Electronic Supplementary Information for:

Mechanistic insights into interfaces and nitrogen vacancies in cobalt

hydroxide/tungsten nitride catalysts to enhance alkaline hydrogen

evolution

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Fig. S1 XRD pattern of Co(OH)₂/CNTs.



Fig. S2 SEM image of Co(OH)₂/c-WN_{1-x}/CNTs catalysts.



Fig. S3 XPS spectra of (a) Co $2p_{3/2}$; (b) W4f; (c) N1s and (d) O1s of Co(OH)₂/*c*-WN_{1-x}/CNTs catalysts

with different mole ratios.



Fig. S4 (a) Polarization curves; (b) Tafel slope and (c) Histogram of overpotential for achieving current density of 10 mA cm⁻², Tafel slope and dot plot of surface atomic ration ((Co+W)/N) for $Co(OH)_2/c$ -WN_{1-x}/CNTs catalysts with different mole ratios.



Fig. S5 CV curves of (a) $Co(OH)_2/c$ -WN_{1-x}/CNTs, (b) c-WN_{1-x}/CNTs and (c) $Co(OH)_2/CNTs$ in the range of 0.166-0.266 V vs. RHE with different scan rates.



Fig. S6 XPS spectra of (a) Co $2p_{3/2}$; (b) W4f; (c) N1s and (d) O1s of Co(OH)₂/*c*-WN_{1-x}/CNTs catalysts

before and after *i*-*t* for 10 min.



Fig. S7 XRD patterns of c-WN/CNTs and c-WN_{1-x}/CNTs annealed at 300, 400 and 500 $^\circ$ C

under H_2 flow.



Fig. S8 SEM images of c-WN_{1-x}/CNTs at different magnifications.



Fig. S9 XPS spectra of (a) W4f; (b) N1s and (c) surface element composition of c-WN/CNTs and c-WN_{1-x}/CNTs annealed at 300, 400 and 500 °C under H₂ flow.



Fig. S10 XRD patterns of *c*-WN_{1-x}/CNTs annealed at 600 $^{\circ}$ C under H₂ flow.



Fig. S11 (a) Polarization curves; (b) Tafel slope of c-WN_{1-x}/CNTs annealed at 300 and 400 °C under H₂ flow.

Catalysts	Loading (mg/cm ²)	Electrolyte	$\eta_{10}(\mathrm{mV})$	Refs.
WN NW/CC (hex)		1 M KOH	130	J. Mater. Chem. A 2017, 5, 19072-19078
WN NA/CC (orthorhombic)	2.5	1 M KOH	285	<i>Electrochimica Acta</i> 154, 2015, 345-351
W ₂ C-NC-WN (hex)	0.2	1 M KOH	145	Int. J. Hydrogen Energy 43, 1, 2018,16-23
WON@NC NAs/CC (cubic)	7.7	1 M KOH	130	<i>ChemSusChem</i> 2015, 8, 2487- 2491
W/N doped C	0.204	0.1 M KOH	85	<i>Adv. Mater.</i> 2018, 30, 1800396
Ni _{0.54} W _{0.26} Se	0.45	1 M KOH	162	<i>Chem. Asian J.</i> 2018, 13, 2040-2045
Ni/WC@NC	0.7	1 M KOH	77	Energy Environ. Sci. 2018, 11, 2114-2123
h-WN/Co _{2.45}	0.196	1 M KOH	76	J. Mater. Chem. A 2018, 6, 10967-10975
WC _x NWs		1 M KOH	122	J. Mater. Chem. A 2017, 5, 13196-13203
WP/W		1 M KOH	133	<i>Chem. Eng. J.</i> 2017, 327, 705- 712
Co(OH) ₂ /c-WN _{1-x} /CNT	1.6	1 M KOH	78	this work

 Table S1 Comparison of hydrogen evolution performance for different tungsten-based