Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Unusual doping induced phase transitions in NiS via solventless synthesis enabling superior bifunctional electrocatalytic activity

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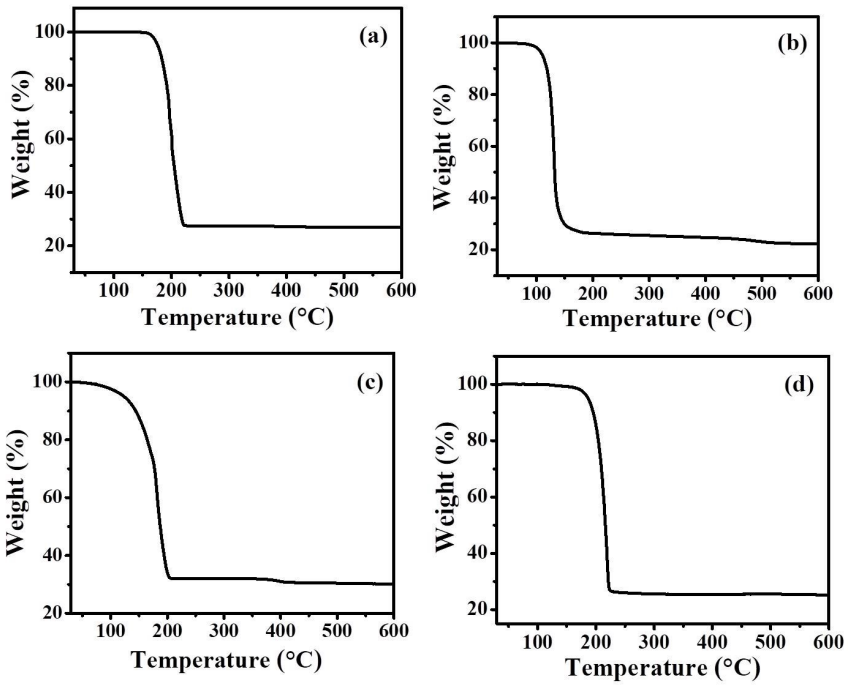

Figure S1. TG plots of (a) complex (**1**), (b) complex (**2**), (c) complex (**3**) and (d) complex (**4**).

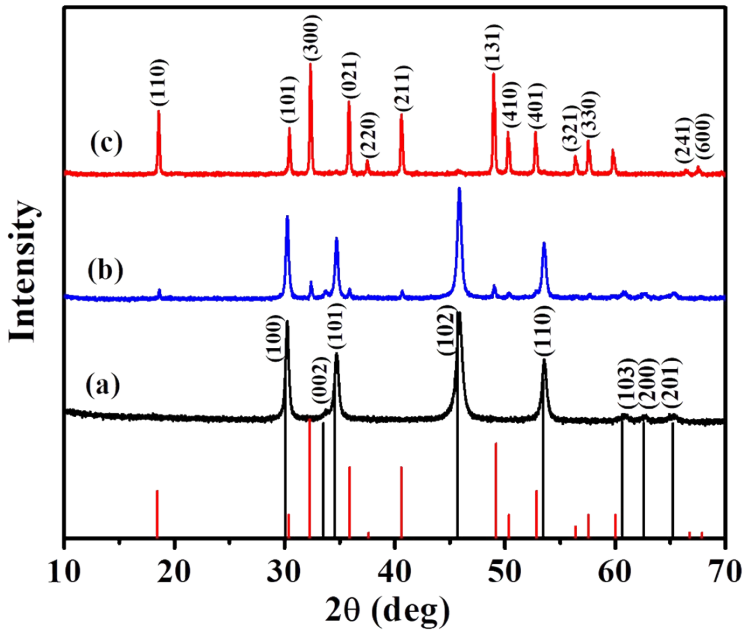

Figure S2. p-XRD patterns of NiS nanoparticles synthesized from complex (**1**) at (a) 200 ºC (ICDD # 03-065-3419), (b) 300 ºC and (c) 400 ºC (ICDD # 00-003-0760).

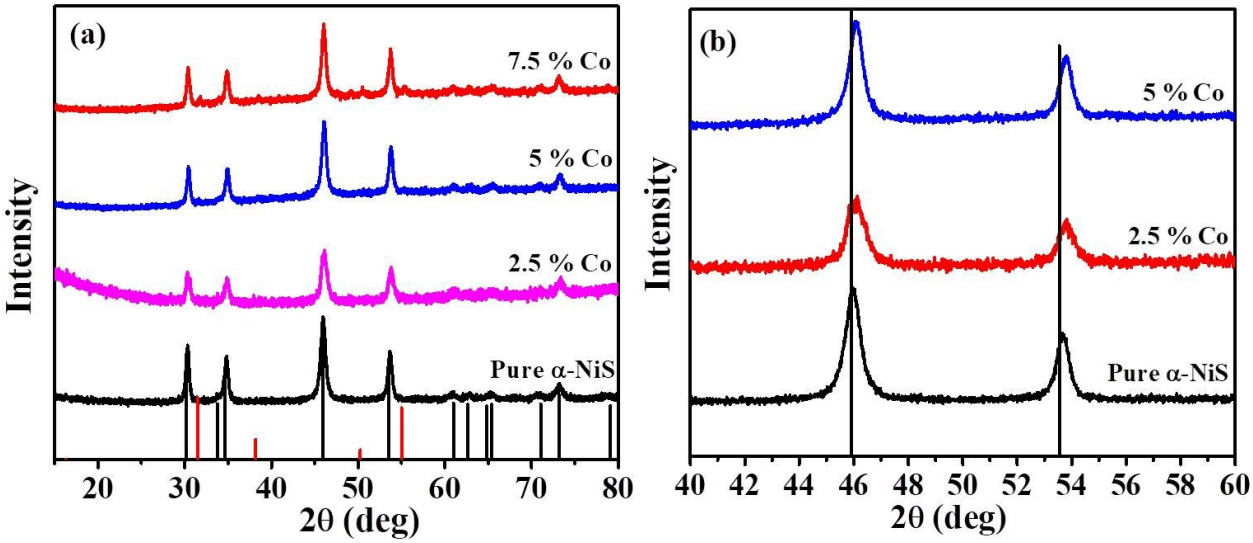

Figure S3. (a) p-XRD patterns of pure α-NiS and Co-doped α-NiS synthesized at 200 °C. (b) Extended part of the diffraction patterns showing a shift in peak positions.

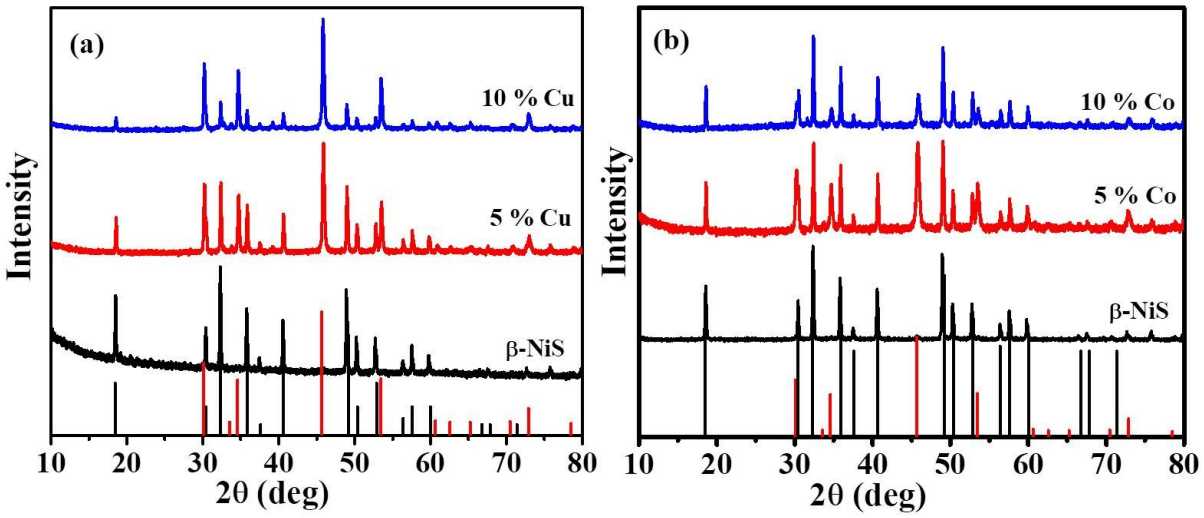

Figure S4. (a) p-XRD patterns of β-NiS and Cu-doped β-NiS synthesized at 400 °C. (b) p-XRD patterns of β-NiS and Co-doped β-NiS synthesized at 400 °C.

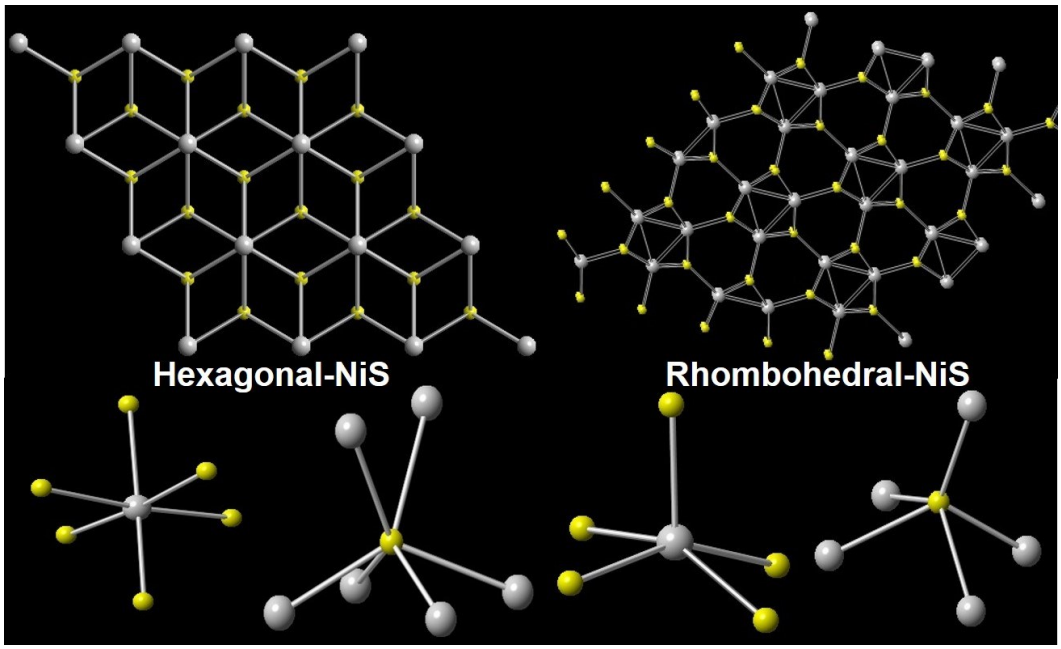

Figure S5. Crystal structures of hexagonal and rhombohedral NiS phases along with their respective nickel and sulfur coordination spheres.

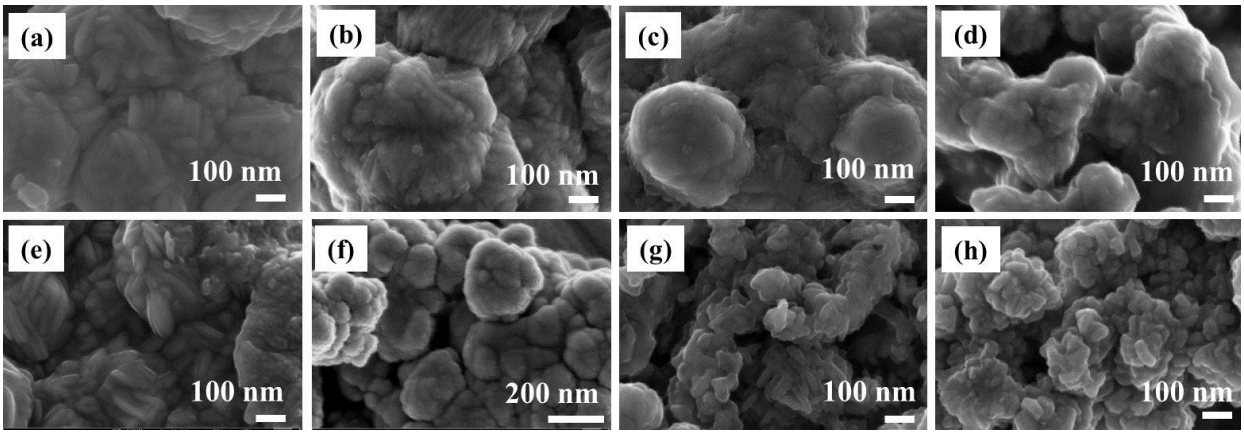

Figure S6. SEM images of (a) α-NiS (b) Cu-doped α-NiS, (c) Co-doped α-NiS, (d) Fe-doped α-NiS synthesized at 200 °C. SEM images of (e) β-NiS (f) Cu-doped β-NiS, (g) Co-doped β-NiS and (h) Fe-doped β-NiS synthesized at 400 °C.

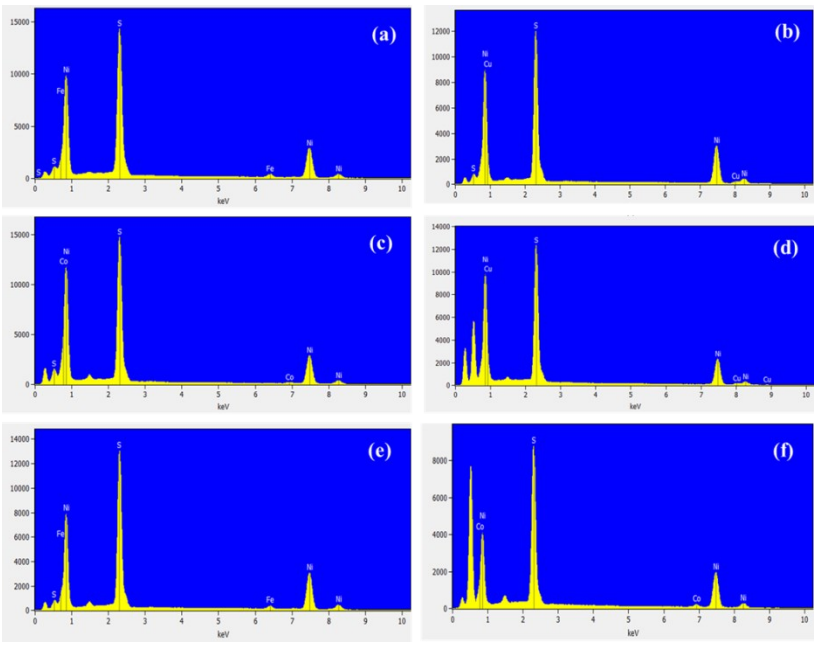

Figure S7. EDX spectra of (a) Fe-doped NiS, (b) Cu-doped NiS, and (c) Co-doped NiS synthesized at 200 °C; and (d) Cu-doped NiS, (e) Fe-doped NiS, and (f) Co-doped NiS synthesized at 400 °C.

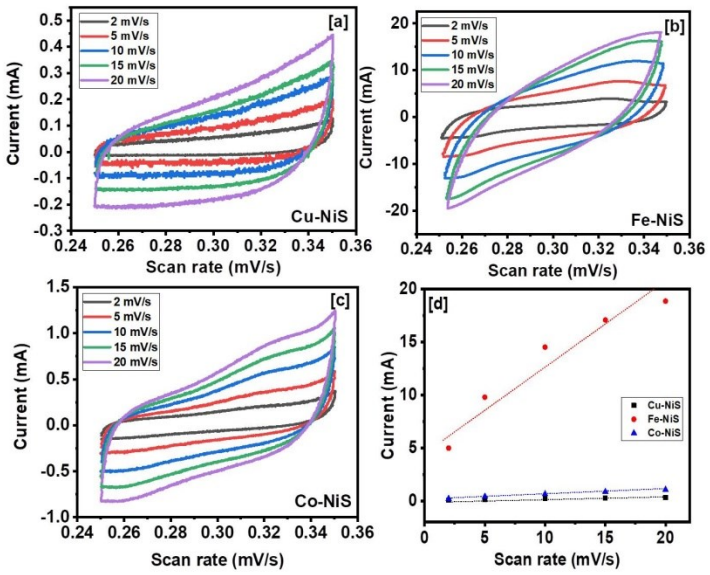

Figure S8. Double-layer capacitance measurements for estimating the electrochemically active surface area. CV curves in a non-Faradaic region for α-NiS doped with 5% (a) Cu (b) Fe and (c) Co. (d) Current vs scan rate plot for all the samples.

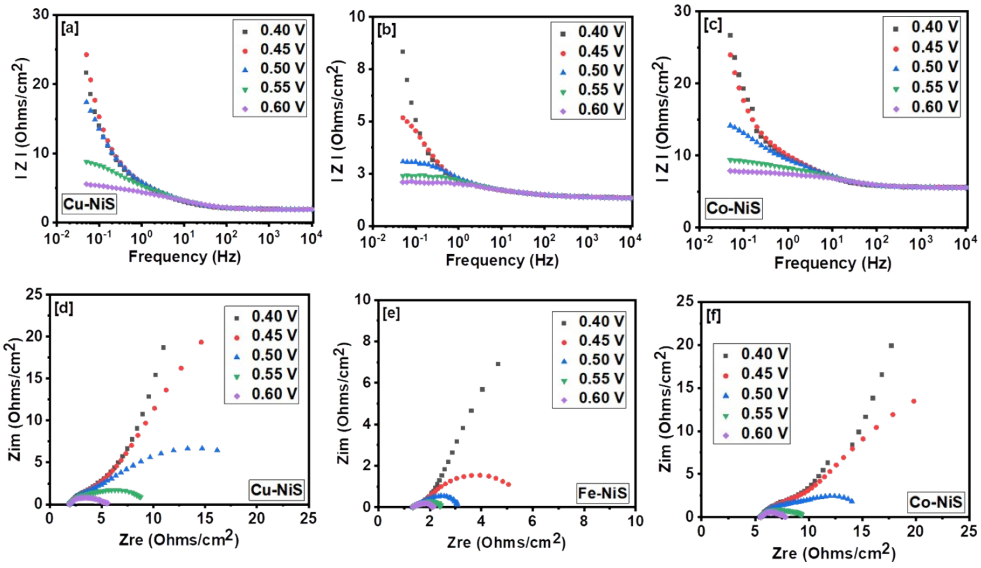

Figure S9. |Z| vs. frequency plots for α-NiS doped with 5% (a) Cu (b) Fe and (c) Co at 200 ºC. Zreal vs. Zimg plots at various potentials for NiS doped with 5% (d) Cu (e) Fe and (f) Co at 200 ºC.

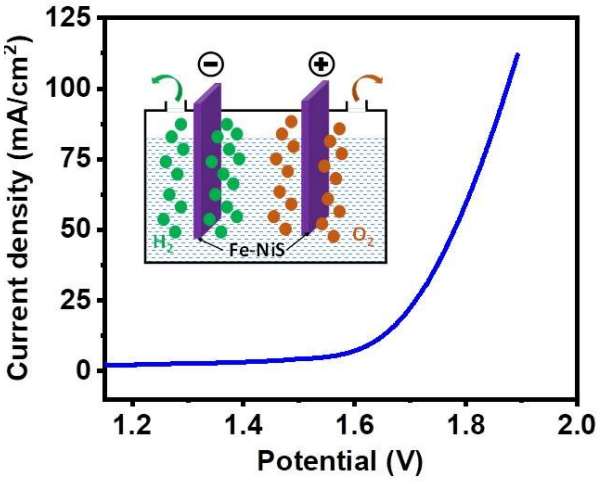

Figure S10. LSV curve for overall water splitting using Fe-doped NiS as both the cathode and anode.

Table S1. Atomic percent composition of Ni, S, Fe, Cu and Co in Fe-doped-, Cu-doped-, and Co-doped NiS synthesized at [a] 200 °C and [b] 400 °C.

	Element	Required At% composition	Obtained At% composition
Fe-doped NiS[a]	Ni	47.5	46.12
	Fe	2.5	2.60
	S	50	51.28
Cu-doped NiS[a]	Ni	47.5	46.23
	Cu	2.5	2.67
	S	50	51.10
Co-doped NiS[a]	Ni	47.5	46.36
	Co	2.5	2.57
	S	50	51.07
Fe-doped NiS[b]	Ni	45.0	46.13
	Fe	5.0	4.72
	S	50	49.15
Cu-doped NiS[b]	Ni	45.0	44.07
	Cu	5.0	4.93
	S	50	50.99
Co-doped NiS[b]	Ni	45.0	44.93
	Co	5.0	4.88
	S	50	50.19

Table S2. A comparison of the specific capacitance observed for TM-doped NiS with other Ni-based electrodes.

Material	Method	Specific capacitance (F/g)	Current density (A/g)	Reference
α-NiS hollow spheres	Hydrothermal	562.3	0.6	[1]
β-NiS hollow spheres	Hydrothermal	501.5	0.6	[1]
β-NiS	Template assisted hydrothermal	668	1	[2]
β-NiS nanoflowers	Hydrothermal	710	2	[3]
β-NiS micro-flowers	Solvothermal	857.76, 512.96	2, 5	[4]
β-NiS/GO	Hydrothermal	109	2.5	[5]
NiS/rGO	Hydrothermal	905.30	0.5	[6]
NiS/C-dot	Hydrothermal	880	2	[3]
α-NiS/CRs	Solvothermal	1092	1	[7]
NiO nanowires	Nano-seed catalyzing mechanism	180	0.5	[8]
NiO/rGO	Electrophoretic and chemical bath deposition	400	2	[9]
NiO hollow spheres	Chemical bath deposition	287	1	[10]

$NiCo_2S_4$@MnO_2	Hydrothermal	520.7	1	[11]
$NiCo_2S_4$@Fe_2O_3	Hydrothermal followed by electro-deposition	285	2.5	[12]
Co-doped NiS	Solventless	1586	0.5	**Present work**
Cu-doped NiS	Solventless	1326	0.5	**Present work**
Fe-doped NiS	Solventless	1314	0.5	**Present work**

Table S3. Comparison of HER performance of the synthesized TM-doped NiS with other Ni-based electrocatalysts.

Catalyst	**Overpotential (mV) at 10 mA/cm^2**	**Tafel Slope (mV/decade)**	**Reference**
NiS	474	124	[13]
NiS_2	454	128	[13]
Ni_3S_2	335	97	[13]
Nitrogen doped-Ni_3S_2 nanowires	196	63	[14]
NiS/$Ni(OH)_2$ composite	350	133	[15]
Fe-NiS/$Ni(OH)_2$	196	118	[15]
NiS_2 micro-architecture	174	63	[16]
NiS_2 nanosheets array on carbon cloth (NiS_2 NA/CC)	243	69	[17]
Ni_3S_2/Ni foam	220	108	[18]

NiS_2/rGO	200	52	[19]
Hierarchically porous Ni_3S_2 nanostructures	200	107	[20]
CoS_x/Ni_3S_2@NF	204	133.32	[21]
$CoNi_2S_4$	255	85	[22]
Fe-doped NiS	146	113	**Present work**
Cu-doped NiS	154	114	**Present work**
Co-doped NiS	156	98	**Present work**

Table S4. Comparison of OER performance of the synthesized TM-doped NiS with other Ni-based electrocatalysts.

Catalyst	**Overpotential (mV) at 10 mA/cm^2**	**Tafel Slope (mV/decade)**	**Reference**
NiS micro architectures	320	59	[16]
NiS@N/S-C nanocomposites	417	48	[23]
Ni_3S_2 nanowires/Ni	317	84.8	[24]
NiO_x nanoparticles	330	54	[25]
Ni-P nanoparticles on Cu foam	325	120	[26]

$NiCo_2O_4$ core-shell nanowires	320	63.1	[27]
Ni_3S_2 NWs/Ni	317	84.8	[24]
Ni-Ni_3S_2/NF	310	63	[28]
Fe doped NiS	266 mV	79	**Present work**

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