Supporting Information

Co_9S_8 nanoparticles embedded in N, S co-doped graphene-unzipped carbon nanotubes composite as a high performance electrocatalyst for hydrogen evolution reaction

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Synthesis of NG-UCNTs and RGO-UCNTs composites

For synthesis of NG-UCNTs, 10 mg of O-UCNTs and 50 mg of GO were dispersed in 30 mL of water, then 4 mmol of urea were added to the suspension. The suspension was sonicated for approximately 2 h at room temperature to achieve a homogeneous suspension, which was dried at 80 °C afterwards. The obtained mixture was thermal treated at 300 °C for 2 h with a heating rate of 2 °C min^{-1} under N_2 atmosphere, then the temperature was elevated to 800 °C at a heating rate of 10 °C min^{-1} and kept for another 1 h. For comparison, RGO-UCNTs composite was synthesized through the identical procedure but without the addition of urea.

Synthesis of Co_9S_8/NSG-UCNTs composite with different mass ratios of GO/O-UCNTs

60 mg mixture of GO and O-UCNTs, in which the weight ratio of GO/O-UCNTs was endowed with different values (1:0, 10:1, 3:1, 1:1, 1:3, 0:1), were dispersed in 30 mL of water, then 0.5 mmol of $Co(NO_3)_2{\cdot}6H_2O$ and 4 mmol of urea were added to the suspension. The suspension was sonicated for approximately 2 h at room temperature to achieve a homogeneous suspension, which was dried at 80 °C afterwards. The obtained mixture was thermal treated at 300 °C for 2 h with a heating rate of 2 °C min^{-1} under N_2 atmosphere, then the temperature was elevated to 800 °C at a heating rate of 10 °C min^{-1} and kept for another 1 h.

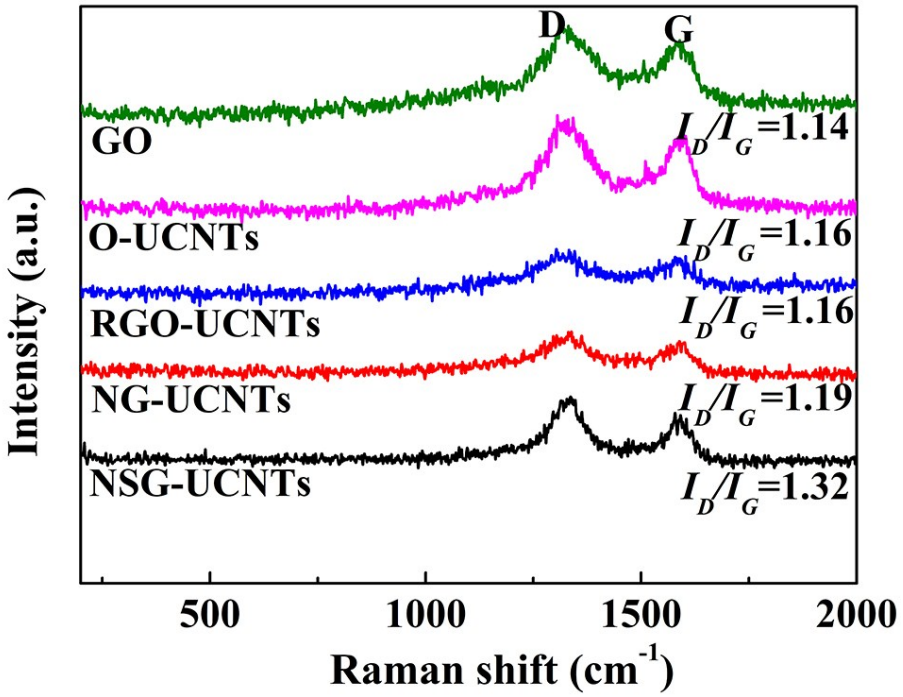

Figure S1 Raman spectra of GO, O-UCNTs, RGO-UCNTs, NG-UCNTs, NSG-UCNTs

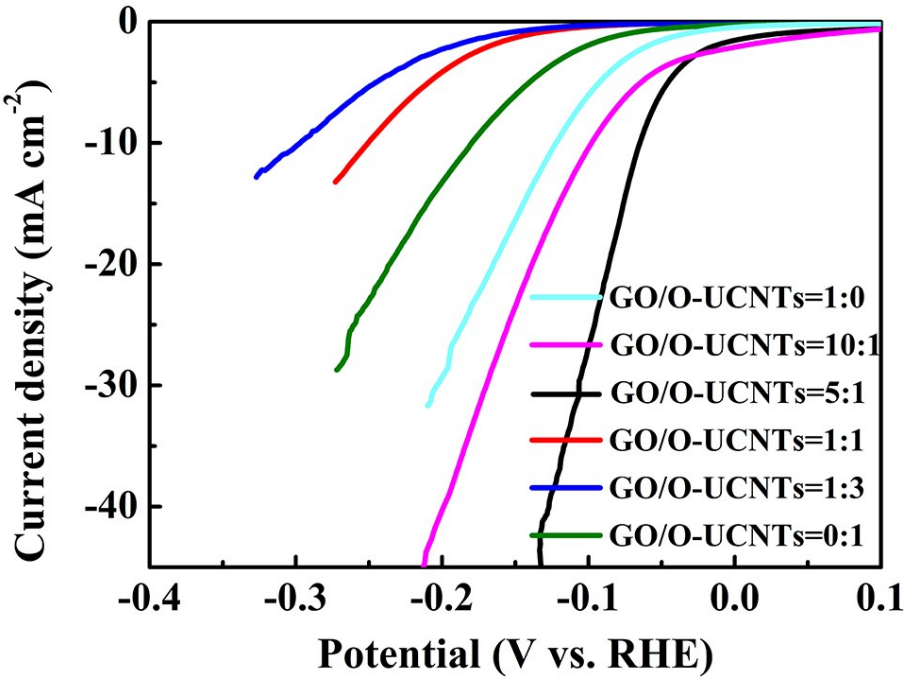

Figure S2 Linear sweep voltammetry curves of Co_9S_8/NSG-UCNTs composites with different mass ratios of GO/O-UCNTs

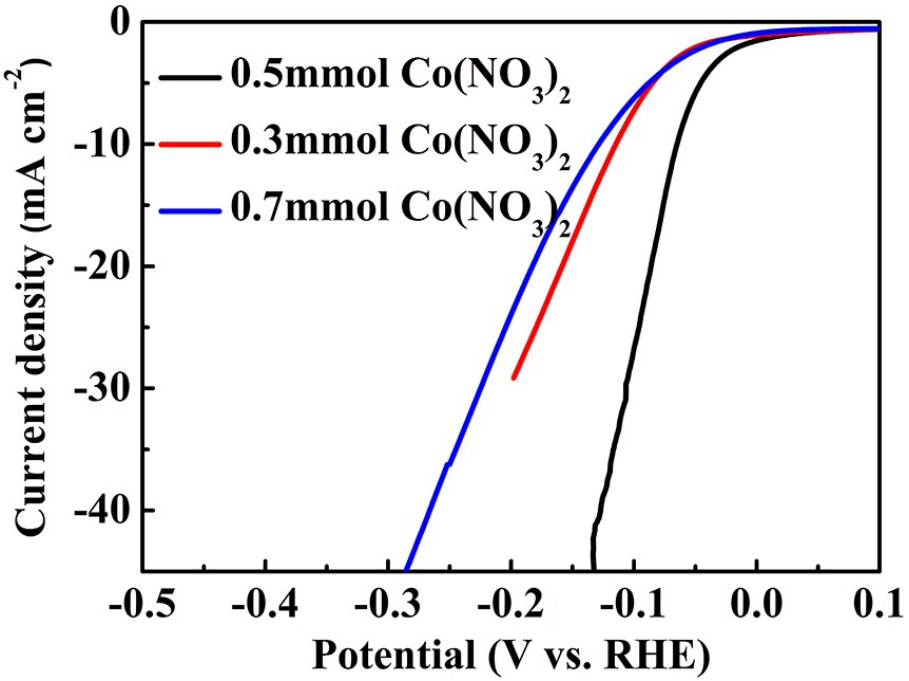

Figure S3 Linear sweep voltammetry curves of Co_9S_8/NSG-UCNTs composites with

different loading of $Co(NO_3)_2$

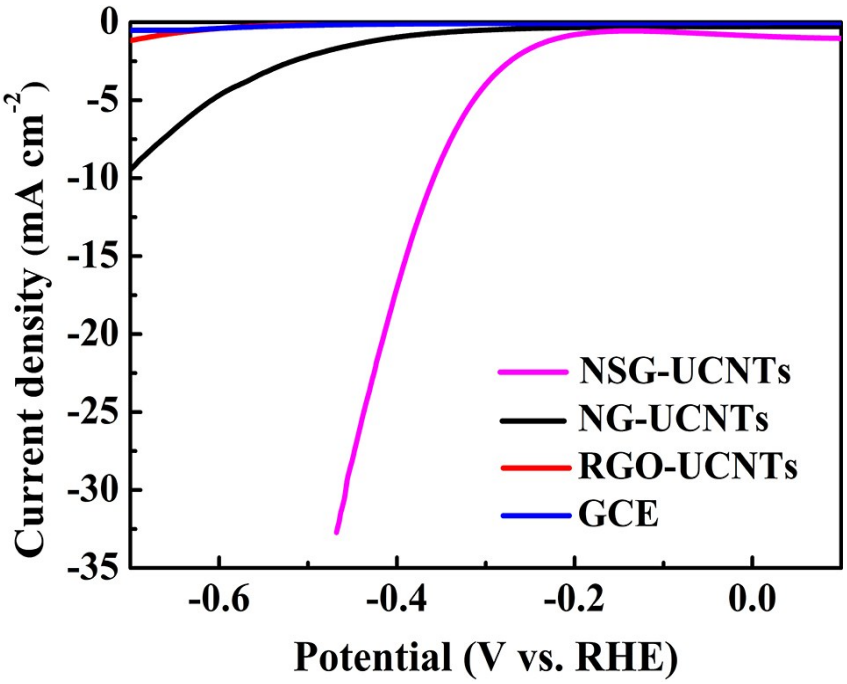

Figure S4 Linear sweep voltammetry curves of NSG-UCNTs, NG-UCNTs, RGO-UCNTs measured in 0.5 M H_2SO_4

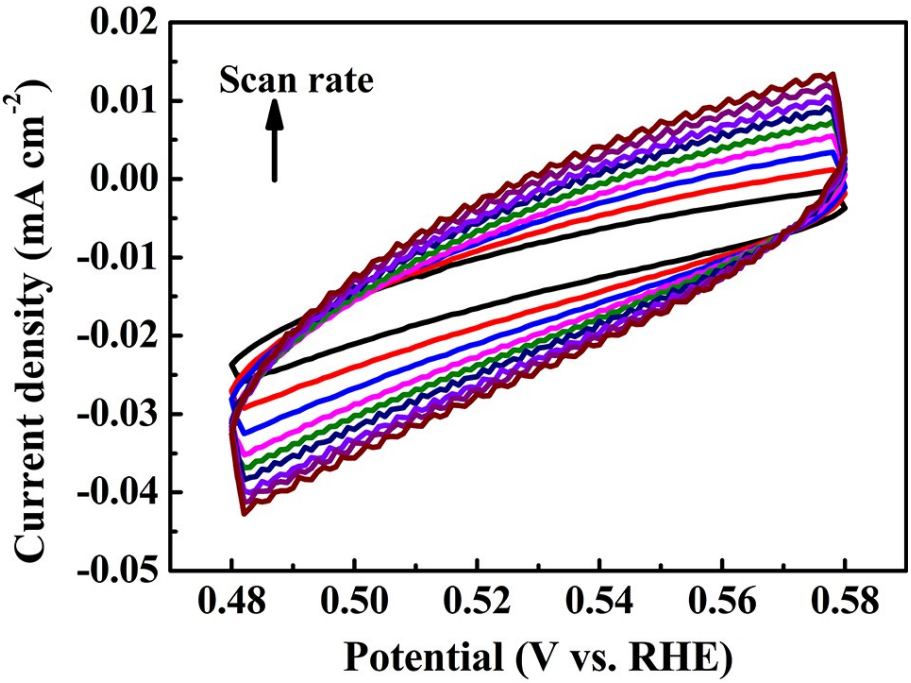

Figure S5 Cyclic voltammograms (0.48−0.58 V) of the Co_9S_8 in 0.5 M H_2SO_4 at various scan rates

Table S1 Comparison of the electrocatalytic activity of Co_9S_8 /NSG-CNT for HER in acid media with some representative recently-reported non-noble metal electrocatalysts

Catalyst	Electrode	Electrolyte	Scan rate (mV s-1)	Loading (mgcm-2)	η at various j (mV)	Reference
Co_9S_8 /NSG-CNT	GCE	0.5 M H_2SO_4	5	0.30	65(10)	This work
Co_9S_8@C	GCE	0.5 M H_2SO_4	50	0.30	240(10)	[1]
CoS_2/RGO-CNT	GCE	0.5 M H_2SO_4	2	0.28	142(10)	[2]
CoP	Ti foil	0.5 M H_2SO_4	2	2.0	90(10)	[3]
CoS_2	graphite	0.5 M H_2SO_4	3	1.7 ± 0.3	145(10)	[4]
$Fe_{0.37}Co_{0.63}S_2$/CNT	GCE	0.5 M H_2SO_4	1	0.4	120(20)	[5]
P-WN/rGO	GCE	0.5 M H_2SO_4	5	0.337	85(10)	[6]
NCo@G	GCE	0.5 M H_2SO_4	5	-	265(10)	[7]
Co@N-C	GCE	1 M$HClO_4$	2	-	200(10)	[8]
MoS_x/NCNT	GCE	0.5 M H_2SO_4	5	0.102	110(10)	[9]
NG-Mo	NG	0.1 M H_2SO_4	-	0.70	140(10)	[10]
CoP/CNTs	GCE	0.5 M H_2SO_4	5	0.285	130(10)	[11]
MoS_2 NA/CC	CC	0.5 M H_2SO_4	2	0.96	196(10)	[12]
Fe-Co_2P/NCNTs	GCE	0.5 M H_2SO_4	5	0.2	104(10)	[13]
CoMoS	GCE	0.5 M H_2SO_4	5	0.285	200(61.9)	[14]
Cu-MoS_2/rGO	GCE	0.5 M H_2SO_4	5	0.285	400(83.6)	[15]
MoS_2/rGO	GCE	0.5 M H_2SO_4	5	0.2	200(23)	[16]
MoS_2/rGO	GCE	0.5 M H_2SO_4	2	0.285	200(40)	[17]
MoS_3/CNT	silver electrode	1.0 M H_2SO_4	1	1.6	300(75)	[18]
NiP_2 NS/CC	CC	0.5 M H_2SO_4	4	4.3	75(10)	[19]

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