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Supporting Information

# A Facile Corrosion Approach to Highly Active $CoO_x$ Water Oxidation Catalysts

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## Chemicals

Chemicals (analytical grade) were obtained from Sigma-Aldrich, Alfa-Aesar or Acros Organics and were used as received without any further purification. Solvents were dried according to the standard literature reported procedure wherever needed. Double distilled water has been used throughout the experiments.

## Instruments

Powder X-Ray diffraction (PXRD) studies were performed on a Bruker AXS D8 Advance instrument using Cu Kα radiation ($\lambda$=1.5418 Å). BET surface area measurements were carried out using a 9-point $N_2$ adsorption analysis on a Micromeritics Gemini with VacPrep 061. The microstructure (morphology, particle size, particle distribution, phase composition, crystallinity) of the samples was studied at the Department of Electron Microscopy (ZELMI), TU Berlin. SEM-images were acquired using a Hitachi S-2700 microscope. For TEM-investigations a small amount of the sample powder was placed on a TEM-grid (carbon film on 300mesh Cu-grid, Plano GmbH, Wetzlar, Germany) and measured with a FEI Tecnai $G^2$ 20 S-TWIN transmission electron microscope (FEI company, Eindhoven, Netherlands) equipped with a $LaB_6$-source at 200kV acceleration voltage. EDX-analysis were carried out with an EDAX r-TEM SUTW Detector (Si (Li)-detector). Data analyses were carried out with the software Digital micrograph (Gatan).ICP-AES was measured on a Thermo Jarrell Ash Trace Scan analyzer. The XAS spectra were collected at cobalt $L_{2,3}$ edge at beam line U49-PGM2 in BESSY-II. The step height for photon scan was 0.1 eV and the data are recorded in total electron yield mode. Two set of measurements are done for each sample before and after electrochemical testing. For the better comparison the background of the spectra are removed and is normalized to highest intense point. The X-ray photoelectron spectroscopy (XPS) were measured using a Kratos Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, UK) with an Al *Kα* monochromatic radiation source (1486.7 eV) and 90° take off angle (normal to analyzer). The spectra were recorded for C1s, O1s, and Co2p levels with pass energy 20 eV and step 0.1 eV. The binding energies have been calibrated relative to C1*s* peak at 285.0 eV. Data analyses were carried out using Casa XPS (Casa Software Ltd.) and Vision data processing program (Kratos Analytical Ltd.).

## Experimental

### Syntheses of the catalysts

*Synthesis of CoO*

Cobalt(II) acetylacetonate (514 mg), cetyltrimethylammonium bromide, CTAB (500 mg) and benzyl amine (15 mL) were placed in a glass tube (Sigma Aldrich, screw capped front seal ACE pressure tube, volume 21 mL) and nitrogen was purged through the mixture for 1 h to remove the air. The tube was sealed with the screw cap in nitrogen environment and placed in an oil bath pre-heated at 180 °C. The mixture was then heated for 3 h and cooled down naturally in atmosphere to room temperature. To this mixture, 50 mL methanol was added and left for 16 h. The obtained solid was centrifuged out at 8000 rpm for 10 minutes, washed with methanol (3 times x 10 mL), chloroform (3 times x 10 mL) and acetone (2 times x 10 mL) [centrifuging performed at 8000 rpm for 10 minutes in each case] and dried in an air oven at 50 °C for 24 h to acquire the brown color solid CoO. The amount of obtained CoO varied from batch to batch from 60-74 mg.

*Synthesis of $CoO_x$*

100 mg of CoO powder was added to 10 mL 0.5 M CAN solution and stirred vigorously for 1 h in air. The solid was centrifuged out at 8000 rpm for 10 minutes, washed with water (3 times x 10 mL) and finally with acetone (2 times x 10 mL) [centrifuging performed at 8000 rpm for 10 minutes in each case] and dried for 16 h at 50 °C. The amount of obtained $CoO_x$ varied from batch to batch from 70-80 mg.

It should be mentioned that the concentration of CAN and the time for CAN treatment, is very important to attain the improved catalytic activity of $CoO_x$. At lower concentration of CAN (0.25 M), transformation of CoO was not prominent as the catalytic activity was not improved while $CeO_2$ precipitated out when 1 M CAN solution was used. Similarly, in 30 min transformation of CoO is not complete and longer time (3 h) of CAN treatment lowers the catalytic activity of $CoO_x$.

*Electrode preparation* [S1]

30 mg of CoO or $CoO_x$ powder was taken in a glass vial, 5 mL of acetone was added followed by 10 mg of iodine. The mixture was sonicated for 30 minutes and the electrode was prepared by electrophoretic deposition for 5 minutes with a potential difference of 10 V on 1x1 $cm^2$ area of fluorinated tin oxide coated glass (FTO, Sigma Aldrich, resistivity 8-12 Ω/sq., both anode and cathode). Amount of catalyst loaded was ~ 2 mg.

## Electrochemical measurements

Catalytic activity was tested in 1 M KOH solution using single-compartment three-electrode electrochemical cell (catalyst deposited on FTO-glass as working electrode, Pt wire as a counter electrode and Hg/$Hg_2SO_4$ as a reference electrode). Test runs were carried out with the typical electrolyte resistance (incl. the electrode) about 40 Ω; *iR* compensation at 80% was applied. The solution was not stirred during the experiments. Chronoamperometric measurements were performed in 1 M KOH at constant potential of 1.55 V vs RHE.

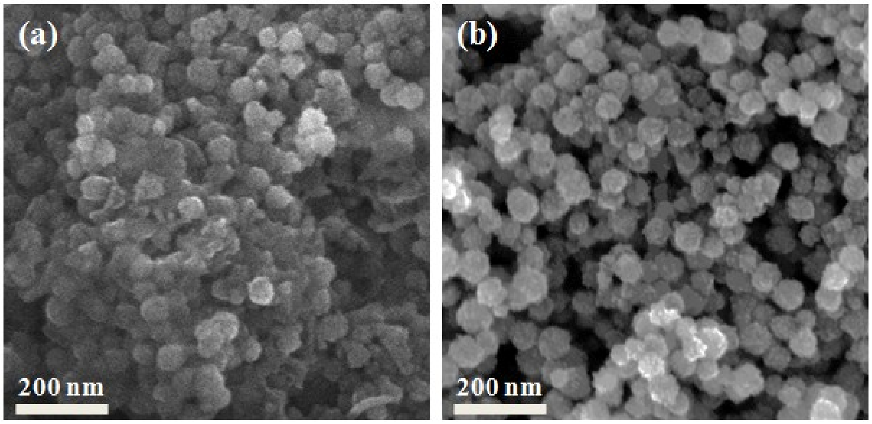


**Fig. S1**. SEM images of (a) CoO and (b) $CoO_x$ showing the retention of the particle morphology after the CAN treatment of CoO.

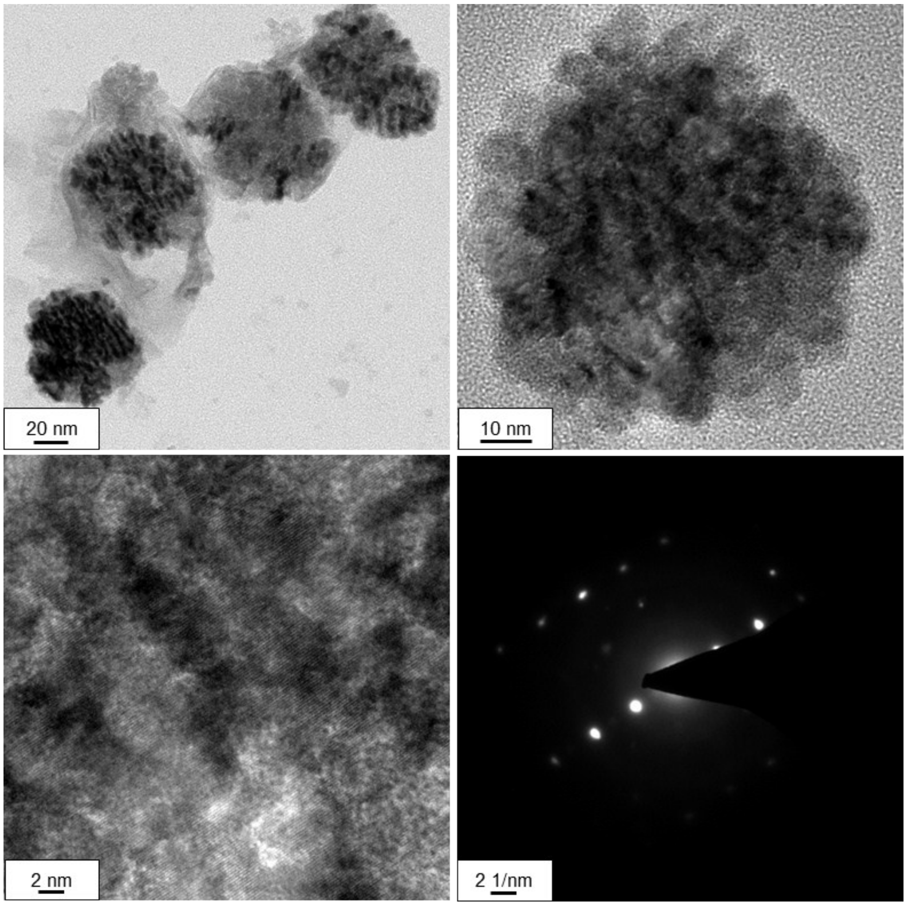


**Fig. S2**. HRTEM images of CoO at different resolutions showing the formation of larger spheroids by the combination of smaller nanoparticles and corresponding selected area electron diffraction patter

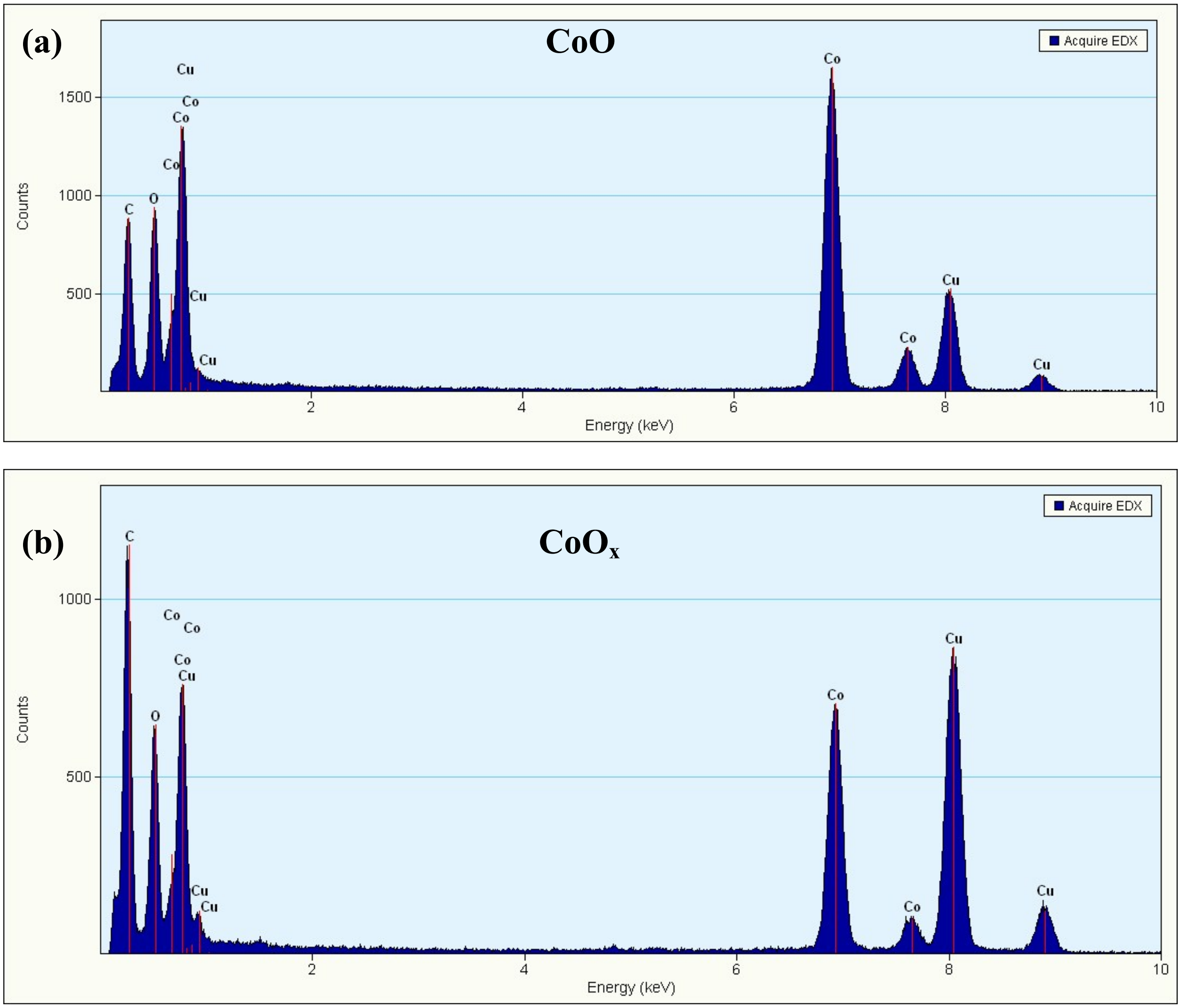


**Fig. S3.** EDX spectra of (a) CoO and (b) CoO$_x$. No cerium was detected in CoO$_x$. The signals for Cu are from the TEM grid.

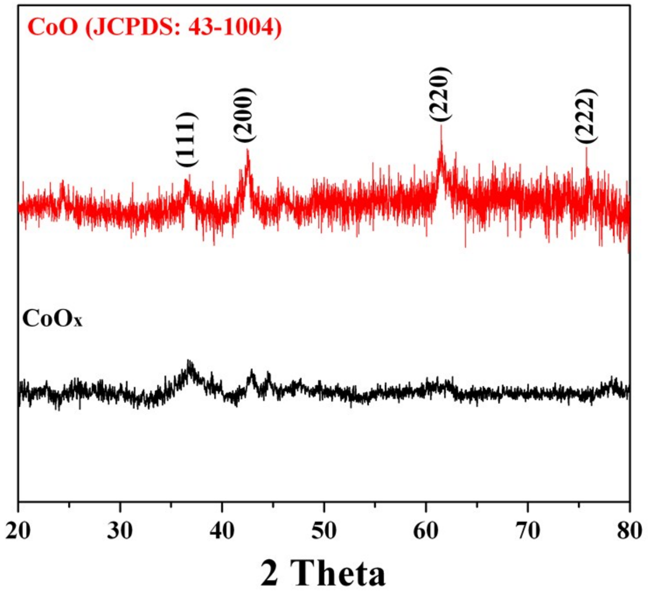


**Fig. S4**. PXRD patterns of CoO and $CoO_x$ showing weak reflections corresponding to smaller particles of cubic CoO. The further confirmation on the structure was also directly deduced from extensive XAS, XPS and TEM analysis.

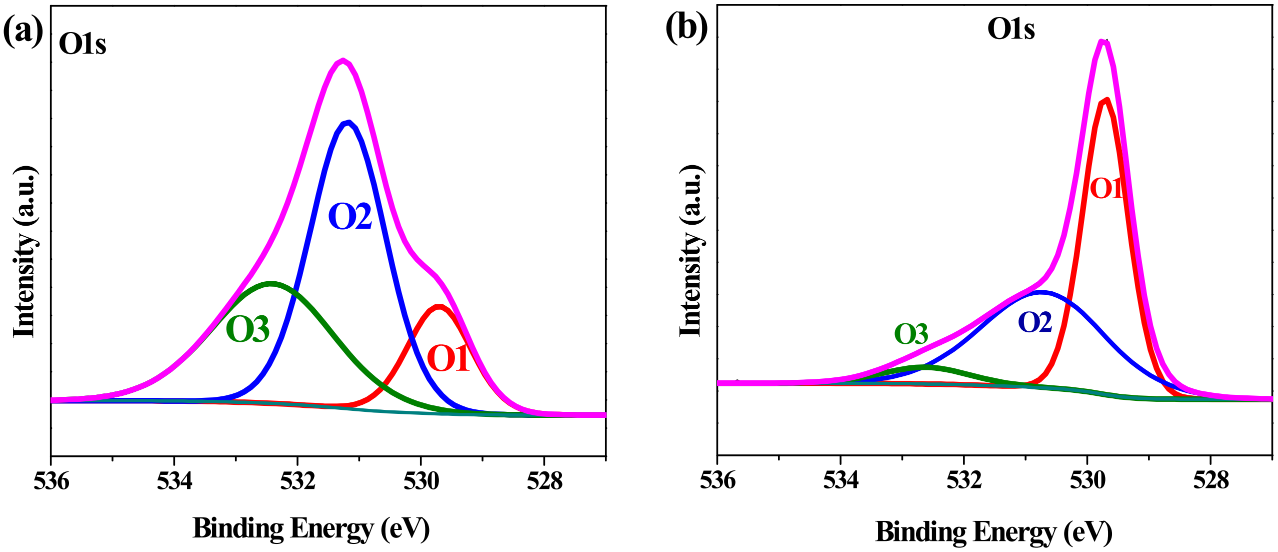


**Fig. S5**. O1s XPS spectra of (a) CoO and (b) $CoO_x$ deconvoluted to metal-oxo (O1), surface-OH (O2) and adsorbed water (O3).

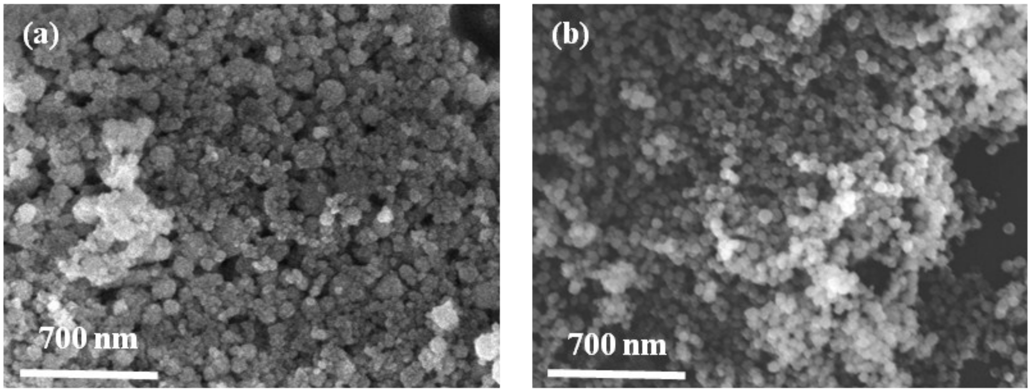


**Fig. S6**. SEM images of (a) CoO and (b) $CoO_x$ particles after the electrphoretic deposition showing minimum deformation of the particle morphology.

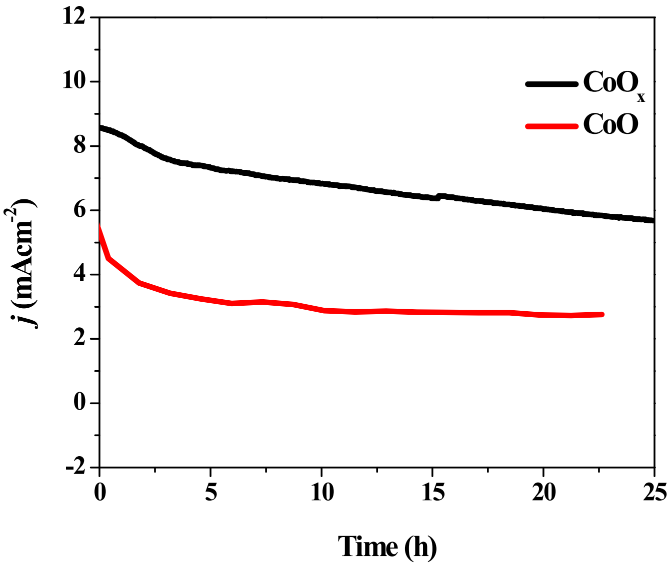


**Fig. S7**. Chronoamperometric studies for OER of CoO and $CoO_x$ at the constant potential of 1.55 V vs. RHE in 1 M KOH solution.

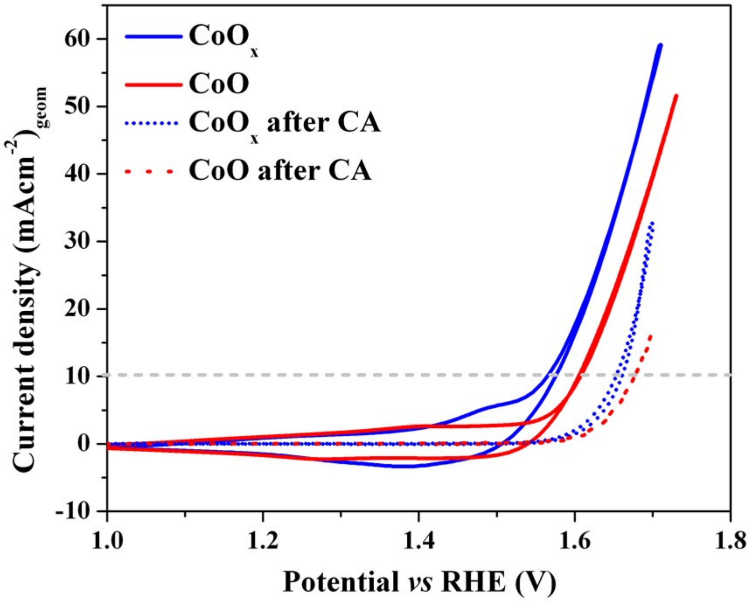


**Fig. S8.** Cyclic voltametric studies of CoO and $CoO_x$ after the chronoamperometric studies for 24 h.

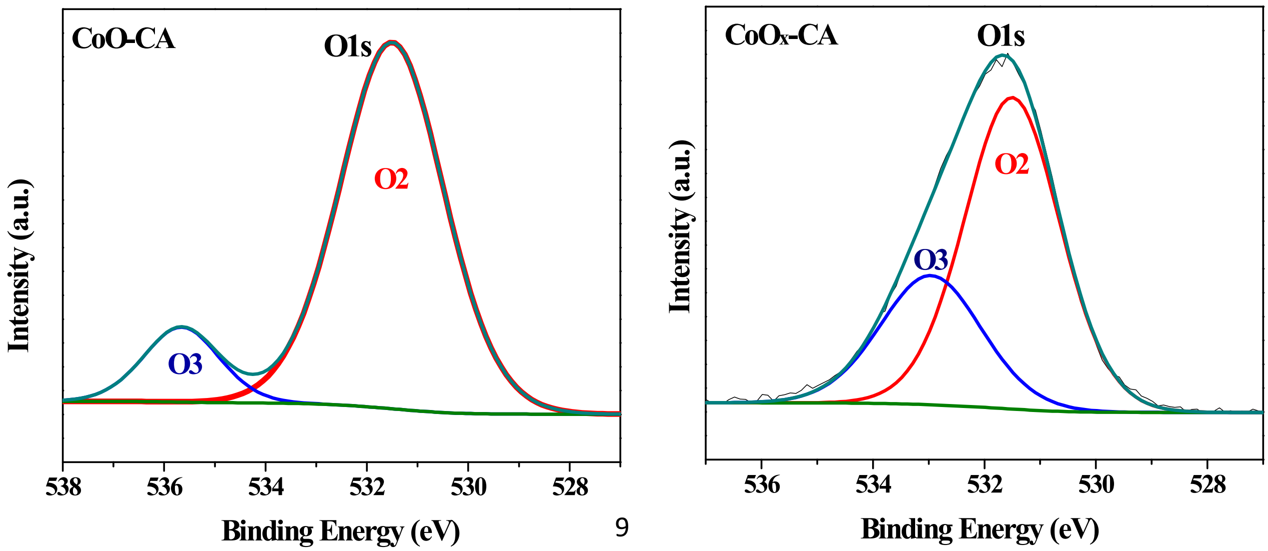
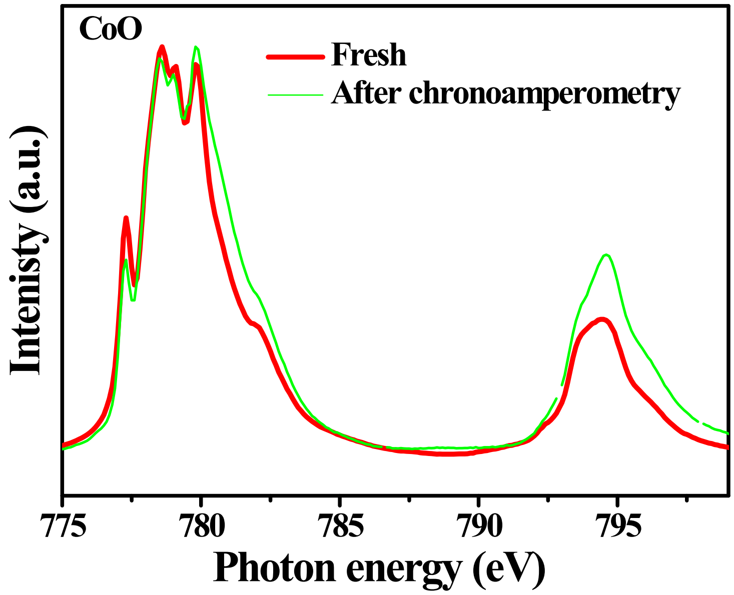


**Fig. S9**. O 1s X-ray photoelectron spectra of CoO and $CoO_x$ after electrochemical CA measurements for 24 h. For CoO and $CoO_x$, the O2/O3 ratio before electrochemistry was 3.3 and 0.88 that was highly increased to 87 and 71, respectively. This shows that a large amount of hydroxylation occurs on the surface of both CoO and $CoO_x$ catalysts.



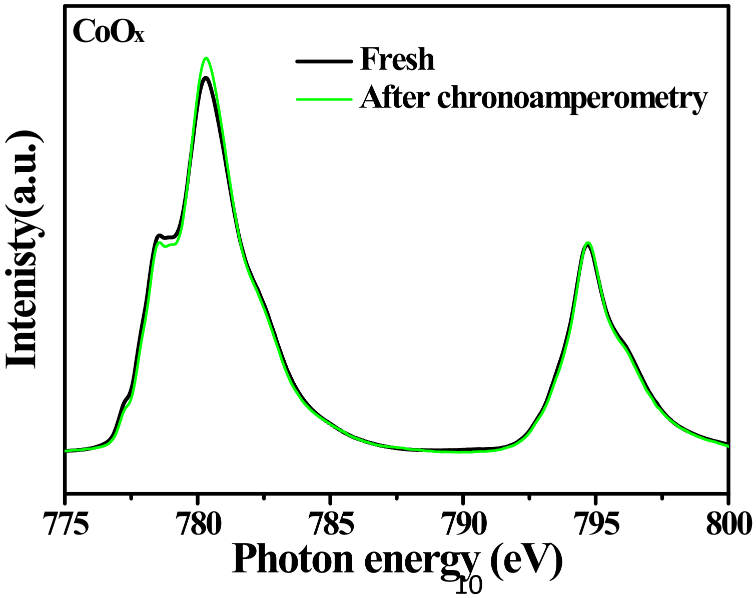


**Fig. S10**. Co $L_{2,3}$ edge X-ray absorption spectra of CoO (top) and $CoO_x$ (bottom) after electrochemical CA measurements for 24 h.

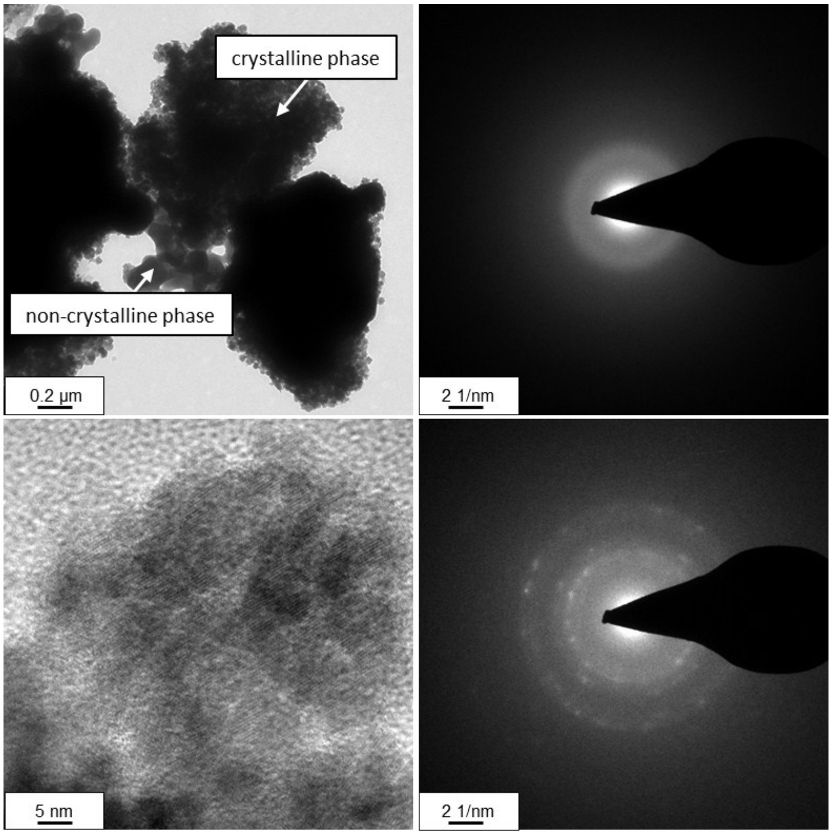


**Fig. S11**. HRTEM images and corresponding diffraction pattern of CoO after chronoamperometric studies at constant potential of 1.55 V vs. RHE for 24 h in 1 M KOH solution. The reflections from the electron diffraction pattern indicate the formation of $Co(OH)_2$ and/or CoOOH.

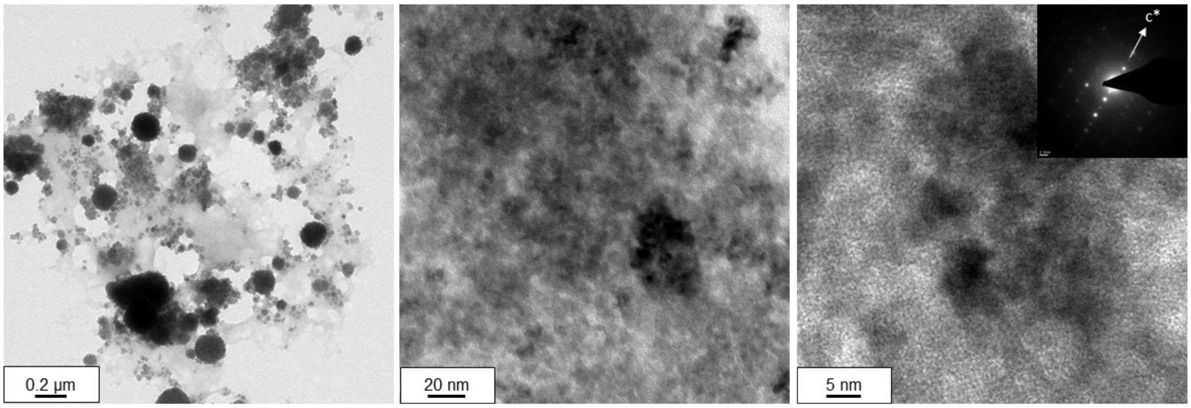


**Fig. S12**. HRTEM images and corresponding diffraction pattern of $CoO_x$ after chronoamperometric studies at constant potential of 1.55 V vs. RHE for 24 h in 1 M KOH solution. The reflections from the electron diffraction pattern (inset) indicate the formation of $Co(OH)_2$ and/or CoOOH.

**Table S1**. Comparison of the catalytic activities of CoO and $CoO_x$ with literature reported transition metal oxide catalysts.

| Catalyst | Electrolyte solution | Current density (mA cm$^{-2}$) | Overpotential at (mV) | Reference |
|---|---|---|---|---|
| $Co_3O_4$/Ni nanofoam | 1 M KOH | 10 | 328 | S2 |
| $Co_3O_4$ | 1 M KOH | 0.5 | 314 | S3 |
| $Co_3O_4$ | 1 M KOH | 13.5 | 507 | S4 |
| $Co_3O_4$ nanochain | 0.1 M KOH | 0.5 | 320 | S5 |
| NiO | 0.5 M KOH | 1 | 280 | S6 |
| Electrodeposited $CoO_x$ | 0.1 M borate buffer | 1 | ~ 400 | S7 |
| $LiCoO_2$ | 1 M KOH | 10 | 420 | S8 |
| $SrCoO_{3-\delta}$ | 0.1 M KOH | 10 | 410 | S9 |
| $Co_3O_4$ nano island | 1 M NaOH | 10 | 376 | S10 |
| $CoO_x$ on Ti | 1 M KOH | 5 | 370 | S11 |
| Co-P/Cu | 1 M KOH | 10 | 345 | S12 |
| NiCo/NS | 1 M KOH | 10 | 334 | S13 |
| NiCo LDH | 1 M KOH | 10 | 367 | S14 |
| $Ni_xCo_{3-x}O_4$ NWs/Ti | 1 M KOH | 10 | 370 | S15 |
| $Co_3O_4$/ $NiCo_2O_4$ DSNCs | 1 M KOH | 10 | 340 | S11 |
| CoP/Cu | 1 M KOH | 10 | 345 | S12 |
| CoCo LDH | 1 M KOH | 10 | 393 | S16 |
| N-G/CoO | 1 M KOH | 10 | 340 | S17 |
| $Co_3O_4$/N-rmGO | 1 M KOH | 10 | 310 | S18 |
| $CoFeO_x$ | 1 M KOH | 10 | 360 | S19 |

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