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Supporting Information

Highly Ordered Mesoporous Co_3O_4 Electrocatalyst for Efficient, Selective, and Stable Oxidation of 5-Hydroxymethylfurfural to 2,5-Furandicarboxylic Acid

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Contents

1. General data:

All solvents and chemicals were used as purchased without further purifications. Chemicals: Pluronic 123 (P123, poly(ethylene glycol)-poly-(propylene glycol)-poly(ethylene glycol), EO:PO:EO = 20:70:20, average Mn ~ 5800; Sigma-Aldrich), Hydrochloric acid (HCl; 37-38%; J.T Baker), Sodium hydroxide (NaOH, reagent, pellet; VWR Chemicals), Potassium hydroxide (KOH, reagent, pellet; VWR Chemicals ≥85%), 1-Butanol (99%; Alfa Aesar), Ethanol (absolute, ≥99.8%; Sigma-Aldrich), Tetraethyl orthosilicate (TEOS; reagent grade, 98%; Sigma-Aldrich), 5-hydroxymethylfurfural (Sigma-Aldrich, 99 %), Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$; ACS reagent, ≥98%; Sigma-Aldrich). Prior to the synthesis, all the flasks were washed with a solution of aqua regia (HCl/HNO_3 = 3:1 v/v) to remove any traces of metal residue, followed by washing with water and acetone, and finally dried at 80 °C overnight. Milli-Q water (18.2 MΩ) was used for all the syntheses and catalysis experiments.

-- **Elemental analysis** was carried out at a commercial analysis laboratory (*Mikroanalytisches Laboratorium Kolbe Fraunhofer Institut UMSICHT, Gebäude G-Osterfelder Str. 3 D-46047 Oberhausen*) with an AAnalyst 200 **Atomic Absorption Spectrometer (AAS).**

--Scanning electron microscopy (SEM) images were taken with a Hitachi S-5500 microscope. The EDX analyses were performed with an SDD-detector and software from Thermo Fisher.

--Scanning transmission electron microscope (STEM) images were taken with a HD 2700 ultrahigh-resolution cold field emission scanning microscope at an acceleration voltage of 200 kV. An EDAX Octane T Ultra W 200mm^2 SDD with TEAM-Software was attached to the instrument.

--**Transmission electron microscopy (TEM)** images of the catalysts were recorded with a Hitachi HF-2000 microscope at an acceleration voltage of 200 kV.

--**Nitrogen adsorption-desorption** measurements were performed on a NOVA 3200e instrument at 77 K. Prior to the measurements, all samples were degassed under vacuum for at least 6 h at 150 °C.

--BET surface areas were calculated from the data in a relative pressure range from 0.05-0.20. By using the Barrett-Joyner-Halenda (BJH) algorithm, the pore volumes and pore size distributions were derived from the adsorption branches of the isotherms (normally desorption is recommended, but the desorption branches could be influenced by the tensile strength effect). The total pore volume was estimated from the amount adsorbed at a relative pressure of 0.95 (might include a small contribution from interparticle voids).

--**X-ray powder diffraction**: Powder X-ray diffraction (XRD) patterns were recorded on a Stoe STADI P θ-θ diffractometer operating in reflection mode with Cu $K_{\alpha 1,2}$ radiation and a secondary graphite monochromator.

--**X-ray photoelectron spectra (XPS)**: XPS measurements were performed with a spectrometer from SPECS GmbH equipped with a PHOIBOS 150 1D-DLD hemispherical energy analyser. The monochromatized Al Kα X-ray source (E=1486.6 eV) was operated at 14 kV and 100W. For the narrow scans, an analyzer pass energy of 20 eV was applied. The medium area mode was used as lens mode. The base pressure during the experiment in the analysis chamber was $5x10^{-10}$ mbar. To account charging effects, all spectra are referred to C 1s at 284.5 eV.

2. Characterization of the catalysts.

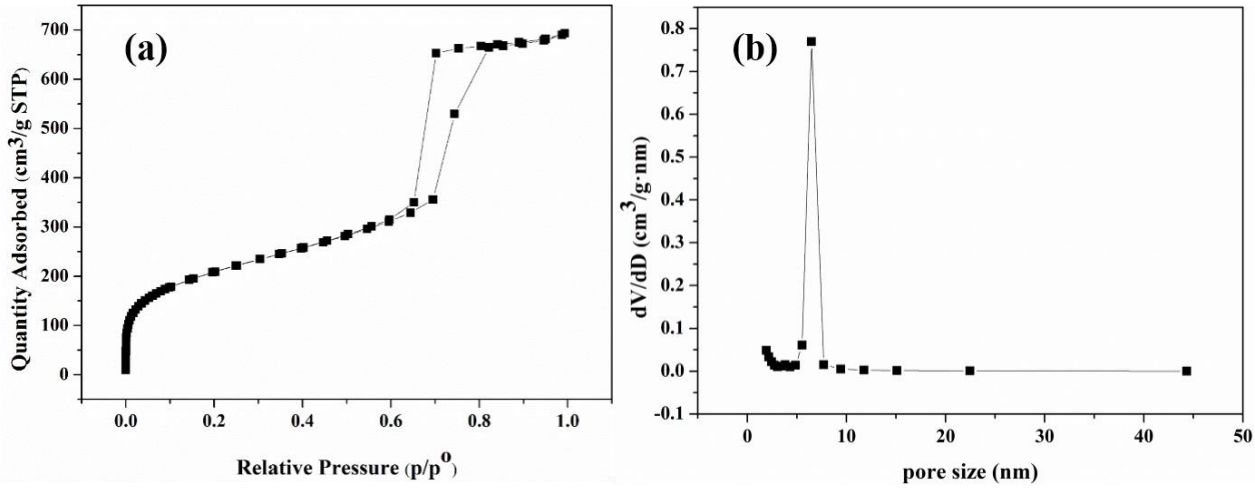


Figure S1. N_2-physisorption analysis of the KIT-6 template. a) N_2 adsorption-desorption isotherms and b) pore size distribution.

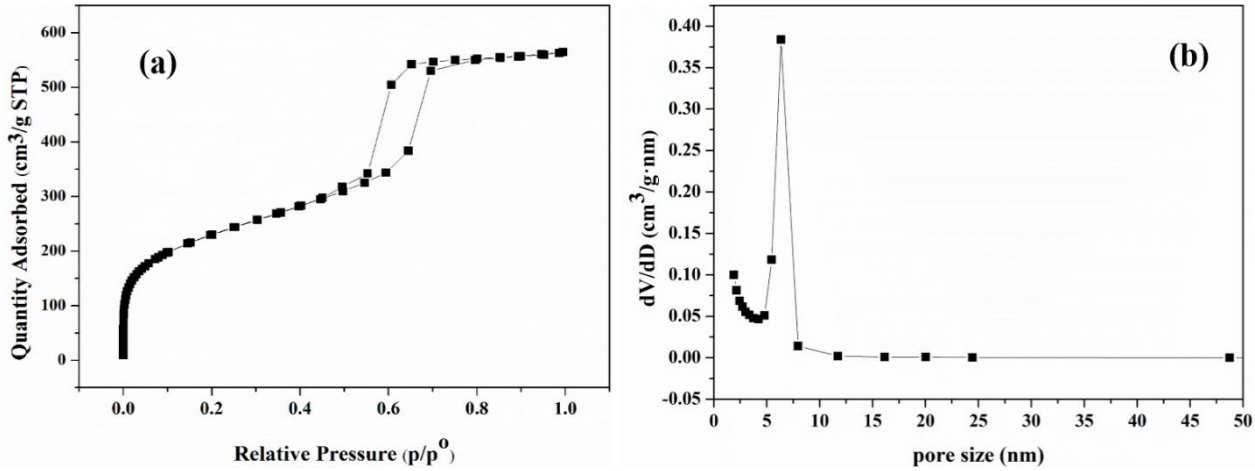


Figure S2. N_2-physisorption analysis of disordered mesoporous SiO_2 template. a) N_2 adsorption-desorption isotherms and b) pore size distribution.

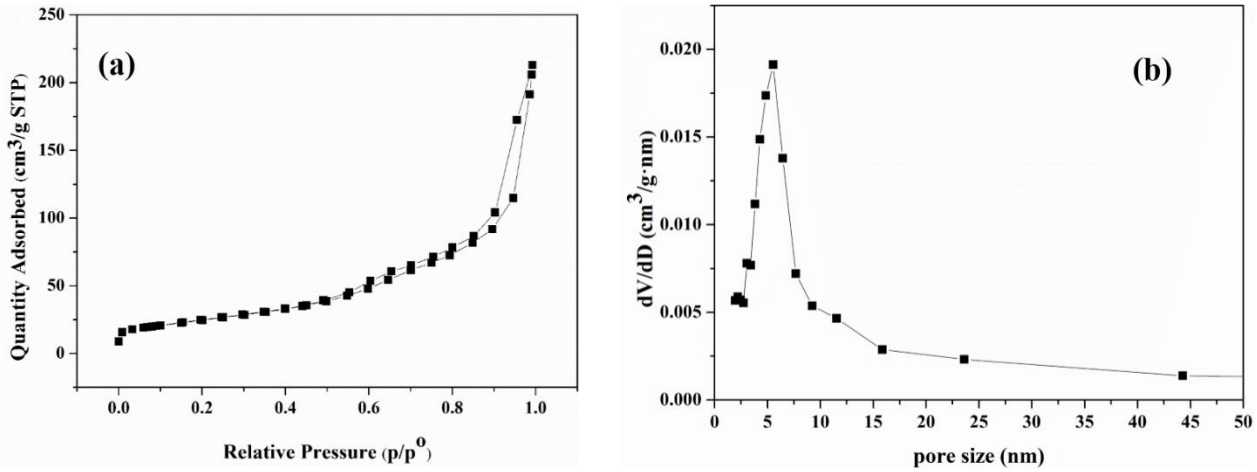


Figure S3. N_2-physisorption analysis of dm-Co_3O_4. a) N_2 adsorption-desorption isotherms and b) pore size distribution.

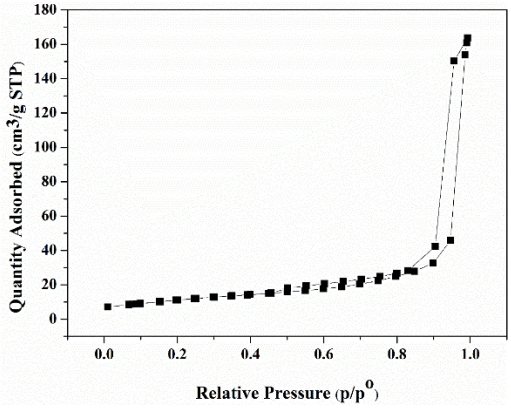


Figure S4. N_2 adsorption-desorption isotherms of bulk Co_3O_4.

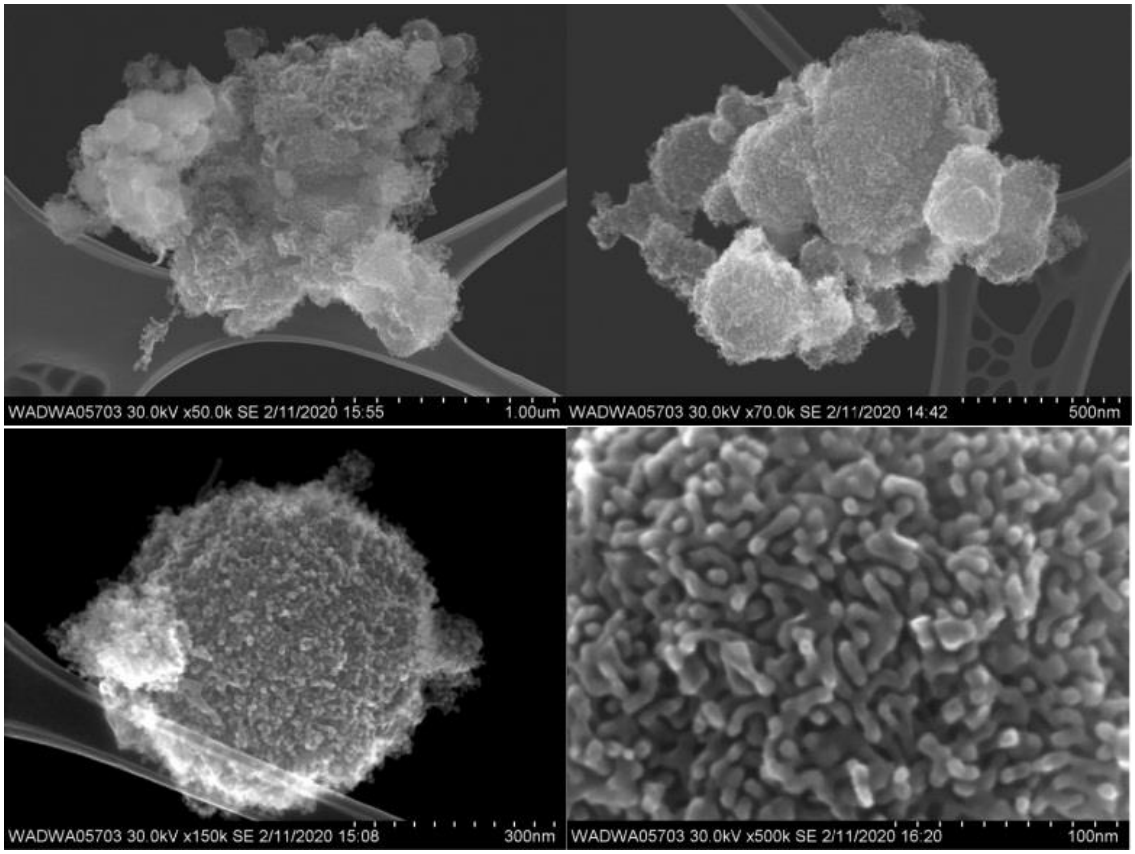


Figure S5. SEM images of disordered mesoporous Co_3O_4 at different magnification.

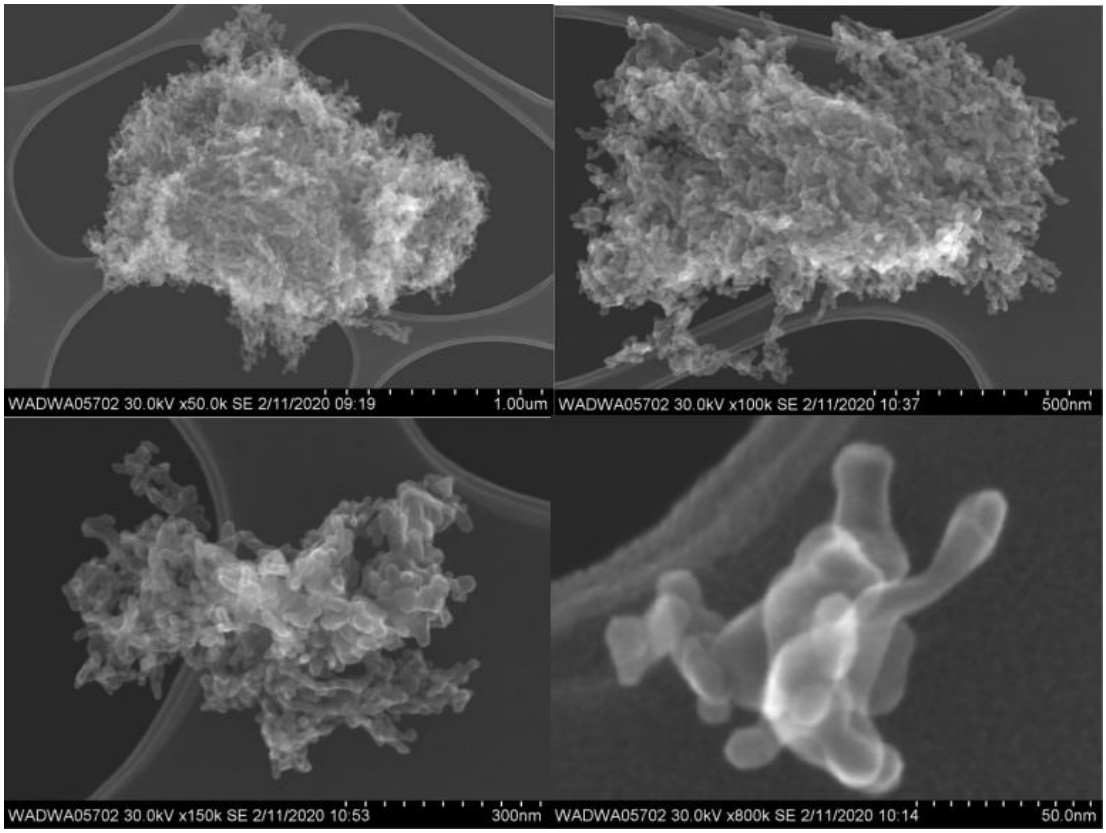


Figure S6. SEM images of bulk Co_3O_4 at different magnification.

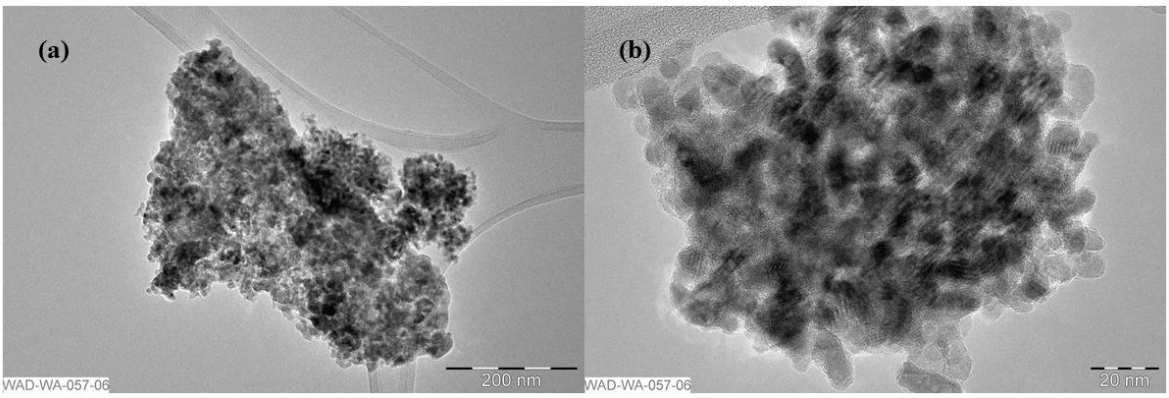


Figure S7. TEM images of disordered mesoporous Co_3O_4 at different magnification.

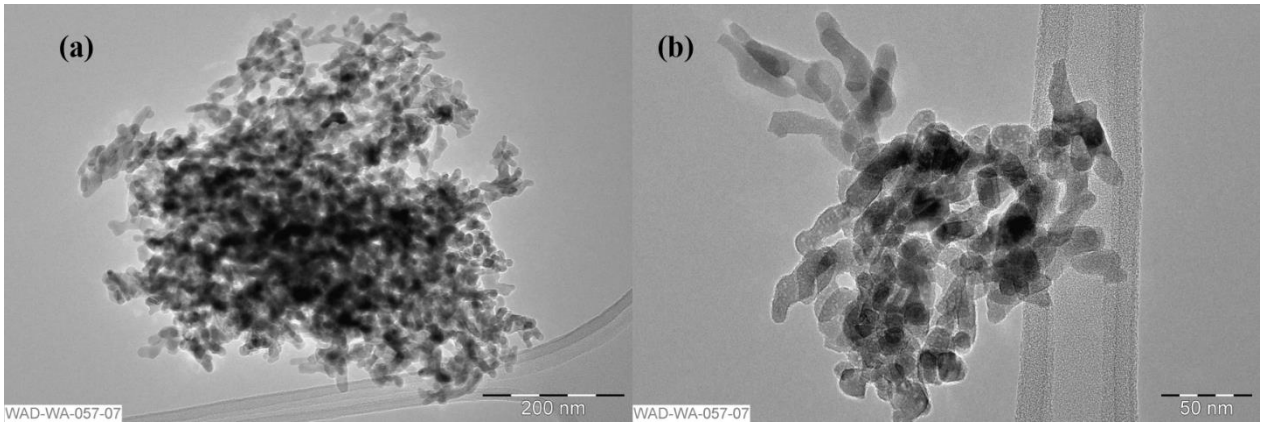


Figure S8. TEM images of bulk Co_3O_4 at different magnification.

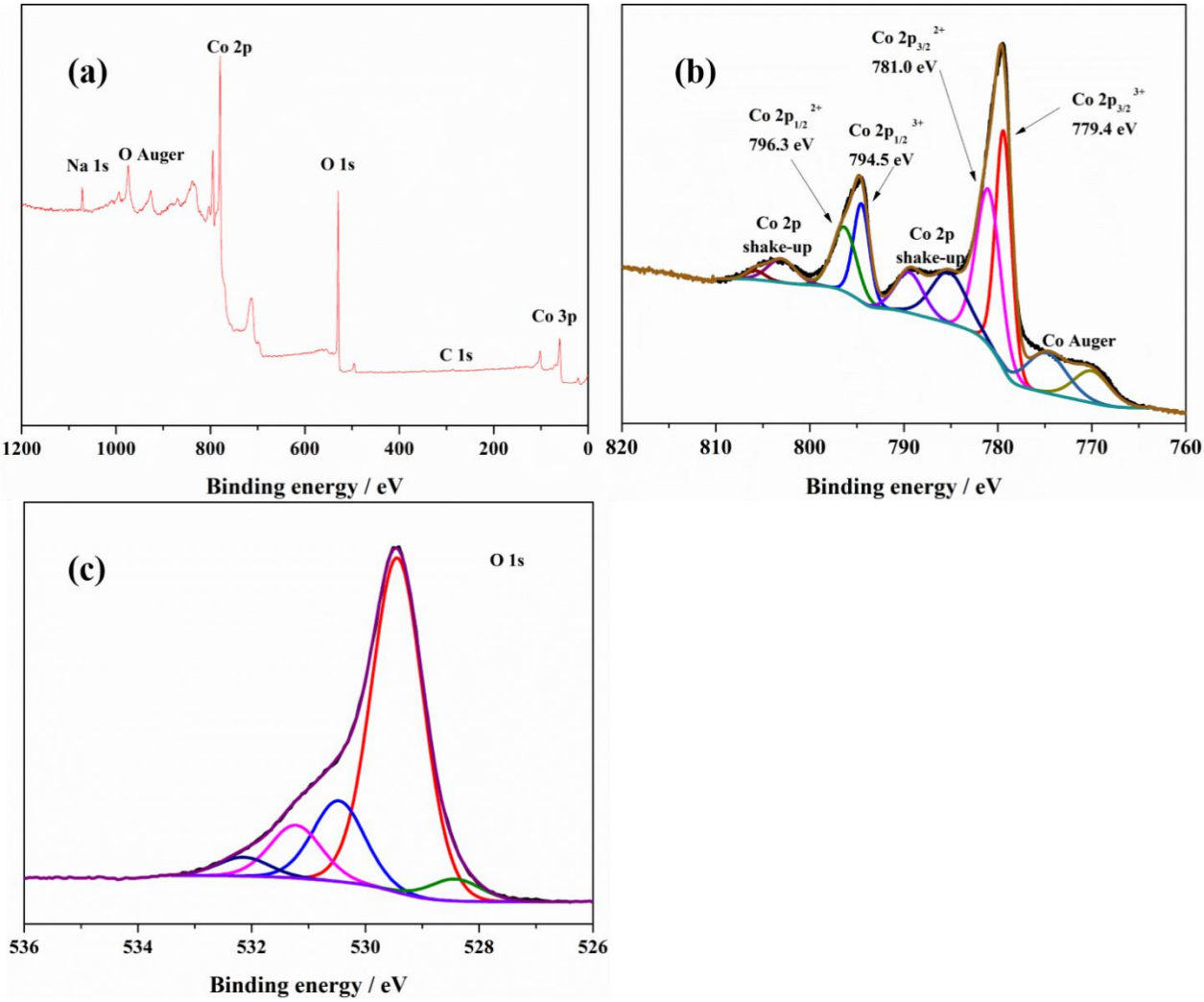


Figure S9. XPS analysis of om-Co_3O_4. a) XPS survey spectrum. b) Co 2p spectrum. c) O 1s spectrum.

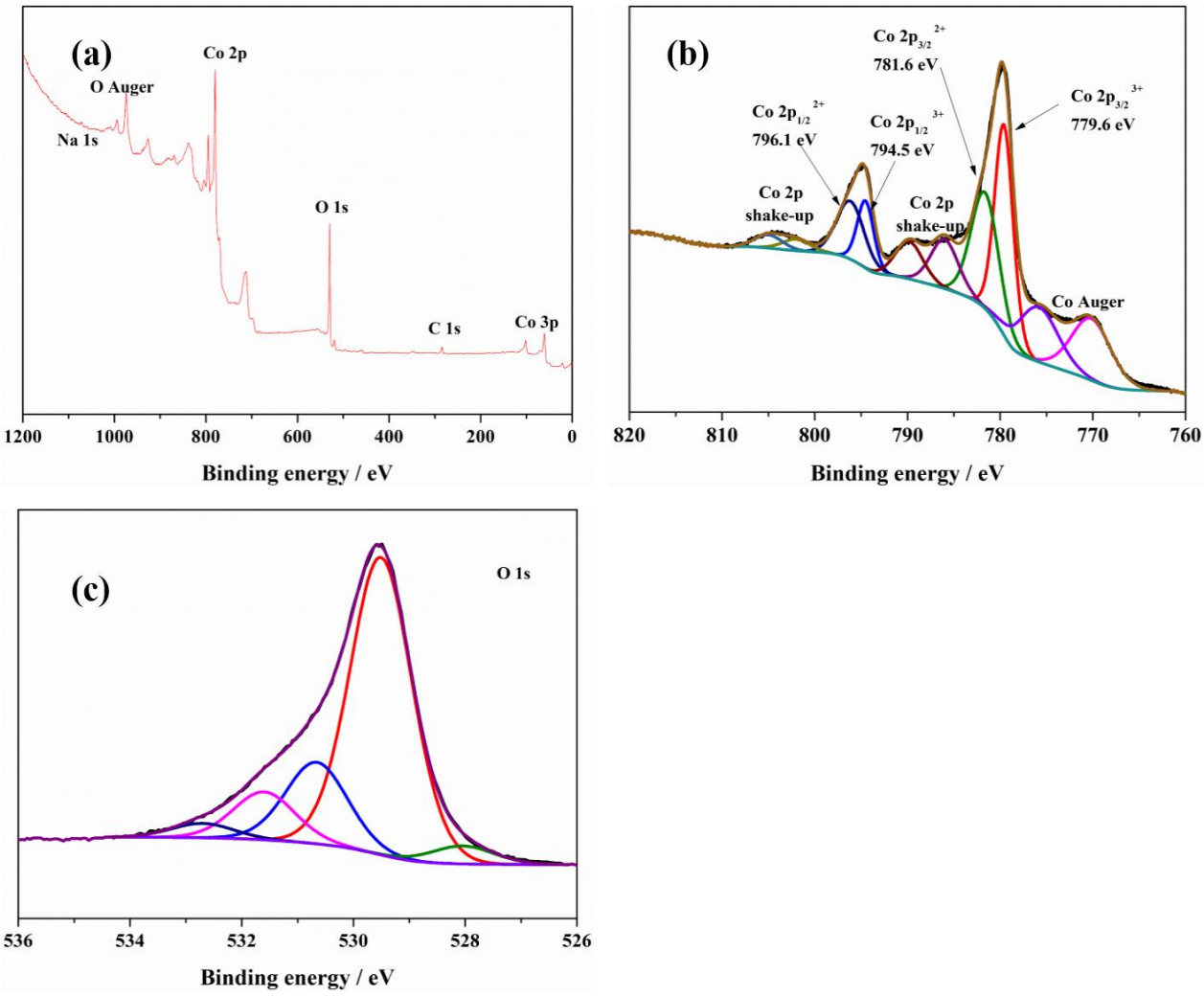


Figure S10. XPS analysis of dm-Co_3O_4. a) XPS survey spectrum. b) Co 2p spectrum. c) O 1s spectrum.

Note: These spectra have been measured with non-monochromatic Al-source (100 W).

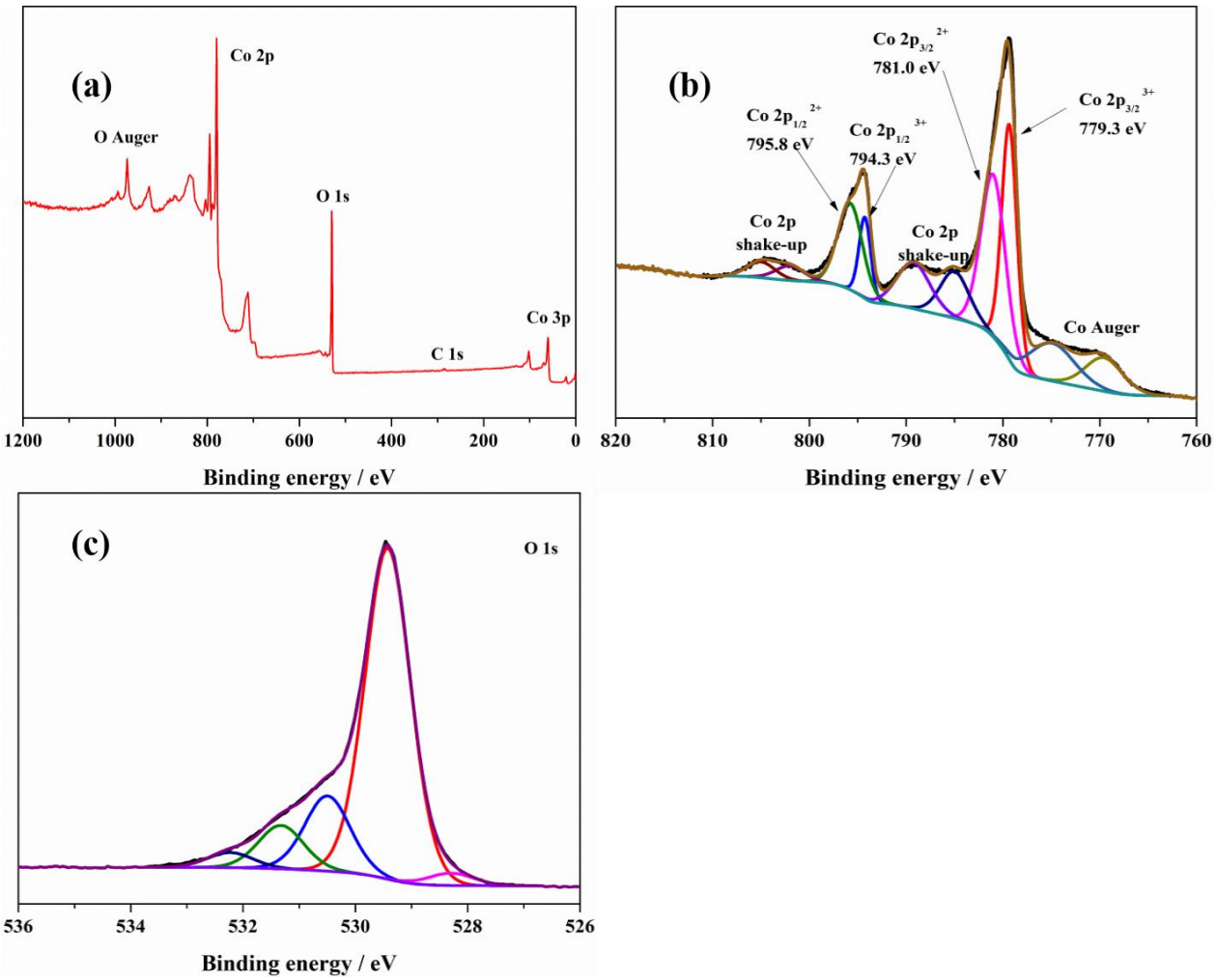


Figure S11. XPS analysis of bulk Co_3O_4. a) XPS survey spectrum. b) Co 2p spectrum. c) O 1s spectrum.

3. Electrochemical oxidation of HMF.

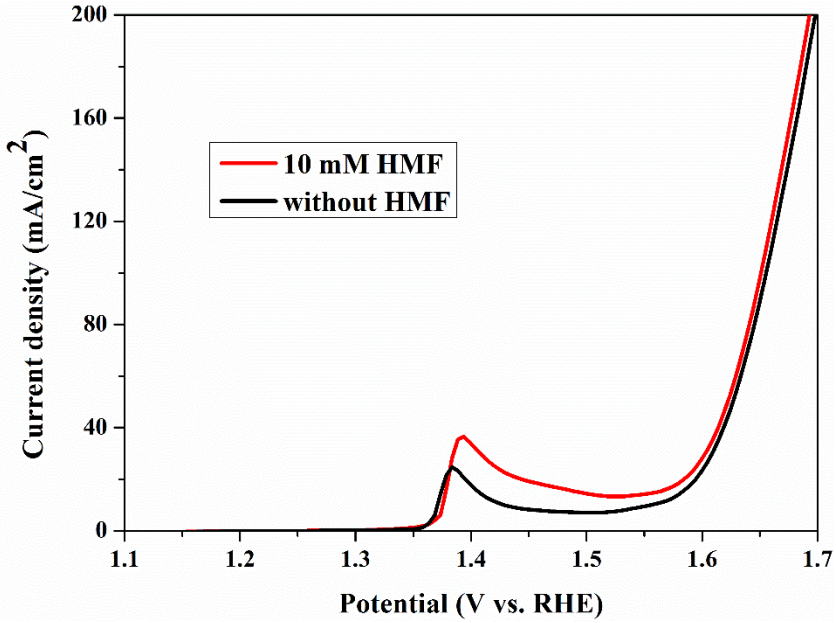


Figure S12. LSV curves for nickel foam in 1 M KOH with and without 10 mM HMF.

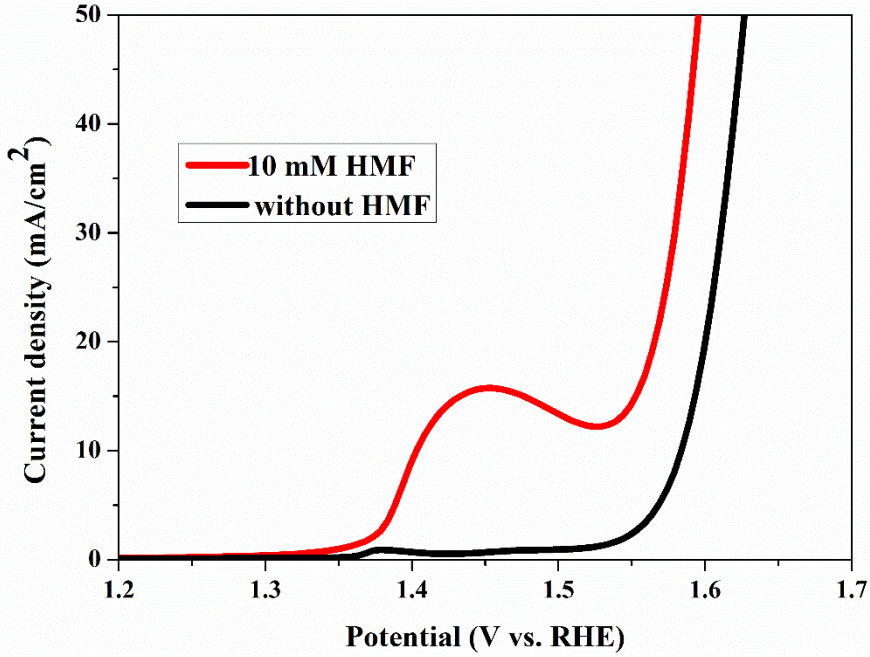


Figure S13. LSV curves of dm-Co_3O_4/NF in 1 M KOH with and without 10 mM HMF.

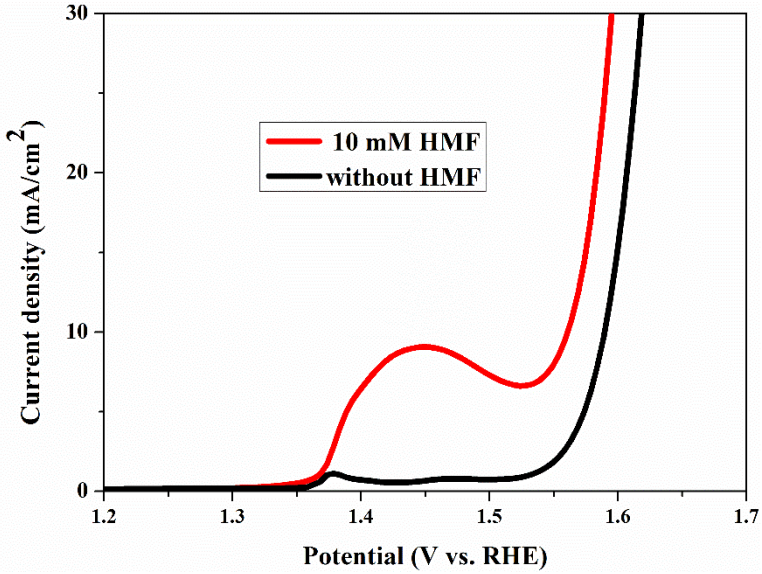


Figure S14. LSV curves of bulk Co_3O_4/NF in 1 M KOH with and without 10 mM HMF.

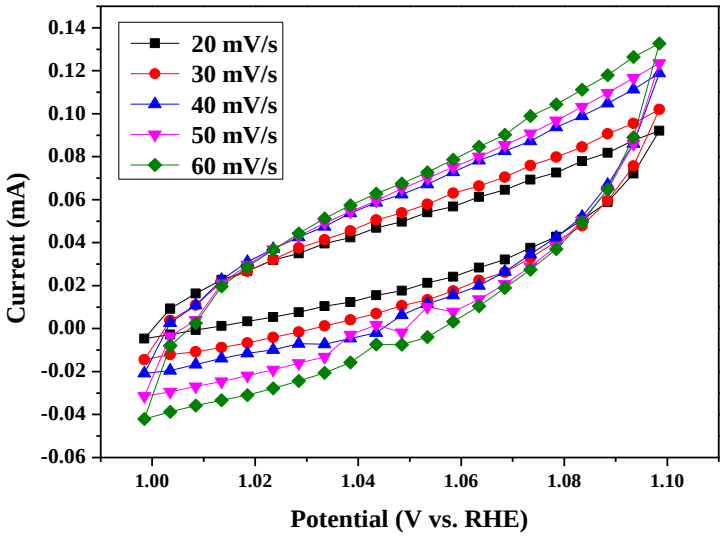


Figure S15. CV curves of bulk Co_3O_4/NF with HMF at different scan rates.

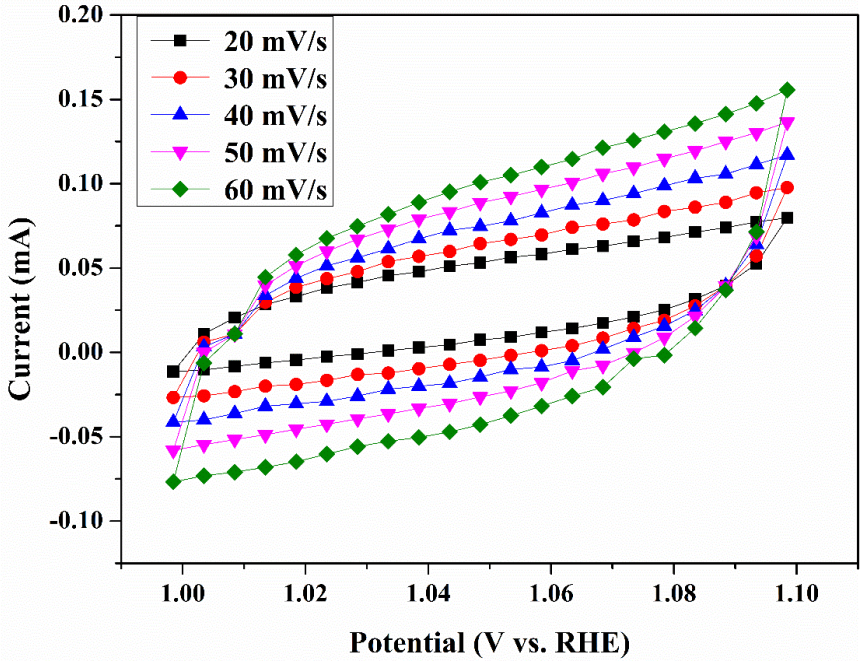


Figure S16. CV curves of dm-Co_3O_4/NF with HMF at different scan rates.

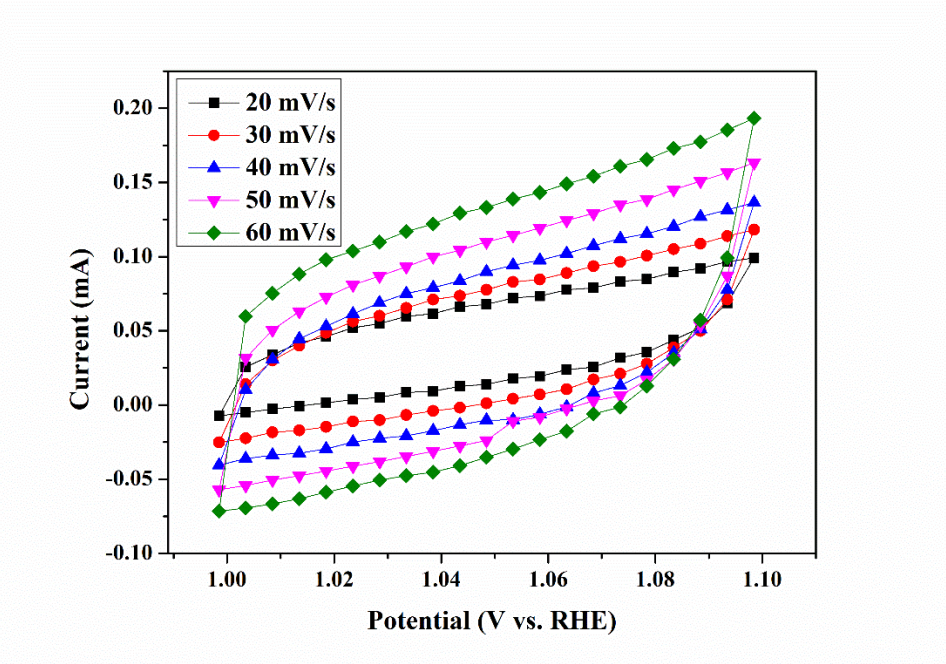


Figure S17. CV curves of om-Co_3O_4/NF with 10 mM HMF at different scan rate.

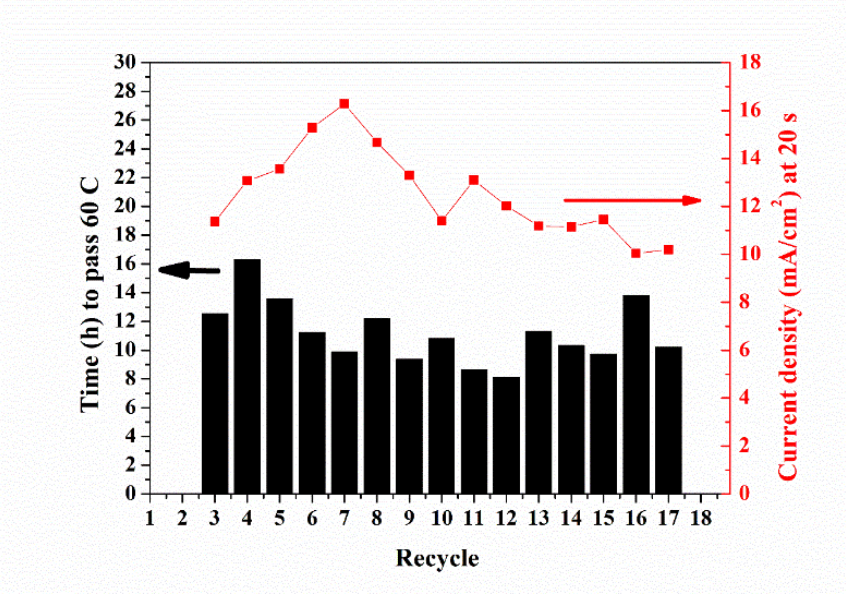


Figure S18: The times required to pass 60 C and the initial current densities for different cycles.

4. Characterizations of om-Co_3O_4 catalyst after electrochemical oxidation of HMF.

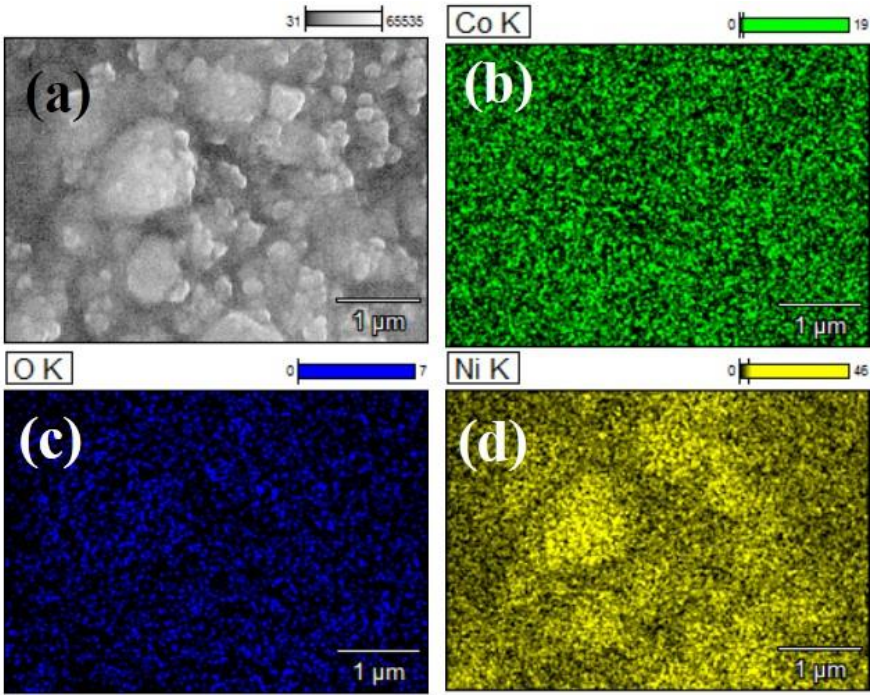
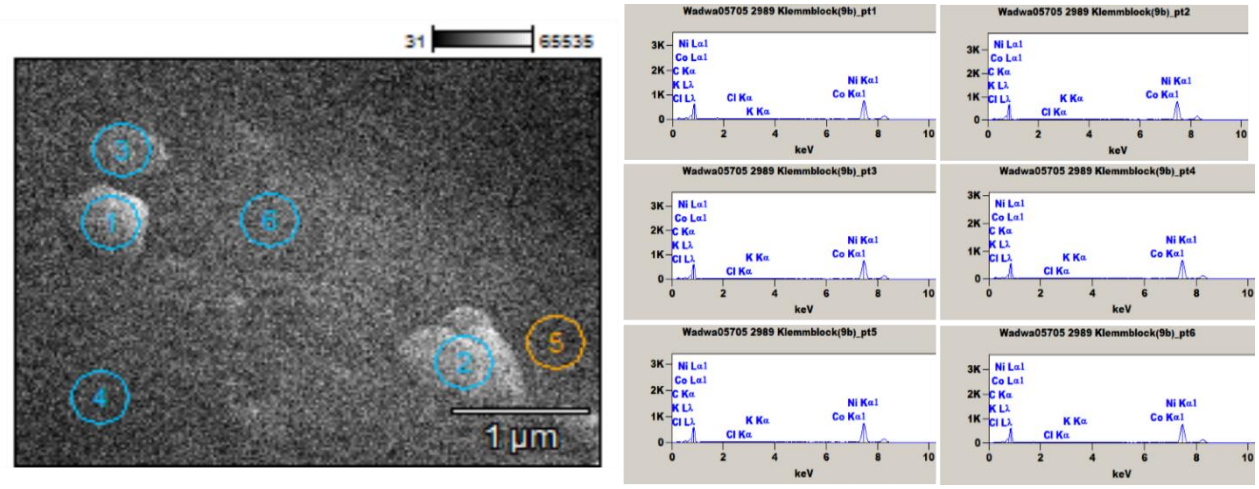


Figure S19. Structural characterizations of om-Co_3O_4/NF electrode after 17 times of electrolysis. a) low-magnification SEM images. b-d) the corresponding elemental mappings of Co, O and Ni.



Atom- %

	C-K	Cl-K	K-K	Co-K	Ni-K
Wadwa05705 2989 Klemmblock(9b)_pt1	72.8	0.3	0.2	0.2	26.5
Wadwa05705 2989 Klemmblock(9b)_pt2	71.9	0.1	0.3	0.2	27.5
Wadwa05705 2989 Klemmblock(9b)_pt3	70.9	0.0	0.2	0.2	28.7
Wadwa05705 2989 Klemmblock(9b)_pt4	71.7	0.0	0.2	0.2	27.8
Wadwa05705 2989 Klemmblock(9b)_pt5	69.1	0.2	0.1	0.2	30.4
Wadwa05705 2989 Klemmblock(9b)_pt6	72.6	0.1	0.2	0.1	26.9

Atom-% Fehler (+/- 2 Sigma)

	C-K	Cl-K	K-K	Co-K	Ni-K
Wadwa05705 2989 Klemmblock(9b)_pt1	±6.8	±0.2	±0.1	±0.1	±0.8
Wadwa05705 2989 Klemmblock(9b)_pt2	±7.3	±0.2	±0.1	±0.1	±0.8
Wadwa05705 2989 Klemmblock(9b)_pt3	±7.4	±0.2	±0.1	±0.1	±0.8
Wadwa05705 2989 Klemmblock(9b)_pt4	±7.9	±0.2	±0.1	±0.1	±0.9
Wadwa05705 2989 Klemmblock(9b)_pt5	±8.0	±0.2	±0.1	±0.2	±0.9
Wadwa05705 2989 Klemmblock(9b)_pt6	±9.5	±0.2	±0.1	±0.1	±0.8

Figure S20. Point and shoot analyses at different places of om-Co_3O_4/NF electrode after 17 times of electrolysis.

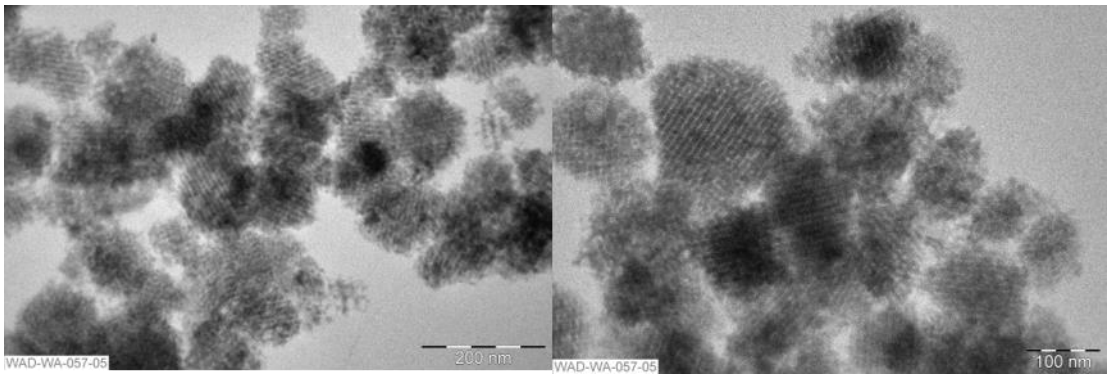


Figure S21. TEM images of om-Co_3O_4 on Lacey film after washing from NF at different magnification (after 17 chronoamperometric runs).