Supporting Information

Hollow Co nanoparticles/carbon nanotubes composite foam for electrocatalytic hydrogen evolution

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1. Experiments

1.1. Acidizing treatment of carbon nanotubes

In this work, carbon nanotubes were acidified and oxidized to enhance the oxygen-containing functional groups on the surface and so improve their dispersibility in water. 6 g MWCNTs are added to 600 mL of mixed strong acid solution with a volume ratio of H_2SO_4 to HNO_3 of 3:1. after uniform mixing, the reaction system is heated to 60 °C and stirred and refluxed for 3 h to form carboxyl and hydroxyl groups on the surface, the mixture is cooled to room temperature[1]. Transfer to a beaker, dilute with deionized water while stirring, and then wash with vacuum filtration until the filtrate is neutral. Finally, the filter residue is ultrasonically dispersed in deionized water, where the acidified carbon is dispersed. The solid concentration of the aqueous dispersion of nanotubes (MWCNTs) is 30 mg mL^{-1}.

1.2. Preparation of polystyrene microspheres

The polystyrene microspheres used in this experiment were prepared by soap-free emulsion polymerization. The following is a typical synthesis procedure: In a three-necked flask, combine 50mL monomer and 500 mL deionized water, then boil the solution while stirring (stirring speed 300 rpm) and heating to remove the air in the flask. The effect of oxygen on the reaction's free radicals. After 3 min of

refluxing, 0.5 g of initiator potassium persulfate powder was added, and the reaction was allowed to run for 3 h to produce a polystyrene mixed solution result. The combined solution was then centrifuged at high speed (10000 rpm) to yield polystyrene microspheres, which were subsequently rinsed with deionized water and dispersed in water many times. The resulting solution had a solid content of about 76.1 mg mL^{-1}.

1.3. Materials Characterization

The morphology and microstructure were observed by scanning electron microscopy (SEM, SIGMA500, ZEISS, Germany) and transmission electron microscope (TEM, JEM2100, JEOL, Japan). The elemental composition was investigated by energy-dispersive X-ray spectroscopy (EDS, Oxford X-Max 80). The crystal structure and phase compositions of the synthesized samples were analyzed using X-ray diffraction (XRD, SmartLab-9kW, RIGAKU, Japan) patterns. The functional groups and element compositions of the samples were determined by X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250, Thermo Electron, UK). Raman spectroscopy (Raman, in Via, Renishaw, UK) were used to collect Raman.

2. Results and discussion

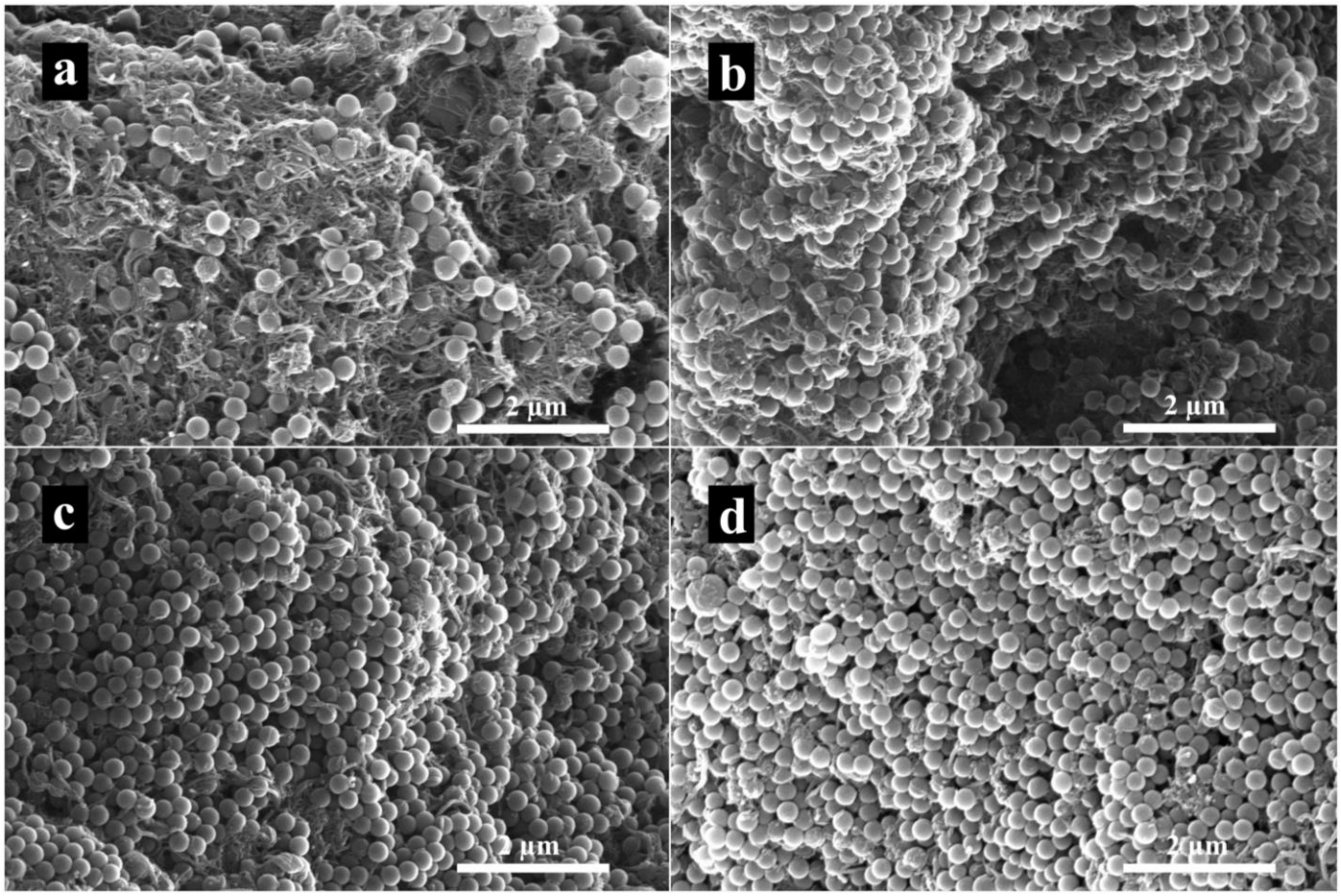

Fig. S1. (a-d) SEM images of Co/NCNT-25 composites with different adding contents of polystyrene microspheres (25, 50, 75, and 100 mg mL^{-1}) before calcination.

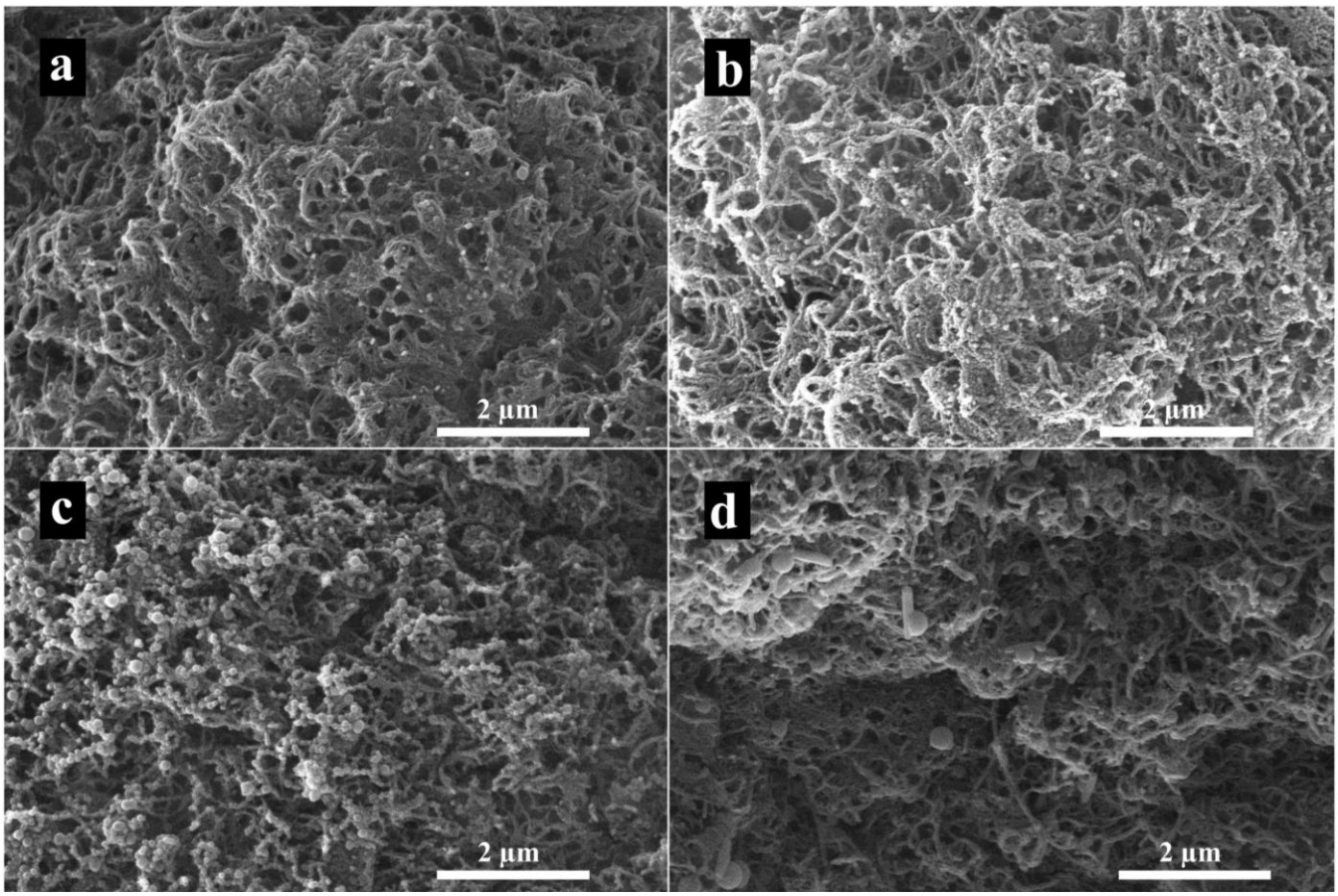

Fig. S2. (a-d) SEM images of Co/NCNT-25 composites with different adding contents of polystyrene microspheres (25, 50, 75, and 100 mg mL^{-1}).

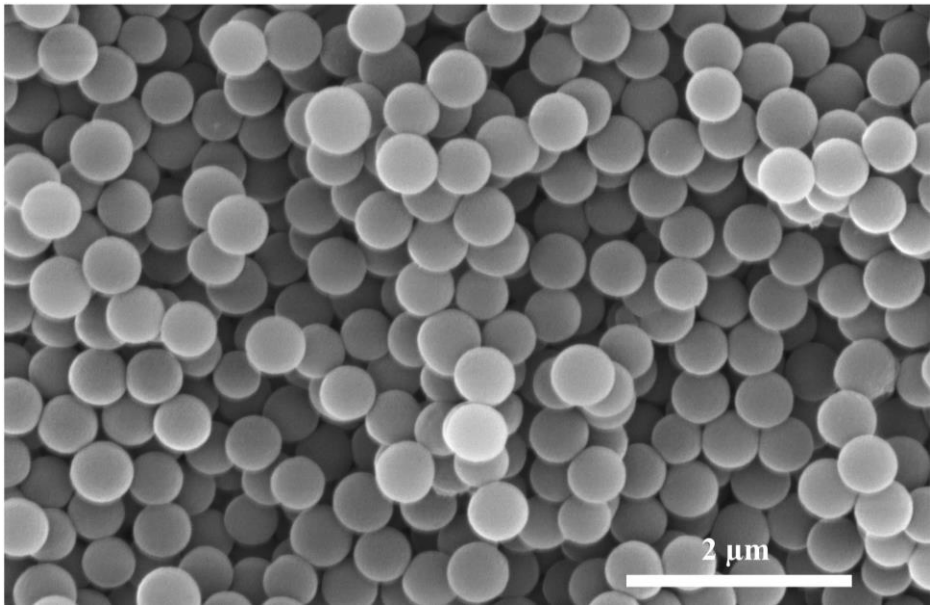

Fig. S3. SEM image of polystyrene microspheres.

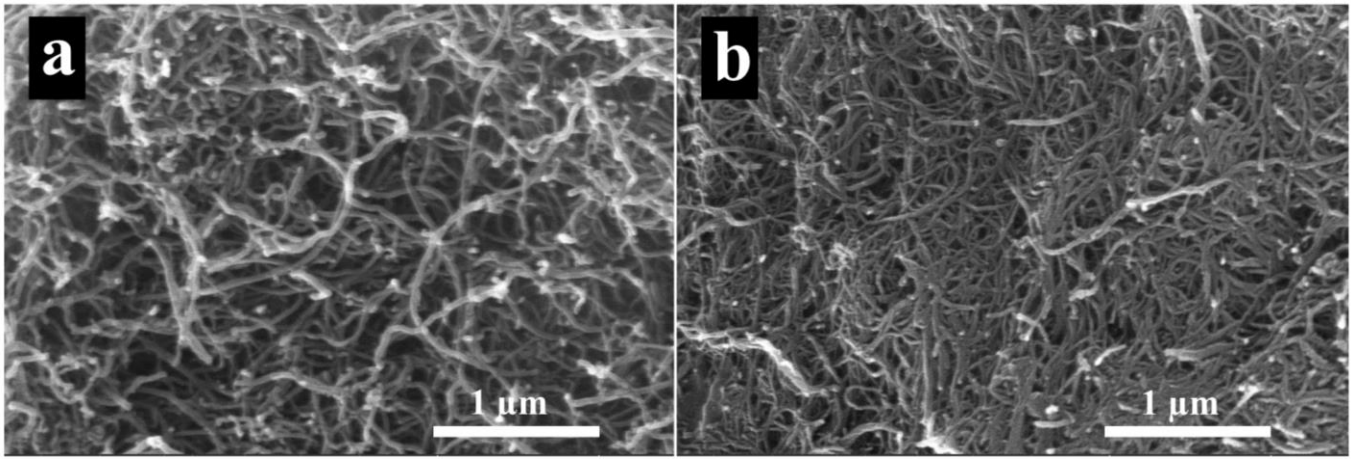

Fig. S4. (a, b) SEM images of raw CNTs and acid-treated CNTs

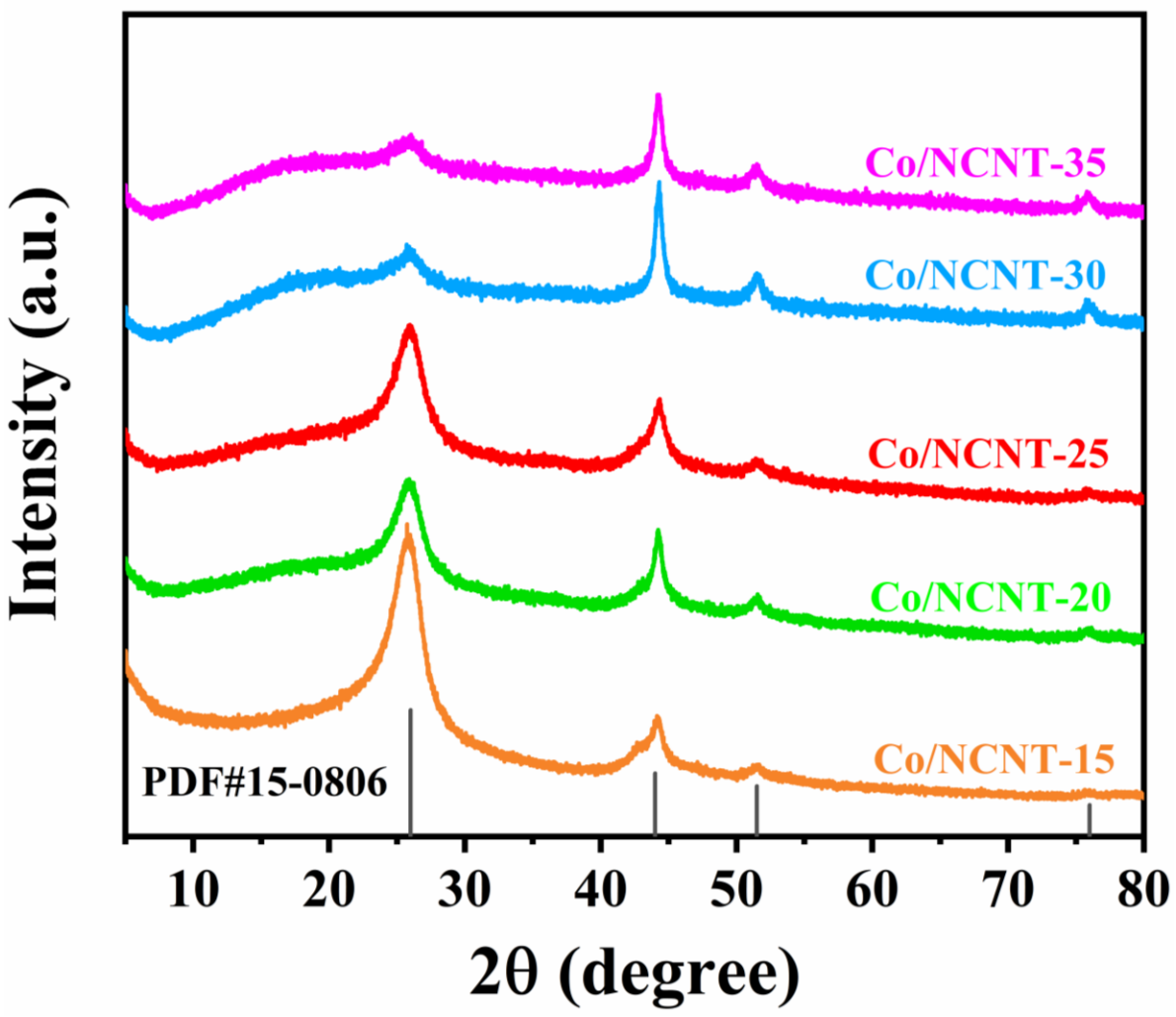

Fig. S5. XRD patterns of the Co/NCNT with different Co amounts.

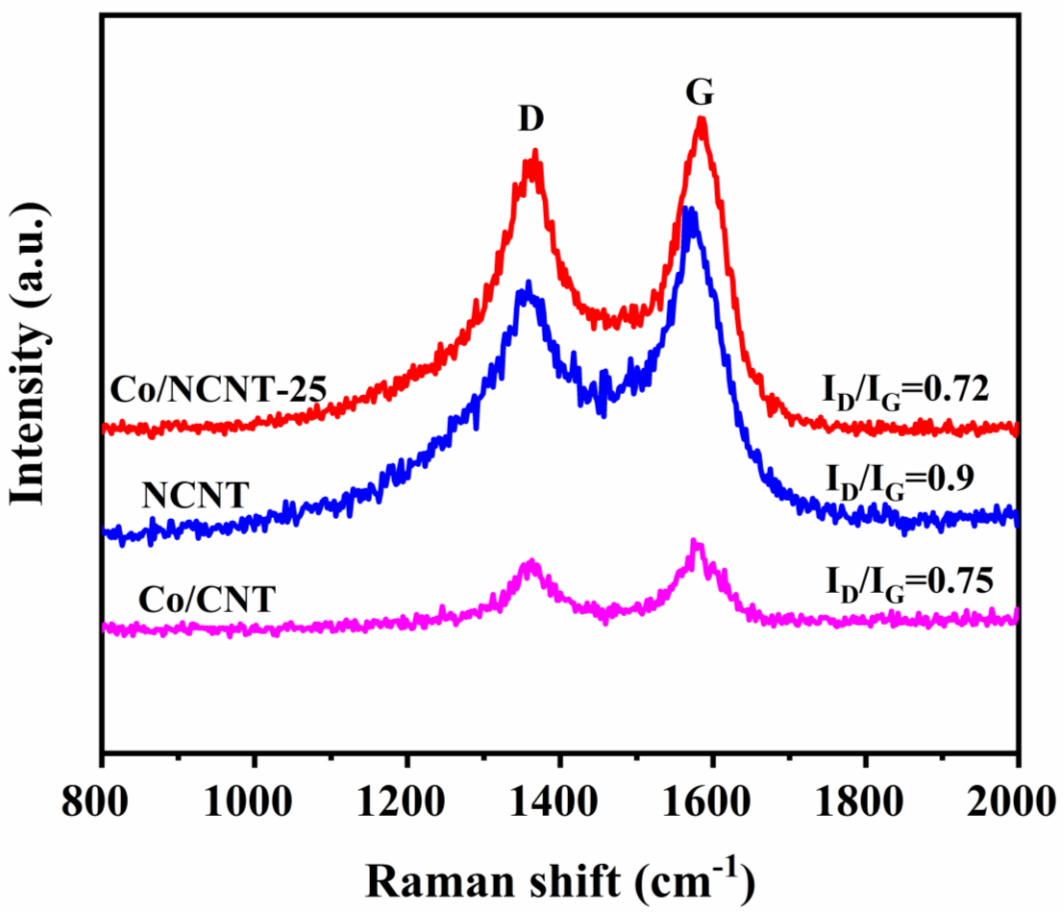

Fig. S6. Raman spectroscopy of the Co/NCNT-25 and NCNT and Co/CNT catalysts.

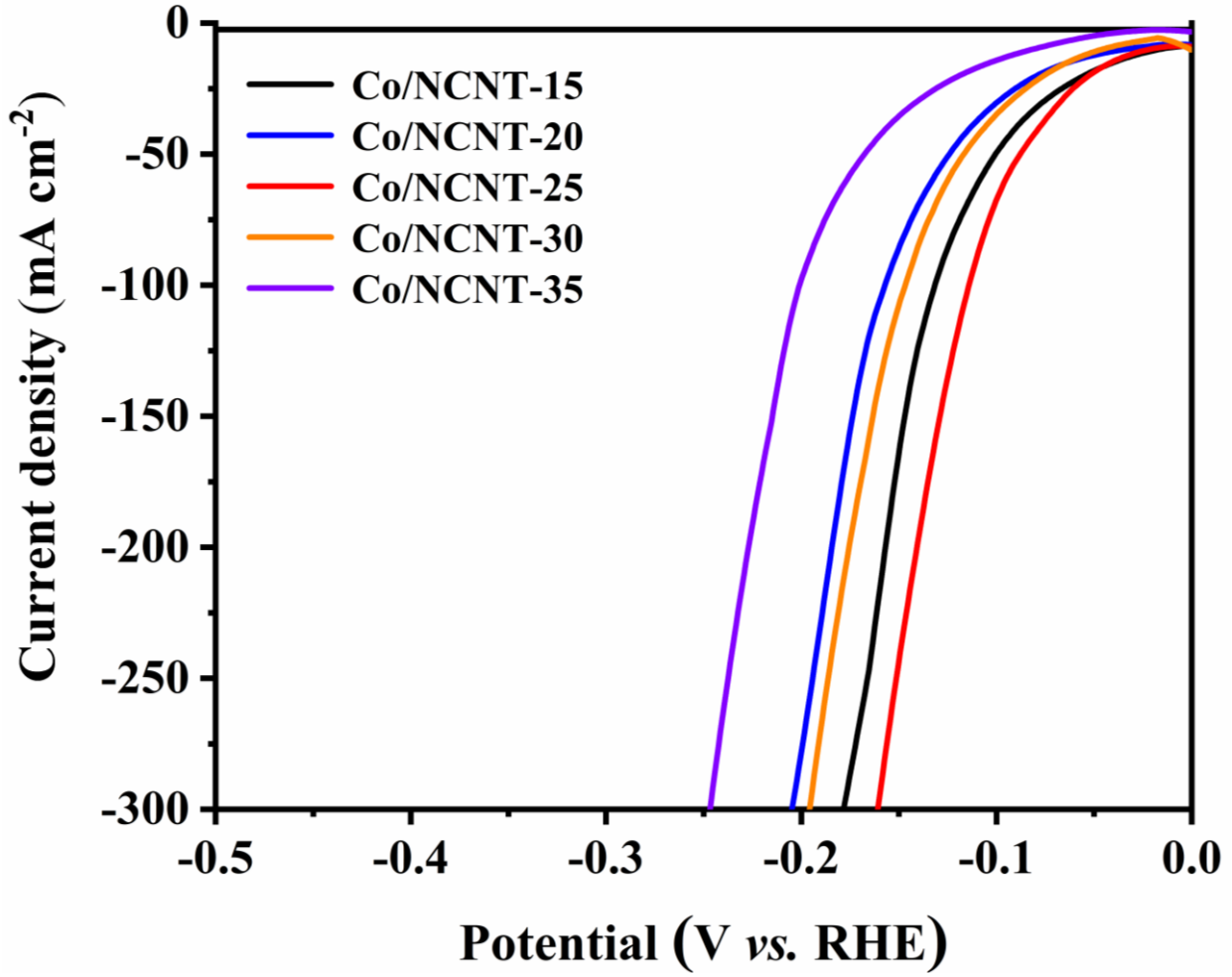

Fig. S7. LSV curves of Co/NCNT samples prepared with different contents in 1M KOH.

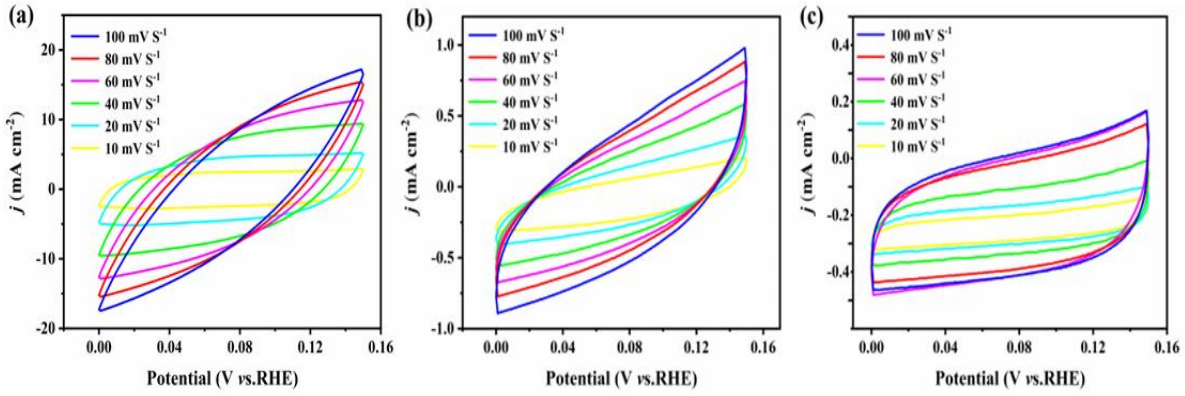

Fig. S8. CVs for(a) Co/NCNT-25, (b) NCNT, and(c) Co/CNT composites at different scan rates.

Table S1. Elemental analysis results of Co /NCNT-25 by XPS.

Samples	C (at%)	N (at%)	O (at%)	Co (at%)
Co/NCNT-25	91.57	2.96	4.34	1.12

Table S2. Comparison of electrochemical performances for the obtained Co/NCNT-25 with those of carbon materials.

Sample	**Electrolyte**	**Overpotential η_{10}(mV vs. RHE)**	**Ref.**
Co/NCNT-25	1 M KOH	20	In this work
Co/NGC-3	0.1M KOH	293	[2]
Co@N-CNTs@rGO	1 M KOH	108	[3]
	0.5MH_2SO_4	87	
Mo/Co@N-C	1M KOH	157	[4]
	0.5MH_2SO_4	187	
Mn-N-Co_9S_8	1 M KOH	102	[5]
NF@$Co_{1-x}V_xP$	1 M KOH	46	[6]
Fe_3C-Co/NC	1 M KOH	238	[7]
Co/N-CNT/VN	1 M KOH	63.4	[8]
CoSP/NC	1 M KOH	183	[9]
CoP-NCNT@MoS_2	1 M KOH	123	[10]
NSP–Co_3FeNx	1 M KOH	23	[11]
Co SAs-Co NPs/NCFs	1 M KOH	205	[12]
	0.5MH_2SO_4	106	
CoNiMn/NC	1 M KOH	191	[13]
Ru/Co-NCNTs	1 M KOH	35	[14]
Co-Mo_2C/N-C	1 M KOH	212	[15]
Co@NSCs	1 M KOH	266	[16]
Co@BNCNTs	1 M KOH	187	[17]
Co@Co-N-C	1 M KOH	178	[18]
$CoPt_3$@Co_2P/Co@NCNT	1 M KOH	19	[19]
Mn/Co-NGC	1 M KOH	116	[20]
Co@NGr	1 M KOH	340	[21]
Co-Mo_2C@NGCS	1 M KOH	161	[22]
Zn_xCo_{1-x}/NC@MoS_2	1 M KOH	130	[23]
CoMoP@N,P-C	1 M KOH	152	[24]
Co/WC@NC	1 M KOH	158	[25]

	$0.5MH_2SO_4$	142	
FeCoCuP@NC	1 M KOH	80	[26]
	$0.5MH_2SO_4$	169	
Co_2P/CoP@Co@NCNT	1 M KOH	118	[27]
NG@Co@Zn	1 M KOH	34	[28]

Table S3. The value of the Co/NCNT-25, NCNT, Co/CNT samples fitted by equivalent circuit components.

Catalysts	**R_s/Ω**	**R_{ct}/Ω**	**W_R**
EIS date obtained in 0.1 M KOH solution			
Co/NCNT-25	1.157	0.7385	7.475
NCNT	1.37	247	1019
Co/CNT	1.094	1.047	2.772

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