Electronic Supplementary Information

Double-wall carbon nanotube assisted phase engineering in CoO_xS_y complex for efficient oxygen evolution reaction

Yucong Huang[a], Zongpeng Wang[b], Shijie Shen[b], Liangai Huang[b], Wenwu Zhong*[ab], Jiaqi Pan*[a], and Chaorong Li*[a]

[a] Key Laboratory of Optical Field Manipulation of Zhejiang Province, and Key Laboratory of ATMMT Ministry of Education, Department of Physics, Zhejiang Sci-Tech University, Hangzhou 310018, P. R. China E-mail: crli@zstu.edu.cn , panjq@zstu.edu.cn

[b] Zhejiang Provincial Key Laboratory for Cutting Tools, Taizhou University, Jiaojiang 318000, Zhejiang, P. R. China. E-mail: zhongww@tzc.edu.cn

Experimental Section

Synthesis of DWCNTs

The solution was prepared with ethanol as carbon source, 3.0 wt.% ferrocene as catalyst and 0.5 wt.% thiophene as cocatalyst, respectively. 1000 sccm argon and 1000 sccm hydrogen were used as carrier gases. The three-temperature-zone tube furnace is used as the reactor, and the temperature of the reactor is 1180 ℃, with the solution injection rate of 12 mL/h. The solid obtained after the reaction was labeled as DWCNTs.

Synthesis of CoO_x and CoS_x

45 mL N,N-Dimethylacetamide (DMAc) was mixed with 30 mL $CoCl_2$ with a concentration of 10 mmol/L, and the mixed solution was ultra-sonicated for 30 minutes. 75 μL NaOH with a concentration of 1 mol/L was then added dropwise to the solution and ultrasonic treatment was continued for 10 minutes. The precipitate obtained by centrifugation was wash with acetone and deionized water and was dried out at room temperature. Subsequently, transfer the powder to tubular furnace, place 300 mg of sublimated sulfur powder in front of it, heat them to 500 ℃ in argon atmosphere, and the heating rate is 2 ℃ per minute. After maintaining the temperature for 2 hours, continue to inject argon until it naturally drops to room temperature and the obtained black solid was labeled as CoS_x. As a contrast, the sample annealed without sublimated sulfur powder was labeled as CoO_x.

Synthesis of CoO_xS_y@DWCNTs and CoO_x@DWCNTs

10 mg DWCNTs were dispersed into a mixed solution of 45 mL DMAc and 30 mL $CoCl_2$ with a concentration of 10 mmol/L, and the mixed solution was ultra-sonicated for 30 minutes. 75 μL NaOH with a concentration of 1 mol/L was then added dropwise to the solution and ultrasonic treatment was continued for 10 minutes. After centrifugation and washing with acetone and deionized water, it was dried out at room temperature to obtain a black solid labeled as Co-DWCNTs. Transfer the powder of Co-DWCNTs to tubular furnace, place 300 mg of sublimated sulfur powder in front of it, heat them to 400, 500 or 600 ℃ in argon atmosphere, and the heating rate is 2 ℃ per minute. After maintaining the temperature for 2 hours, continue to inject argon until it naturally drops to room temperature, and the obtained black solid was labeled as CoO_xS_y@DWCNTs-400, 500 or 600, respectively, according to the reaction temperature. As a contrast, the sample annealed at 500 ℃ without sublimated sulfur powder was labeled as CoO_x@DWCNTs-500.

Characterizations

Material Characterizations

The morphology characterizations were conducted on the scanning electron microscopy (Hitachi S4800) and high-resolution transmission electron microscopy (FEI Talos F200S). X-ray diffraction (XRD) data were measured by X-ray diffraction (D/MAX 2500). Raman spectra and XPS spectra date were measured by Raman spectrometer (Horiba LabRam HR Evolution) and X-ray photoelectron spectrometer (Thermo Scientific K-Alpha) respectively.

Electrochemical Characterizations

Electrochemical tests were carried out on electrochemical workstation (CHI-660E) based on the three-electrode system. A Pt plate electrode and an Ag/AgCl were chosen as the counter electrode and the reference electrode respectively. 5 mg sample and 50 μL Nafion solution were uniformly dispersed in 1 mL *N, N*-Dimethylacetamide to prepare the electrocatalyst ink. Subsequently, 5 μL

electrocatalyst ink was dropped on the surface of the 3 mm diameter glassy carbon electrode and dried out at room temperature to obtain the working electrode. 1 mol/L KOH (pH = 13.8) was used as the electrolytes. The *iR*-corrected linear sweep voltametric (LSV) curves were tested at the scan rate of 5 mV/s and the Tafel slope is obtained by linear fitting the points in the Tafel region of the LSV data. The Tafel slope is obtained by linear fitting the points in the Tafel region of the LSV data. Electrochemical impedance spectra Nyquist plots were measured at a potential of 1.3 V from 1 MHz to 0.1 Hz. Cyclic voltammetry curves were measured at different scan rates (20 mV/s, 40 mV/s, 80 mV/s, 120 mV/s, 160 mV/s and 200 mV/s).

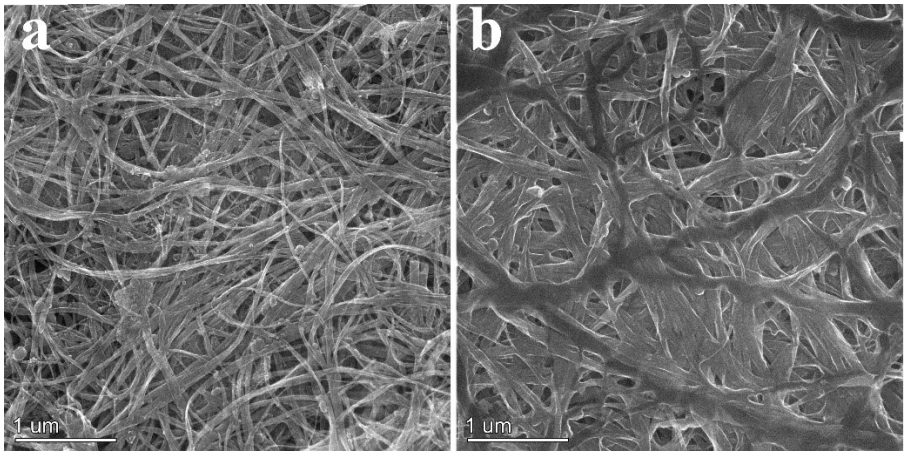

Figure S1. SEM image of (a) CoO_xS_y@DWCNTs-400 and (b) CoO_xS_y@DWCNTs-600 Both outer wall and inner wall of DWCNTs.

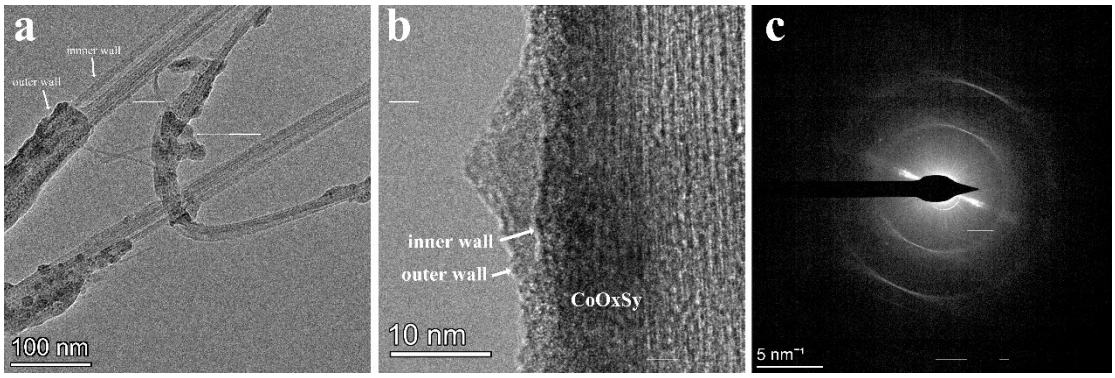

Figure S2. (a, b) TEM images of CoO_xS_y@DWCNTs-500 showing both outer wall and inner wall of DWCNTs, (c) selected area electron diffraction image of CoO_xS_y@DWCNTs-500.

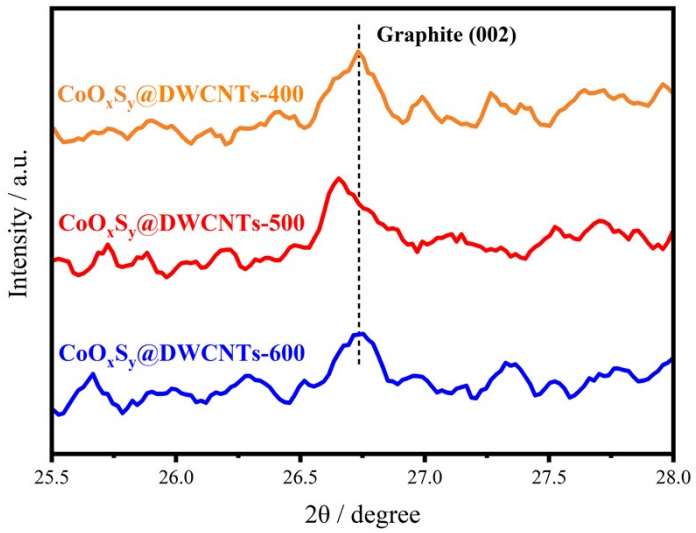

Figure S3. Partial zoomed image of XRD results, showing characteristic peaks of graphite (002) at 26.7°.

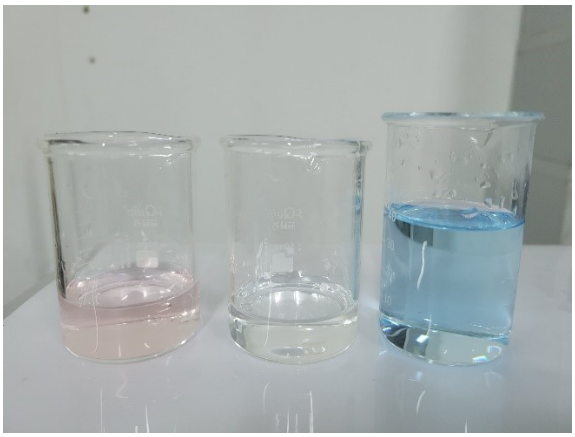

Figure S4. $CoCl_2$ solution with a concentration of 10 mmol/L (left), N,N-Dimethylacetamide (middle) and their complex formed after mixing (right).

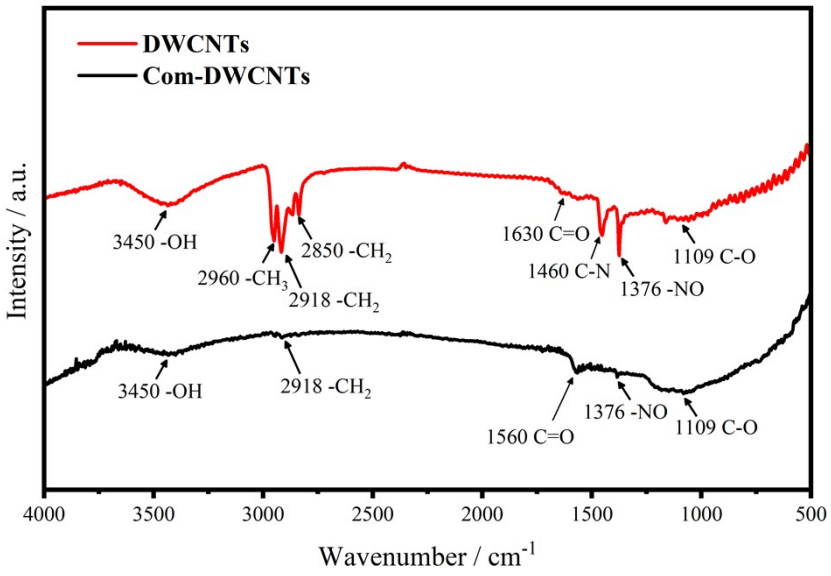

Figure S5. Fourier-transform infrared spectra of DWCNTs and commercial double walled carbon nanotubes.

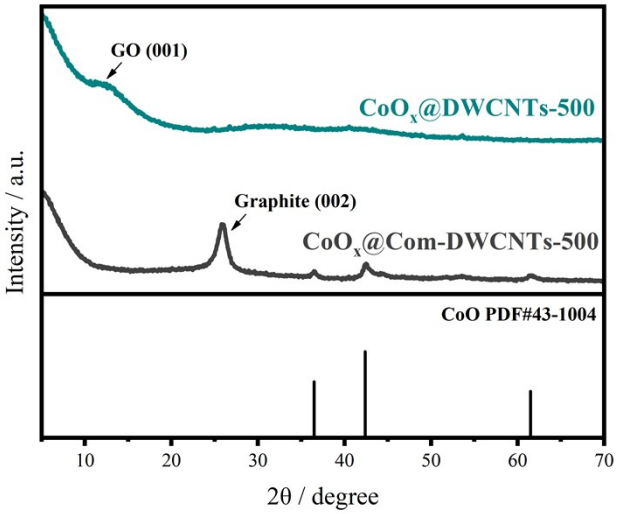

Figure S6. XRD patterns of CoO_x@DWCNTs-500 and its counterpart synthesized with commercial double walled carbon nanotubes.

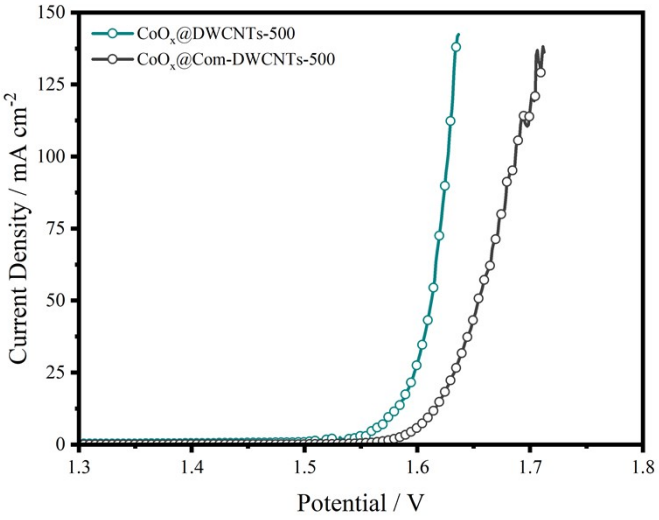

Figure S7. Linear sweep voltammetry plot of CoO_x@DWCNTs-500 and its counterpart synthesized with commercial double walled carbon nanotubes.

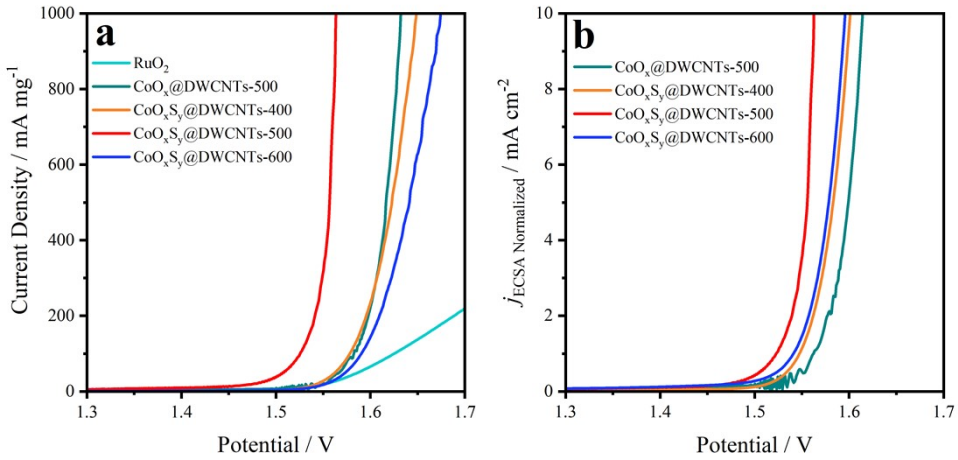

Figure S8. Linear sweep voltammetry plots with (a) current mass ratio and (b) ECSA normalized current density.

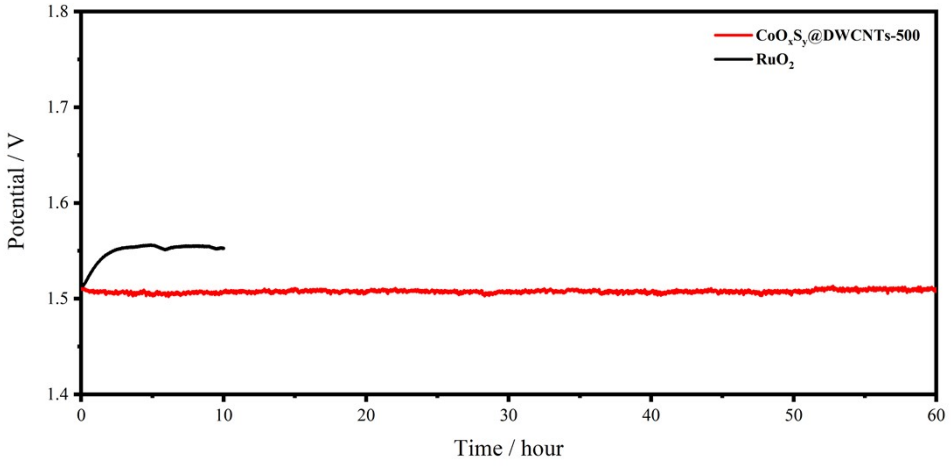

Figure S9. Electrochemical stability test at constant current density of 10 mA cm^{-2} of CoO_xS_y@DWCNTs-500.

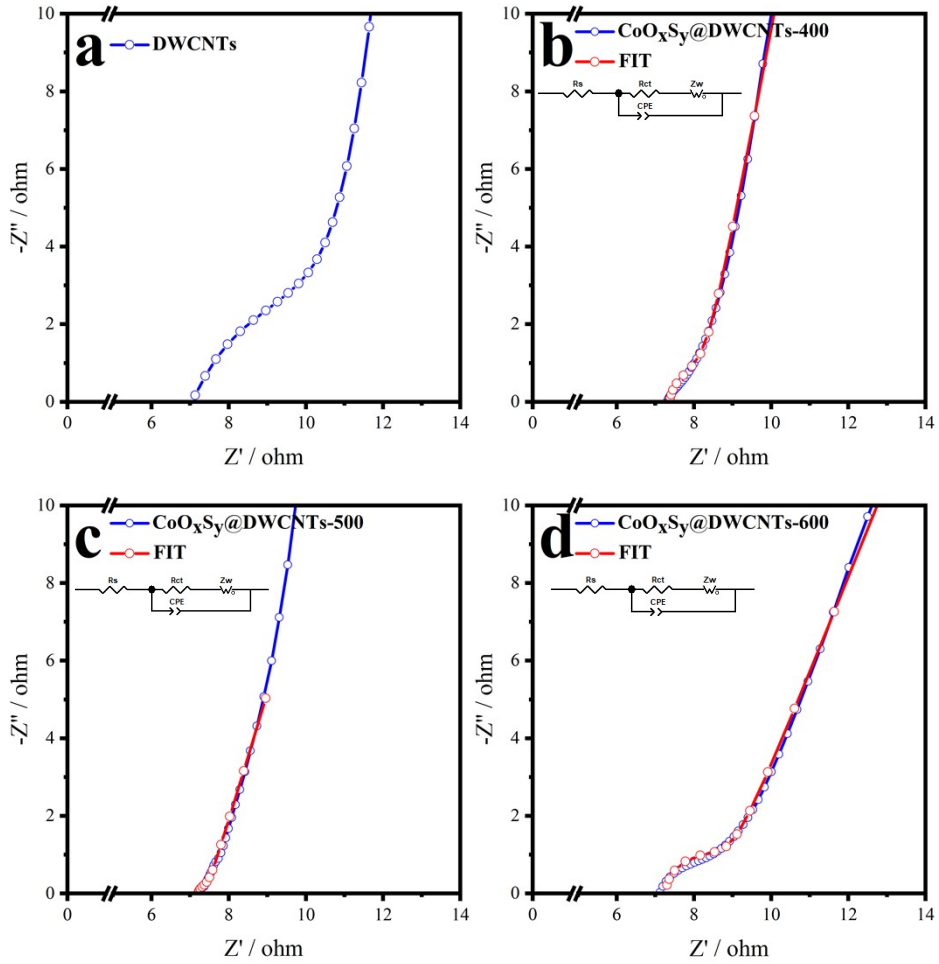

Figure S10. (a) Nyquist plot of DWCNTs and (b-d) electrochemical impedance spectroscopy fitting of CoO_xS_y@DWCNTs-400, 500 and 600.

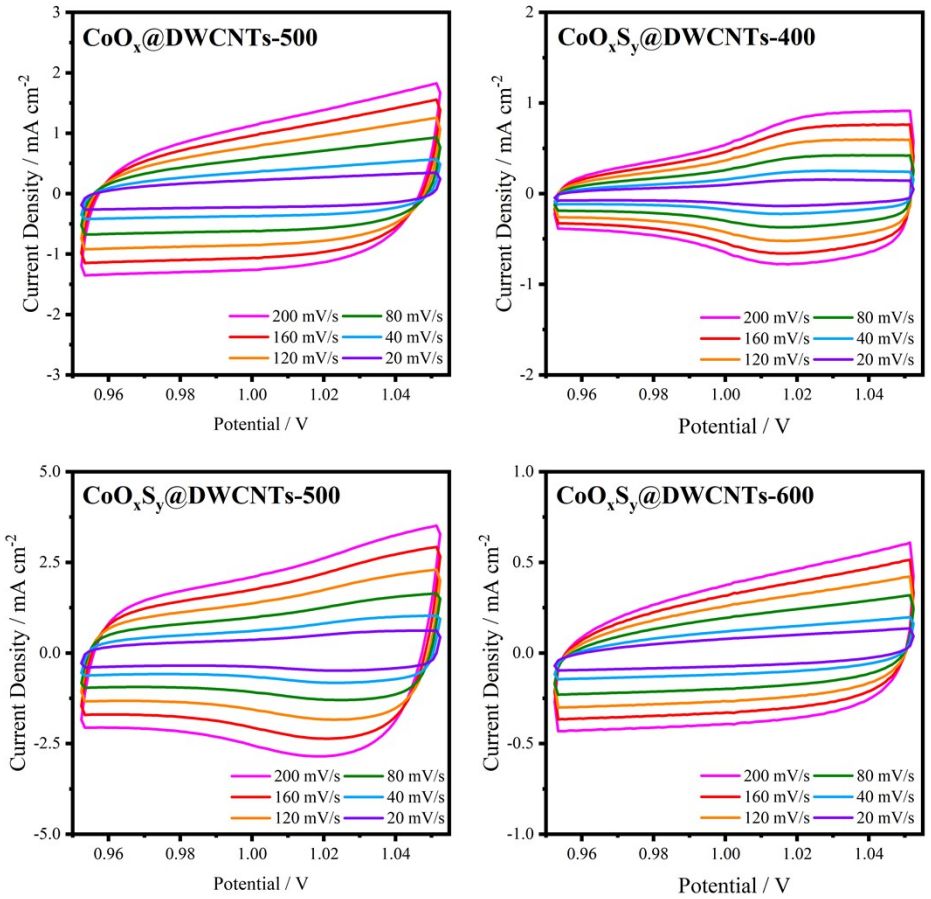

Figure S11. Cyclic voltammetry curves in different scan rates of CoO_xS_y@DWCNTs-400, 500 and 600 (vs. RHE).

Table S1. Different atomic content measured by the X-ray photoelectron spectroscopy.

Sample	C Atomic / %	O Atomic / %	S Atomic / %	Co Atomic / %
CoO_xS_y@DWCNTs-400	90.13	6.34	2.96	0.58
CoO_xS_y@DWCNTs-500	84.80	9.97	4.01	1.22
CoO_xS_y@DWCNTs-600	84.82	11.52	2.34	1.33

Table S2. Different parameters fitting by Electrochemical impedance spectroscopy.

Sample	R_s	R_{ct}
CoO_xS_y@DWCNTs-400	7.367	1.785
CoO_xS_y@DWCNTs-500	7.205	0.468
CoO_xS_y@DWCNTs-600	7.267	1.822

Table S3. Comparison of OER performance of recently reported cobalt-based electrocatalyst in alkaline electrolytes.

Electrocatalyst	Overpotential (mV) at 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	Refs.
CoO_xS_y@DWCNTs	290	50.8	This work
30% Pt/$LiCoO_2$	285	46.8	1
$CuCo_2S_4$	310	86	2
Cobalt sulfide	312	69	3
Co_3O_4/$NiCo_2O_4$	340	88	4
CoFe LDH	331	52	5
CoMn LDH	324	43	6
CO/NCO/NF	320	84	7
Co@Co_9S_8	350	55	8
Co_xP_y	287	70	9
Co_3S_4	363	90	10

Table S4. Loading mass of these electrocatalyst on test electrodes.

Sample	Loading mass (mg)
RuO_2	0.048
CoO_x@DWCNTs-500	0.009
CoO_xS_y@DWCNTs-400	0.008
CoO_xS_y@DWCNTs-500	0.008
CoO_xS_y@DWCNTs-600	0.009

Supplementary references

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