

Supporting Information

Selective Catalytic Electro-oxidation of Water with Cobalt Oxide in Ion Impermeable Reduced Graphene Oxide Porous Electrodes

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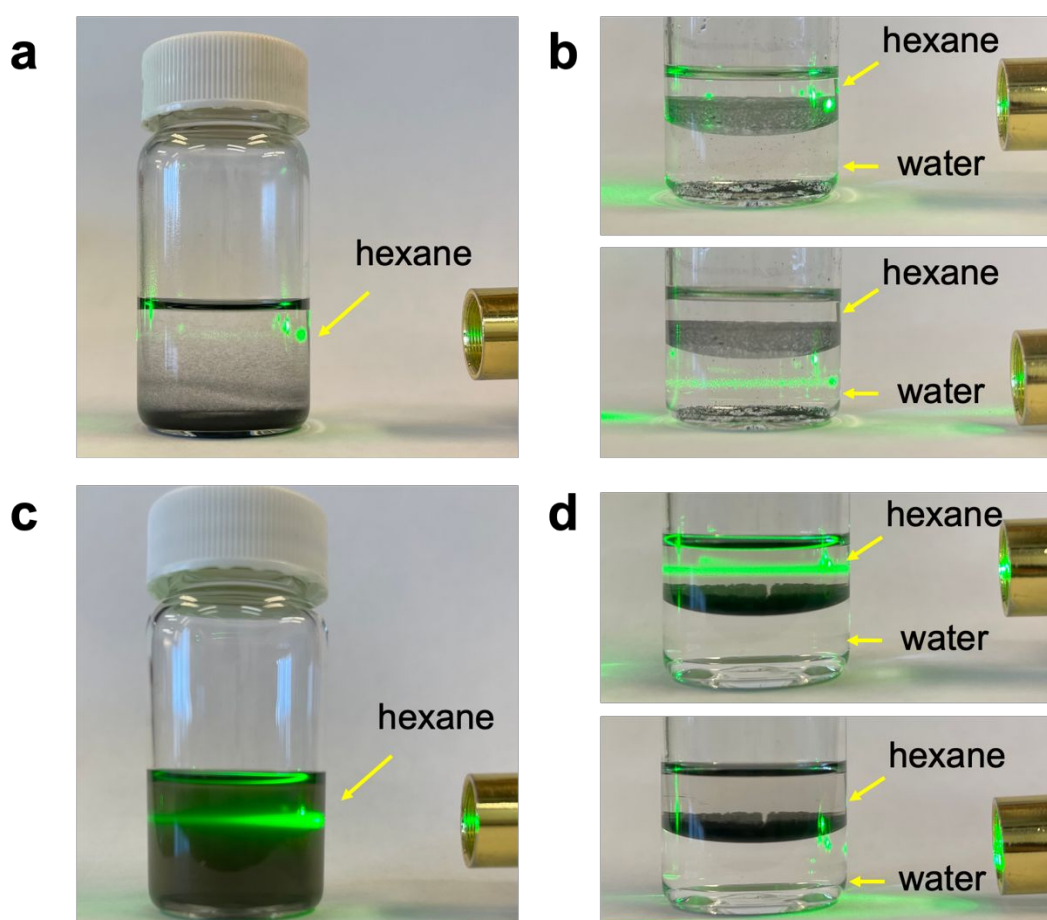


Figure S1. Digital photographs showing (a) pristine Co_3O_4 particles in hexane, (b) pristine Co_3O_4 particles in hexane (top) and water (bottom) after shaking, (c) $\text{Co}_3\text{O}_4/\text{SA}$ particles in hexane, (d) $\text{Co}_3\text{O}_4/\text{SA}$ particles in hexane (top) and water (bottom) after shaking. A green laser is pointed at the vials to evaluate the Tyndall effect in the dispersions. A clear solution without suspended particles shows no light scattering. In panel b, the absence of light scattering in the hexane phase (top) suggests the absence of dispersed Co_3O_4 particles in this medium after shaking. In panel d, the strong Tyndall effect observed in the hexane phase together with the absence of the Tyndall effect in the water phase after shaking suggests that the dispersion of $\text{Co}_3\text{O}_4/\text{SA}$ particles in the hexane phase and at the hexane/water interface.

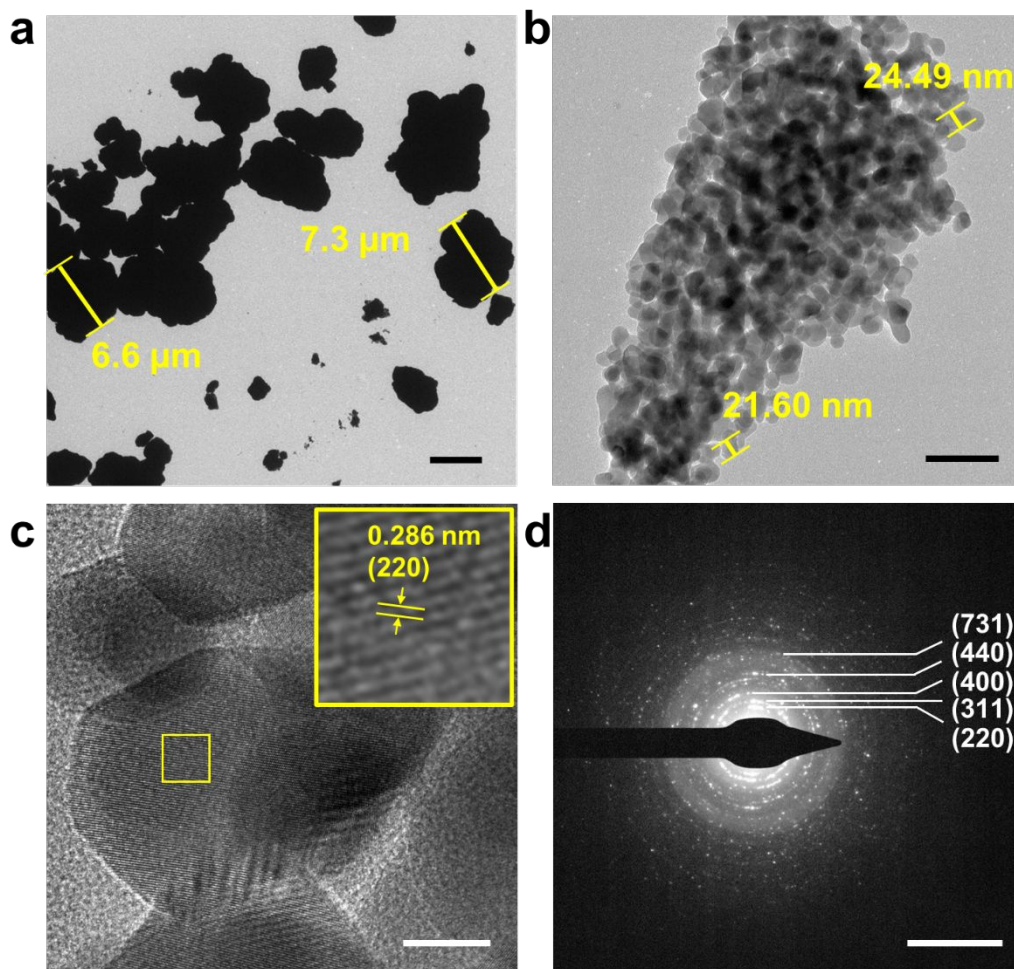


Figure S2. (a-b) Representative TEM images of aggregates of pristine Co₃O₄ particles. (c) HRTEM analysis of Co₃O₄ particles. The magnification of the area highlighted by the yellow square, shown as an inset figure, allows to measure the *d*-spacing and identify the (220) diffraction planes of the Co₃O₄ cubic phase (JCPDS 00-42-1467). (d) The selected area electron diffraction (SAED) patterns obtained from Co₃O₄ particles reflect the diffraction bands of the cubic Co₃O₄ lattice, whose most prominent zone axes are labelled and indicated by solid lines. The SAED patterns in panel (d) and Figure 2d are identical within the experimental error. Scale bars: 5 μm (a), 100 nm (b), 10 nm (c), and 10 nm⁻¹ (d).

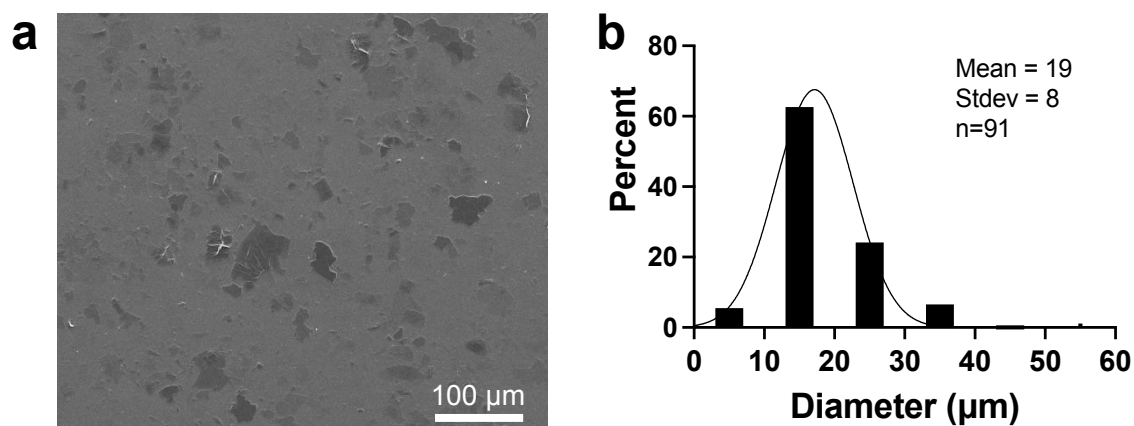


Figure S3. (a) SEM image of the GO flakes used in this study. (b) GO flake size distribution and nonlinear regression based on a Gaussian model. The flake size is shown as the effective diameter of a circle that has the same area as the GO flake, as observed in the SEM.

Table S1. Surface chemistry from XPS survey data of GO and GO/CTAB (n=3 experiment points).

	GO	GO/CTAB
O1s (atom%)	39±3	31.5±0.5**
C1s (atom%)	60±2	66.7±0.4**
N1s (atom%) ^{a)}	1.3±1.2	1.8±0.2

^{a)} Nitrogen on the original GO is the trace impurity from the sodium nitrate in the Hummers' method for GO preparation.

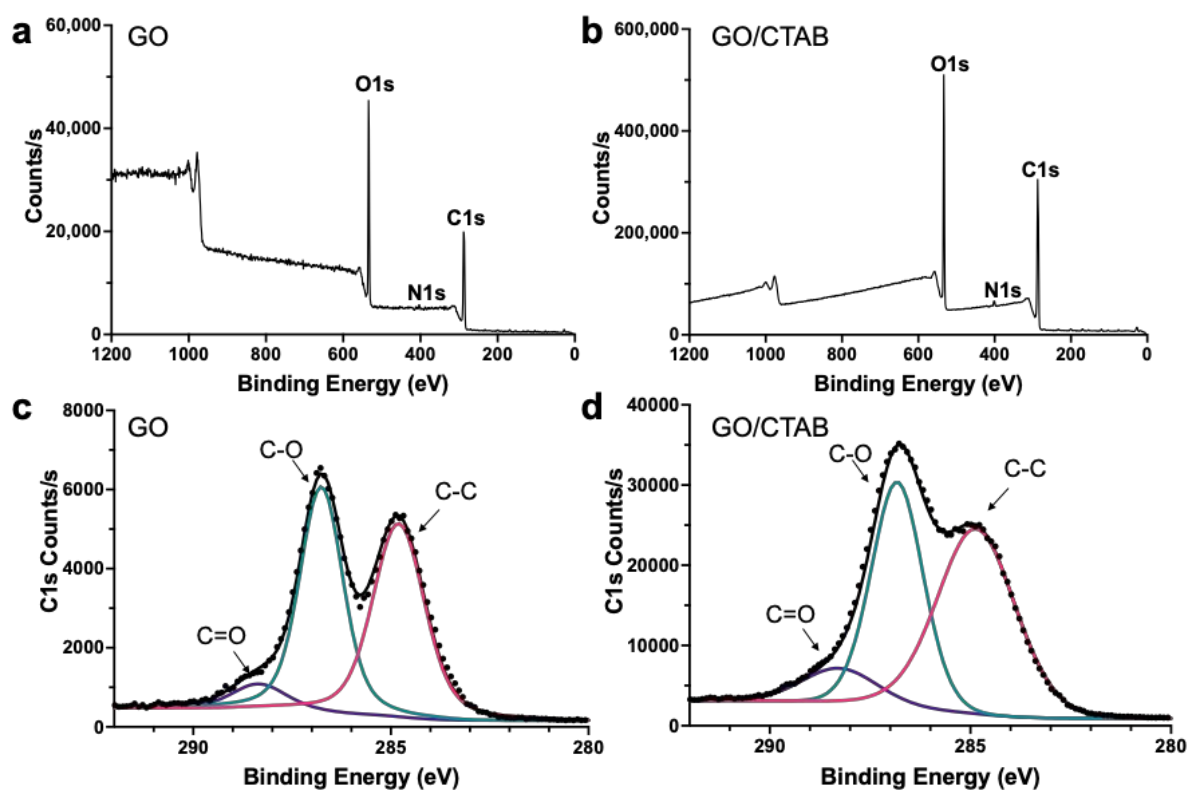


Figure S4. Representative XPS survey spectra of (a) GO and (b) GO/CTAB. XPS high-resolution C1s spectra of (c) GO and (d) GO/CTAB.

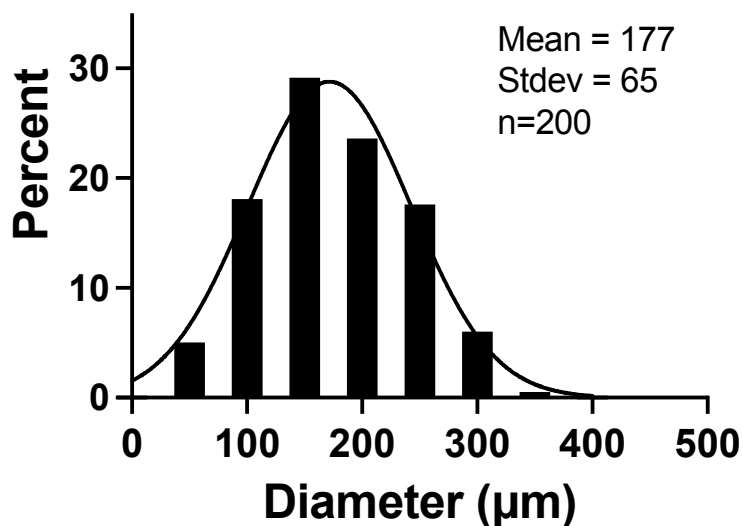


Figure S5. Pore diameter distribution of rGO/CoOx aerogels and nonlinear regression based on Gaussian model. The pore diameter is calculated based on the analysis of 200 pores observed in SEM images.

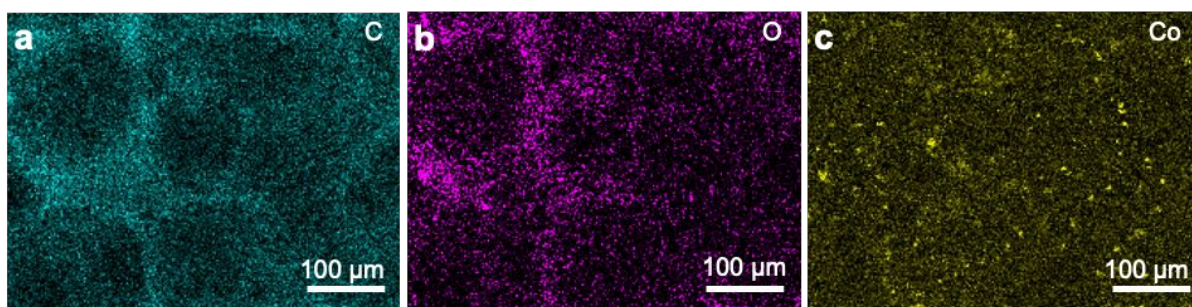


Figure S6. (a-c) EDS mapping of carbon and oxygen of the SEM image of rGO/CoO_x aerogel shown in Figure 3b.

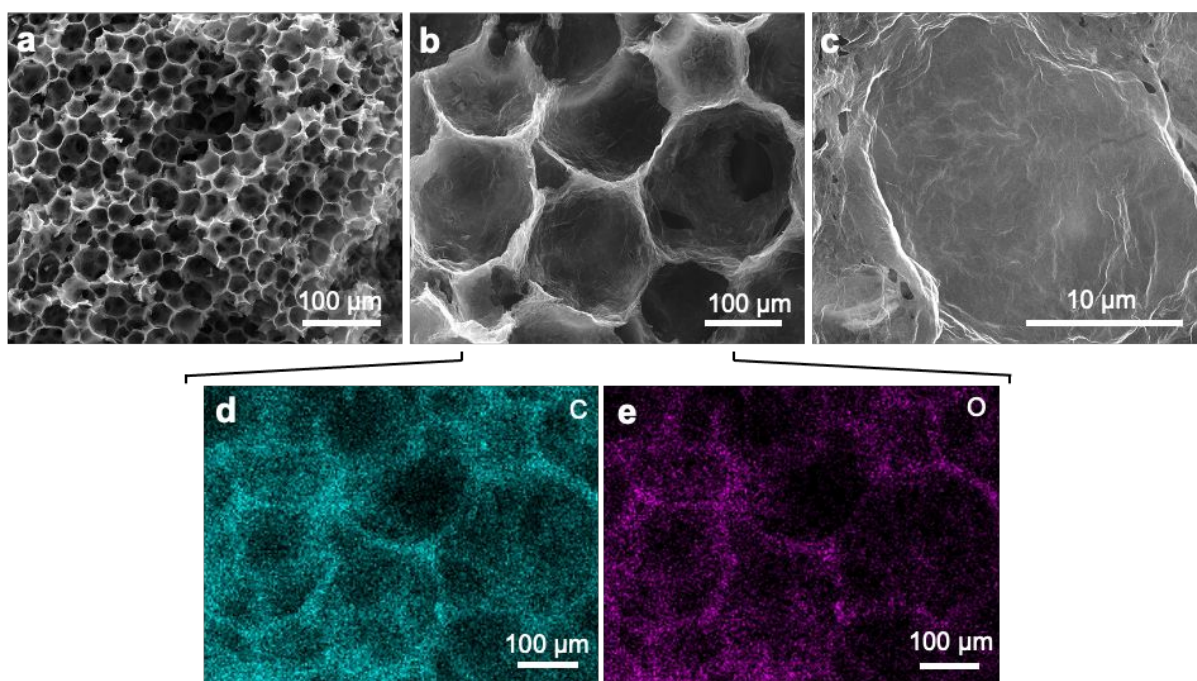


Figure S7. (a-c) SEM images of rGO aerogel synthesized without Co₃O₄ particles (control sample) at different magnifications. (d, e) EDS mapping of carbon and oxygen.

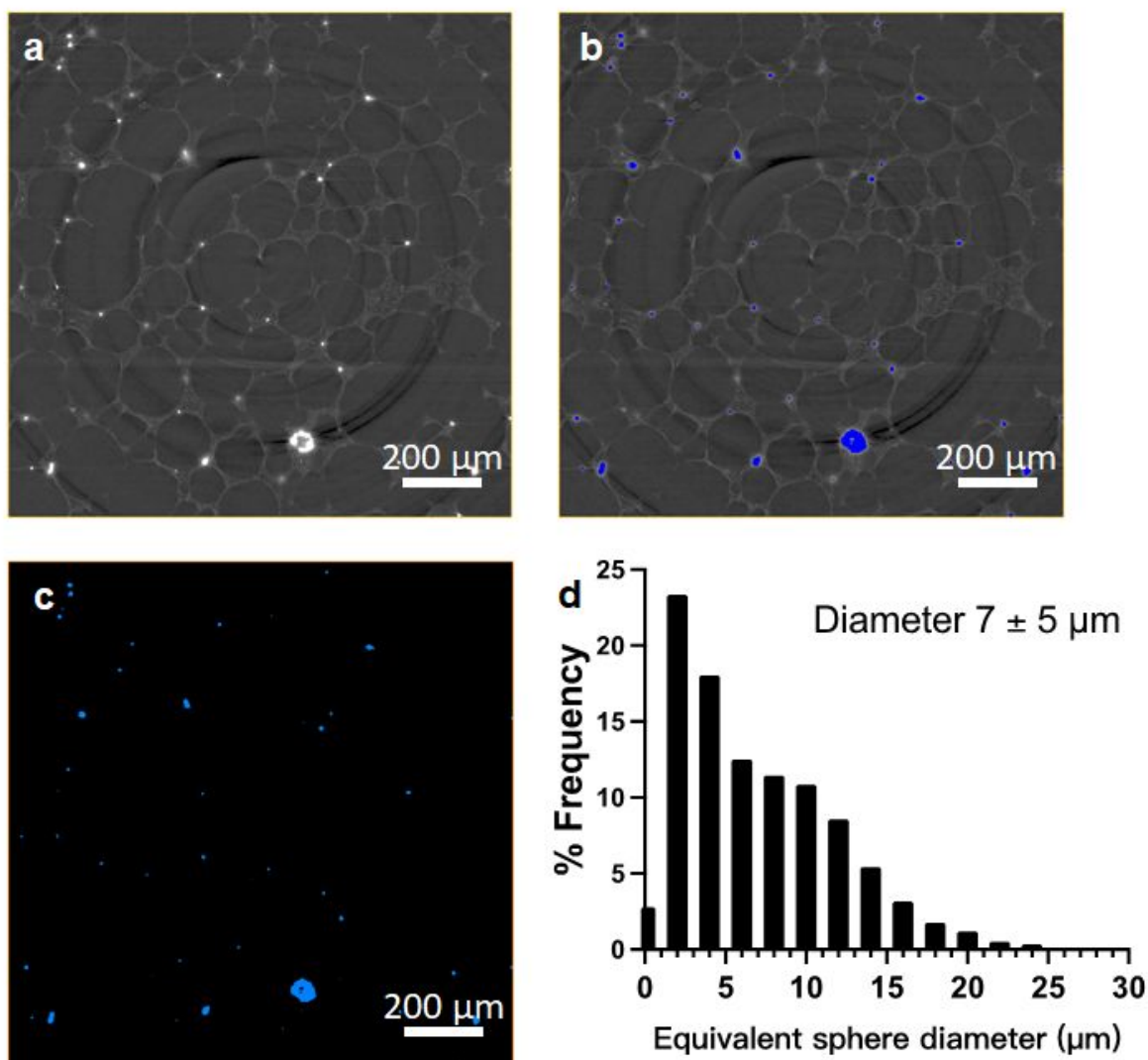


Figure S8. Phase contrast image (PCI) analysis of rGO/CoOx scaffolds. (a) Greyscale reconstruction slice (8-bit) showing the rGO pores as grey contour and CoOx particles as bright dots. Because of the higher X-ray absorption of cobalt oxide, the CoOx particles show with higher contrast. (b) With the interactive thresholding module in Avizo software, we set a certain grey level range (200-255) as a threshold (highlighted in blue) that only includes bright particles in the greyscale image. (c) After applying the interactive thresholding, the greyscale image is transformed into a binary image showing the CoOx in light blue. (d) With the label analysis module in Avizo, we obtain the volume of visualized particles, and thus the equivalent sphere diameter of particles. The equivalent diameter is equal to the diameter of a sphere that has the same volume of the particle.

We do not report X-ray powder diffraction (XRD) results because the diffraction pattern of rGO-CoOx samples varied from one measurement to another and we were not able to define a “representative” measurement. The isolated cobalt oxide particles in the scaffold behave as single crystals, each one immobilized in a particular random orientation. The result is not a powder XRD pattern – where all the possible grain orientations are statistically sampled throughout the compressed powder – nor a single crystal XRD, where the crystal orientation is controlled. XRD revealed a limited number of diffraction peaks, and often their relative peak intensities did not match the reference patterns in the literature. For this reason, we performed high resolution TEM characterization coupled with selected area electron diffraction (SAED) to clarify the composition and phases of the particles present in the electrodes.

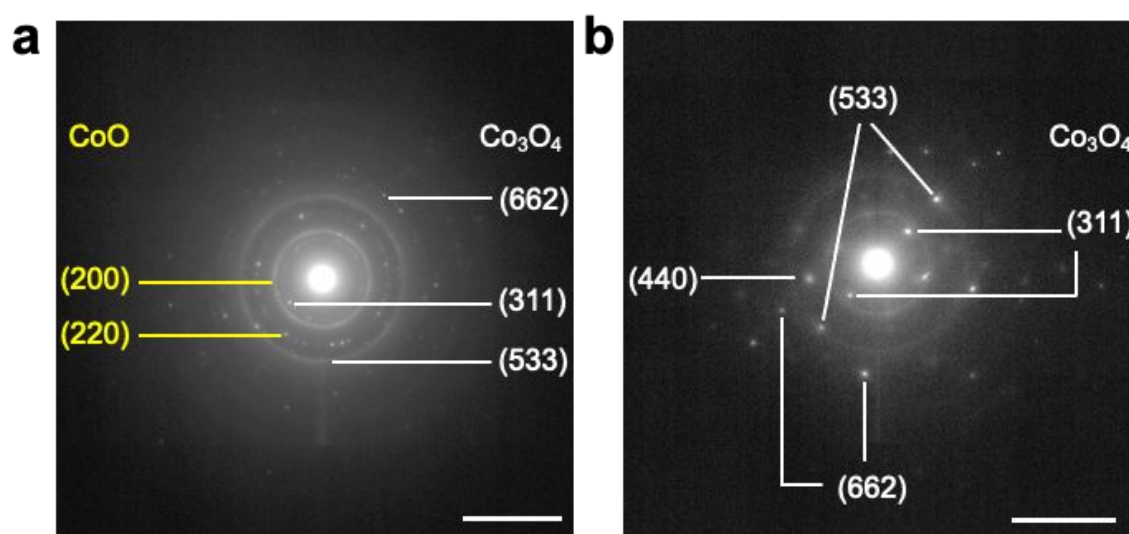


Figure S9. SAED patterns and the most prominent diffraction bands obtained from CoOx particles inside the rGO/CoOx aerogel shown in Figure 3h (a) and 3i (b) of the main text. (a) The SAED pattern of the aggregate highlighted with a yellow circle in Figure 3h contains the most prominent diffraction bands of both the cubic Co_3O_4 (JCPDS 00-42-1467) and cubic CoO (JCPDS 00-043-1004) crystalline phases, indicated by the white and yellow labels, respectively. (b) The SAED pattern of the octahedral particles highlighted with a yellow circle in Figure 3i matches the interlayer spacing of a single-crystal Co_3O_4 cubic phase, and its four most intense diffraction planes are indexed in white. Scale bars: 10 nm^{-1} .

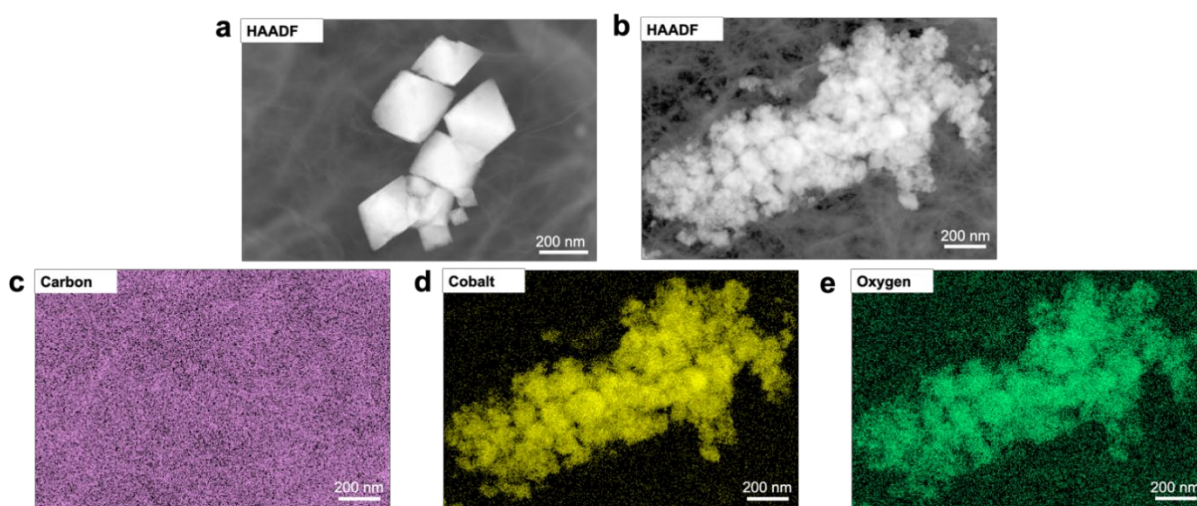


Figure S10. (a) HAADF image the CoOx particles shown in Figure 3i. (b) HAADF image and (c-e) the corresponding EDS elemental maps of CoOx particles shown in Figure 3h.

Table S2. Surface chemistry from XPS survey data of rGO and rGO/CoOx (n=3 experiment points). XPS analysis was carried out on the interior structure of purposely broken rGO and rGO/CoOx aerogels, to ensure that the results are representative of the bulk electrodes. Even though the XPS probe depth is <10 nm^[1], the spot analysed with XPS is 400 μ m in diameter and includes not only the surface of CoOx particles but also that of several rGO pores.

	rGO	rGO/CoOx
O1s (atom%)	7.3 $\pm$ 0.9	10 $\pm$ 1
C1s (atom%)	82 $\pm$ 2	79 $\pm$ 2
N1s (atom%)	11 $\pm$ 1	9 $\pm$ 2
Co2p (atom%) ^a	----	2.0 $\pm$ 0.2

^a The high nitrogen content arises from the reaction of ammonia vapors with the CO₂ generated from GO reduction during the hydrothermal treatment. It is likely present in the form of ammonium carbonate nanoparticles inside the rGO scaffold rather than as a doping element of the rGO sheets, as the temperature of the hydrothermal treatment is far below the one required to achieve nitrogen doping of graphitic materials.

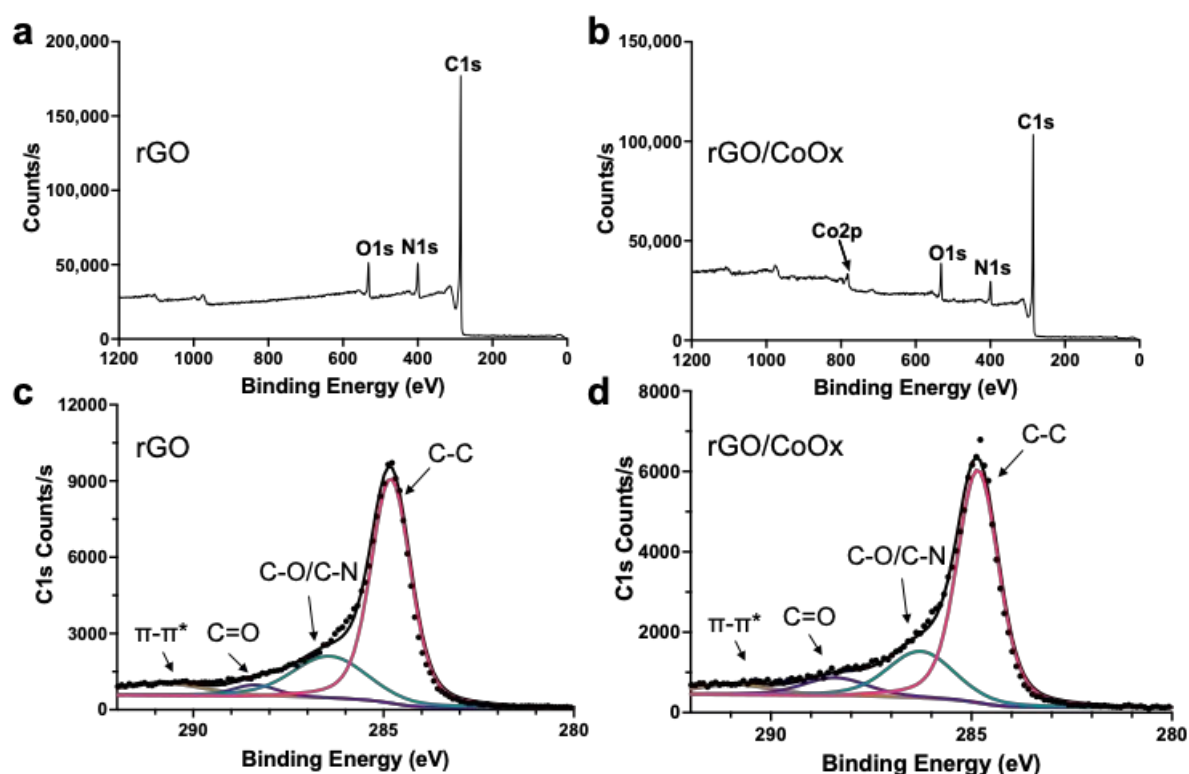


Figure S11. Representative XPS survey spectra of (a) rGO and (b) rGO/CoOx. XPS high-resolution C1s spectra of (c) rGO and (d) rGO/CoOx.

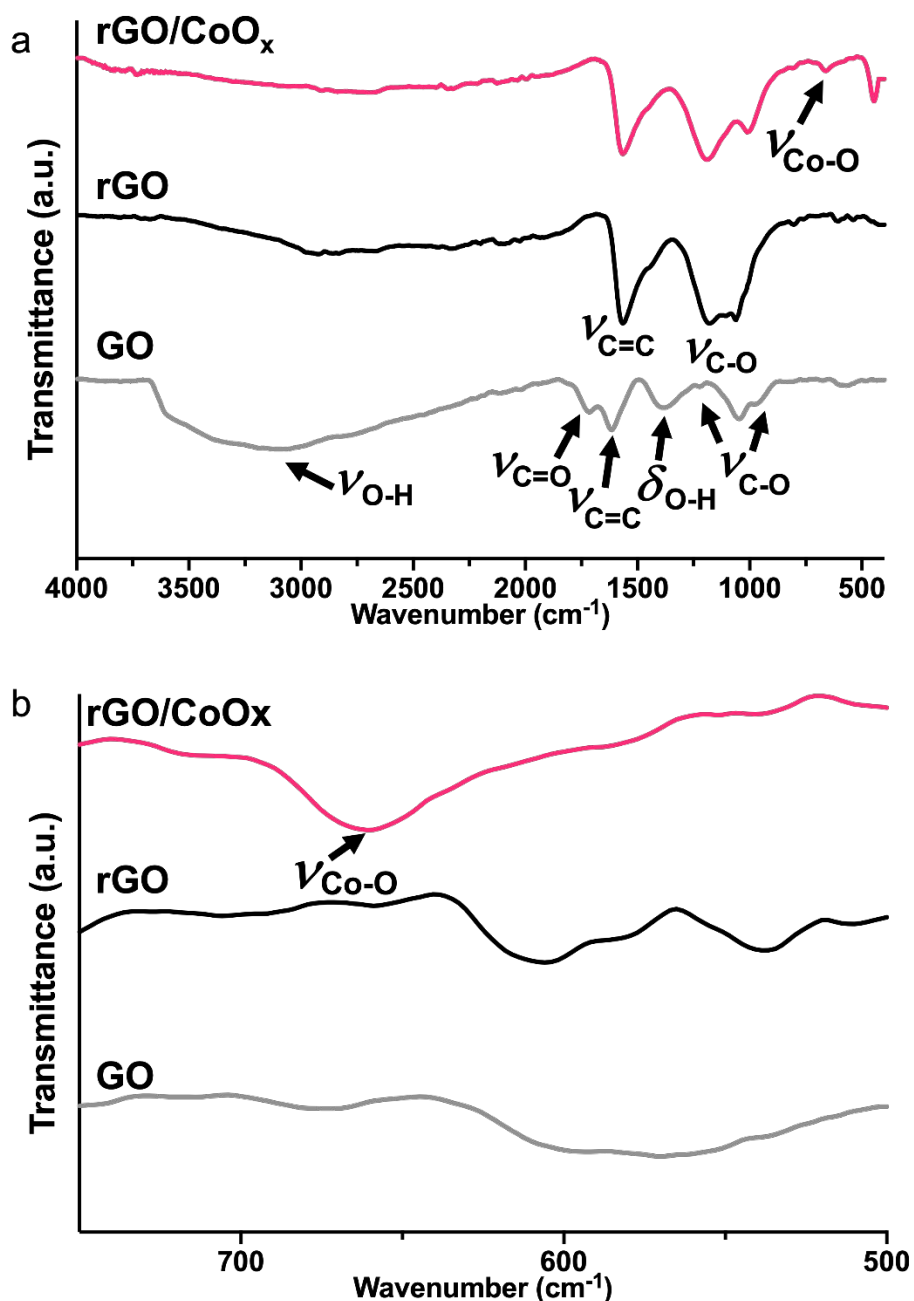


Figure S12. (a) FTIR spectra of pristine GO, rGO, and rGO/CoO_x aerogels; (b) zoom-in into the low wavenumber region where the Co–O vibrations are visible. These spectra provide further evidence of the reduction of GO after the HT and the presence of cobalt oxide. After HT, the peaks assigned to $\nu(\text{C=O})$ and $\delta(\text{O–H})$ disappear, and the broad peak related to $\nu(\text{O–H})$ decreases. A broad band spanning from 560 to 660 cm^{-1} , which corresponds to $\nu(\text{Co–O})$, appears in the rGO/CoO_x aerogel spectra.^[2-4]

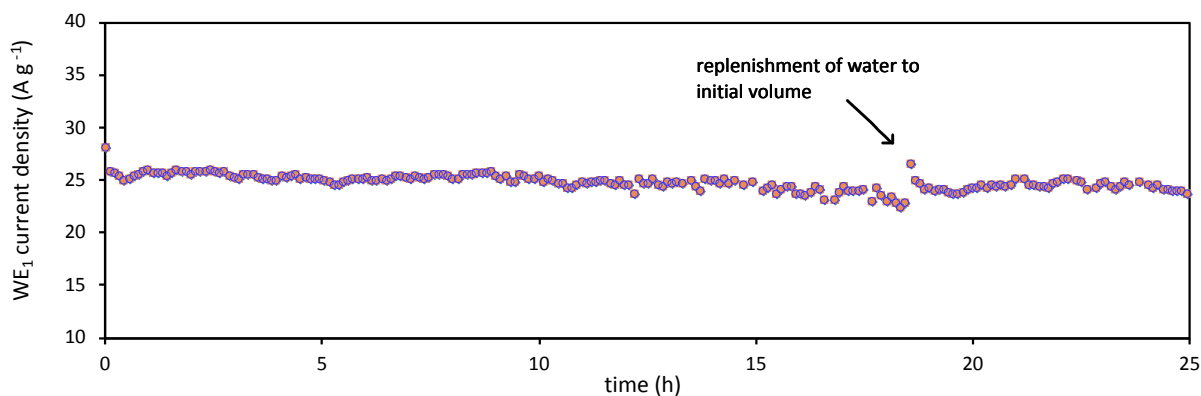


Figure S13. Durability test of Ag_m/rGO/CoOx electrode during selective water oxidation of simulated seawater, consisting of NaCl 0.5 M + KOH 1 M electrolyte. The chronoamperometric measurement is performed at room temperature, with the working electrode biased at +1.2 V vs Ag/AgCl.

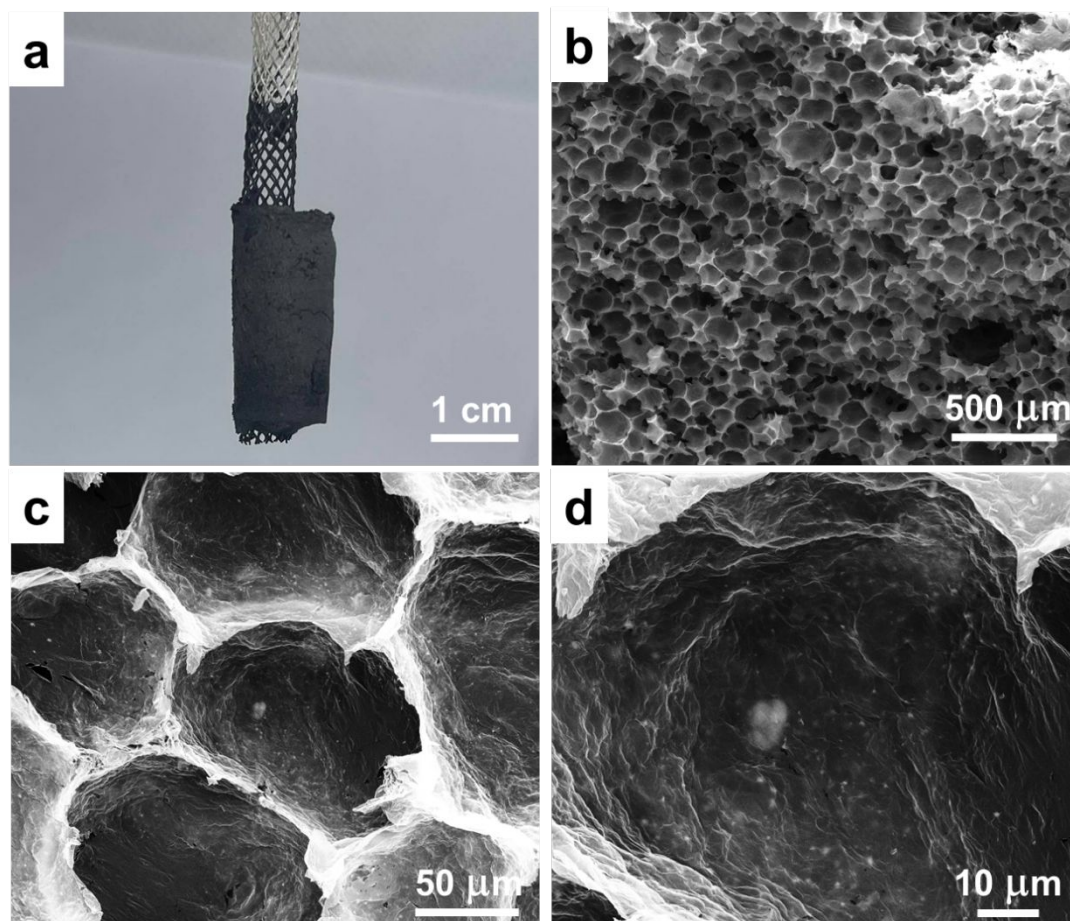


Figure S14. Structural characterization of Ag_m/rGO/CoOx electrode after selective water oxidation of simulated seawater for 25 hours, and subsequent washing in DI water before analysis. (a) Photograph and (b-d) SEM images of the electrode at different magnifications. The intact electrode porous structure and the particles embedded in the rGO pore walls closely resemble those recorded before electrolysis (Figures 3 and S7).

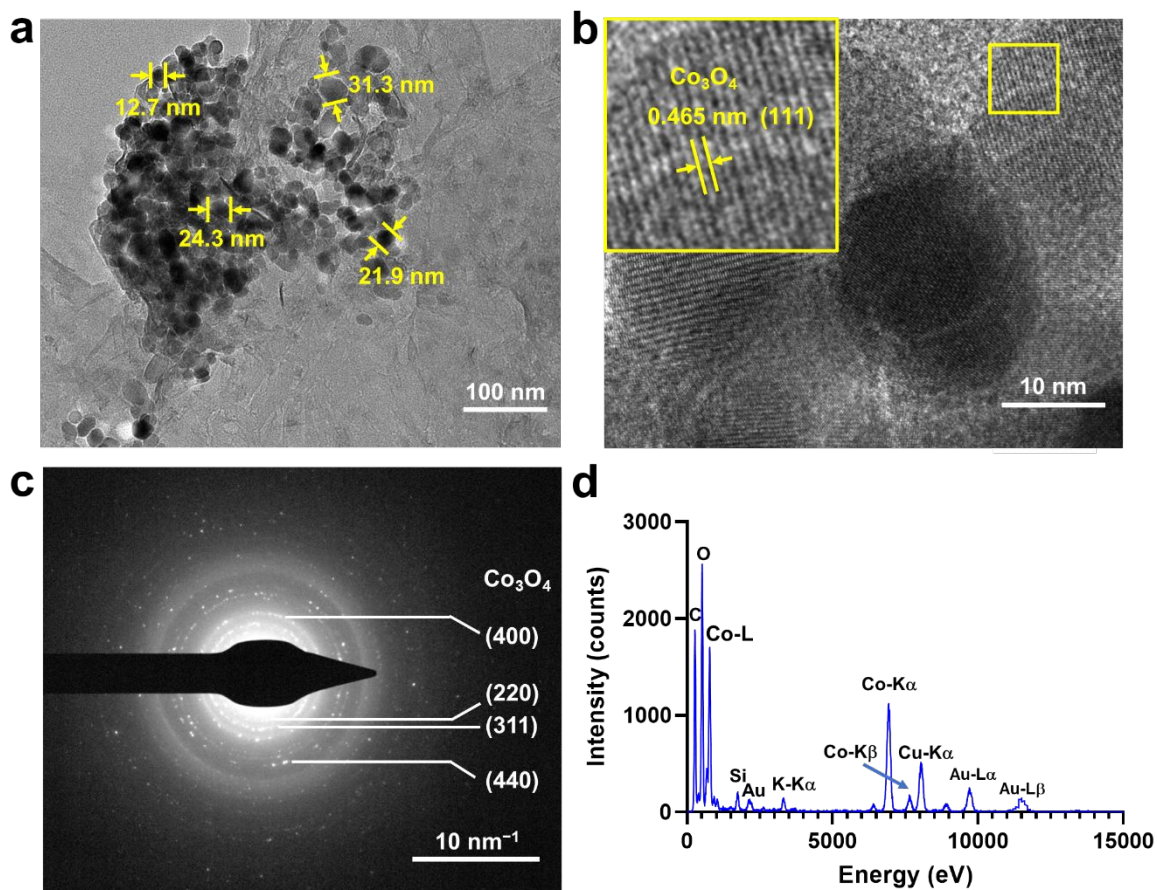


Figure S15. Characterization of the catalytic particles inside the Ag_m/rGO/CoO_x structure after selective water oxidation of simulated seawater for 25 hours, and subsequent washing in DI water before analysis. (a) TEM image of representative aggregates of cobalt oxide nanoparticles embedded in the rGO flakes. These sub-micrometric aggregates are similar to those imaged before electrolysis (Figures 3 and S10). (b) HRTEM analysis of the cobalt oxide particles shown in panel a. The magnification of the area highlighted by the yellow square, shown as the inset figure, allows to measure the d -spacing of the nanoparticle and identify the (111) diffraction planes of the Co_3O_4 phase (JCPDS 00-42-1467). (c) The SAED patterns obtained from the particles in panel b reflect the most prominent diffraction bands of the cubic Co_3O_4 lattice. (d) EDS spectrum of the particles shown in panel a. The Au and Cu signals arise from the TEM grids utilized. After the electrolytic process, the physicochemical composition and morphology of the cobalt oxide catalytic particles in the electrode appear substantially unchanged.

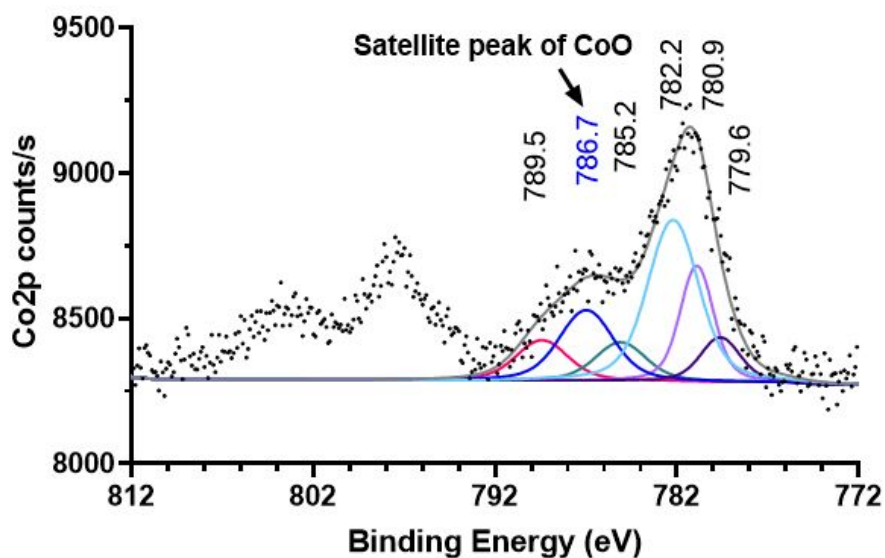


Figure S16. High-resolution XPS Co2p spectrum of the Ag_m/rGO/CoO_x electrode after selective water oxidation of simulated seawater for 25 hours. The satellite peak at 786.7 eV indicates the presence of CoO, as it has been observed prior to electrolysis (Figure 4b), suggesting that the electrolytic process does not affect the composition and phases of the catalyst particles.

To estimate the limit of detection of free chlorine with our method, we conservatively assume an electric current of -0.5 mA cm^{-2} recorded on the electrode WE_2 to be the smallest that can be significantly distinguished from the background current recorded in the absence of free chlorine, i.e. -0.25 mA cm^{-2} (Figure 5e). The ClO^- production/detection rate can be calculated as:

$v_{\text{ClO}^-} [\text{mol h}^{-1}] = j [\text{C s}^{-1} \text{ cm}^{-2}] \times A [\text{cm}^2] \times 3600 [\text{s h}^{-1}] / n \times F [\text{C mol}^{-1}]$, where j is the net current density measured on WE_2 during the chronoamperometry (the reference current measured in the absence of free chlorine being subtracted), A is the area of WE_2 immersed in the electrolyte solution, n is the number of moles of e^- exchanged per mole of reactant (ClO^-), and F is the Faraday constant. In our experiment, $j = 0.25 \text{ mA}$, $A = 2 \text{ cm}^2$, and $n = 2$ (the reduction of ClO^- to Cl^- is a bielectronic process, see equation 2 in the main article), which results in $v_{\text{ClO}^-} = 9.3 \text{ } \mu\text{mol h}^{-1}$.

The ClO^- detection rate can be expressed in ppm as follows: $v_{\text{ClO}^-} [\text{ppm h}^{-1}] = v_{\text{ClO}^-} [\text{mol h}^{-1}] \times 10^6 / \text{mol}_{\text{H}_2\text{O}} [\text{mol}]$, where water molecules alone are considered as reference. In our setup, the working electrode compartment contains 30 ml of electrolyte, which approximately corresponds to 1.67 mol of water ($\text{MW}_{\text{H}_2\text{O}} = 18 \text{ Da}$). In these conditions, the lowest ClO^- concentration detectable with our amperometric method (v_{ClO^-}) is 5.6 ppm h^{-1} .

Table S3. Comparison between rGO/CoOx and the most active electrocatalysts reported for selective oxidation of alkaline simulated seawater (KOH 1 M + NaCl 0.5 M, pH = 14), at room temperature. Most of the catalytic activities in the literature are reported normalized by electrode area, but in the case of an extended 3D GO structure, it is more appropriate to compare specific activity per unit mass. All the catalysts chosen for this comparison are supported on thin sheets of nickel foam (1-1.5 mm thick) with areal density ranging from 35 to 45 g cm⁻². The operational potentials of all the catalysts for comparison were *iR* compensated (85-95%) and referenced to the reversible hydrogen electrode (RHE) or reported as overpotentials (η) for the O₂ evolution reaction. At pH 14, the potentials of the RHE and Ag/AgCl/KCl 3.5 M reference electrodes are -0.827 and +0.205 V vs SHE, respectively, and the thermodynamic onset of the OH⁻ oxidation to O₂ is +0.402 V vs SHE. The values here reported (second column) are calibrated to the Ag/AgCl/KCl 3.5 M electrode using either one of the following equations: $E_{\text{Ag/AgCl}} = E_{\text{RHE}} - 0.827 - 0.205$ or $E_{\text{Ag/AgCl}} = \eta + 0.402 - 0.205$.

Catalyst	E vs Ag/AgCl (V)	j (mA cm ⁻²)	Areal density (g cm ⁻²)	j (A g ⁻¹)	Reference
Fe-Ni(OH) ₂ /Ni ₃ S ₂	+0.52	100	0.035-0.045*	2.2-2.9	5
Ni ₂ P-Fe ₂ P	+0.49	100	0.035	2.9	6
	+0.54	500	0.035	14.3	
NiMoN@NiFeN	+0.48	100	0.035	2.9	7
	+0.54	500	0.035	14.3	
NiFe/NiS _x -Ni (Ni ³)	+0.80	400	0.042	9.5	8
	+1.00	800	0.042	19.0	
	+1.15	1000	0.042	23.8	
Ag_m/rGO/CoOx	+0.54	-	-	~9 ^a	This work
	+1.00	-	-	~19.5 ^a	
	+1.20	-	-	25 ± 5	

* As the value of catalyst areal density was not reported in this work, we calculated two values of current density per mass of catalyst, based on the lowest and the highest areal densities of commercial nickel foams.

^a These values of current density per mass of catalyst do not result from chronoamperometric measurements and are rather estimated from the sweep voltammetric profile of the electrode.

At a low overpotential of 0.34 V, corresponding to 0.54 V vs Ag/AgCl, benchmark electrocatalysts such as Ni₂P-Fe₂P and NiMoN@NiFeN show superior specific activity compared to rGO/CoOx, 14.3 (both catalysts) versus ~9 A g⁻¹, respectively. Also, the closed-pore structure of rGO/CoOx is responsible for a smaller rate of current increase versus applied potential as compared to Ni foam-based catalysts, for example, from ~9 to 25 A g⁻¹ over 0.65 V for rGO/CoOx versus a comparable 9.5 to ~24 A g⁻¹ over a 0.35 V change for NiFe/NiS_x-Ni. However, Ni foam-based catalysts are not intrinsically selective against chloride competition, which limits their application to a small potential range, while rGO/CoOx electrodes can work in a wider potential range and pH window, thanks to the intrinsic selectivity resulting from their pore structure, as also discussed in the main article.

References

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