ADVANCED MATERIALS INTERFACES

Supporting Information

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Plasma-Assisted Synthesis of Co_3O_4-Based Electrocatalysts on Ni Foam Substrates for the Oxygen Evolution Reaction

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§ S-1. Material characterization

§ S-1.1. X-ray diffraction (XRD)

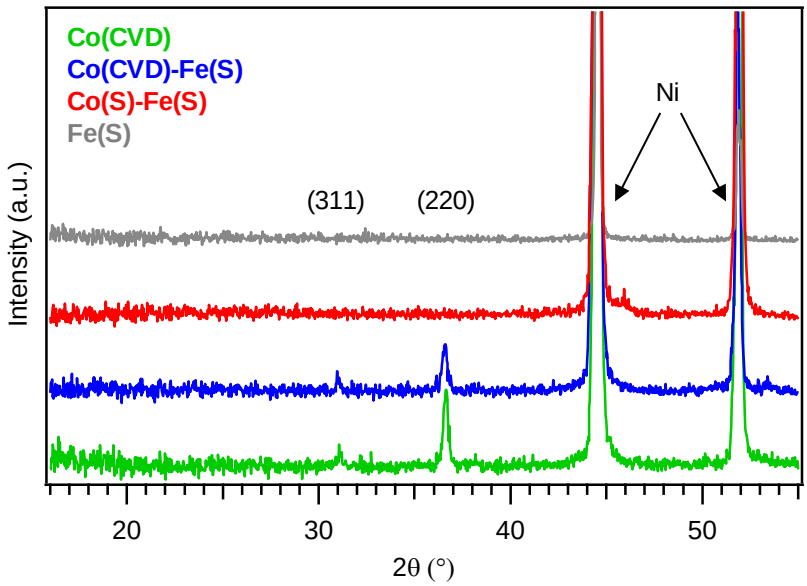

Figure S1. XRD patterns for the specimens investigated in the present work. The Ni foam diffraction peaks[1-3] are marked for clarity. XRD patterns were vertically shifted without altering their relative intensity.

§ S-1.2. X-ray photoelectron spectroscopy (XPS)

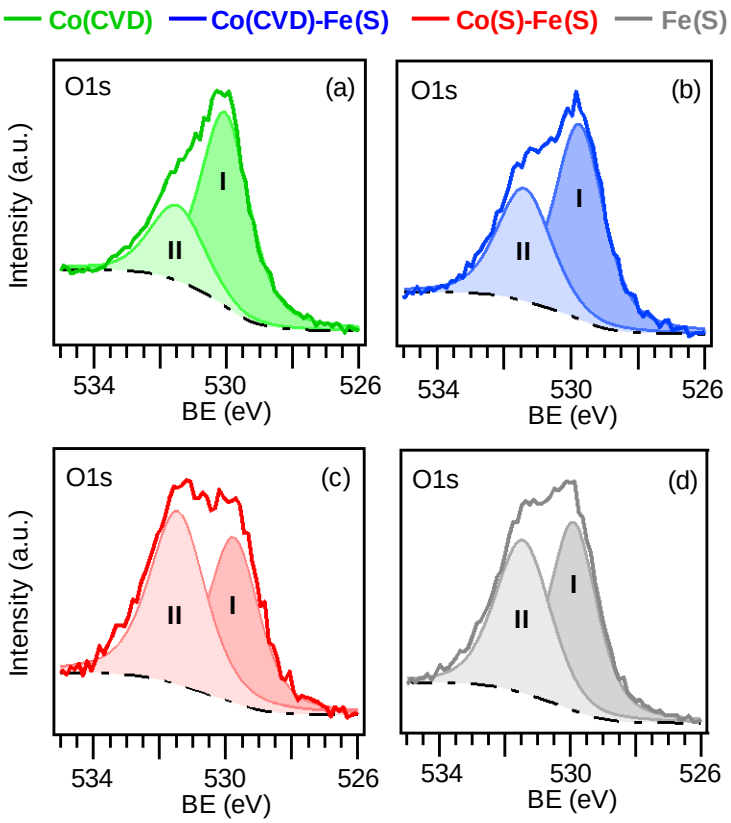

Figure S2. O1s photoelectron peaks, along with the resulting fitting components, for specimens Co(CVD) (a), Co(CVD)-Fe(S) (b), Co(S)-Fe(S) (c), and Fe(S) (d).

	Atomic percentages (at. %)			
Sample	**Co at.%**	**Fe at.%**	**Ni at.%**	**O at.%**
Co(CVD)	41.2	//	//	58.8
Co(CVD)-Fe(S)	13.0	19.2	//	67.8
Co(S)-Fe(S)	17.6	10.5	9.4	62.5
Fe(S)	//	30.2	12.4	57.4

Table S1. XPS atomic percentages for Co, Fe, Ni, O for the target samples.

§ S-1.3. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDXS)

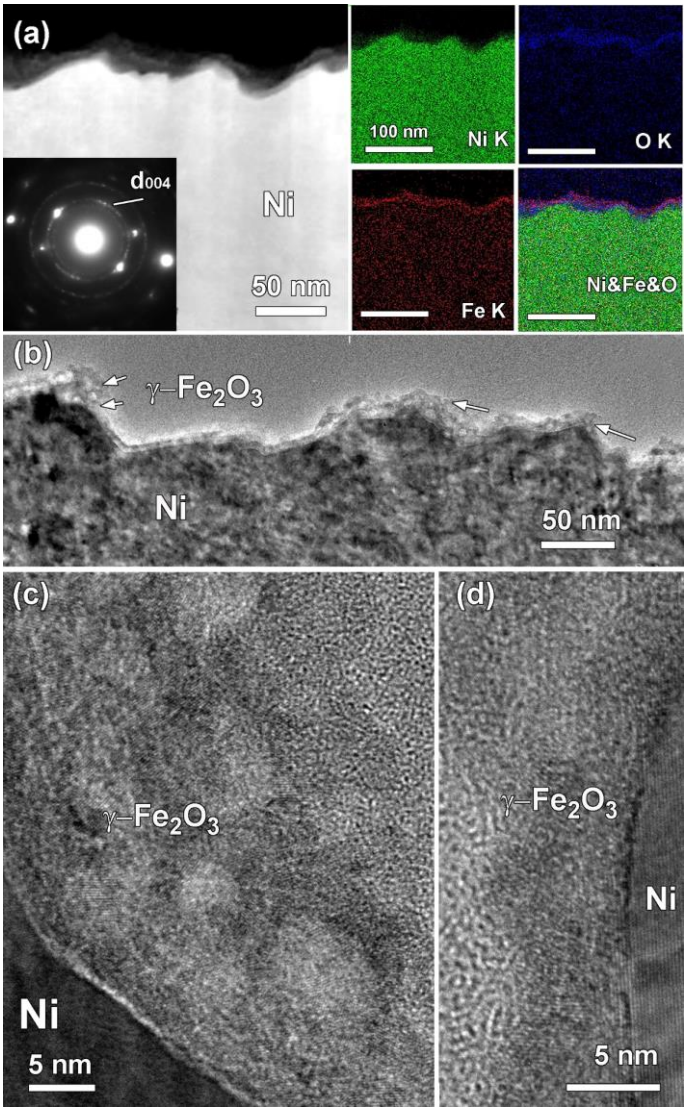

Figure S3. (a) Low magnification high angle annular dark field (HAADF)-STEM cross-sectional image, and EDXS elemental maps for sample Fe(S). The electron diffraction (ED) pattern in the bottom left corner of panel (a) results from the superimposition of Ni substrate diffraction spots and ring pattern of γ-Fe_2O_3 nanoparticles. (b) Medium and (c,d) high resolution bright field TEM images evidencing the Ni substrate coverage by γ-Fe_2O_3 nanoparticles. In panel (b), white arrows mark the iron oxide deposit (average thickness = 10-20 nm), composed of randomly oriented crystallites of 5-10 nm.

§ S-2. Electrochemical tests

§ S-2.1. Cyclic voltammetry (CV)

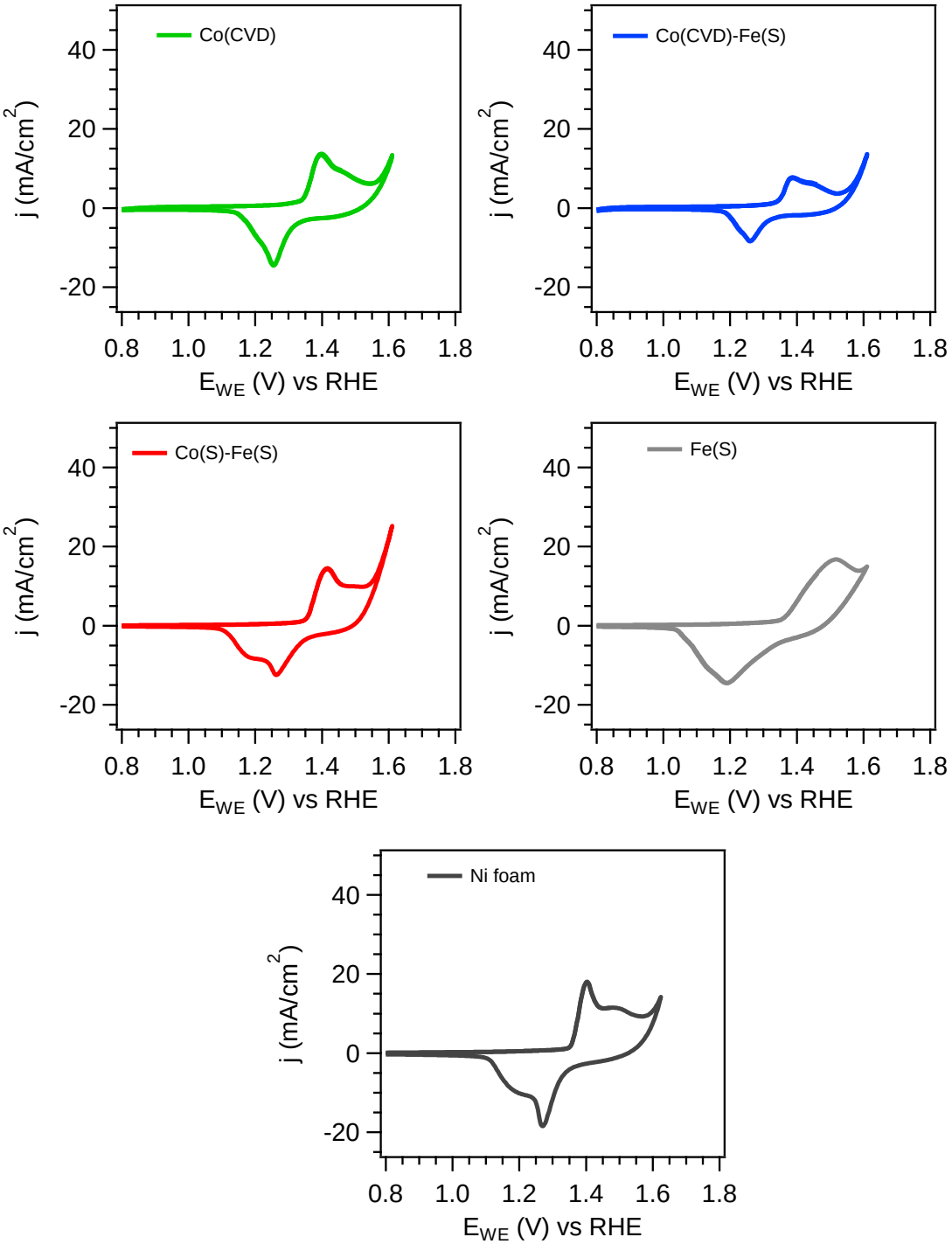

Figure S4. CV curves of Co(CVD), Co(CVD)-Fe(S), Co(S)-Fe(S), Fe(S) and bare Ni foam collected in 1.0 M KOH aqueous solution at a scan rate of 50 mV/s. LSV curves in Figure 6a (recorded at a scan rate of 5 mV/s) were overlapped to the "return" scans of CV cycles, indicating that the contribution of capacitive currents is negligible.

§ S-2.2. Electrochemical impedance spectroscopy (EIS)

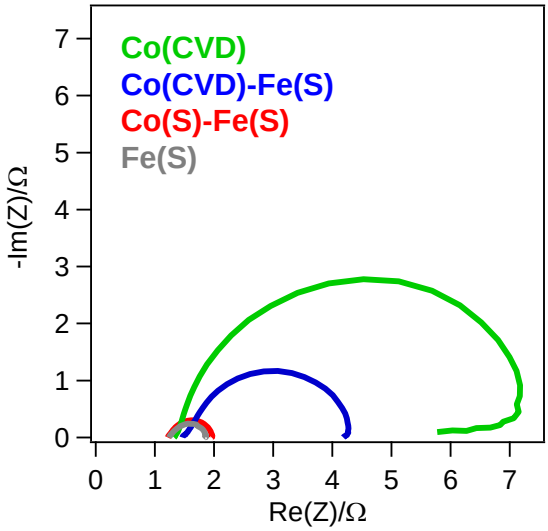

Figure S5. EIS spectra of the target samples recorded in 1.0 M KOH, at 1.55 V *vs*. the reversible hydrogen electrode (RHE) in the frequency range 10^6-0.01 Hz. The shift in the origin of the Nyquist plot for Co(CVD) and Co(CVD)-Fe(S) with respect to the other samples is due to the higher resistivity of CVD-derived Co_3O_4.

§ S-2.2. Linear sweep voltammetry (LSV)

Material	Electrolyte	Overpotential at 10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Ref.
Ni foam	1.0 M KOH	404	80	Present work
Co(CVD)		396	71	
Co(CVD)-Fe(S)		382	60	
Co(S)-Fe(S)		355	62	
Fe(S)		366	66	
Co_3O_4	1.0 M KOH	339	82	[4]
$NiCo_2O_4$	1.0 M KOH	290	53	[5]
CoP-MNA	1.0 M KOH	290	65	[6]
Co_3O_4/N-rmGO	1.0 M KOH	310	67	[7]
CoO_x@CN	1.0 M KOH	260	n.a.	[8]
Co_3O_4	1.0 M KOH	350	38	[9]
Co_3O_4/Fe_2O_3	1.0 M KOH	254	33	[9]

Table S2. Comparison of OER performances for the materials developed in the present work with selected literature data for other Co-containing electrocatalysts on Ni foams operated in alkaline solutions. Acronyms: CoP-MNA = Co phosphide mesoporous nanorod arrays; N-rmGO = N-doped reduced mildly oxidized graphene oxide; CoO_x@CN = cobalt-cobalt oxide/N-doped carbon hybrids; n.a. = not available.

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