

## Supporting Information

### Interface engineering for NiO/CeO<sub>2</sub>@NF heterostructure to boost the electro-oxidation of 5-hydroxymethylfurfural

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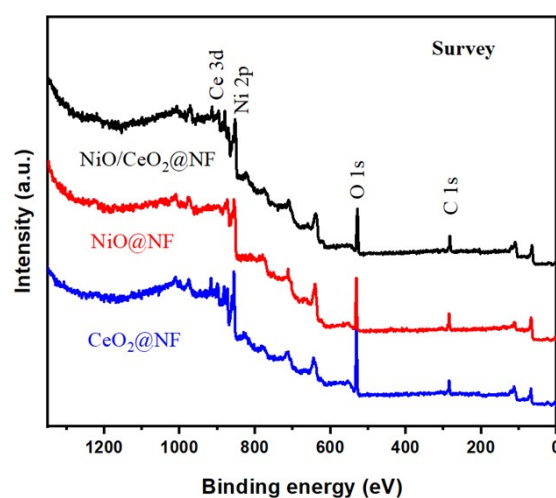


Figure S1. XPS survey spectra of the NiO/CeO<sub>2</sub>@NF, NiO@NF and CeO<sub>2</sub>@NF.

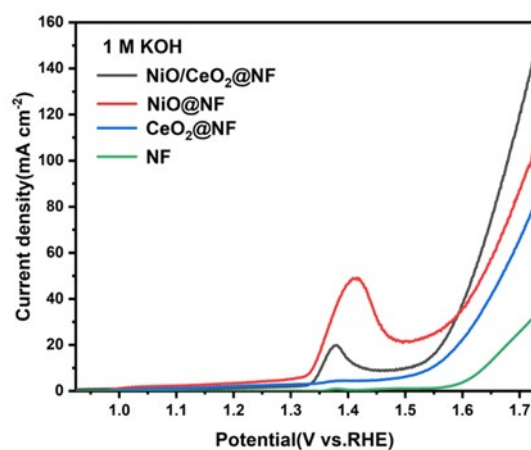


Figure S2. LSV curves of NiO/CeO<sub>2</sub>@NF, NiO@NF and NiO/CeO<sub>2</sub>@NF in 1 M KOH.

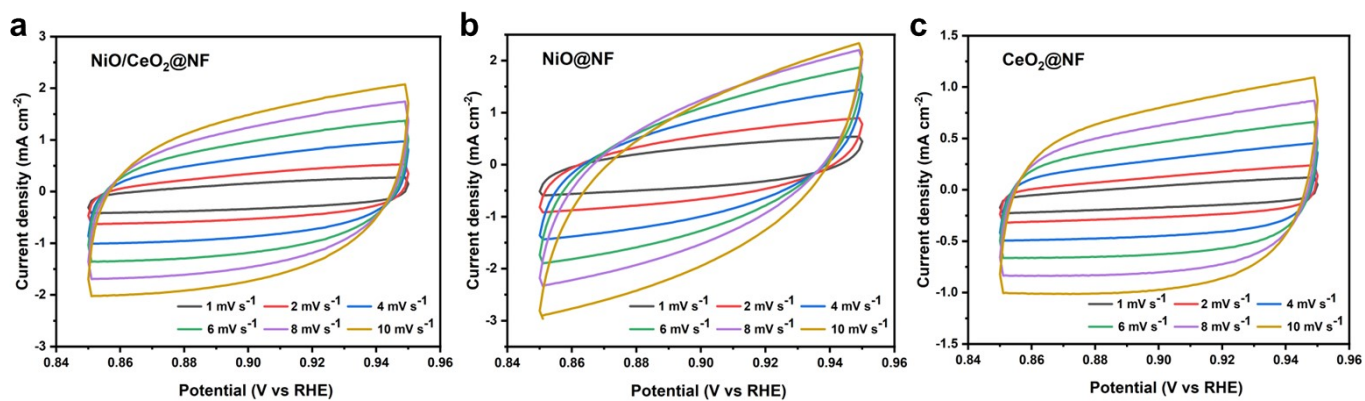


Figure S3. CV curves of (a) NiO/CeO<sub>2</sub>@NF, (b) NiO@NF and (c) CeO<sub>2</sub>@NF with 50 mM HMF at different scan rates.

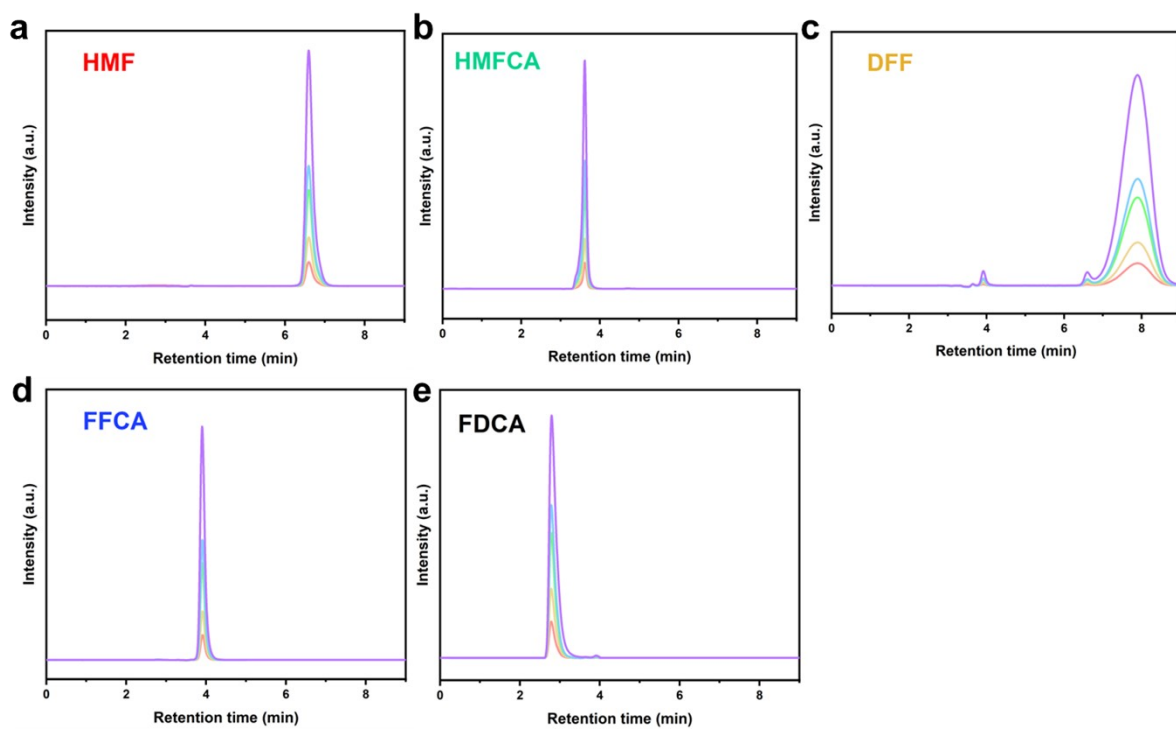


Figure S4. HPLC standard curves for (a) HMF, (b) HMFCA, (c) DFF, (d) FFCA and (e) FDCA.

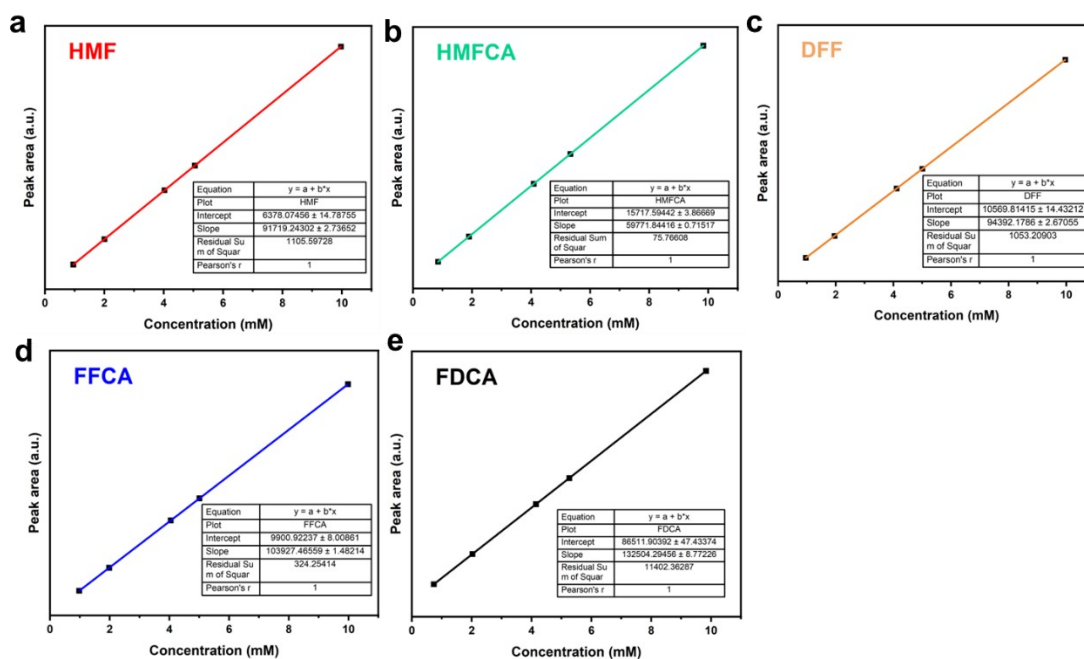


Figure S5. HPLC calibration curves for (a) HMF, (b) HMFCa, (c) DFF, (d) FFCA and (e) FDCA.

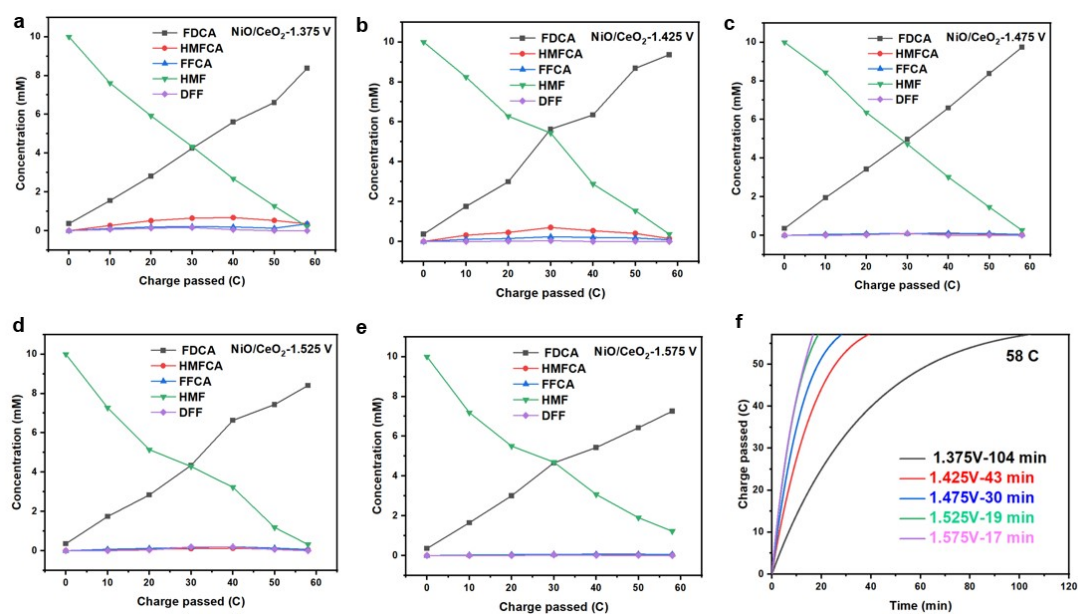


Figure S6. The concentrations of (a) HMF, (b) HMFCa, (c) FFCA, (d) DFF, and (e) FDCA with different electrolysis potentials under the fixed theoretical charge of 58 C. (f) The time to reach theoretical charge (58 C) at different potentials.

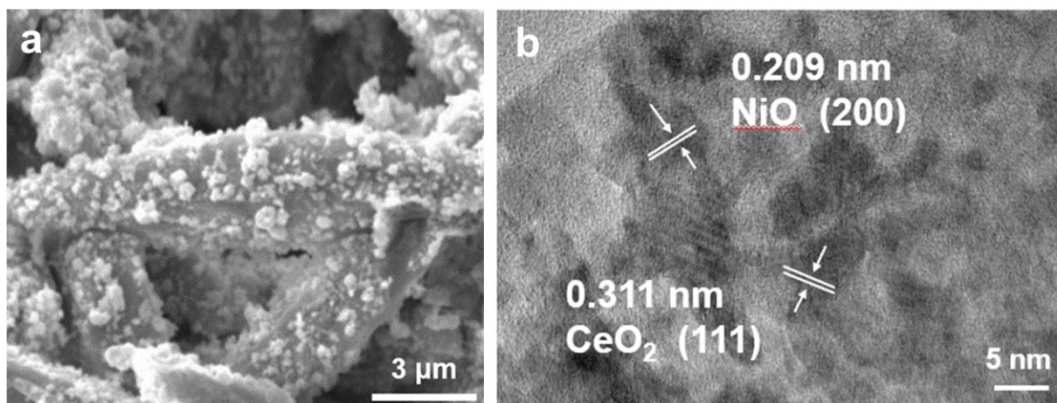


Figure S7. (a) SEM, (b) HRTEM images of the NiO/CeO<sub>2</sub>@NF sample after 10 cycles of electrolysis.

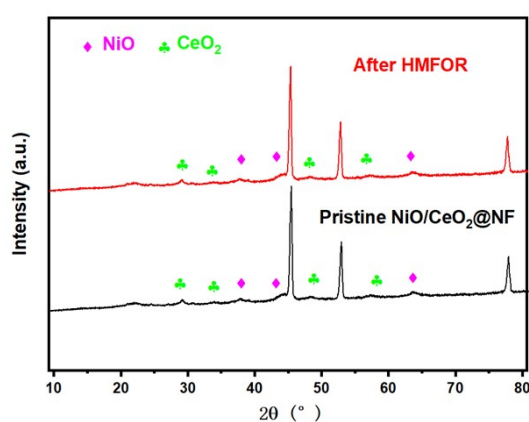


Figure S8. XRD patterns of the as-synthesized NiO/CeO<sub>2</sub>@NF before and after HMF electrooxidation.

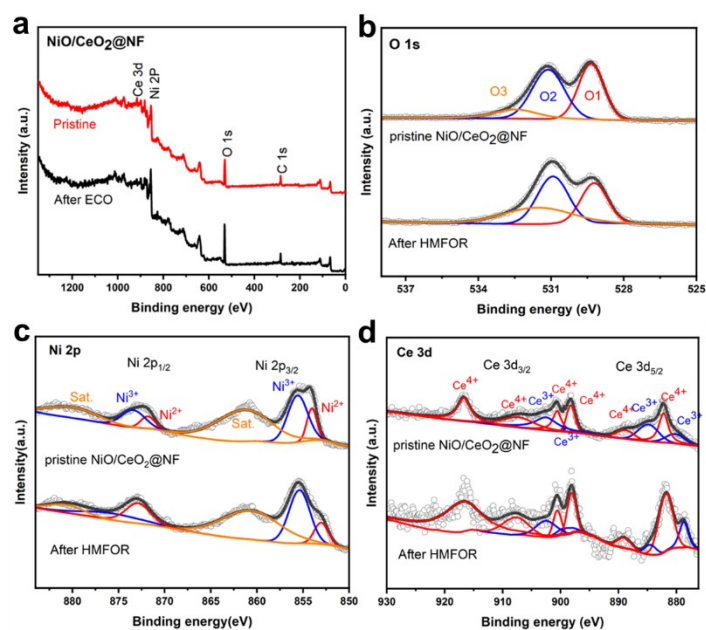


Figure S9. (a) XPS survey spectra, (b) O 1s, (c) Ni 2p and (d) Ce 3d XPS spectra of the NiO/CeO<sub>2</sub>@NF sample before and after 10 cycles of electrolysis.

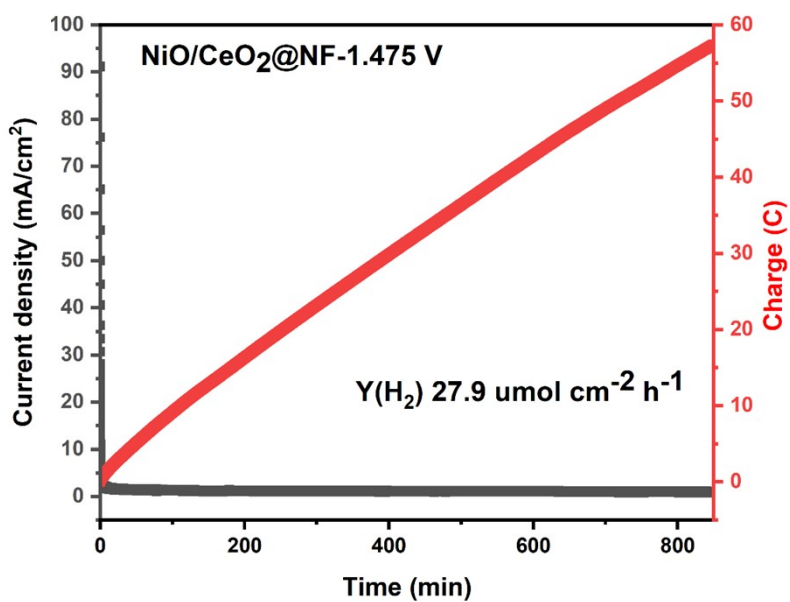


Figure S10. The current-time and charge-time curves during water splitting without HMF.

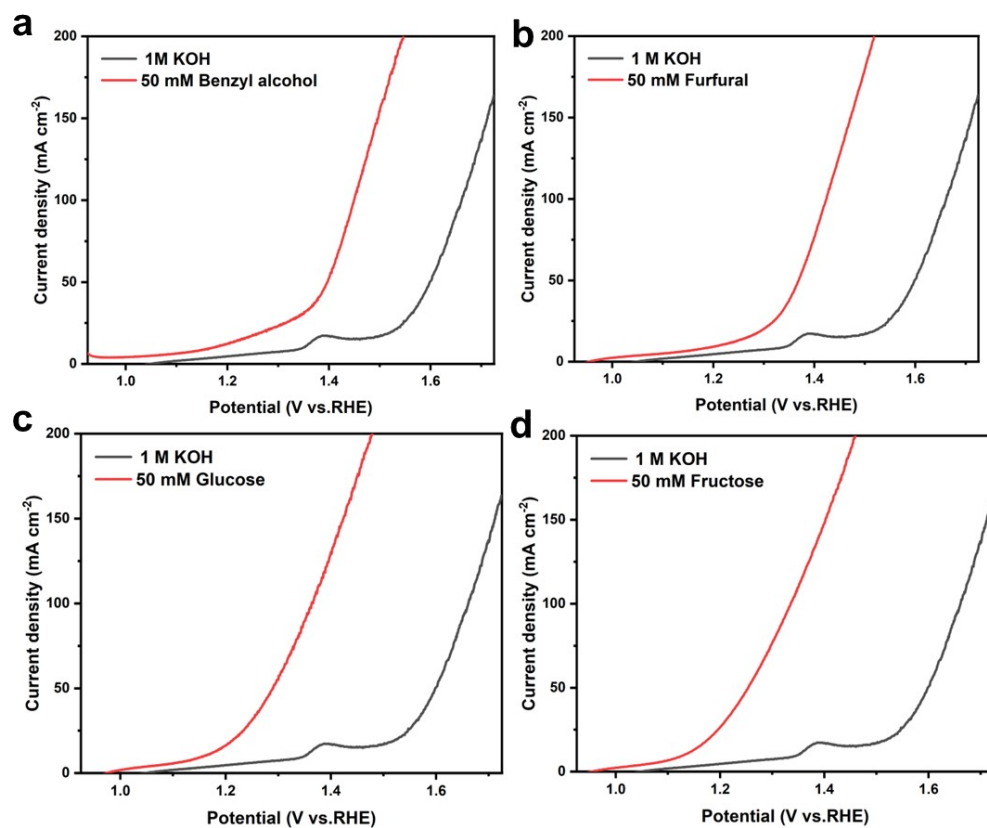


Figure S11. (a-d) LSV curves of the NiO/CeO<sub>2</sub>@NF at a scan rate of 5 mV s<sup>-1</sup> in 1.0 M KOH with and without benzyl alcohol, furfural, glucose and fructose.

Table S1. The ratio of Ni<sup>3+</sup>/Ni<sup>2+</sup>, Ce<sup>4+</sup>/Ce<sup>3+</sup> and O2 was obtained from XPS results.

NiO/CeO <sub>2</sub> @NF	Ni <sup>3+</sup> /Ni <sup>2+</sup>	Ce <sup>4+</sup> /Ce <sup>3+</sup>	O2
pristine	3.0	2.7	0.46
After HMFOR	2.3	4.3	0.4

Table S2. The FDCA yield rates on the NiO/CeO<sub>2</sub>@NF catalyst under different potentials.

Potential (V vs. RHE)	1.375	1.425	1.475	1.525	1.575
FDCA yield rate (μmol cm <sup>-2</sup> h <sup>-1</sup> )	49.31	125.1	197.92	282.5	302.96

Table S3. The comparison of activity for NiO/CeO<sub>2</sub>@NF and other reported HMF electrochemical oxidation catalysts.

Catalyst	Potential (V vs RHE)	C <sub>HMF</sub> (mM)	HMF Conversion (%)	FDCA Yield (%)	Faradic Efficiency (%)	Ref.
NiO/CeO <sub>2</sub> @NF	1.475	10	100	99.0	98.96	This work
NiCo <sub>2</sub> O <sub>4</sub> /NF	1.43	5	99.6	90.4	90.8	1
Ni <sub>3</sub> S <sub>2</sub> /NF	1.498	10	100	98	94	2
NiFe-LDH	1.48	10	97.4	96.8	84.5	3
NiCoFe-LDHS	1.55	10	95.5	95	90	4
NiO-Co <sub>3</sub> O <sub>4</sub>	1.45	10	100	98	96	5
Ni <sub>2</sub> P NPA/NF	1.423	10	100	98	98	6
NiCoP	1.464	300	98.7	98.8	96.1	7
CoNiS@NF	1.45	10	100	100	99.1	8
NF@Co <sub>3</sub> O <sub>4</sub> /CeO <sub>2</sub>	1.4	50	98	94.5	97.5	9

Ni <sub>3</sub> N@C	1.45	10	100	98	99	10
CoP/Ni <sub>2</sub> P- NiCoP@NC	1.45	5	100	98.1	97.6	11
Co-NixP@C	1.56	10	-	100	98.9	12
NiS <sub>x</sub> /Ni <sub>2</sub> P	1.46	10	100	98.5	95.1	13
Co <sub>9</sub> S <sub>8</sub> -Ni <sub>3</sub> S <sub>2</sub>	1.4	10	100	98.8	98.6	14
Ni/NiO	1.45	50	95	91	95	15

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