***Electronic Supplementary Information (ESI) for*:**

Enhanced urea oxidization on spinel cobalt oxide nanowires via on-site electrochemical defect engineering

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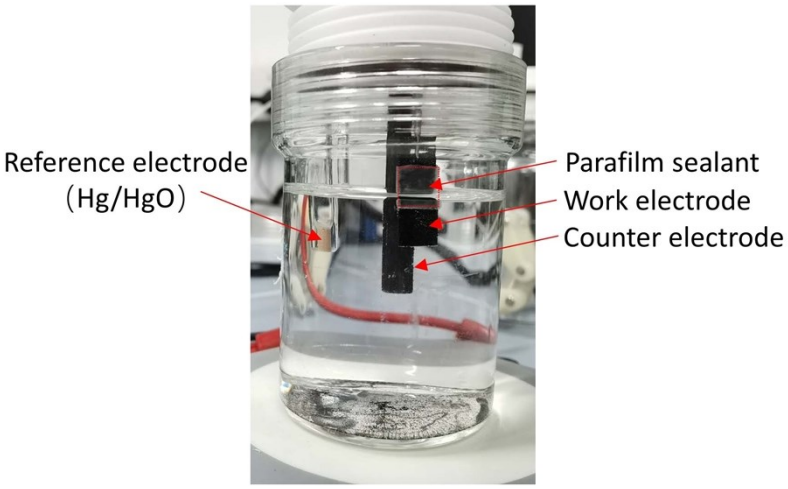

Figure S1. The 3-electrode electrochemical test setup.

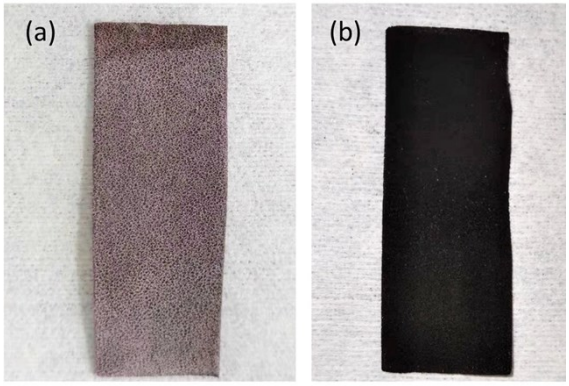

Figure S2. Photograph of (a) cobalt hydroxide precursor and (b) cobalt oxide supported on NF.

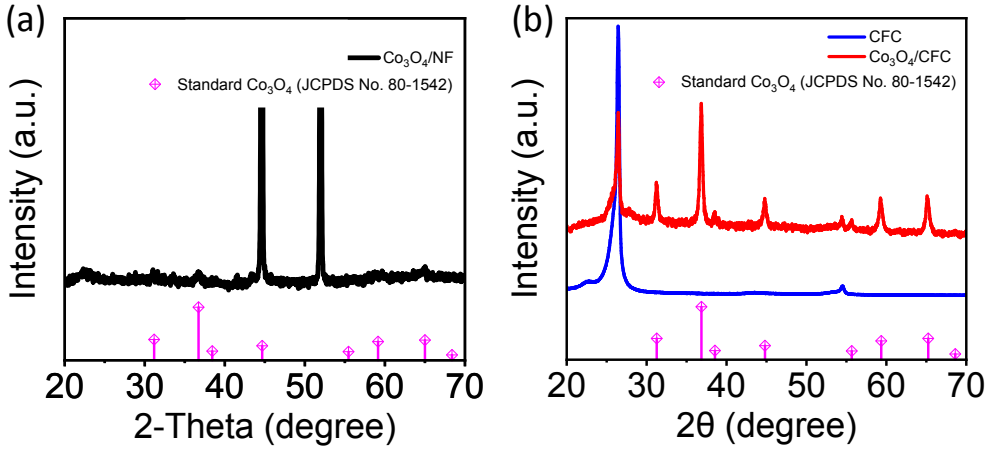

Figure S3. XRD pattern of Co_3O_4 supported on (a) NF and (b) CFC with the reference of standard powder diffraction card.

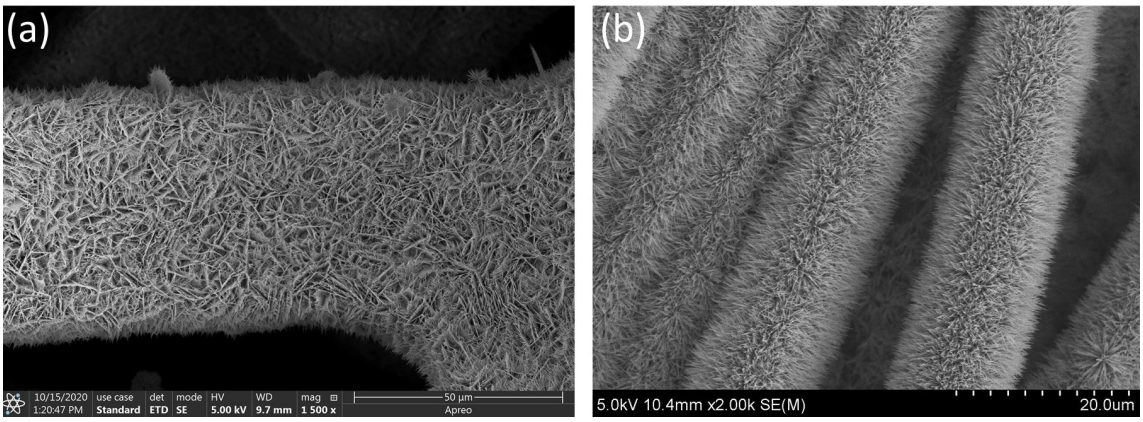

Figure S4. Low-magnification SEM images of Co_3O_4 wire arrays supported on different substrates: (a) NF and (b) CFC.

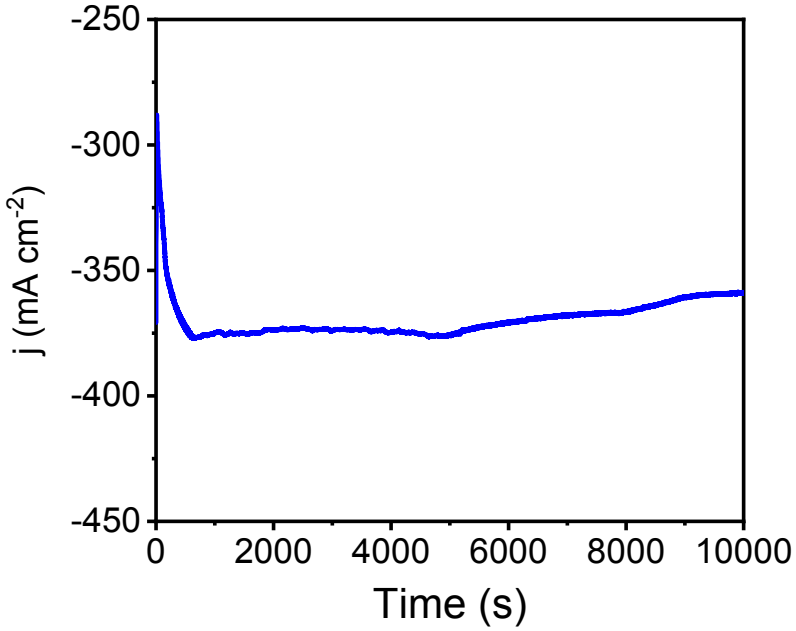

Figure S5. The typical chronoamperometric curve of Co_3O_4/NF corresponding to the cathodic treatment at a constant potential of -1.5 V vs. Hg/HgO.

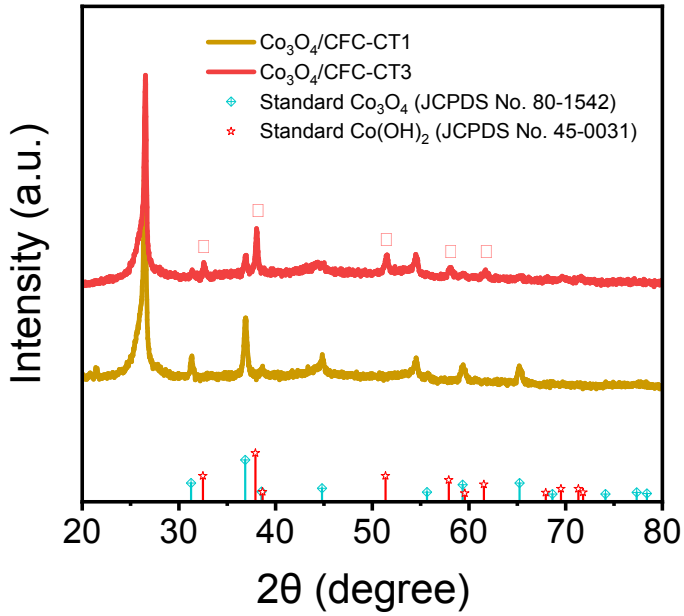

Figure S6. XRD patterns of Co_3O_4-CT1, and Co_3O_4-CT3 supported on CFC.

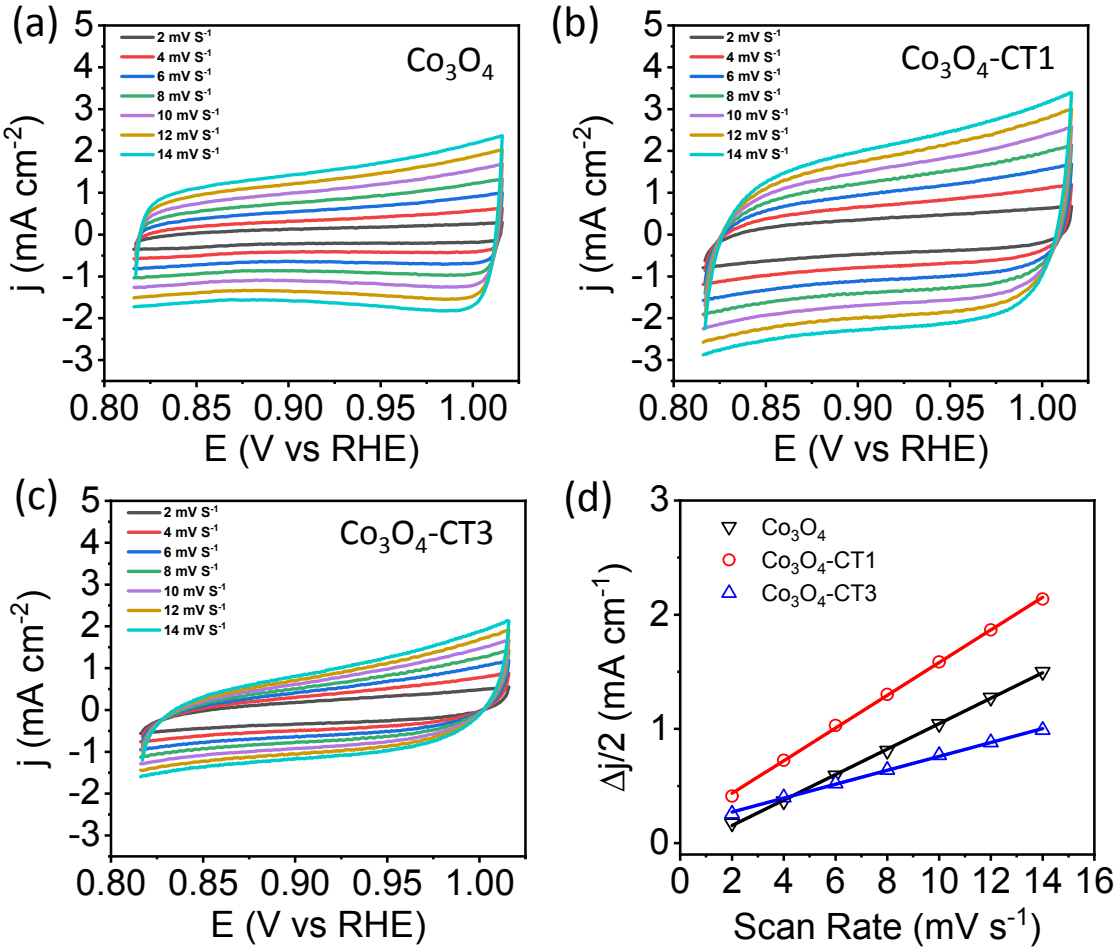

Figure S7. (a-c) CV curves of Co_3O_4, Co_3O_4-CT1, and Co_3O_4-CT3 recorded with different scanning rate at the non-faradaic region; (d) linear fitting of the current density at 0.9 V vs RHE against different scan rates.

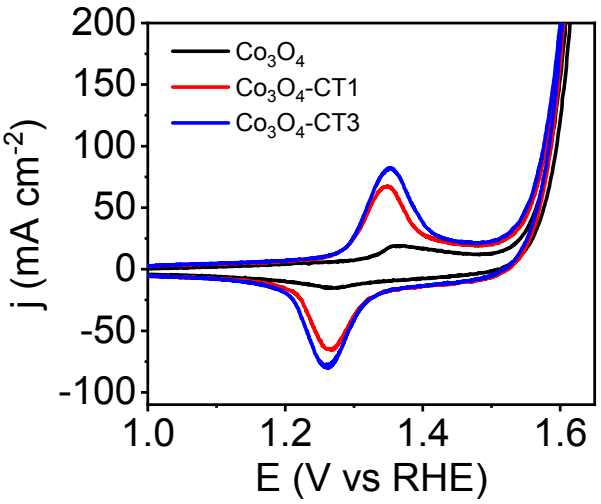

Figure S8. CV curves of Co_3O_4, Co_3O_4-CT1, and Co_3O_4-CT3 measured in pure 1 M KOH solution at the scan rate of 10 mV/s.

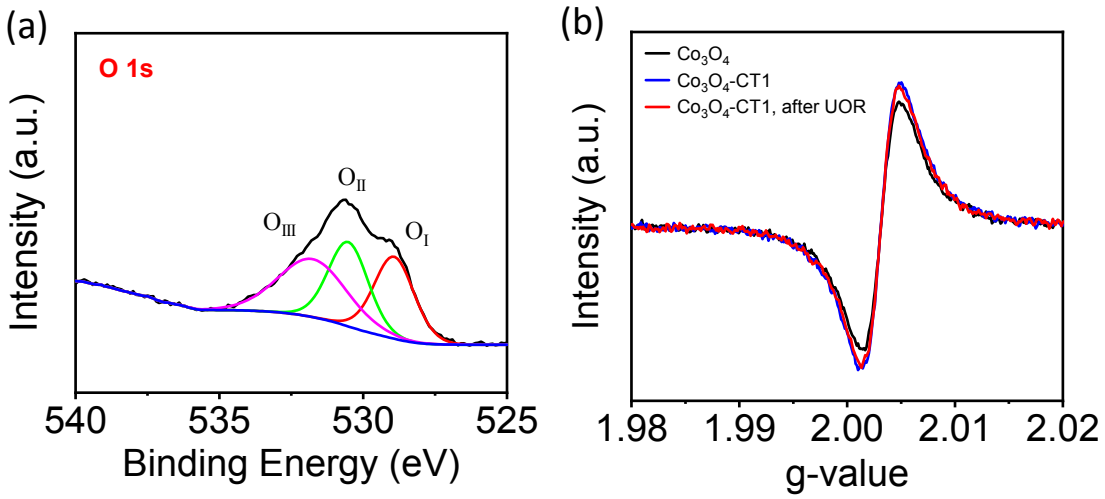

Figure S9. (a) O 1s spectrum of Co_3O_4-CT1 after CV the V-t test for UOR, and (b) EPR spectra Co_3O_4-CT1 before and after the UOR test, with Co_3O_4 as a reference.

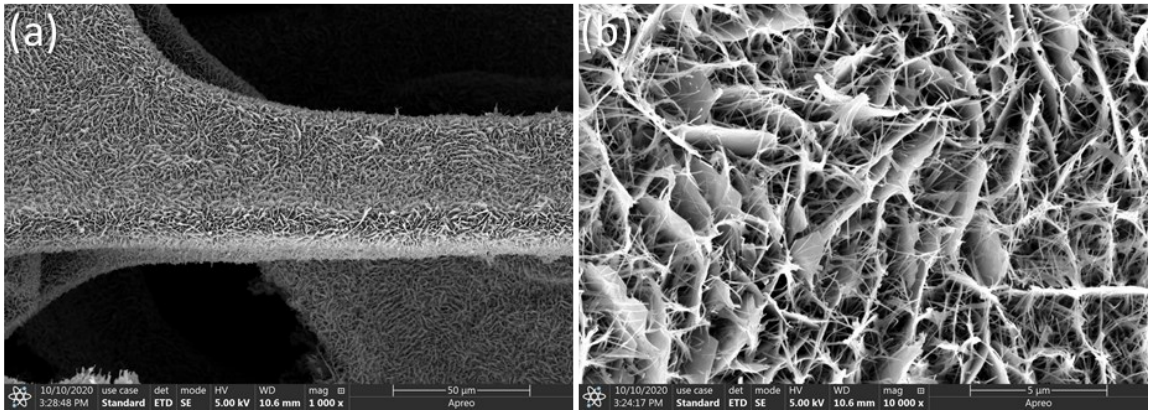

Figure S10. SEM images of Fe-Co_3O_4 nanosheet/wire arrays supported on NF.

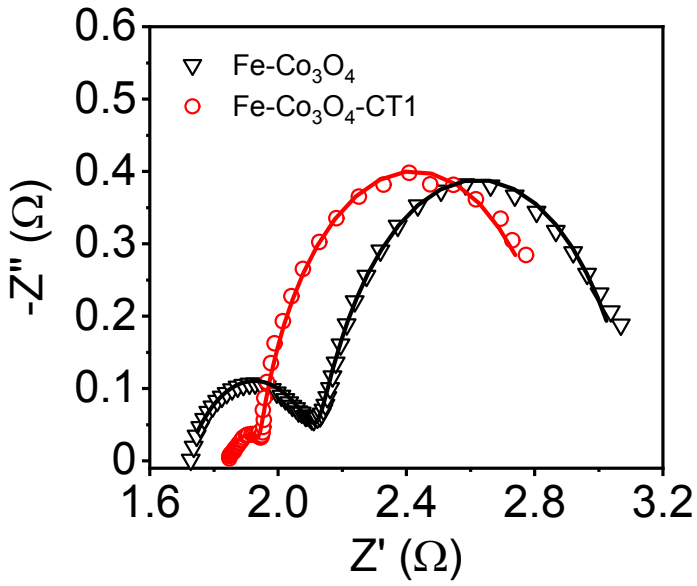

Figure S11. EIS spectra of Fe-Co_3O_4 and Fe-Co_3O_4-CT1.

Table S1. Comparison of the electrocatalytic performance of UOR catalysts reported recently.

Catalysts	Substrate	Electrolyte	*j* (mA cm^{-2})	Potential (V vs. RHE)	iR-Compensation	Reference
CoFeCr LDH	Nickel foam	1.0 M KOH 0.33 M urea	10	1.31	*yes*	*Appl. Catal. B Environ. 2020, **272**,118959.*
$NiMoO_3S$	Nickel foam	1.0 M KOH 0.5 M urea	10	1.34	*yes*	*Chem. Commun., 2020, **56**, 11038*
Rh-NCs/NiO-NSs	Glassy carbon	1.0 M KOH 0.33 M urea	52.05	1.5	*ye*	*Appl. Catal. B Environ. 2020, **265**, 118567*
$NiSe_2$-NiO 350	Glassy carbon	1.0 M KOH 0.33 M urea	10	1.53	*no*	*Appl. Catal. B Environ. 2020, **276**,119165*
V_O-rich $CoMoO_4$	Nickel foam	1.0 M KOH 0.5 M urea	288	1.63	*unknown*	*Appl. Catal. A: General, 2020, **602**, 117670.*
Ni_3N	Nickel foam	1.0 M KOH 0.5 M urea	100	1.40	*unknown*	*ACS Appl. Mater. Interfaces 2019, **11**, 13168*
Mo-Co-S-Se	Carbon fiber cloth	1.0 M KOH 0.5 M urea	10	1.40	*unknown*	*ACS Sustainable Chem. Eng. 2019, 7, 16577*
CoS_2-MoS_2	Nickel foam	1.0 M KOH 0.5 M urea	10	1.29	*yes*	*Adv. Energy Mater. 2018, 1801775*
NiMoO-Ar	Nickel foam	1.0 M KOH 0.5 M urea	10 100	1.38 1.42	*yes*	*Energy Environ. Sci. 2018, **11**, 1890*
r-$NiMoO_4$	Nickel foam	1.0 M KOH 0.5 M urea	249.5	1.62	*unknown*	*ACS Catal. 2018, **8**, 1*
Ni-MOF	Nickel foam	1.0 M KOH 0.33 M urea	10	1.37	*unknown*	*Chem. Commun. 2017,**53**, 10906*
S-MnO_2	Graphen-nickel foam	1.0 M KOH 0.5 M urea	10	1.33	*yes*	*Angew. Chemie Int. Ed. 2016, **55**, 3804.*
Rh-Ni electrode	Nickel foil	1.0 M KOH 0.3 M urea	50	1.40	*unknown*	*J. Power Sources 2011, **196**, 9579*
Co_3O_4-CT1	**Nickel foam**	**1.0 M KOH 0.5 M urea**	**100**	**1.34**	**yes**	**This work**

Table S2. Fitting parameters obtained by the EIS spectra in Figure 3d with the proposed 2TS equivalent circuit.

Sample	R_s	R_1	T_1	P_1	R_{ct}	T_2	P_2	C_{dl}^{*EIS}
Co_3O_4	1.664	0.3338	0.0093	0.5708	0.6152	0.2704	0.8226	187.4
Co_3O_4-CT1	1.663	0.0615	0.4301	0.5089	0.5290	0.4869	0.7725	308.4
Co_3O_4-CT3	1.706	0.0644	0.7265	0.4895	0.57207	0.5201	0.7928	358.5
Fe-Co_3O_4	1.714	0.4181	0.0062	0.6150	0.9869	0.2905	0.8454	221.1
Fe-Co_3O_4-CT1	1.849	0.0931	0.0312	0.7657	0.9634	0.4036	0.8818	338.9

Note: a*) C_{dl}^{*EIS} was calculated by using equation 2; b) units for R and C_{dl}^{*EIS} are ohm (Ω) and mF cm^{-2}, respectively.*