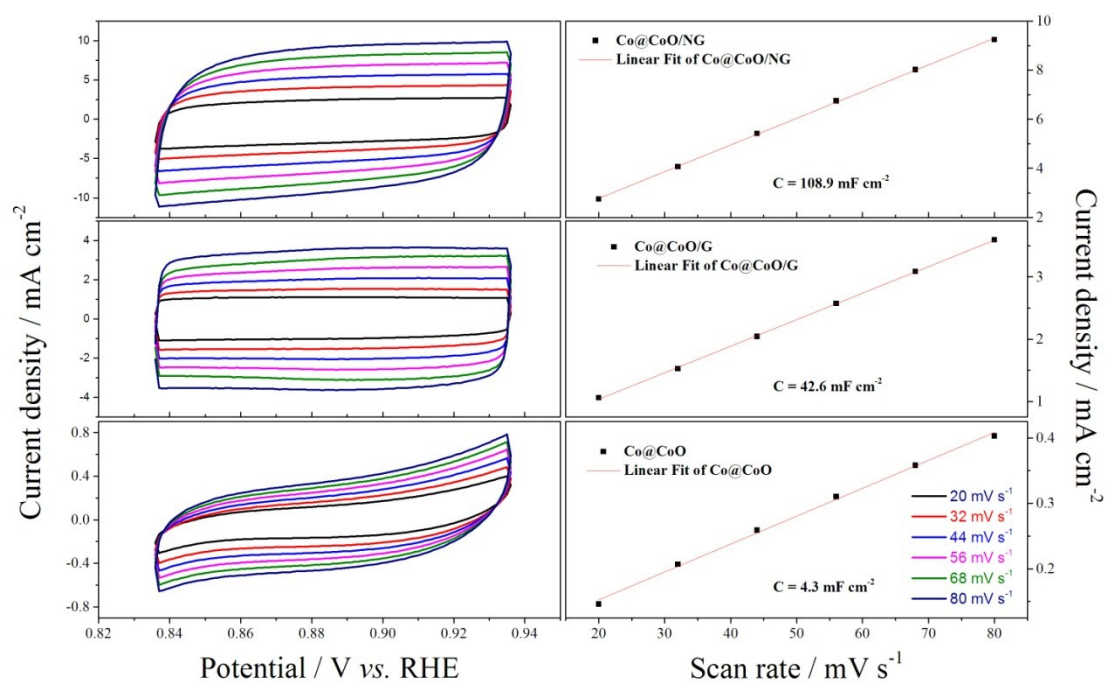


Figure S12 Cyclic voltammographs for Co@CoO/NG, Co@CoO/G and Co@CoO in the region of 0.836-0.936 V vs. RHE in 1M KOH. The differences in current density ($\Delta J = J_a - J_c$) at 0.89 V vs. RHE plotted against scan rate fitted to a linear regression allows for the estimation of C_{dl} .

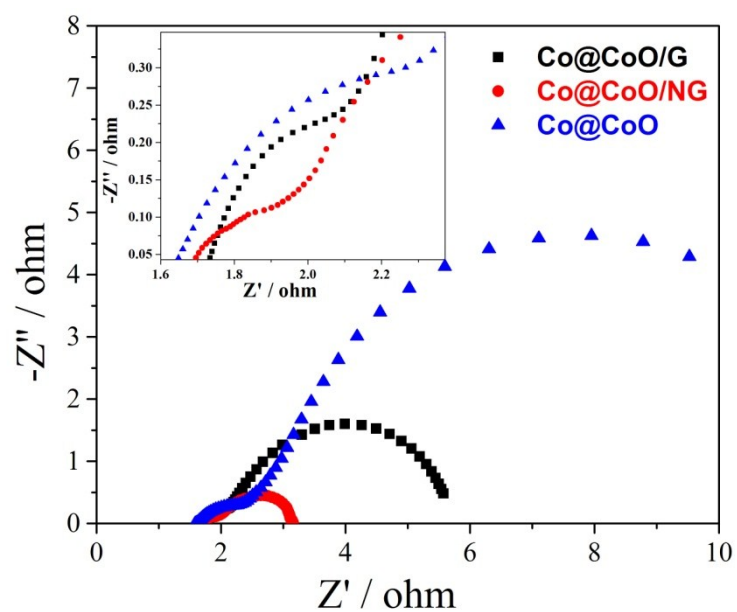


Figure S13 Nyquist plots of Co@CoO/NG, Co@CoO/G and Co@CoO at η_{OER} of 300 mV.

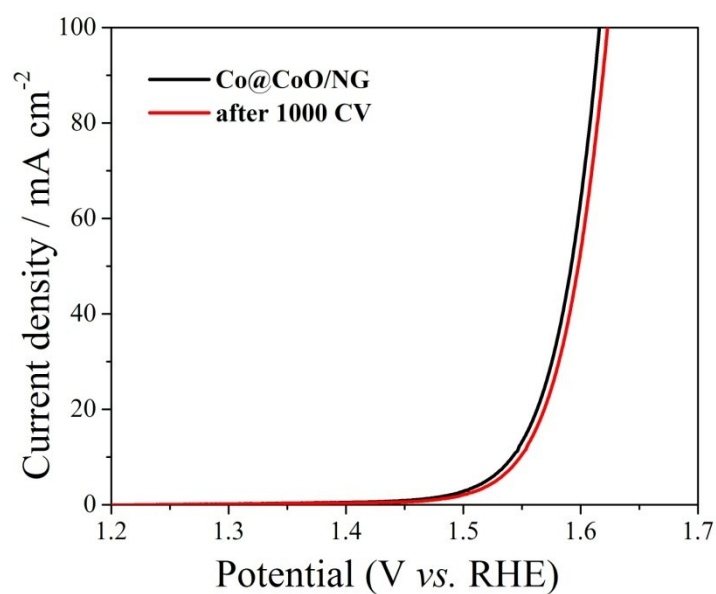


Figure S14 Stability test for the Co@CoO/NG by CV scanning for 1000 cycles in 1.0 M KOH solution at a scan rate of 50 mV s⁻¹.

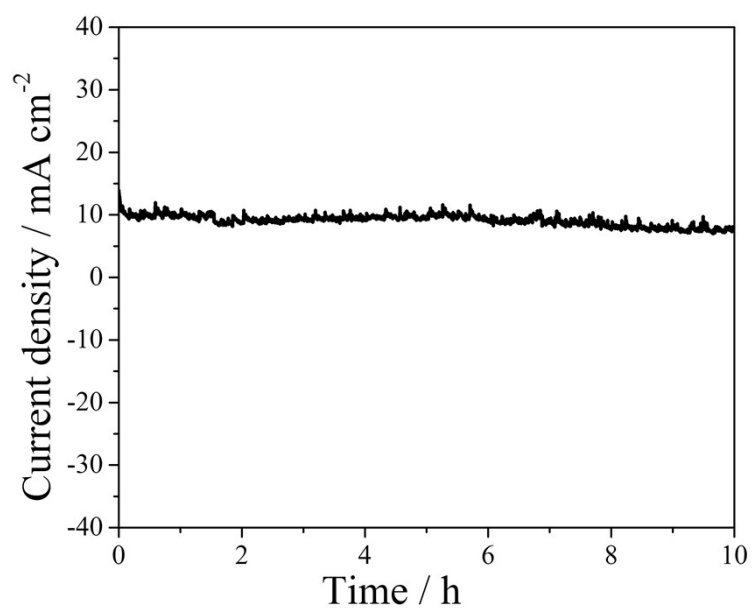


Figure S15 Time-dependent current density curve for the Co@CoO/NG under a static overpotential of 318 mV over 10 h.

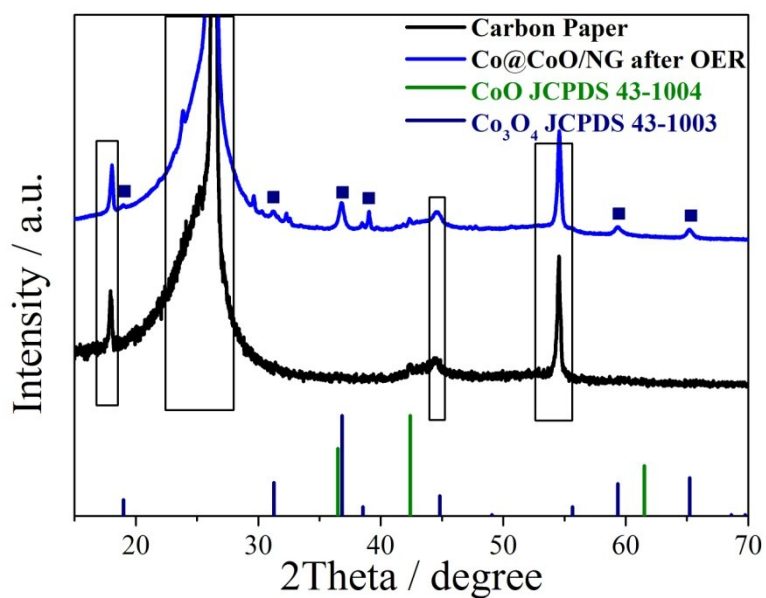


Figure S16 Comparison of XRD patterns of Co@CoO/NG before and after OER. The peaks indicated by square line come from carbon paper electrode.

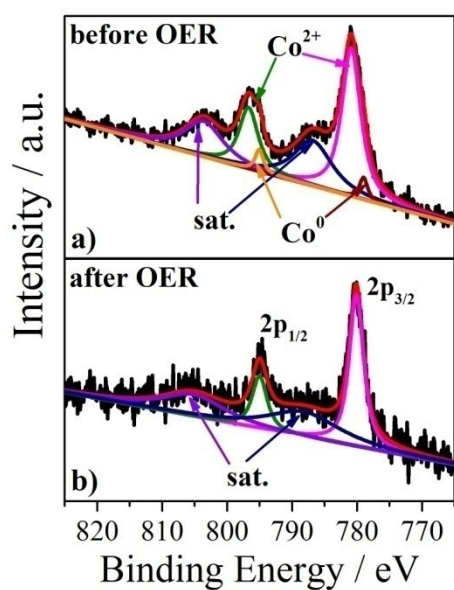


Figure S17 Comparison of XPS spectra of Co 2p core level of Co@CoO/NG before and after OER.

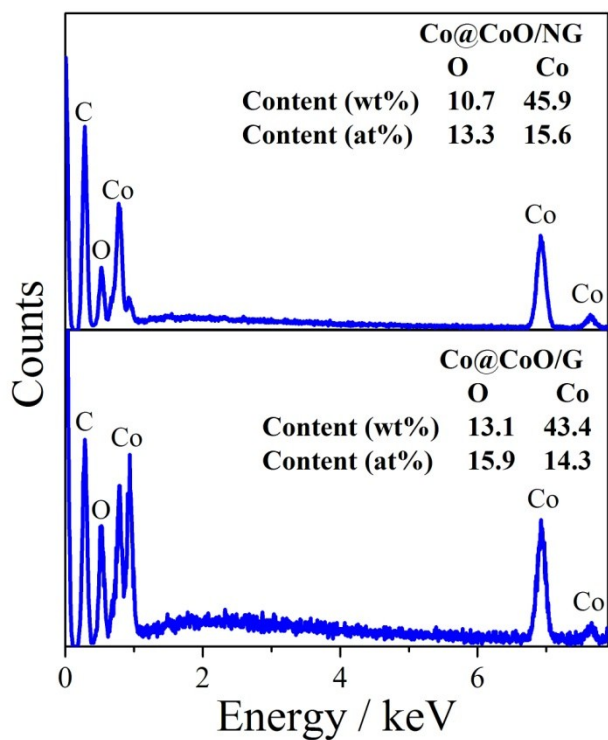


Figure S18 EDS patterns of Co@CoO/NG and Co@CoO/G

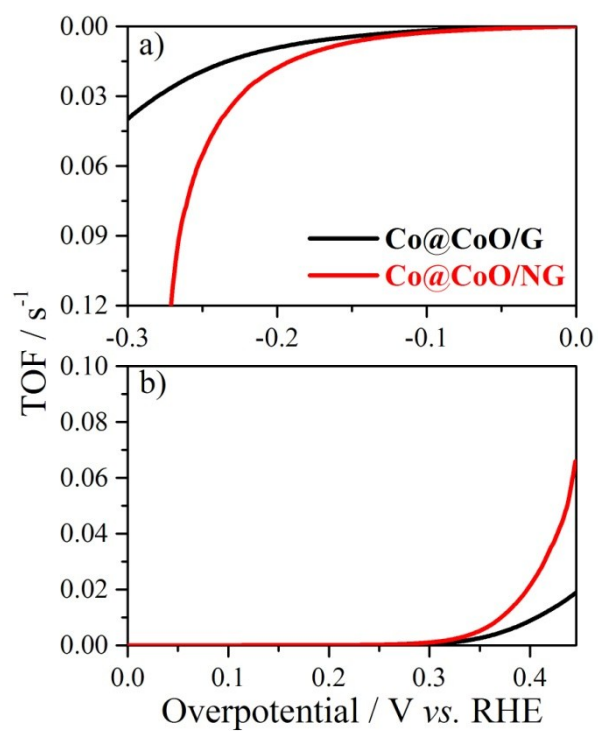


Figure S19 TOFs of Co@CoO/NG and Co@CoO/G

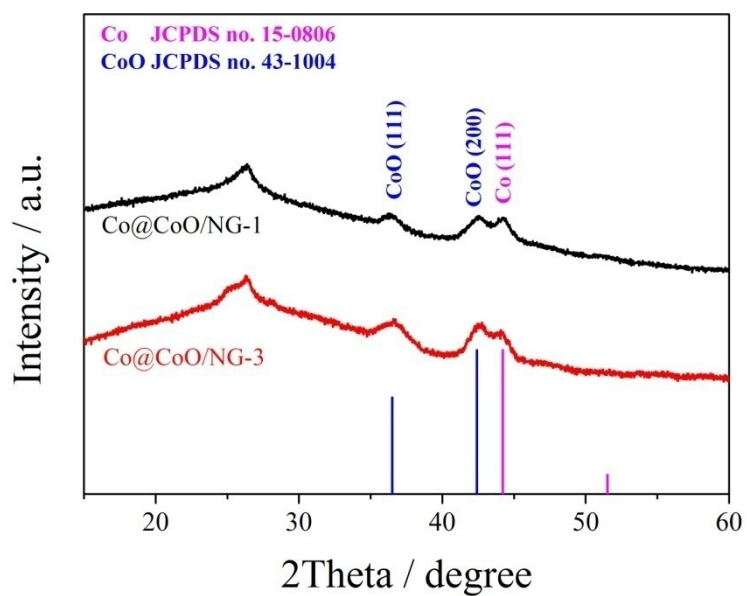


Figure S20 XRD patterns of Co@CoO/NG-1 and Co@CoO/NG-3.

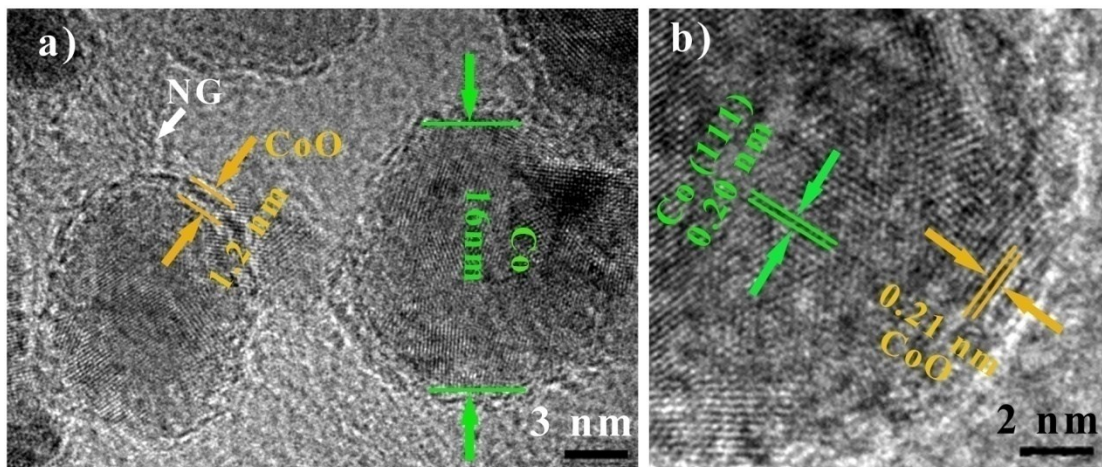


Figure S21 TEM images of patterns of Co@CoO/NG-1. a) High-magnification TEM image and b) HRTEM image.

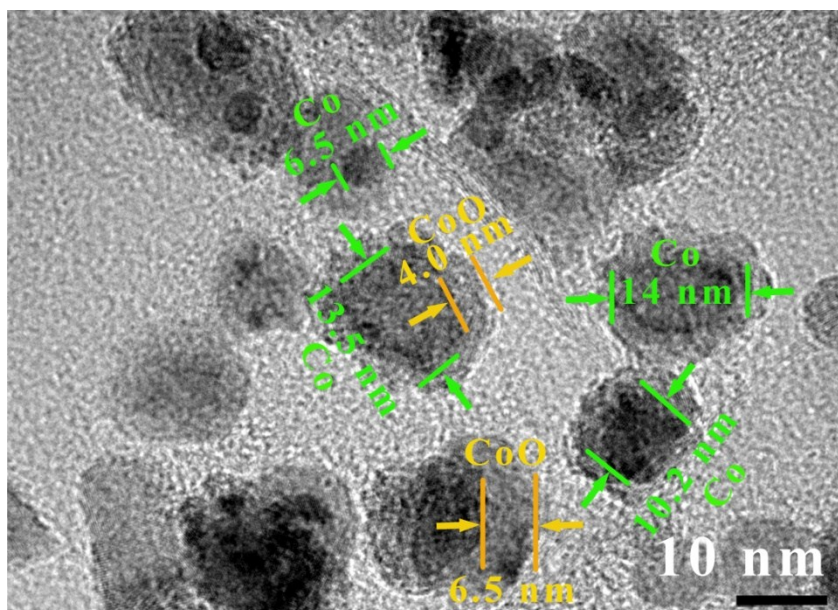


Figure S22 TEM image of patterns of Co@CoO/NG-3.

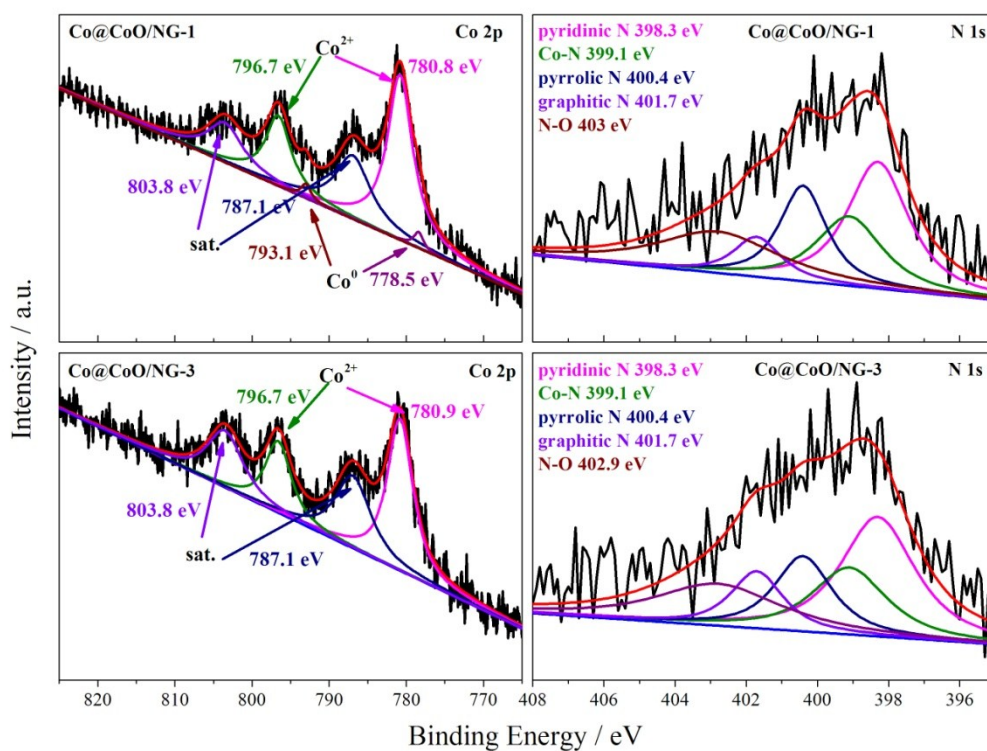


Figure S23 XPS spectra of Co 2p and N 1s of Co@CoO/NG-1 and Co@CoO/NG-3

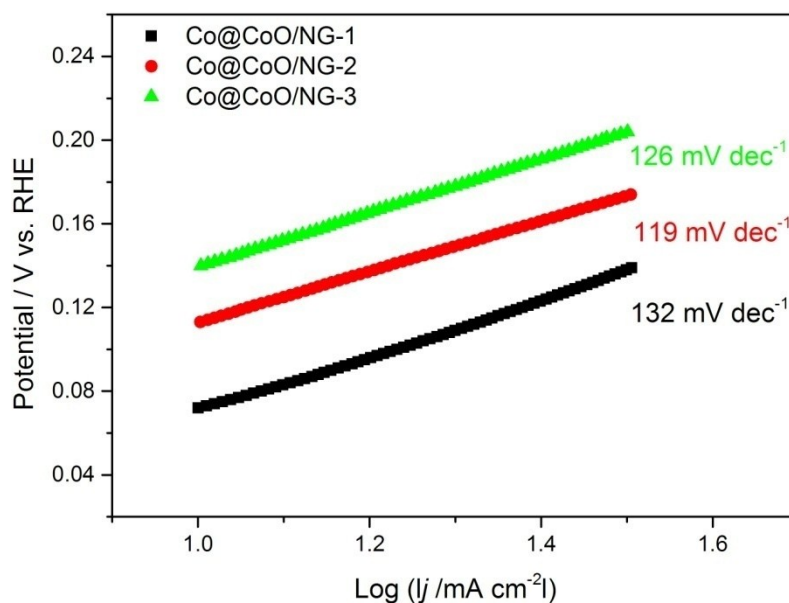


Figure S24 Tafel slopes of Co@CoO/NG-1, Co@CoO/NG-2 and Co@CoO/NG-3

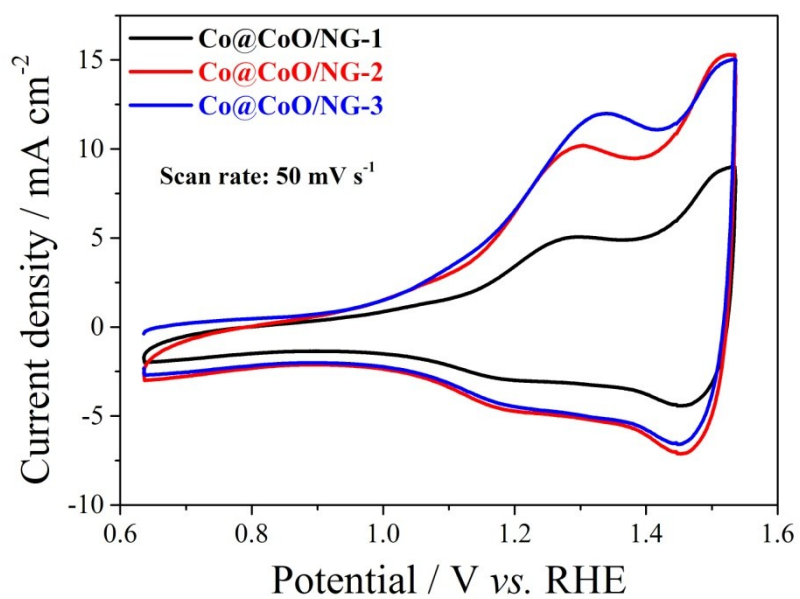


Figure S25 The CV curve of Co@CoO/NG electrodes at a scan rate of 50 mV s⁻¹.

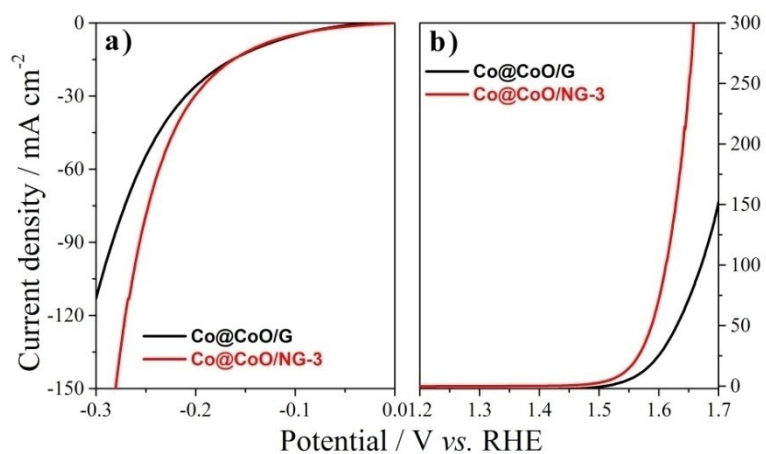


Figure S26 Comparison of HER (a) and OER (b) activities of Co@CoO/G to Co@CoO/NG-3.

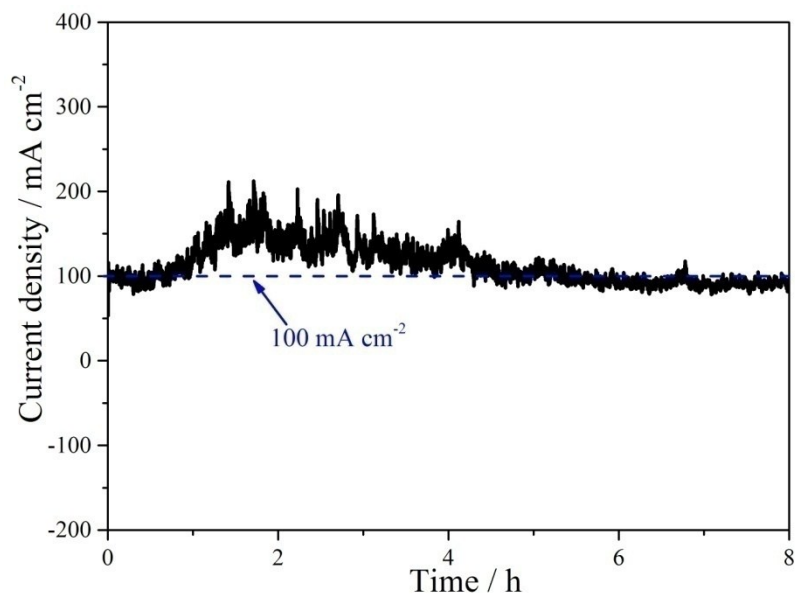


Figure S27 The stability of Co@CoO/NG electrodes at 1.7 V.

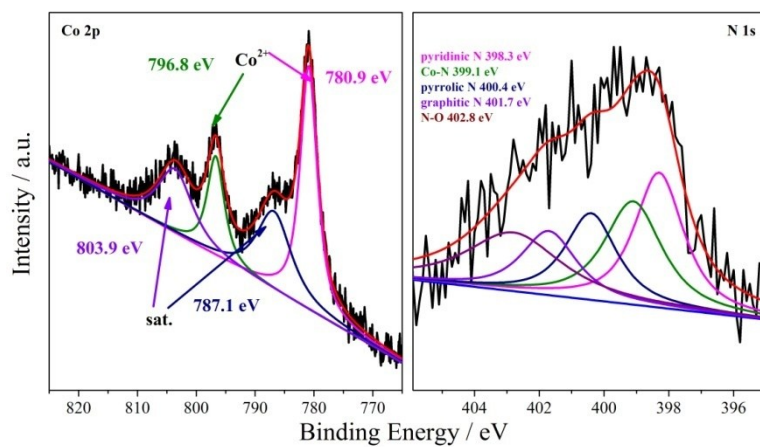


Figure S28 Co 2p and N 1s XPS spectra of Co@CoO/NG-4.

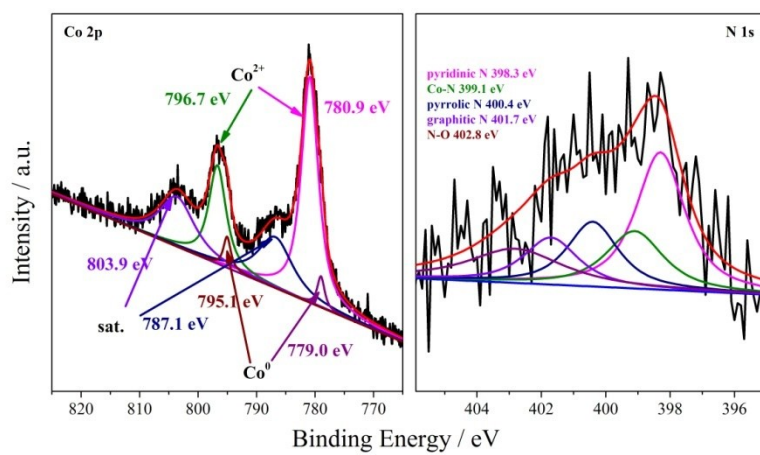


Figure S29 Co 2p and N 1s XPS spectra of Co@CoO/NG-5.

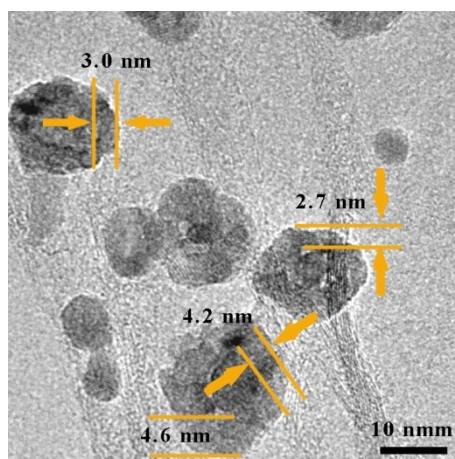


Figure S30 TEM image of Co@CoO/NG-4

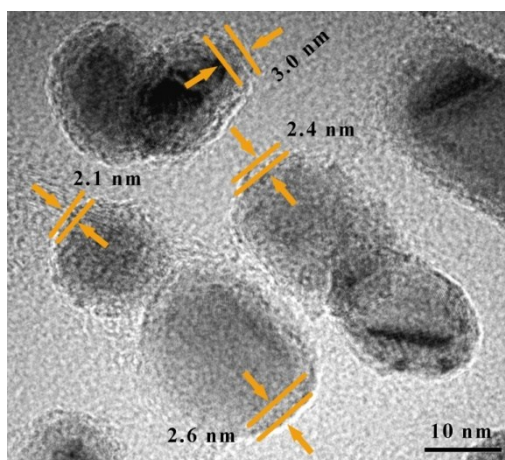


Figure S31 TEM image of Co@CoO/NG-5

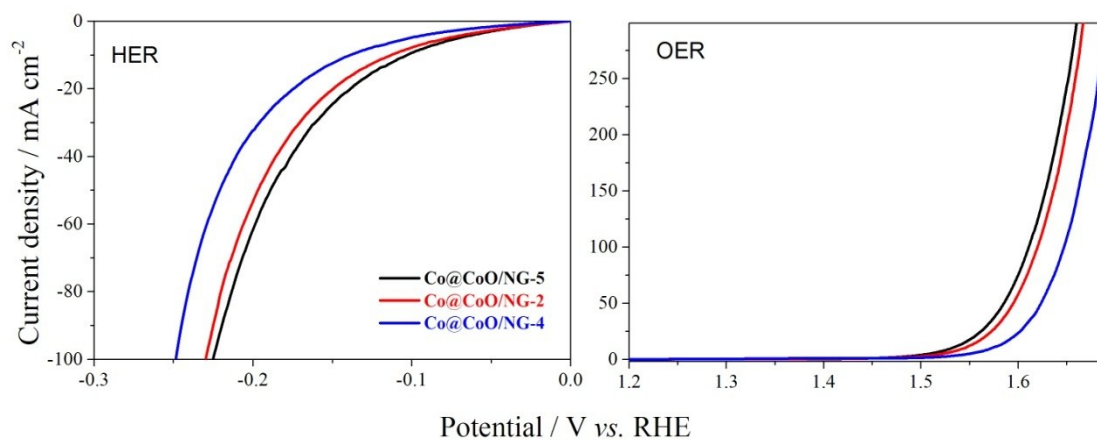


Figure S32 Comparison of HER and OER activities of Co@CoO/NG-2, Co@CoO/NG-4 and Co@CoO/NG-5.

Table S1. Comparison of the HER activities of the Co@CoO/NG in 1.0 M KOH with those of other HER catalysts recently published.

Catalysis	Tafel slope (mV dec ⁻¹)	η_{10} (mV)	η_{100} (mV)	Electrolyte	Refs.
Co@CoO/NG-1	122	72	221	1.0 M KOH	This work
Co@CoO/NG-2	119	112	230		
Co@CoO/NG-3	120	139	261		
Co-NRCNTs	--	~350	--	1.0 M KOH	<i>Angew. Chem., Int. Ed.</i> , 2014, 53 , 4372–4376.
Co-NRCNTs	80	260	--	0.5 M KOH	<i>Angew. Chem., Int. Ed.</i> , 2014, 53 , 4372–4376.
CoP/CC	129	209	550	1.0 M KOH	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 7587–7590.
CoP/CC	51	67	204	0.5 M H ₂ SO ₄	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 7587–7590.
CoNi@CN	104	142	--	0.1 M H ₂ SO ₄	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 2100–2104.
CoP/CNT	54	122	--	0.5 M H ₂ SO ₄	<i>Angew. Chem. Int. Ed.</i> , 2014, 53 , 6710–6714.
CoP	76	225	--	0.5 M H ₂ SO ₄	<i>Angew. Chem. Int. Ed.</i> , 2014, 53 , 6710–6714.
CoP/Ti	50	72	--	0.5 M H ₂ SO ₄	<i>Angew. Chem. Int. Ed.</i> , 2014, 53 , 5427–5430.
CoS ₂ film	51.4	190	--	0.5 M H ₂ SO ₄	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 10053–10061.
CoS ₂ -MW	58	158	--	0.5 M H ₂ SO ₄	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 10053–10061.
CoS ₂ -NW	51.6	145	200	0.5 M H ₂ SO ₄	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 10053–10061.
Co ₉ S ₈ @MoS ₂ /CNFs	110	190	--	0.5 M H ₂ SO ₄	<i>Adv. Mater.</i> , 2015, 27 , 4752–4759.
MoS ₂ /CNFs	110	342	--	0.5 M H ₂ SO ₄	<i>Adv. Mater.</i> 2015, 27 , 4752–4759.
Co ₉ S ₈ /CNFs	203	--	--	0.5 M H ₂ SO ₄	<i>Adv. Mater.</i> , 2015, 27 , 4752–4759.
NiSe/NF	120	96	--	1.0 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 9351–9355.
CoP	42	94	~145	1.0 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 6251–6254

Co-PCPTF	53	150	--	0.5 M H ₂ SO ₄	<i>Adv. Mater.</i> , 2015, 27 , 3175–3180.
Co-PCPTF	--	370	--	1.0 M KOH	<i>Adv. Mater.</i> , 2015, 27 , 3175–3180.
Ni-NiO/N-rGO	46	135	--	1.0 M KOH	<i>Adv. Funct. Mater.</i> , 2015, 25 , 5799–5808.
Co-NiO/N-rGO	51	160	--	1.0 M KOH	<i>Adv. Funct. Mater.</i> , 2015, 25 , 5799–5808.
PANiCo _{750A}	55	140	210	0.5 M H ₂ SO ₄	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 15070–15073.
600FeCo	74	262	--	0.5 M H ₂ SO ₄	<i>Energy Environ. Sci.</i> , 2015, 8 , 3563–3571.
Co(OH) ₂ @PANI	91.6	85	240	1.0 M NaOH	<i>Adv. Mater.</i> , 2015, 27 , 7051–7057.
Ni ₂ P/Ni/NF	72	98	175	1.0 M KOH	<i>ACS Catal.</i> , 2016, 6 , 714–721.
CoO _x @N-doped carbon	115	232	--	1.0 M KOH	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 2688–2694
CoO _x @AC	--	260	--	1.0 M KOH	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 2688–2694

Table S2. Comparison of the OER activities of the Co@CoO/NG in 1.0 M KOH with recently published results.

Catalysis	Tafel slope (mV dec ⁻¹)	η_{10} (mV)	η_{100} (mV)	Electrolyte	Refs.
Co@CoO/NG-1	68	1.566	1.637	1.0 M KOH	This work
Co@CoO/NG-2	73	1.545	1.62		
Co@CoO/NG-3	73	1.538	1.621		
Co ₉ S ₈ @MoS ₂ /CNFs	61	430	--	1.0 M KOH	<i>Adv. Mater.</i> , 2015, 27 , 4752–4759.
MoS ₂ /CNFs	80	--	--	1.0 M KOH	<i>Adv. Mater.</i> , 2015, 27 , 4752–4759.
Co ₉ S ₈ /CNFs	78	512	--	1.0 M KOH	<i>Adv. Mater.</i> , 2015, 27 , 4752–4759.
Co ₃ O ₄ @CoO SC	89	430	--	0.5 M KOH	<i>Nat. Commun.</i> , 2015, 6 , 8106.
G-Co ₃ O ₄	56	313	--	1.0 M KOH	<i>Sci. Rep.</i> , 2015, 5 , 7629.
Au@Co ₃ O ₄	60	380	--	0.1 M KOH	<i>Adv. Mater.</i> , 2014, 26 , 3950–3955.
NG-NiCo	614	--	500	0.1 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2013, 52 , 13567–13570.
CoO _x @CN	--	260	--	1.0 M KOH	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 2688–2694.
Mn ₃ O ₄ /CoSe ₂	49	~450	--	0.1 M KOH	<i>J. Am. Chem. Soc.</i> , 2012, 134 , 2930–2933.
Co ₃ S ₄ (csatn)	48	--	--	0.1 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 11231–11235.
Ni–Co Hydroxide	145	460	--	0.1 M KOH	<i>Adv. Funct. Mater.</i> , 2014, 24 , 4698–4705.
NiCo _{2.7} (OH) _x	65	350	--	1.0 M KOH	<i>Adv. Energy Mater.</i> , 2015, 5 , 1401880.
Ni-Co-O ₂	39	325	--	1.0 M NaOH	<i>ACS Nano</i> , 2014, 8 , 9518–9523.
NiSe/NF	75	--	314	1.0 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 9351–9355.
Co-P	47	345	~430	1 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 6251–6254.
Co-PCPTF	65	300	--	1.0 M KOH	<i>Adv. Mater.</i> , 2015, 27 , 3175–3180.
Ni-NiO/N-rGO	43	~240	--	0.1 M KOH	<i>Adv. Funct. Mater.</i> , 2015, 25 , 5799–5808.

Co-CoO/N-rGO	68	~400	--	0.1 M KOH	<i>Adv. Funct. Mater.</i> , 2015, 25 , 5799–5808.
FeNi@NC	70	280	430	1.0 M NaOH	<i>Energy Environ. Sci.</i> , 2016, 9 , 123–129.
Ni ₂ P/Ni/NF	--	200	268	1.0 M KOH	<i>ACS Catal.</i> , 2016, 6 , 714–721.
Ni _{0.9} Fe _{0.1} O _x	30	336		1.0 M KOH	<i>J. Am. Chem. Soc.</i> , 2012, 134 , 17253–17261.

Table S3. Comparison of the electrochemical performance of Co@CoO/NG-2|Co@CoO/NG-2 as bifunctional catalysts for overall water splitting in 1.0 M KOH with recently published results.

Catalysis	η_{10} (V)	η_{100} (V)	Electrolyte	Refs.
Co@CoO/NG-2	1.58	1.7	1.0 M KOH	This work
NiSe	1.63	--	1.0 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 9351–9355.
CoP	1.64	1.744	1.0 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 6251–6254.
Ni ₂ P/Ni/NF	1.49	1.68	1.0 M KOH	<i>ACS Catal.</i> , 2016, 6 , 714–721.
CoP nanoparticles/Carbon	1.587	--	1.0 M KOH	<i>ACS Catal.</i> , 2015, 5 , 6874–6878
Co-P/ N-doped carbon matrices	~1.7	--	1.0 M KOH	<i>Chem. Mater.</i> , 2015, 27 , 7636–7642
NiSe Nanowire/ Nickel Foam	1.63	--	1.0 M KOH	<i>Angew. Chem. Int. Ed.</i> , 2015, 54 , 9351–9355
NiCo ₂ S ₄ nanowires array	1.68	--	1.0 M KOH	<i>Nanoscale</i> , 2015, 7 , 15122–15126