

Supporting Information

Selective Acid Leaching: A Simple Way to Engineer Cobalt Oxide Nanostructure for Electrochemical Oxygen Evolution Reaction

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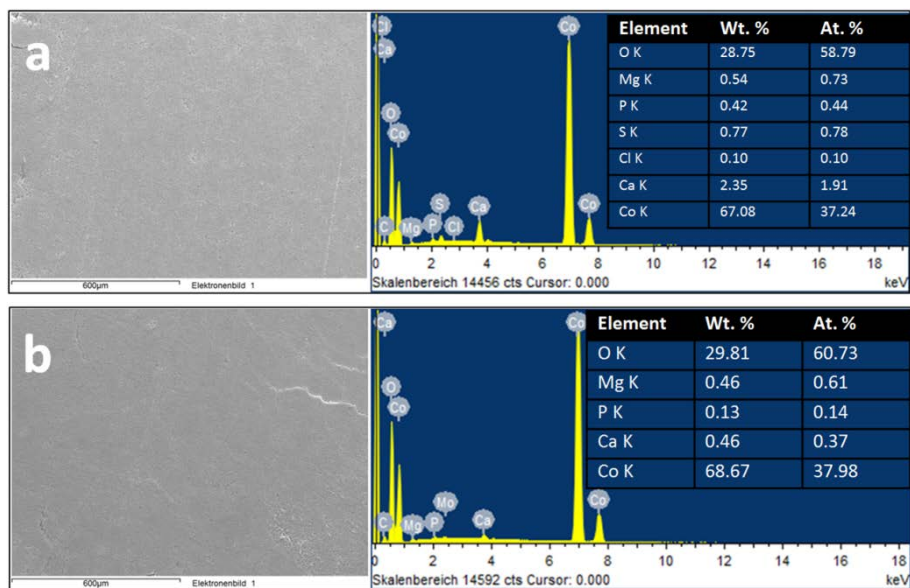


Figure S1. SEM images with corresponding EDX analysis of CW-templated Co_3O_4 before (a) and after (b) leaching by 0.1 M HCl solution for 2 h.

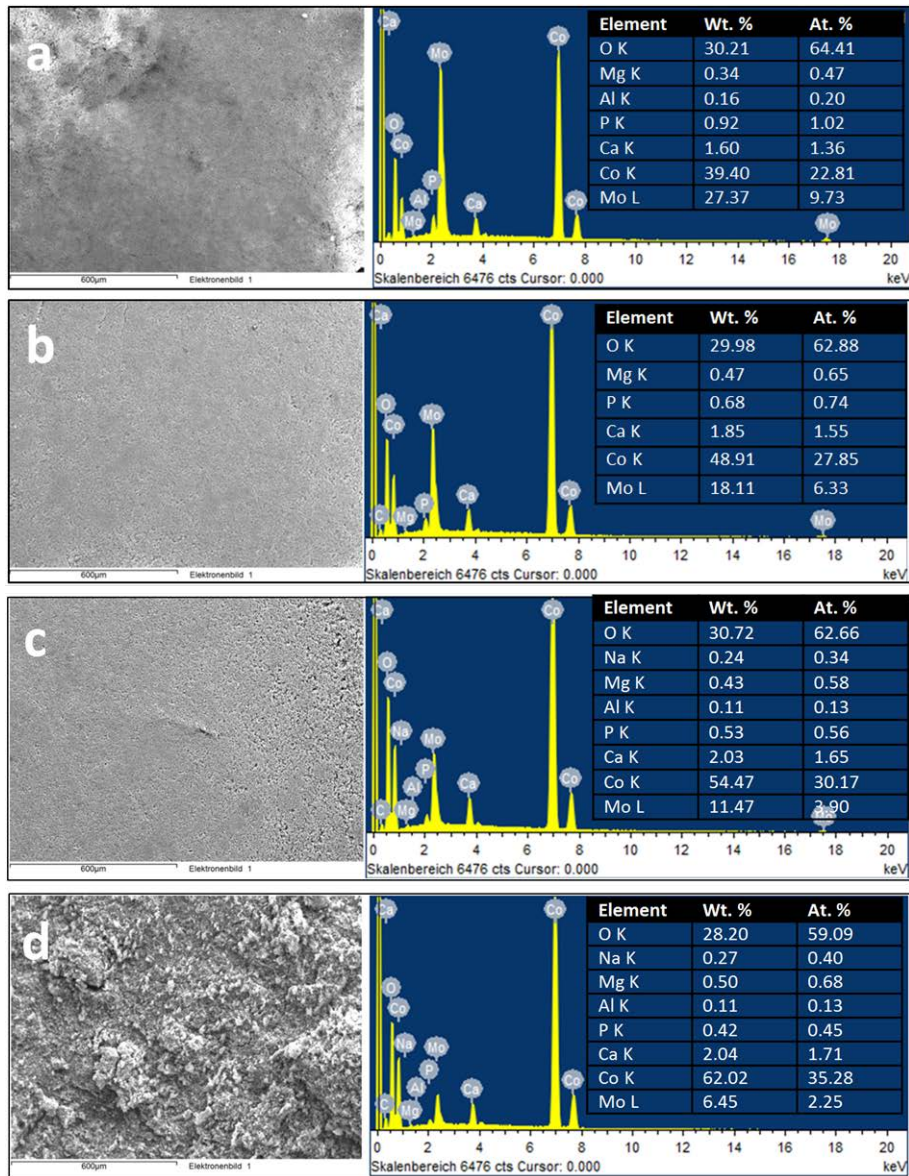


Figure S2. SEM images with corresponding EDX analysis of CW-templated Co-Mo oxides as obtained after calcination: (a) Co₂Mo oxide, (b) Co₄Mo oxide, (c) Co₈Mo oxide, (d) Co₁₆Mo oxide.

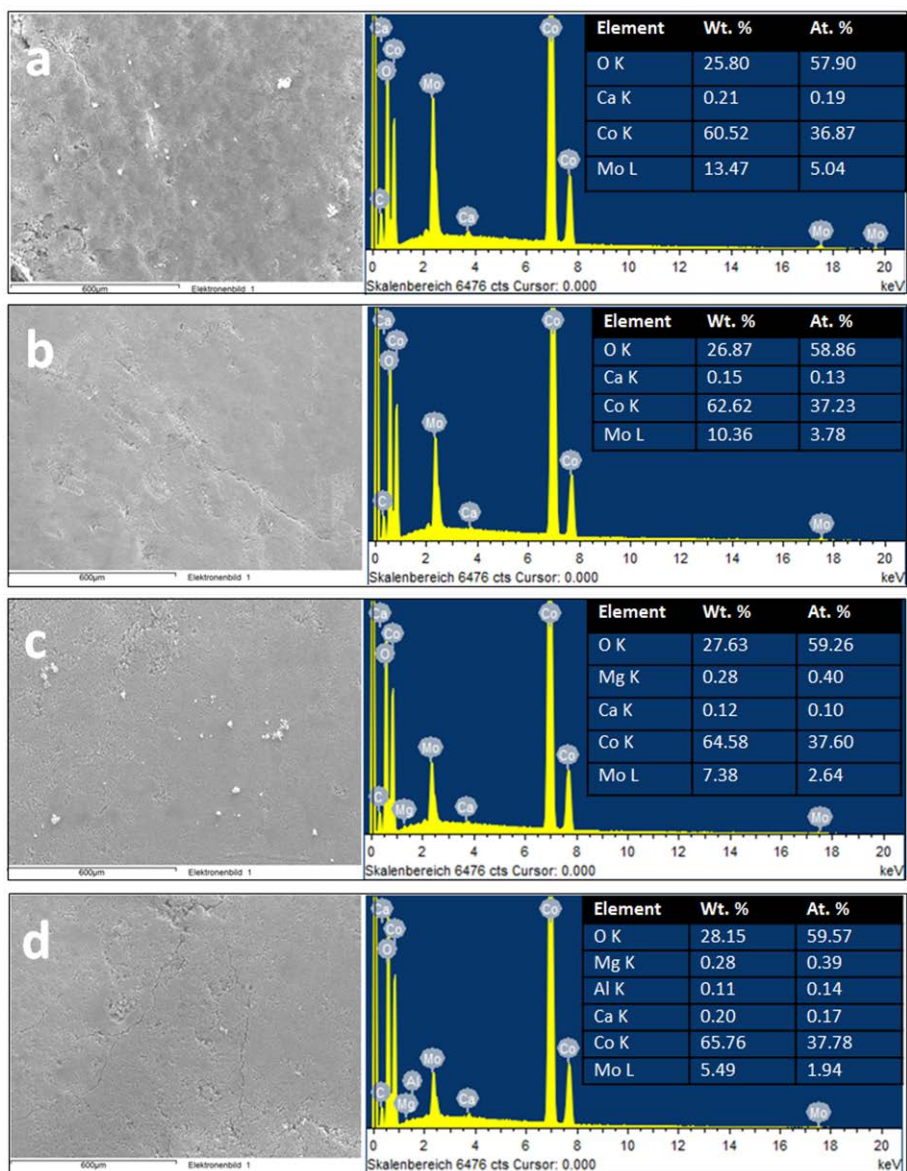


Figure S3. SEM images with corresponding EDX analysis of CW-templated Co-Mo oxides after leaching by 0.1 M HCl solution for 2h: (a) Co₂Mo oxide, (b) Co₄Mo oxide, (c) Co₈Mo oxide, (d) Co₁₆Mo oxide.

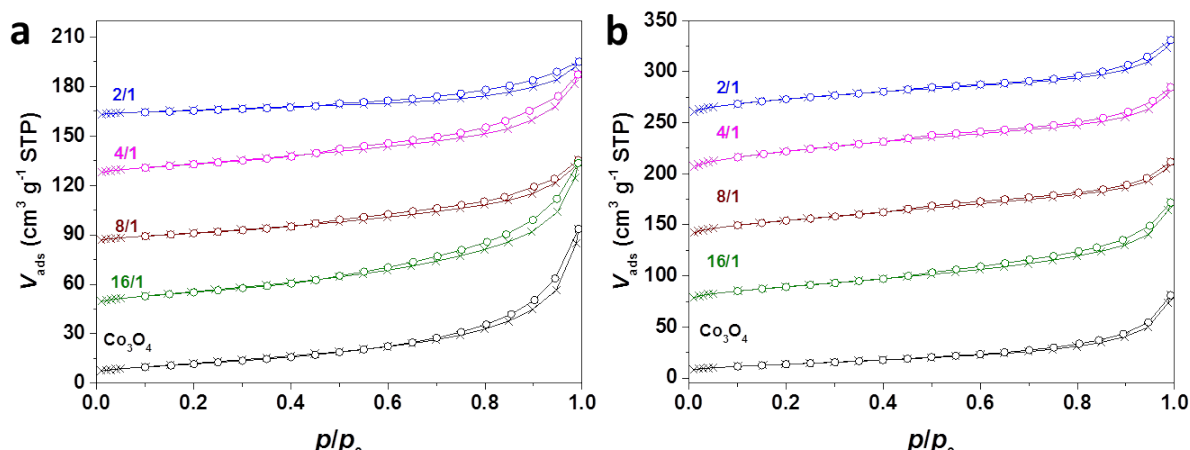


Figure S4. Nitrogen sorption isotherms of CW-templated oxides before (a) and after (b) leaching by 0.1 M HCl solution for two hours. An offset of $40 \text{ cm}^3 \text{ g}^{-1}$ and $60 \text{ cm}^3 \text{ g}^{-1}$ was applied to the isotherms in (a) and (b), respectively.

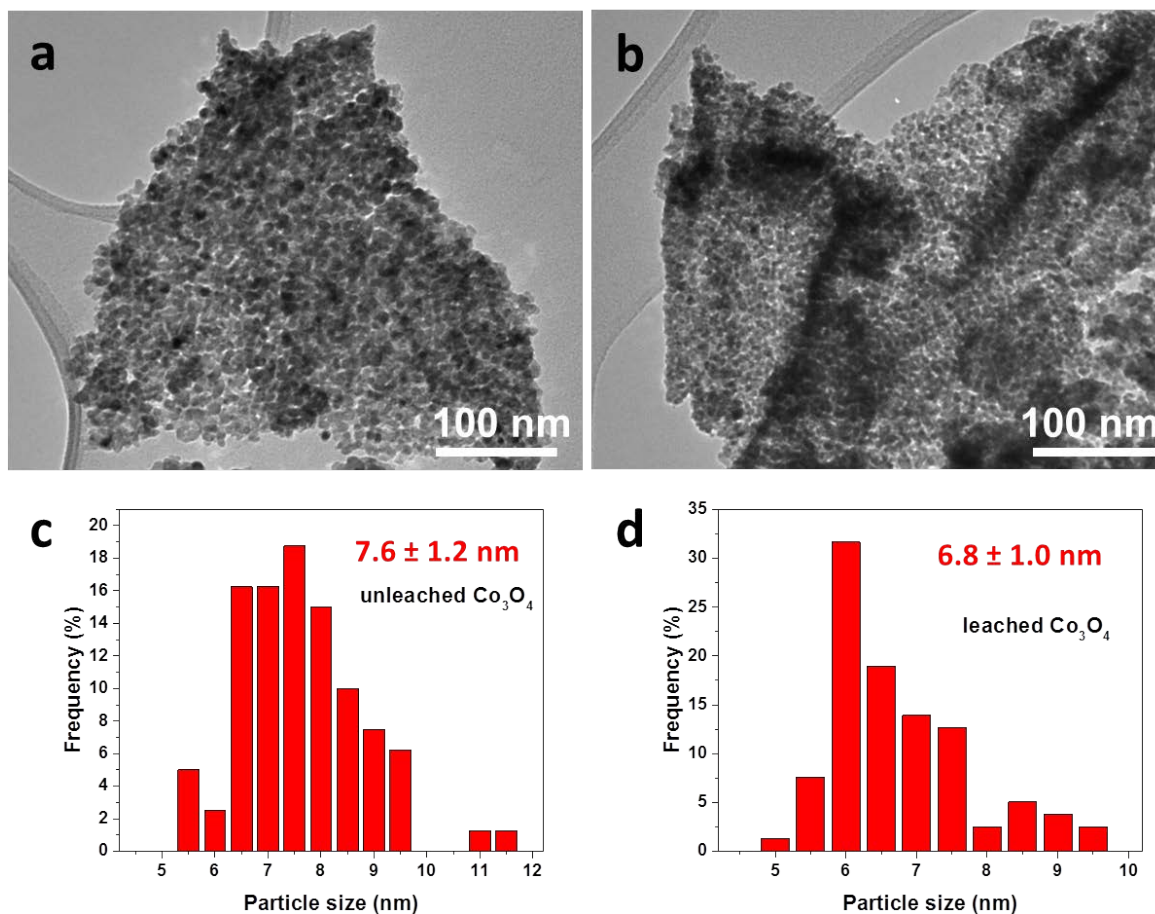


Figure S5. TEM images of CW-templated cobalt oxide before (a) and after (b) leaching with 0.1 M HCl solution for two hours. The corresponding particle size distribution are shown in (c) and (d) for pristine and leached cobalt oxides, respectively.

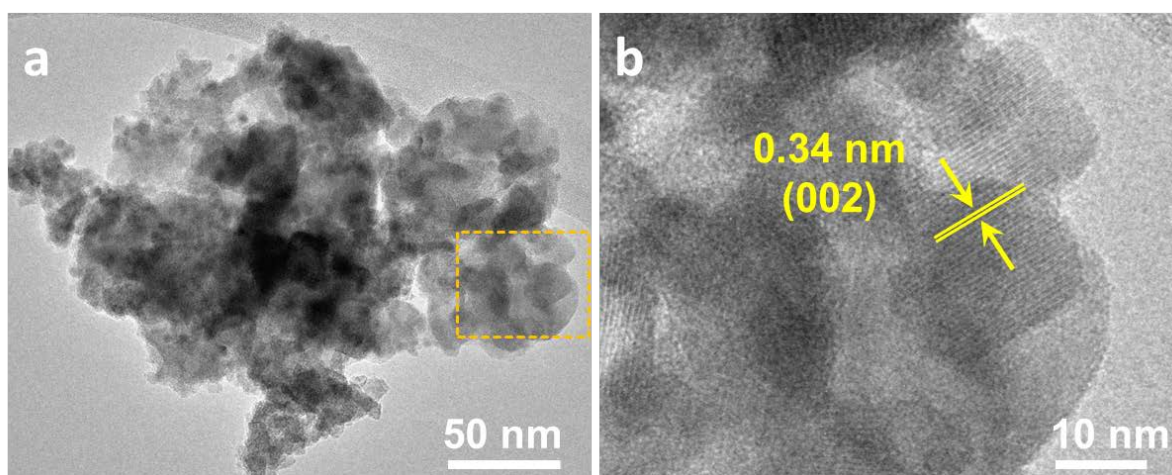


Figure S6. (a) High resolution TEM image of pristine Co_4Mo oxide. (b) Closeup of the marked rectangle in (a), showing the lattice fringe of cubic CoMoO_4 with crystal domain of around 20-30 nm.

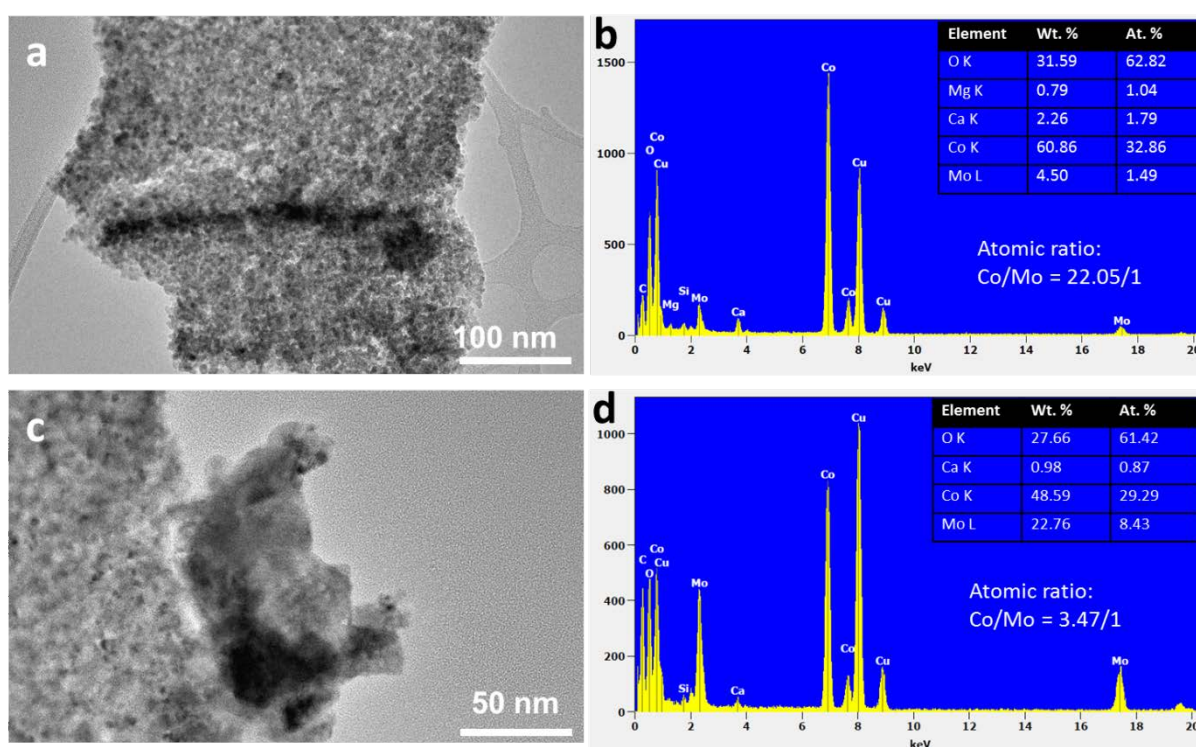


Figure S7. (a, c) High resolution TEM image of pristine Co_4Mo oxide in different areas. (b, d) local EDX analysis according to the areas in (a) and (c), respectively. Image (a) shows the samples comprising mostly small nanoparticles (~ 7 nm) with a high ratio of Co/Mo (22.05/1). In image (c), both smaller Co_3O_4 and larger CoMoO_4 particles were shown, where a much higher content of Mo was detected.

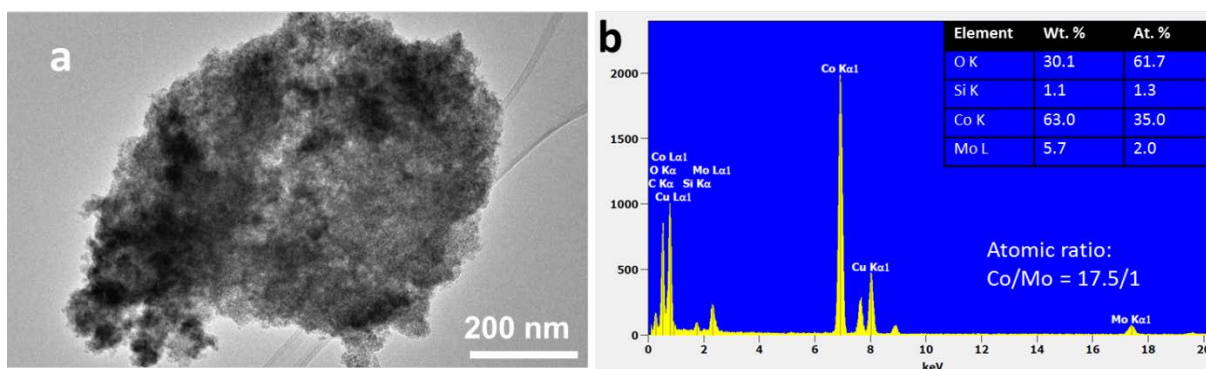


Figure S8. (a) High Resolution TEM image of acid-leached Co_4Mo oxide. (b) local EDX analysis according to the area in (a). The Co_4Mo oxide after leaching was composed of mostly small Co_3O_4 nanoparticles with a very low Mo content.

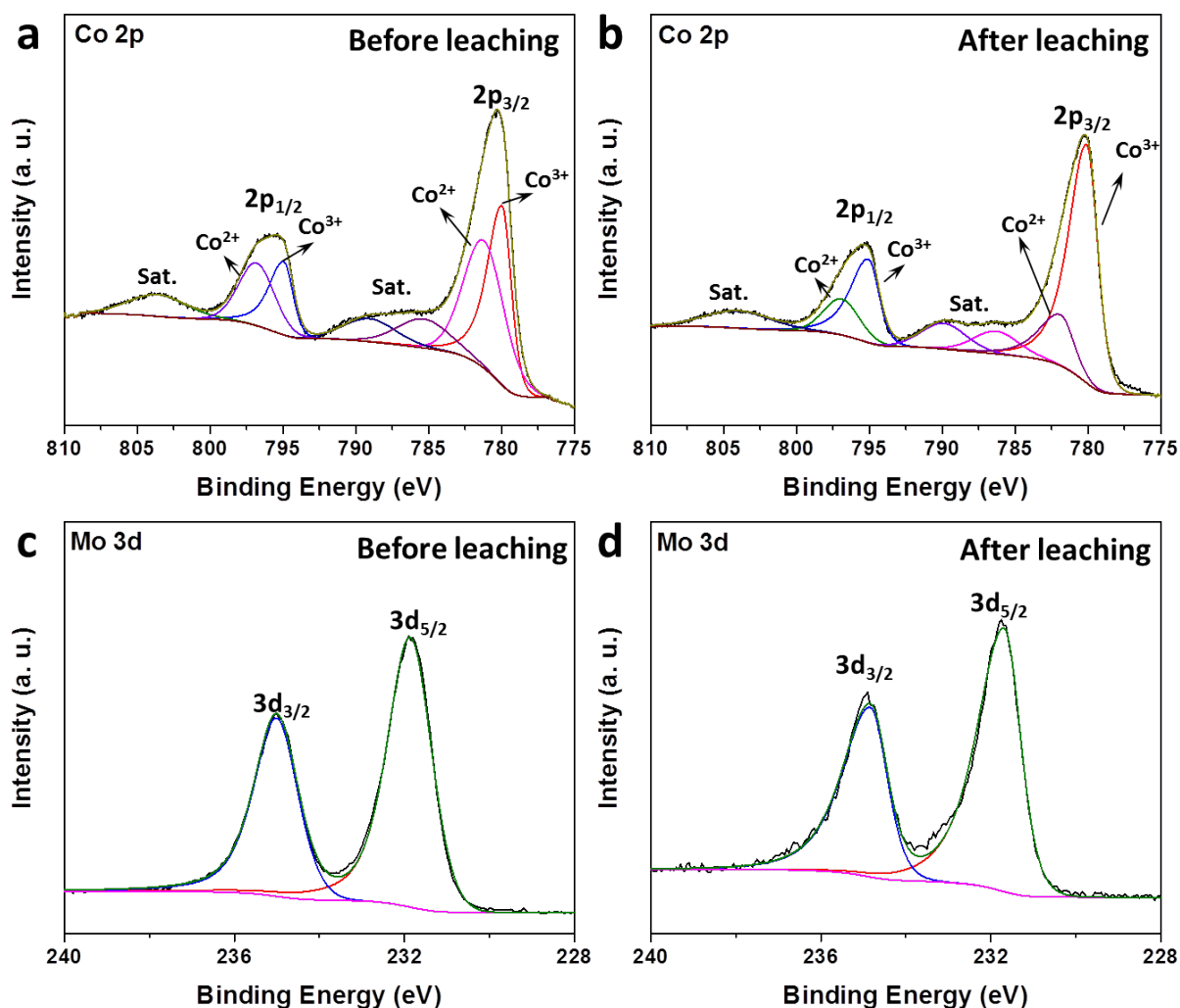


Figure S9. XPS spectra of Co 2p (a, b) and Mo 3d (c, d) for Co_4Mo oxide before and after leaching with 0.1 M HCl solution for two hours.

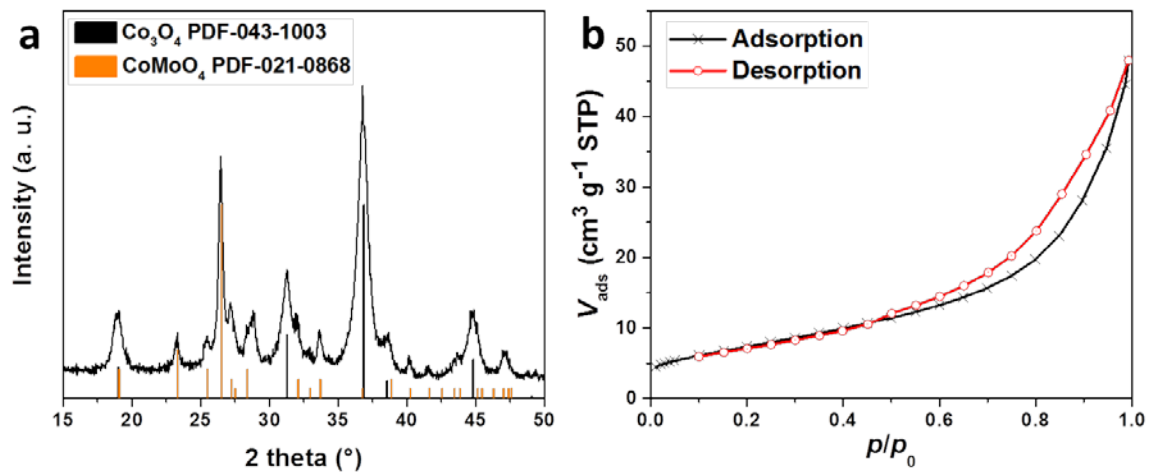


Figure S10. Wide-angle XRD (a) and nitrogen sorption isotherms (b) of CW-templated Co₄Mo oxide in a large batch, which was employed to be treated with various leaching conditions for optimizing leaching profile.

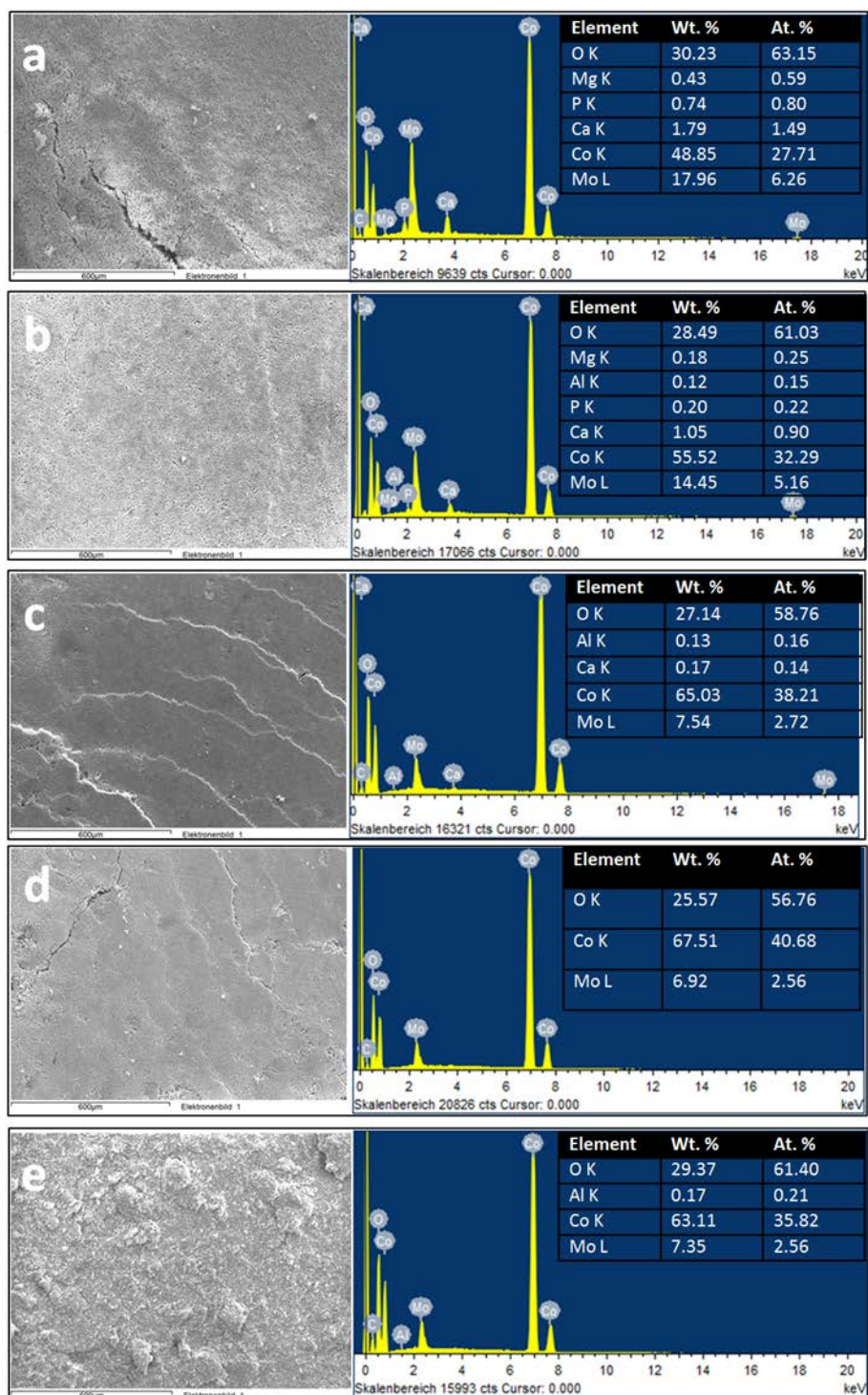


Figure S11. SEM images with corresponding EDX analysis of (a) CW-templated Co_4Mo oxides and the oxides after leaching by HCl solution with different concentrations for 2h: (b) 0.01 M, (c) 0.05 M, (d) 0.1 M, (e) 0.2 M.

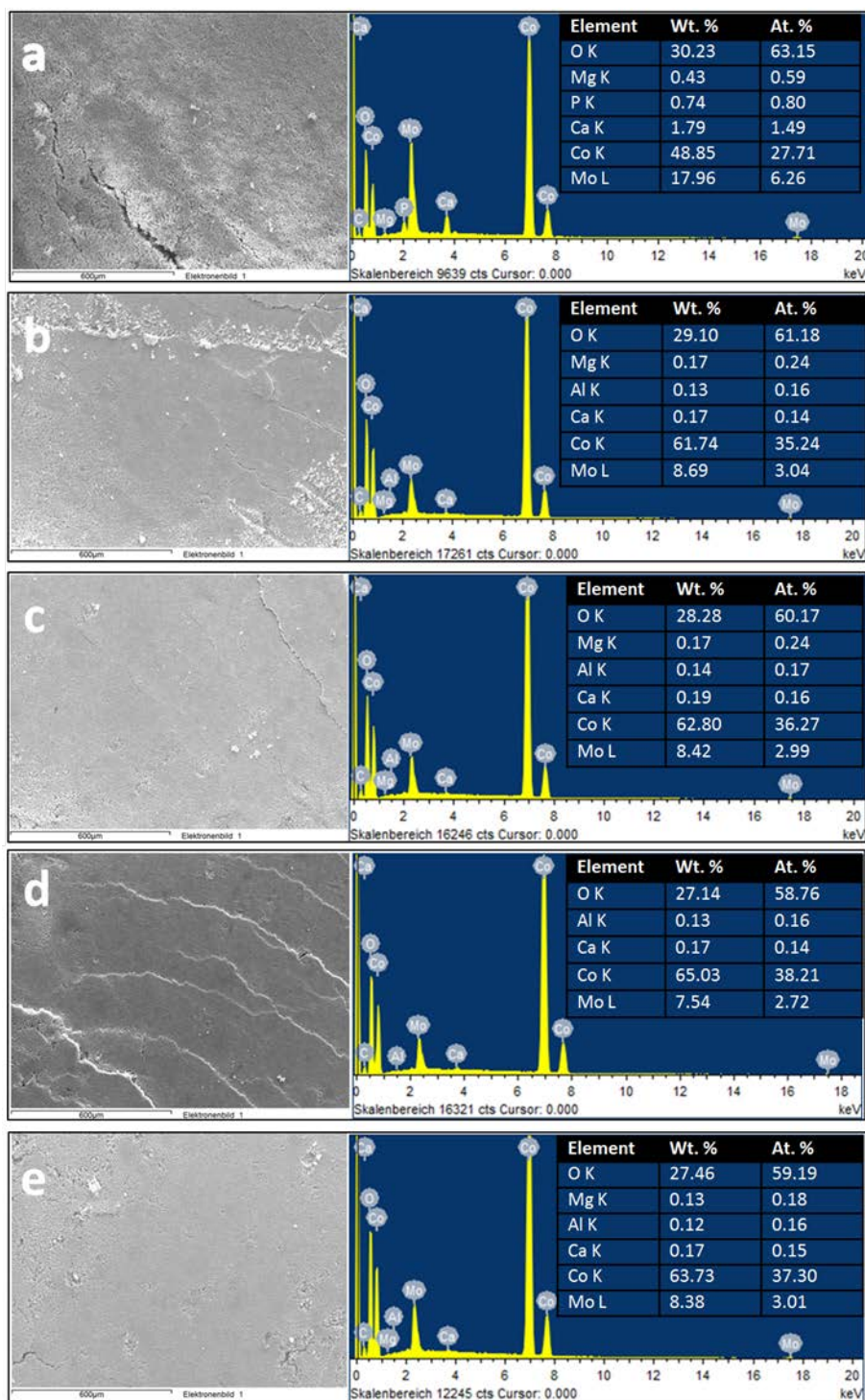


Figure S12. SEM images with corresponding EDX analysis of (a) CW-templated Co_4Mo oxides and the oxides after leaching by 0.05 M HCl solution for different time: (b) 5 min, (c) 30 min, (d) 2 h, (e) 6 h.

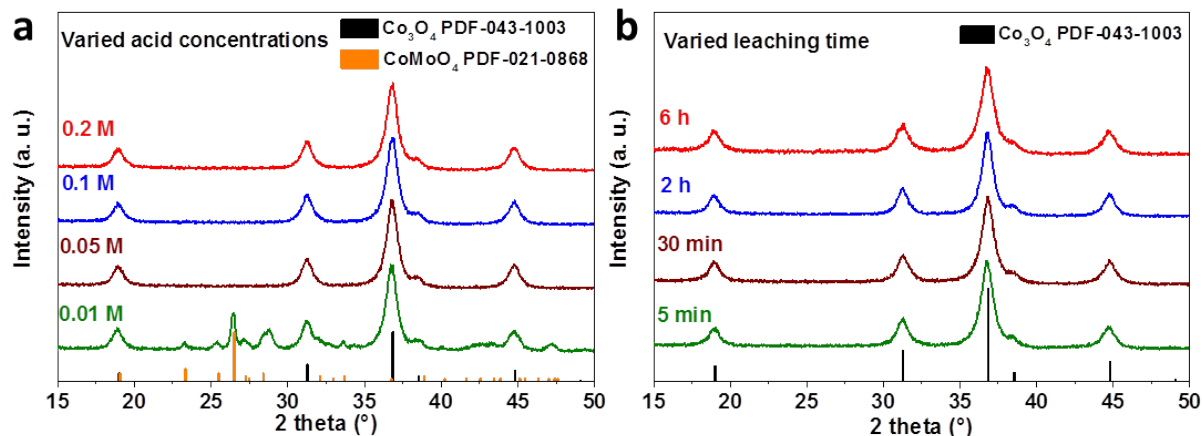


Figure S13. Wide-angle XRD patterns of CW-templated Co_4Mo oxide after leaching by various leaching profiles. (a) 2 h leaching using 0.01, 0.05, 0.1 and 0.2 M HCl solution. (b) Leaching with 0.05 M HCl solution for 5 min, 30 min, 2 h and 6 h.

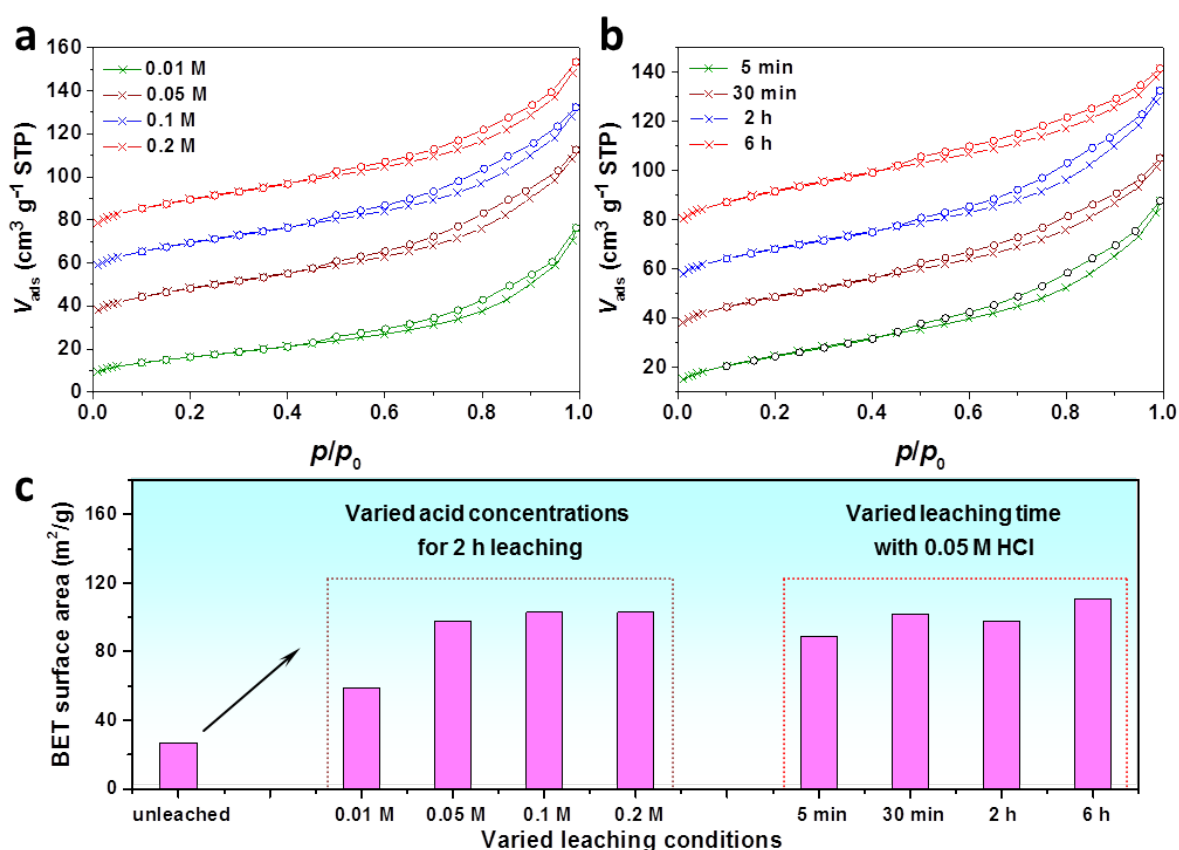


Figure S14. Nitrogen sorption isotherms of coffee waste templating oxides after leaching by various leaching condition. (a) 2 h leaching using 0.01, 0.05, 0.1 and 0.2 M HCl solution. (b) Leaching with 0.05 M HCl solution for 5 min, 30 min, 2 h and 6 h. An offset of $20 \text{ cm}^3 \text{ g}^{-1}$ was applied to the isotherms in (a) and (b). (c) Summarized BET surface areas of Co_4Mo oxide before and after leaching by various leaching profiles.

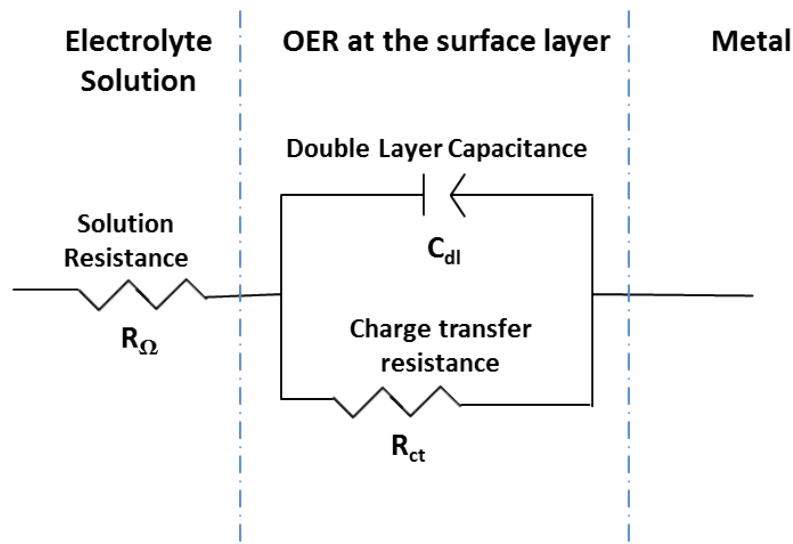


Figure S15. Equivalent circuit according to Randel model for cobalt based oxide electrocatalysts, where R_{Ω} and R_{ct} represent the solution and charge transfer resistance, respectively. C_{dl} models the double-layer capacitance.

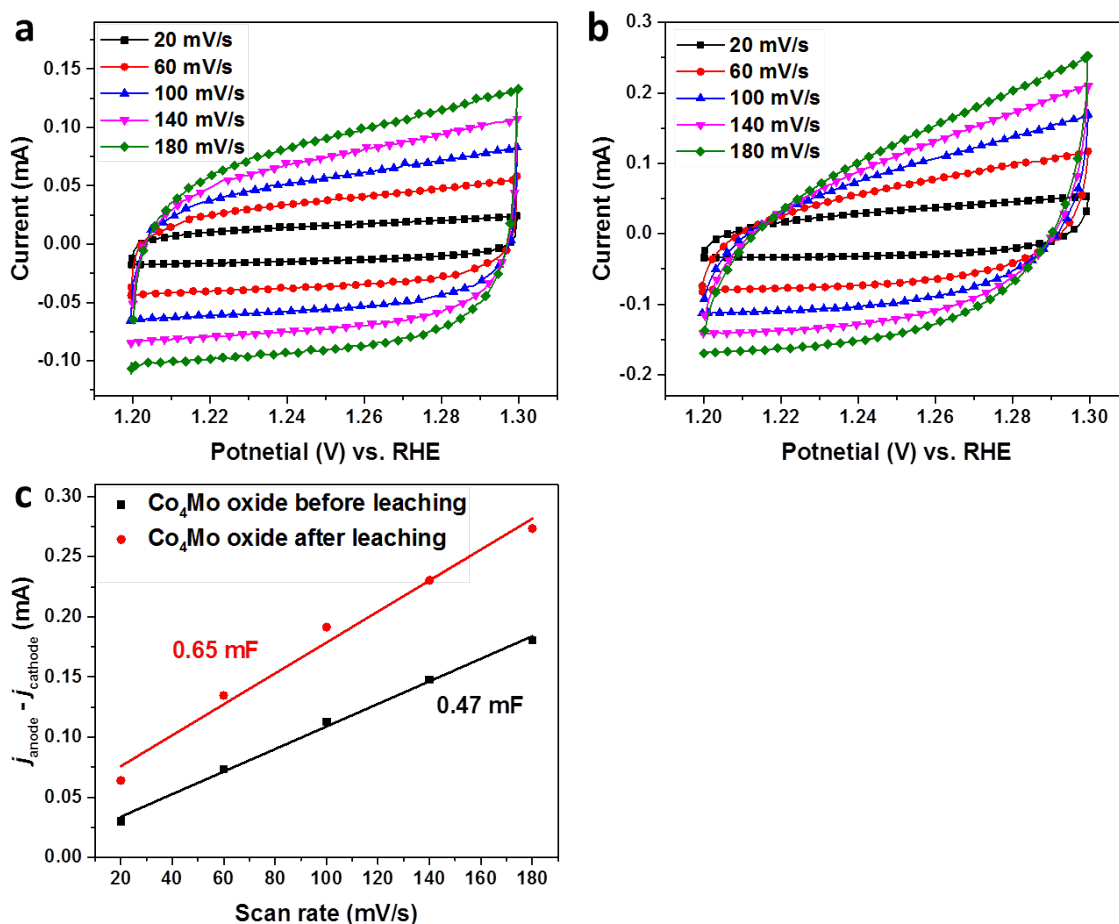


Figure S16. CV curves of Co_4Mo oxide before (a) and after (b) acid leaching at different scan rates. (c) corresponding plots of capacitive current at 1.25 V vs. RHE against scan rates.

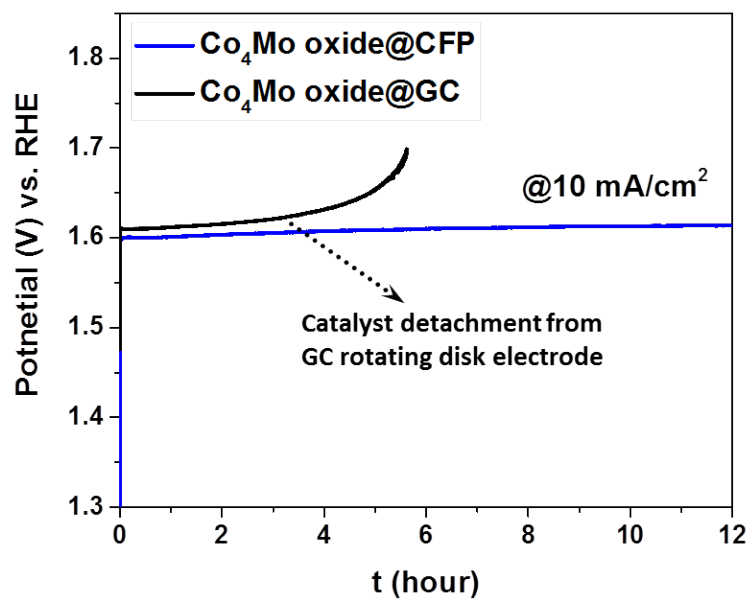


Figure S17. Chronopotentiometric curves of the acid-leached Co₄Mo oxide on GC and CFP electrodes, with keeping a current density at 10 mA/cm².

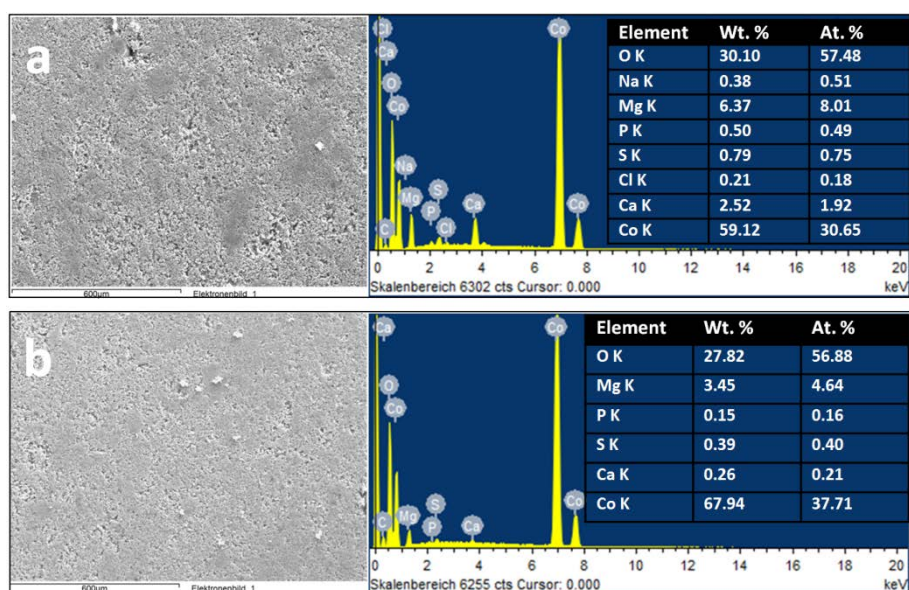


Figure S18. SEM images with corresponding EDX analysis of (a) CW-templated Co₄Mg oxides and the oxides after leaching by 0.1 M HCl solution for 2 h.

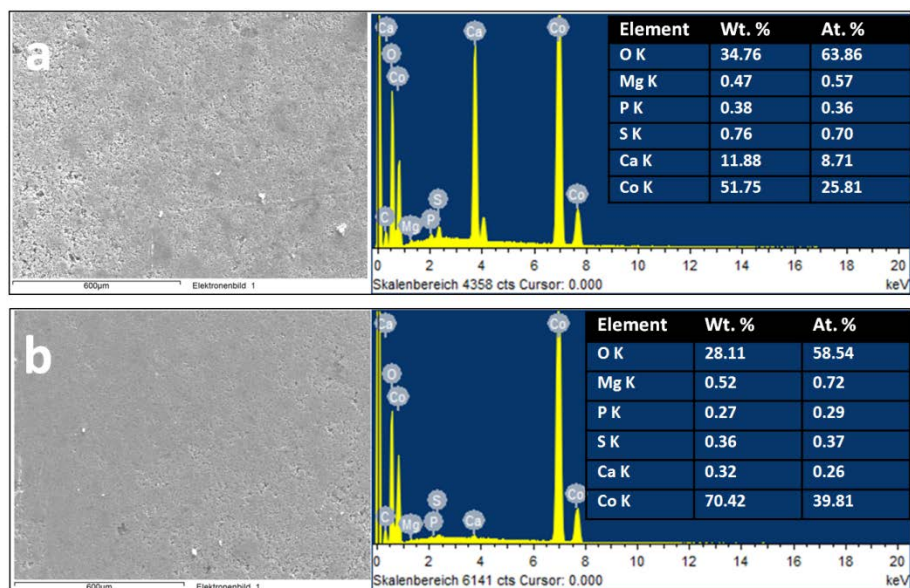


Figure S19. SEM images with corresponding EDX analysis of (a) CW-templated Co_4Ca oxides and the oxides after leaching by 0.1 M HCl solution for 2 h.

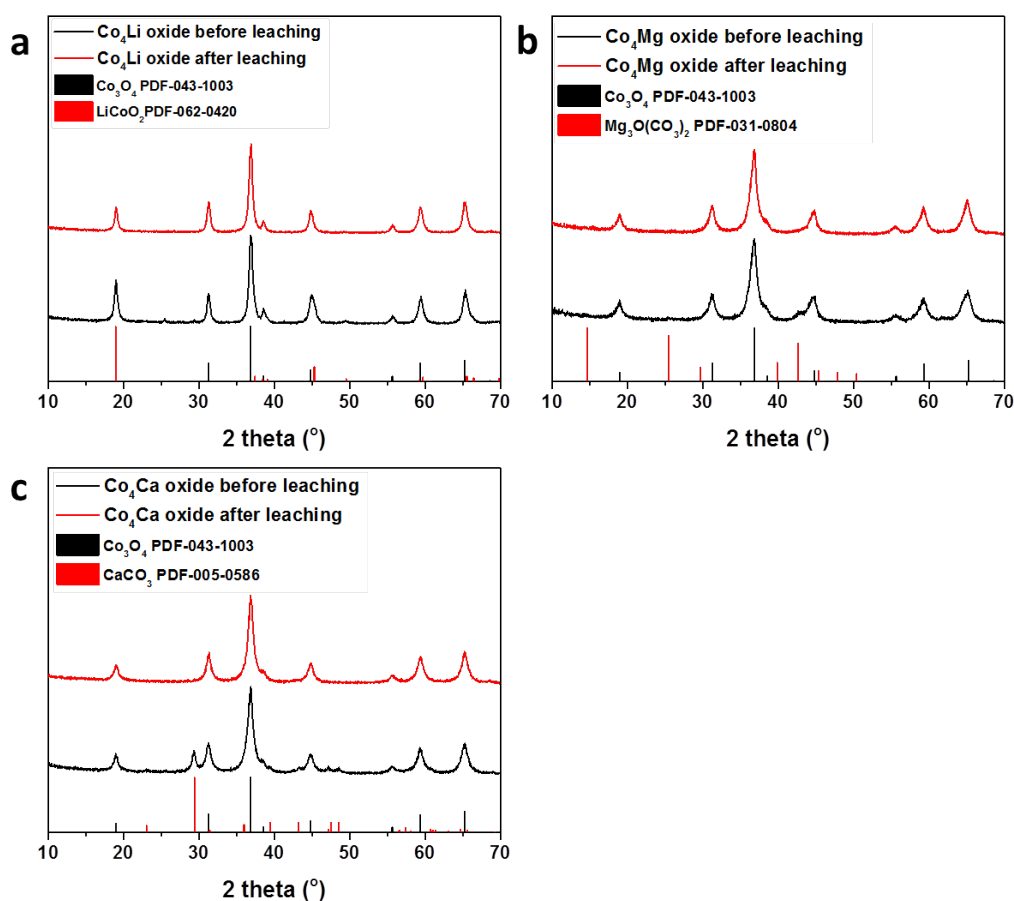


Figure S20. Wide-angle XRD patterns of (a) Co_4Li oxide, (b) Co_4Mg oxide, (c) Co_4Ca oxide before and after leaching process with 0.1 M HCl solution for 2 h.

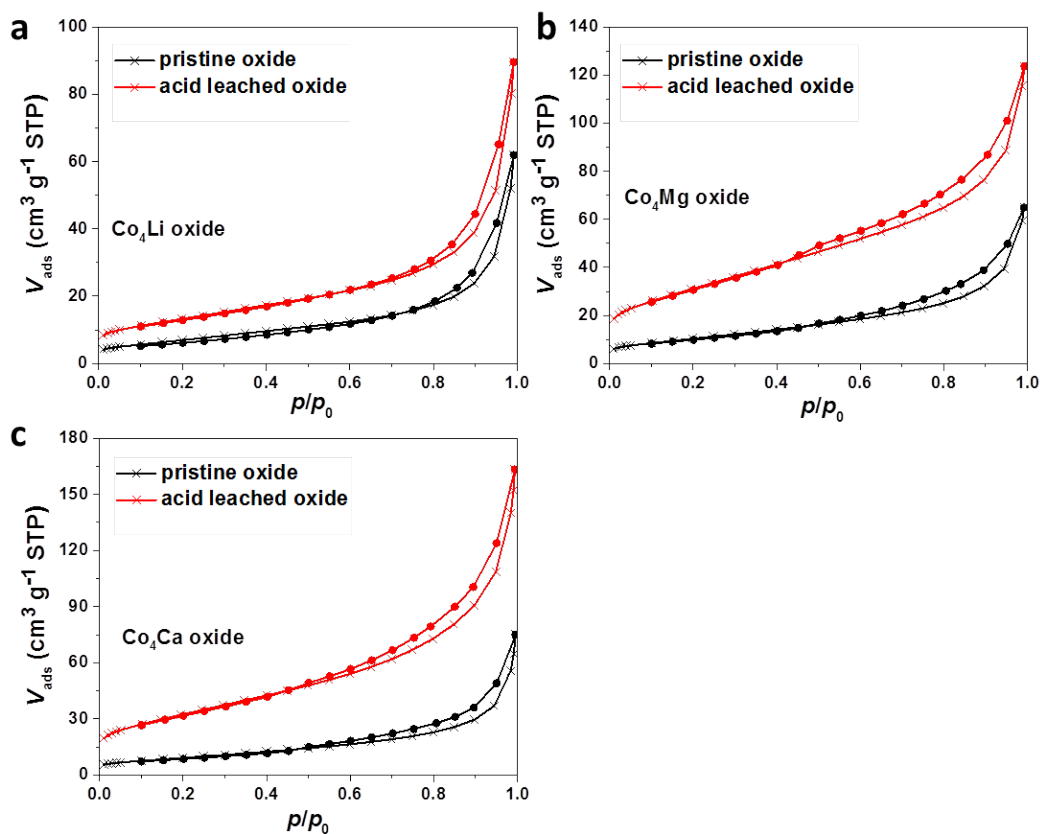


Figure S21. Nitrogen sorption isotherms of coffee waste templating mixed oxides before and after leaching by 0.1 M HCl solution for 2 h. (a) Co_4Li oxide. (b) Co_4Mg oxide. (c) Co_4Ca oxide.

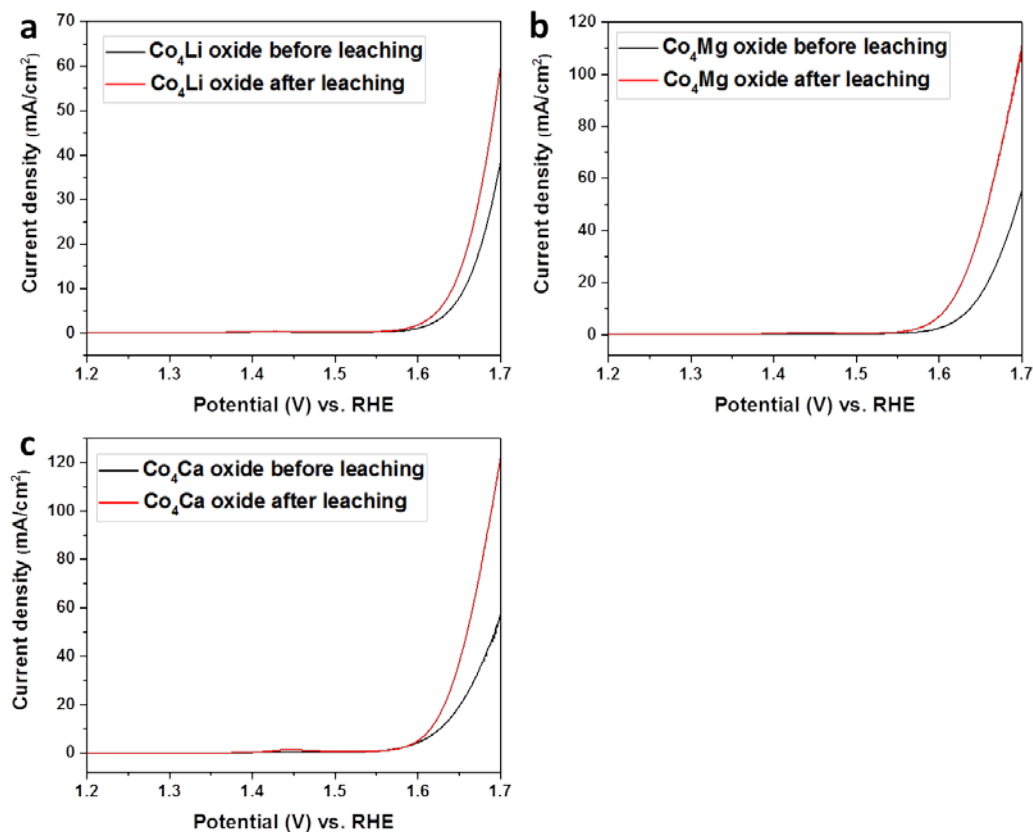


Figure S22. LSV curves of CW-templated mixed oxides before and after leaching by 0.1 M HCl solution for 2 h. (a) Co_4Li oxide. (b) Co_4Mg oxide. (c) Co_4Ca oxide.

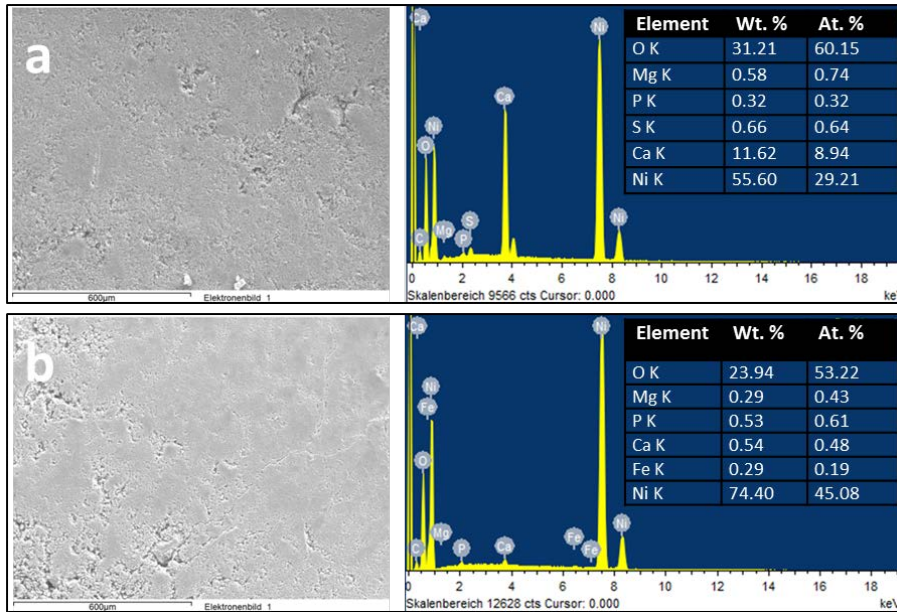


Figure S23. SEM images with corresponding EDX analysis of (a) CW-templated Ni₄Ca oxides and the oxides after leaching by 0.1 M HCl solution for 2 h.

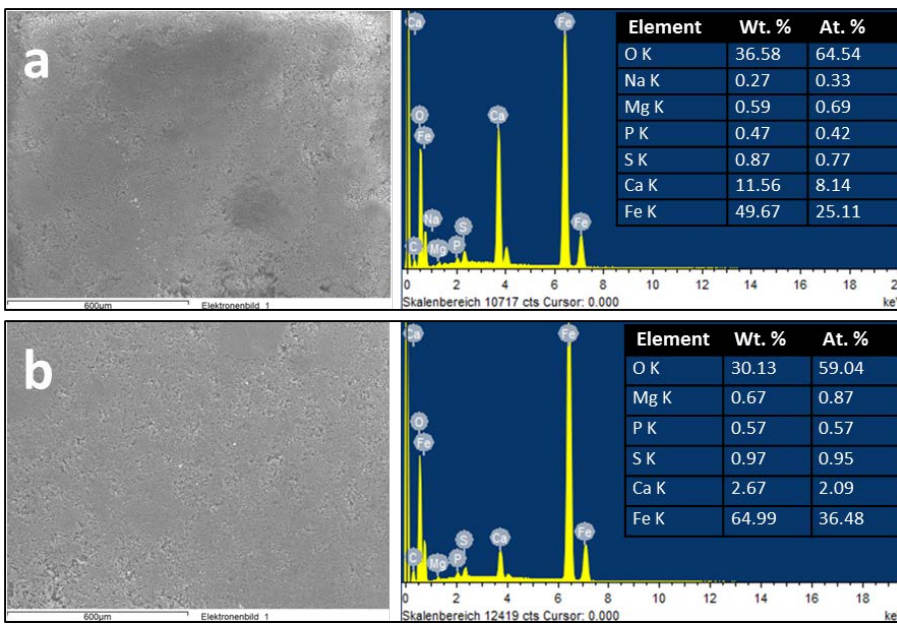


Figure S24. SEM images with corresponding EDX analysis of (a) CW-templated Fe₄Ca oxides and the oxides after leaching by 0.1 M HCl solution for 2 h.

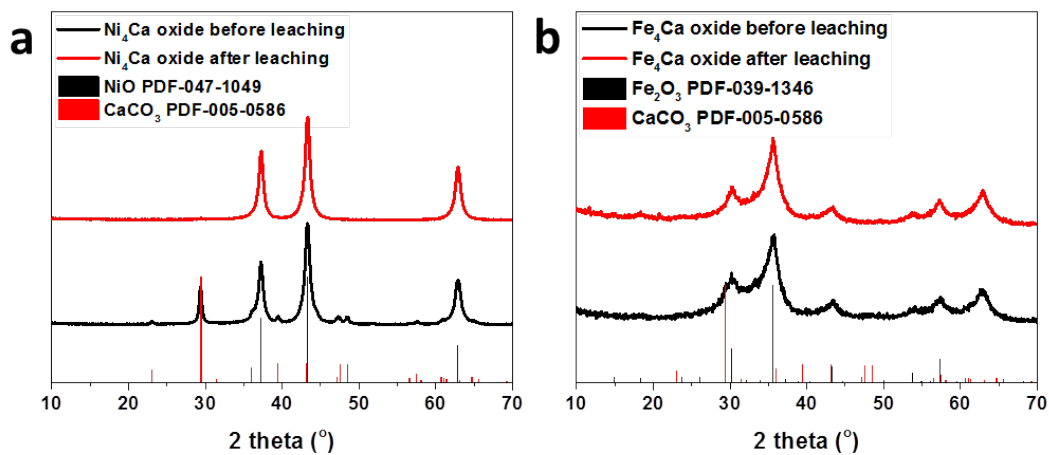


Figure S25. Wide-angle XRD patterns of (a) Ni_4Ca oxide, (b) Fe_4Ca oxide before and after leaching process with 0.1 M HCl solution for 2 h.

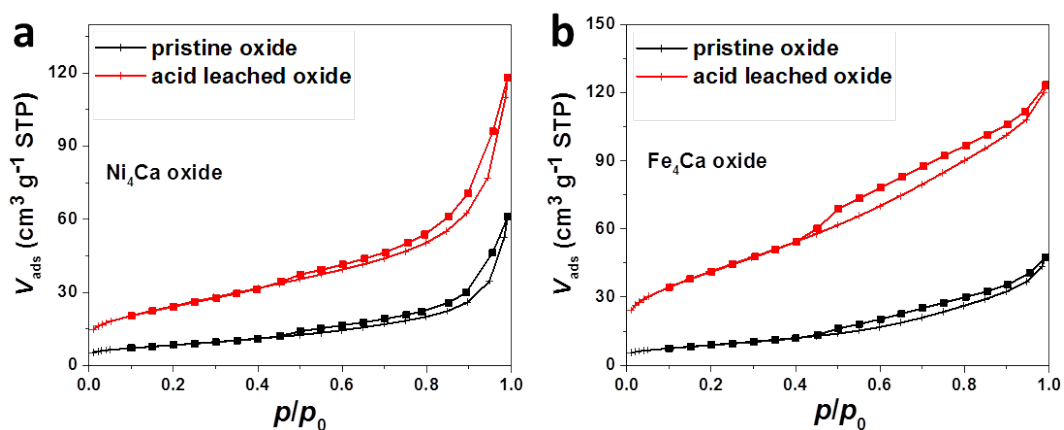


Figure S26. Nitrogen sorption isotherms of coffee waste templating mixed oxides before and after leaching by 0.1 M HCl solution for 2 h. (a) Ni_4Ca oxide, (b) Fe_4Ca oxide.

Table S1. Elemental analysis results and textural parameters of CW-templated Co-Mo oxides without leaching process, derived from EDX and N₂ sorption results, respectively.

	Co ₃ O ₄	Co/Mo 16/1	Co/Mo 8/1	Co/Mo 4/1	Co/Mo 2/1	Co/Mo 1/1
Actual ratio of Co/Mo	-	15.7/1	7.7/1	4.4	2.2	1.1
Total impurities (at. %)	4.0	3.4	3.3	2.9	3.1	2.9
BET surface area (m²/g)	45	55	41	49	36	27
Pore volume (cm³/g)	0.15	0.15	0.09	0.11	0.06	0.07

Note: impurities are the additional elements except of Co, Mo, and O in the oxides, which were contained in the coffee waste template.

Table S2. Elemental analysis results and textural parameters of CW-templated Co-Mo oxides after leaching by 0.1 M HCl solution for 2 h, derived from EDX and N₂ sorption results, respectively.

	Co ₃ O ₄	Co/Mo 16/1	Co/Mo 8/1	Co/Mo 4/1	Co/Mo 2/1	Co/Mo 1/1
Actual ratio of Co/Mo	-	19.5	14.2	9.8	7.3	1.3
Total impurities (at. %)	1.3	0.7	0.5	0.1	0.2	0.9
BET surface area (m²/g)	61	103	122	150	118	23
Pore volume (cm³/g)	0.15	0.16	0.12	0.13	0.12	0.07

Table S3. Elemental analysis results and textural parameters of CW-templated Co₄Mo oxides after 2 h' s leaching by different concentration of HCl solution, derived from EDX and N₂ sorption results, respectively.

HCl concentration	unleached	0.01 M	0.05 M	0.1 M	0.2 M
Actual ratio of Co/Mo	4.4/1	6.3/1	14.1/1	15.9/1	14.0/1
Total impurities (at. %)	2.9	1.5	0.3	0	0.2
BET surface area (m²/g)	27	59	98	103	102
Pore volume (cm³/g)	0.08	0.12	0.13	0.13	0.13

Table S4. Elemental analysis result and textural parameter of CW-templated Co₄Mo oxides after leaching by 0.05 M HCl solution for various time, derived from EDX and N₂ sorption results, respectively.

Leaching time	unleached	5 min	30 min	2 h	6 h
Actual ratio of Co/Mo	4.4/1	6.8/1	12.1/1	14.1/1	12.4/1
Total impurities (at. %)	2.9	0.6	0.6	0.3	0.6
BET surface area (m²/g)	27	89	102	98	111
Pore volume (cm³/g)	0.08	0.13	0.12	0.13	0.11

Table S5. Summarized electrochemical data of CW-templated Co₄Mo oxides before and after 2 hours leaching by 0.1 M HCl solution.

	Co ₃ O ₄	Co/Mo 16/1	Co/Mo 8/1	Co/Mo 4/1	Co/Mo 2/1
<i>j</i> _{@1.7 V vs. RHE} (mA/cm ²) before leaching	72	66	63	86	56
<i>j</i> _{@1.7 V vs. RHE} (mA/cm ²) after leaching	80	92	102	123	102
Overpotential _{@10mA/cm²} (mV) before leaching	405	391	388	380	399
Overpotential _{@10mA/cm²} (mV) after leaching	401	389	380	375	387
Tafel (mV/dec) before leaching	62	66	71	72	68
Tafel (mV/dec) after leaching	62	55	59	56	50

Table S6. Elemental analysis result and textural parameter of CW-templated Co₄M oxides (M = Li, Mg, Ca) before and after leaching by 0.1 M HCl solution for 2 h, derived from EDX and N₂ sorption results, respectively.

	Co/Li 4/1	Co/Mg 4/1	Co/Ca 4/1
Actual ratio of Co/M before leaching	-	3.8/1	3.0/1
Actual ratio of Co/M after leaching	-	8.1/1	153/1
BET surface area (m ² /g) before leaching	27	39	34
BET surface area (m ² /g) after leaching	48	114	117
Pore volume (cm ³ /g) before leaching	0.10	0.10	0.08
Pore volume (cm ³ /g) after leaching	0.14	0.19	0.25

Note: lithium is not detectable in EDX analysis.

Table S7. Elemental analysis result and textural parameter of CW-templated M₄Ca oxides (M = Ni, Fe) before and after leaching by 0.1 M HCl solution for 2 h, derived from EDX and N₂ sorption results, respectively.

	Ni/Ca 4/1	Fe/Ca 4/1
Actual ratio of M/Ca before leaching	3.3/1	3.1/1
Actual ratio of M/Ca after leaching	93.9/1	17.5
BET surface area (m ² /g) before leaching	30	33
BET surface area (m ² /g) after leaching	88	150
Pore volume (cm ³ /g) before leaching	0.09	0.07
Pore volume (cm ³ /g) after leaching	0.18	0.18