Supporting Information

Phase and Interface Engineering of Nickel Carbide Nanobranches for Efficient Hydrogen Oxidation Catalysis

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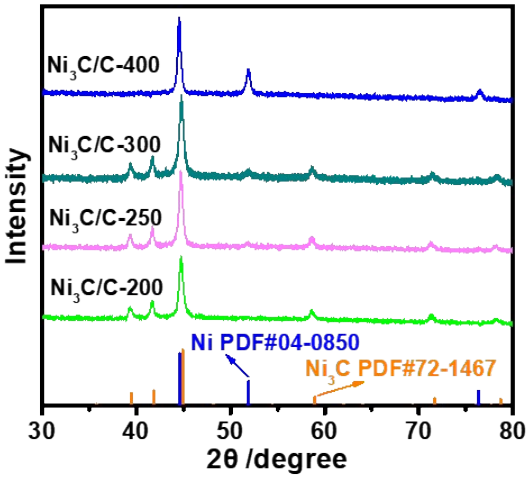

Figure S1. XRD patterns of Ni_3C/C after annealed at different temperatures in 5 % H_2/Ar.

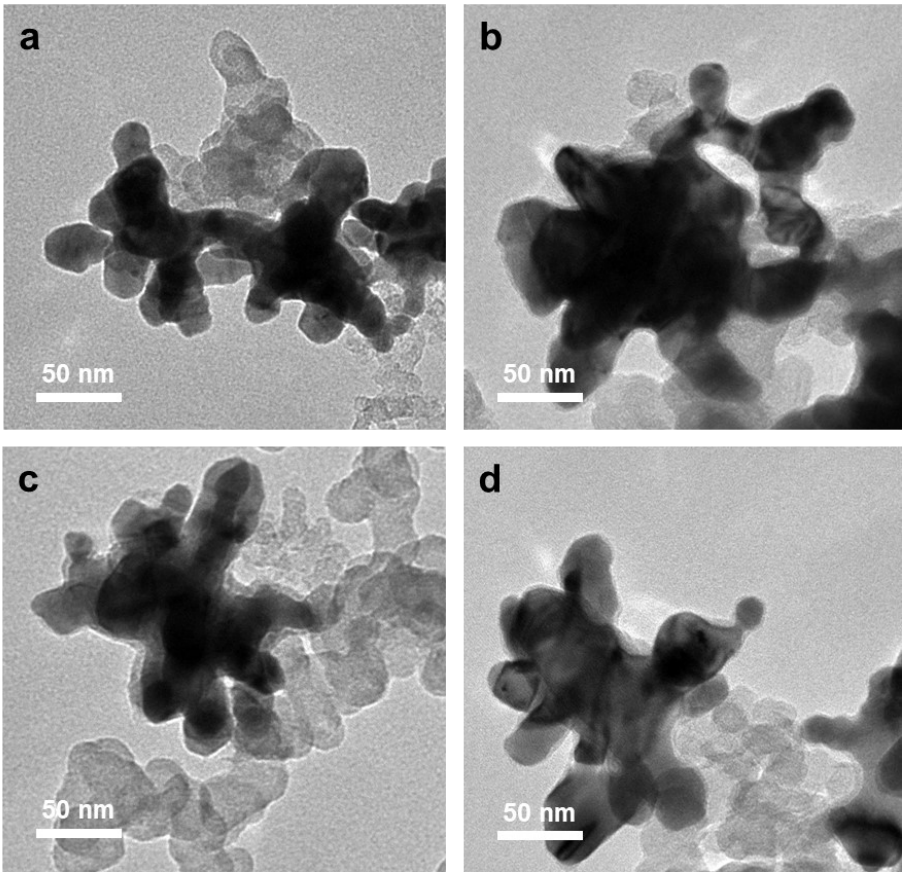

Figure S2. TEM images of Ni_3C/C after annealing at (a) 200 °C, (b) 250 °C, (c) 300 °C, and (d) 400 °C in 5 % H_2/Ar.

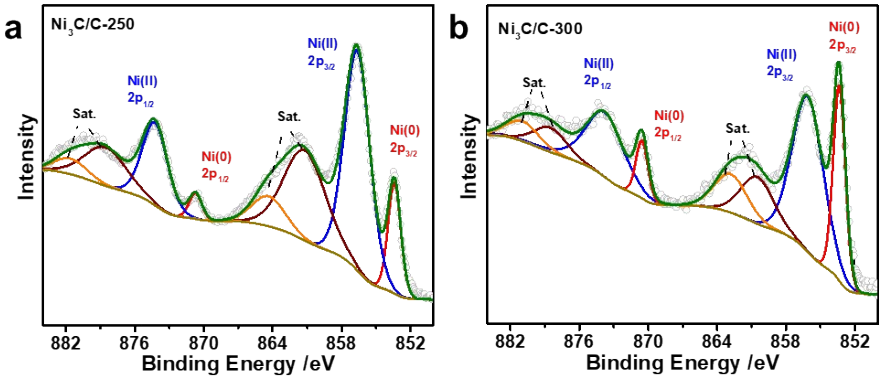

Figure S3. XPS spectra of (a) Ni_3C/C-250 and (b) Ni_3C/C-300.

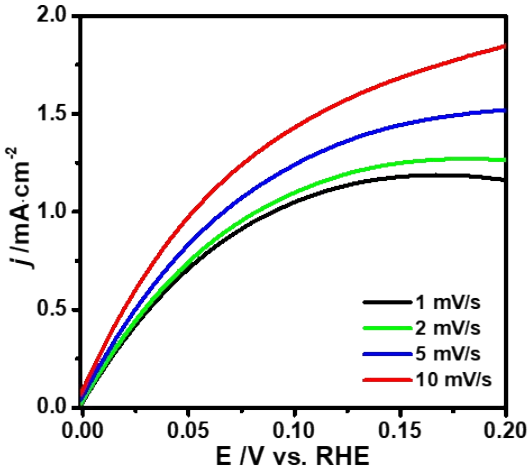

Figure S4. HOR polarization curves of Ni_3C/C-350 in H_2-saturated 0.1 M KOH at a rotating speed of 1600 rpm with different scan speeds.

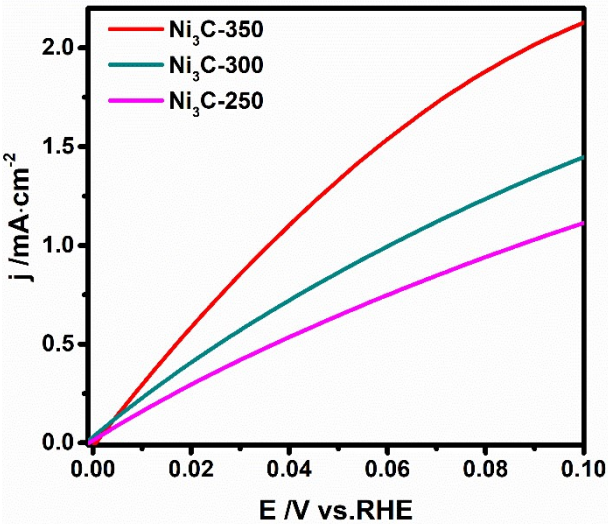

Figure S5. HOR polarization curves of Ni_3C/C-250 and Ni_3C/C-300 in H_2-saturated 0.1 M KOH at a rotating speed of 1600 rpm.

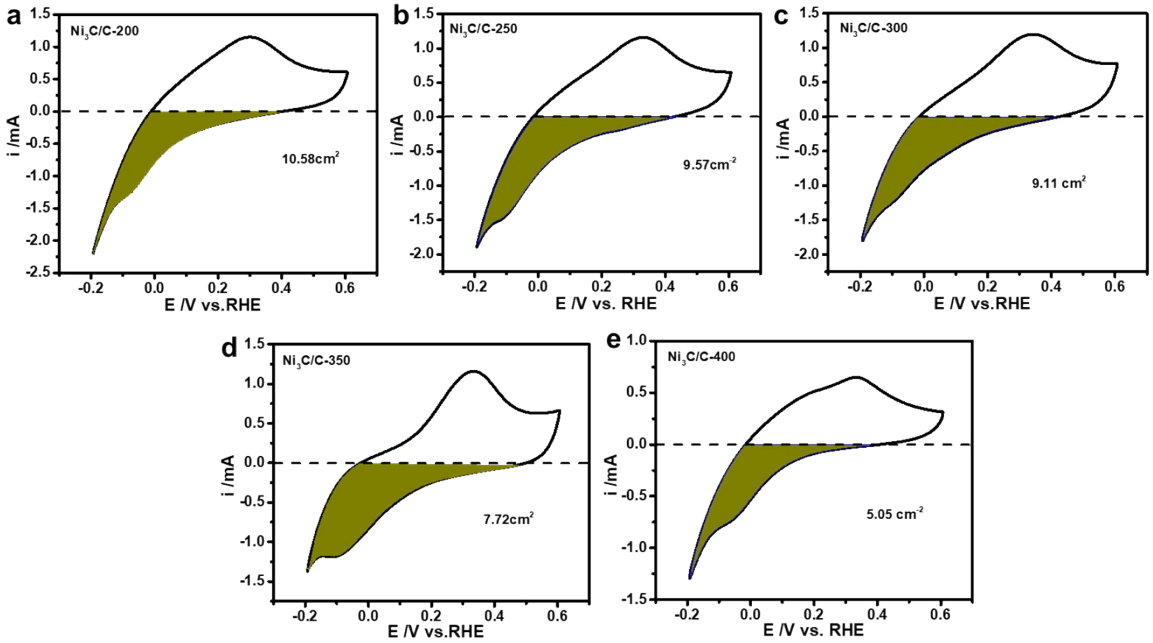

Figure S6. CV curves of different catalysts. (a) ECSA for Ni_3C/C-200 (10.58 cm^2, catalyst loading: 0.2 mg/cm^2), (b) ECSA for Ni_3C/C-250 (9.57 cm^2, catalyst loading: 0.2 mg/cm^2), (c) ECSA for Ni_3C/C-300 (9.11 cm^2, catalyst loading: 0.2 mg/cm^2), (d) ECSA for Ni_3C/C-350 (7.72 cm^2, catalyst loading: 0.2 mg/cm^2), and (e) ECSA for Ni_3C/C-400 (5.05 cm^2, catalyst loading: 0.2 mg/cm^2).

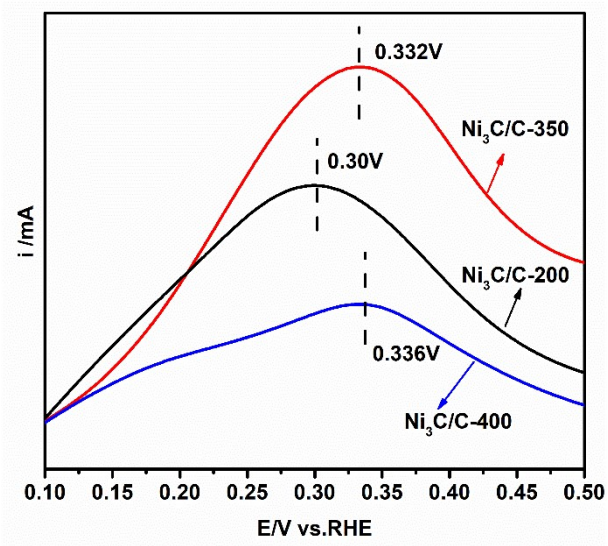

Figure S7. Anodic LSV scans in 0.1 M Ar-saturated KOH electrolyte showing the OH_{ads} oxidative adsorption peaks (scan rate: 50 $mV \cdot s^{-1}$) of Ni_3C/C-200, Ni_3C/C-350 and Ni_3C/C-400.

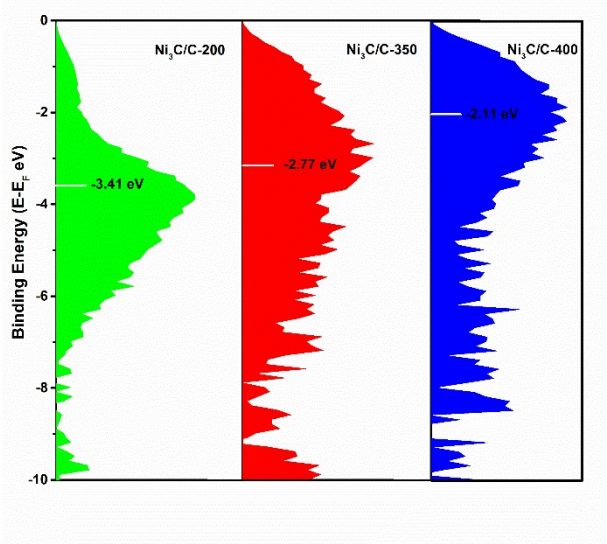

Figure S8. Surface valence band photoemission spectra of Ni_3C/C-200, Ni_3C/C-350 and Ni_3C/C-400.

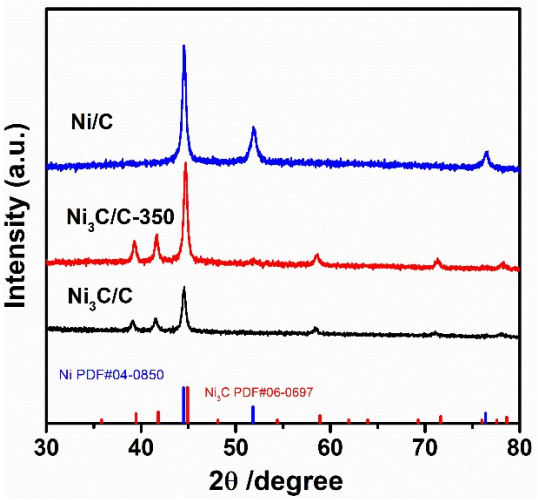

Figure S9. XRD patterns of of Ni/C, Ni_3C/C and Ni_3C/C-350.

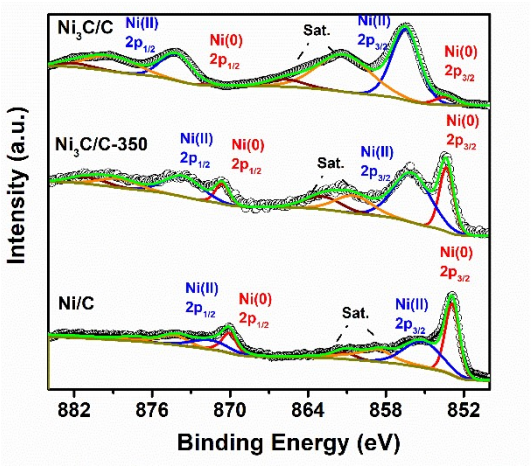

Figure S10. XPS spectra of Ni_3C/C, Ni_3C/C-350 and Ni/C.

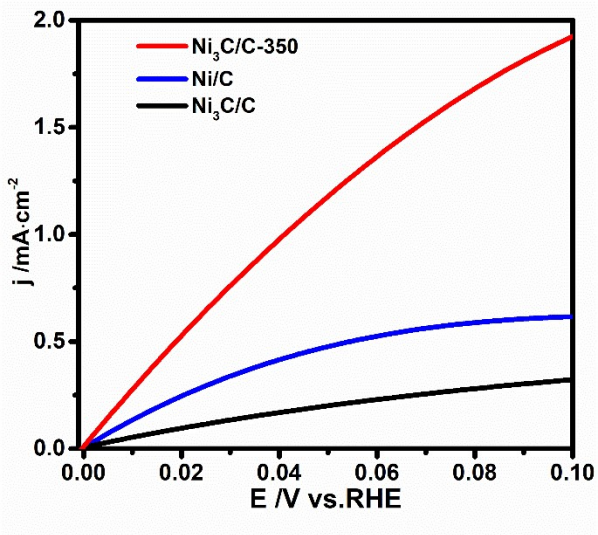

Figure S11. HOR polarization curves of Ni/C, Ni_3C/C and Ni_3C/C-350 in H_2-saturated 0.1 M KOH at a rotating speed of 1600 rpm.

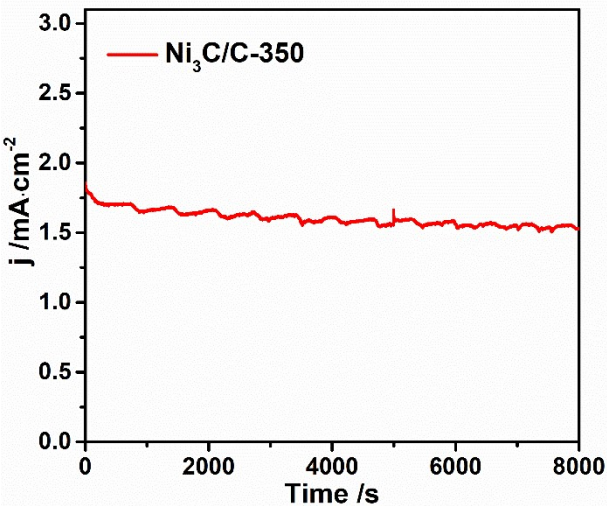

Figure S12. Relative current-time chronoamperometry response of Ni_3C/C-350 at 0.05 V versus RHE.

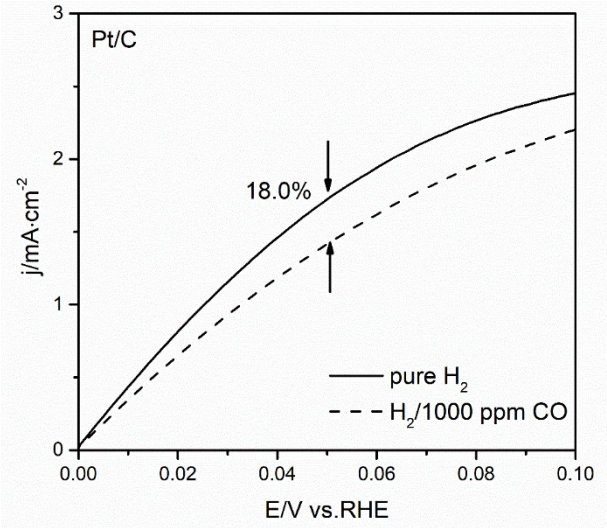

Figure S13. The polarization curves of Pt/C colleted with and without 1000 ppm CO. The scan rate is 1 mV/s and the rotation speed is 1600 rpm.

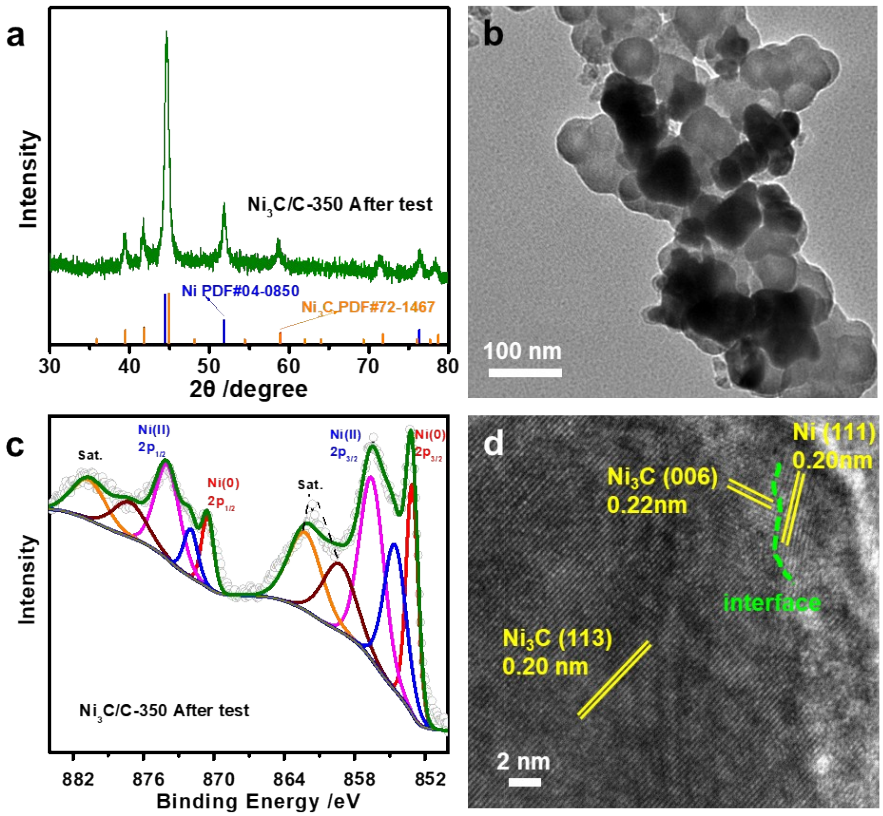

Figure S14. (a) XRD pattern, (b) TEM image, (c) XPS spectrum and (d) HRTEM of the spent Ni_3C/C-350 after long-term durability test.

Table S1. The ratio of Ni^0:Ni^{2+}obtained from XPS fitting.

Samples	Ni_3C/C-200	Ni_3C/C-250	Ni_3C/C-300	Ni_3C/C-350	Ni_3C/C-400
Ni^0:Ni^{2+}	0.17	0.29	0.45	0.49	1.17

Table S2. Results from EXAFS fitting.

Sample	Path	CN	R(Å)	σ^2($\times10^{-3}$Å^2)	$\triangle E_0$ (eV)	R factor
Ni foil	Ni-Ni	12	2.48±0.01	6.0±0.2	5.6±0.4	0.002
Ni_3C/C-200	C-Ni		1.79±0.03	10.6±7	-8.3±4.7	0.005
	Ni-Ni	6.3±1.4	2.60±0.02	12.5±2.0	1.5±1.8	
Ni_3C/C-350	C-Ni	1.6±1.5	1.78±0.04	6.3±1.9	7.6±1.4	0.005
	Ni-Ni	8.5±2.2	2.51±0.03	9.2±2.7	5.8±2.3	
Ni_3C/C-400	Ni-Ni	8.7±0.1	2.48±0.05	4.3±0.5	6.2±0.9	0.009

Table S3. Comparison of Ni_3C/C-350 and the reported catalysts for HOR in 0.1 M KOH.

Catalyst	Loading (mg cm^{-2})	Rotating Speed (rpm)	j^k (mA cm^{-2})	j^0 (mA cm^{-2})	j^0_{ECAS} (mA cm^{-2})	Ref.
Ni_3C/C-350	0.2	1600	2/72	0.96	0.031	This work
Ni_3C/C-400	0.2	1600	2.18	0.81	0.031	This work
Ni/N-CNT	0.25	2500	2.33	0.8857	0.028	Nat. Commun., 2016, **7**, 10141.
CeO_2(r)-Ni/C-1	0.141	2500	1.73	1.07	0.038	Angew. Chem. Int. Ed., 2019, **58**, 14179.
Ni_4Mo	0.5	1600	33.8	3.41	0.065	Nat. Commun., 2020, 11, 4789
Ni_4Mo	0.2	1600	10.72	2.82	-	Angew. Chem. Int. Ed., 2021, **60**, 5771
Ni-H_2-2%	0.116	2500	5.85	2.9	0.028	Angew. Chem. Int. Ed., 2020, **59**, 10797.
np-Ni_3N	0.16	1600	4.76	1.65	-	Energy Environ. Sci., 2019, **12**, 3522.
Ni_3N/C	0.16	2500	3.90	1.89	0.014	Angew. Chem. Int. Ed., 2020, **58**, 7745
Ni/NiO/C-700	0.32	1600	1.59	-	0.026	Angew. Chem. Int. Ed., 2019, **58**, 10644.
Ni_9Mo_1/KB	0.1	1600	-	-	0.027	J. Mater. Chem. A, 2017, **5**, 24433.
$Ni_{95}Cu_5$/KB	0.1	1600	-	-	0.025	Sustain. Energy Fuels, 2018, **2**, 2268.
NiB-300	0.142	2500	-	-	0.026	Chem. Sci., 2020, **11**, 12118
Ni_3@BN/C	0.25	2500	-	0.84	0.023	Chem. Sci., 2017, **8**, 5728