Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Topotactic Transition of α-$Co(OH)_2$ to β-$Co(OH)_2$ Anchored on CoO Nanoparticles During Electrochemical water Oxidation : Synergistic Electrocatalytic Effects

SumanaKundu,[a,b]#* Bibhudatta Malik,[a]# Amrutha Prabhakaran,[a] Deepak K. Pattanayak,[a,b]* and Vijayamohanan K. Pillai[a,b]*

[a] CSIR-Central Electrochemical Research Institute, Karaikudi, Tamilnadu, 630006, India.

[b] Academy of Scientific & Innovative Research, Chennai, Tamilnadu, 600113, India

Email : vijay@cecri.res.in

deepak@cecri.res.in

kundusumana@yahoo.com

 # equal authorship

Experimental Section:

Chemicals:

Cobalt acetate tetrahydrate ($Co(CH_3COO)_2.\ 4H_2O$), Hexamethylenetetramine (HMT) and urea were used from Sigma Aldrich while Sodium dodecyl sulfate (SDS) was bought from the STREM chemicals. And the milli Q water of (18 Ω) has been used in the whole experiment. All the purchased chemicals were analytical grade and have been used without further purification.

Material synthesis:

One step Synthesis of $Co(OH)_2$ @ CoO :

In a typical synthesis of α-$Co(OH)_2$ @ CoO, 0.5 g of $Co(CH_3COO)_2.4H_2O$ and 0.15 g of SDS were mixed with 15 mL of de-ionized (DI) water and 15 mL of ethanol and ultrasonicated for 10 minutes. Then 1 g urea was added to this solution under constant stiring for 15 m to get a clear pink colored solution. Finally the entire mixture was transferred to a Teflon-lined stainless steel vessel and heated upto 16 hours at 150^o C in an electric oven. Subsequently, the products were washed several times with DI water and ethanol and finally dried in a vacuum oven at 80^o C for 12 hours. This dried pink coloured solid was characterized by various techniques and studied for electrochemical measurements.

Synthesis of $Co(OH)_2$:

For synthesizing $Co(OH)_2$, 0.1 g of Cobalt acetate tetrahydrate and HMT was thoroughly mixed with 25 mL of DI water and ethanol (1:1) using a stirrer and subsequently 2 mL of 0.1 M NaOH was added to the solution under stirring then the whole solution transferred to a 50 mL hydrothermal vessel and heated at 180^{o}C for 20 hours and brought down to the room temperature. This was finally

washed several times with water followed by ethanol and dried at 80°C for 12 hours. This product was confirmed as β-$Co(OH)_2$ through powder XRD.

Materials Characterization:

High Resolution Transmission electron microscopy (HRTEM) of α-$Co(OH)_2$ -CoO was carried out using a Make-FEI TEM (Model-TECNAI G^2 20, Voltage-200 kV, Wave length- 0.0024 nm) while Powder XRD (PXRD) was done using a powder X-ray Diffractometer by Bruker with Al K_α (1.54 Å) X-ray. X-ray Photoelectron Spectroscopy was carried out in ESCALAB of Al K_α and Mg K_α as the X-ray source.

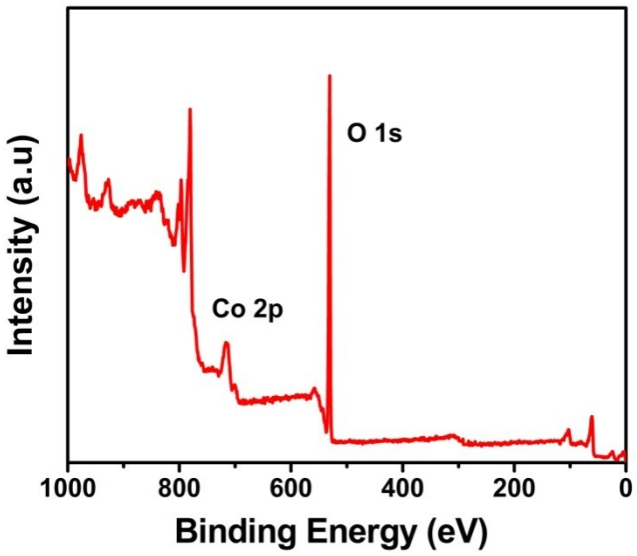

Figure S1: XPS (survey spectrum) of α-$Co(OH)_2$ - CoO

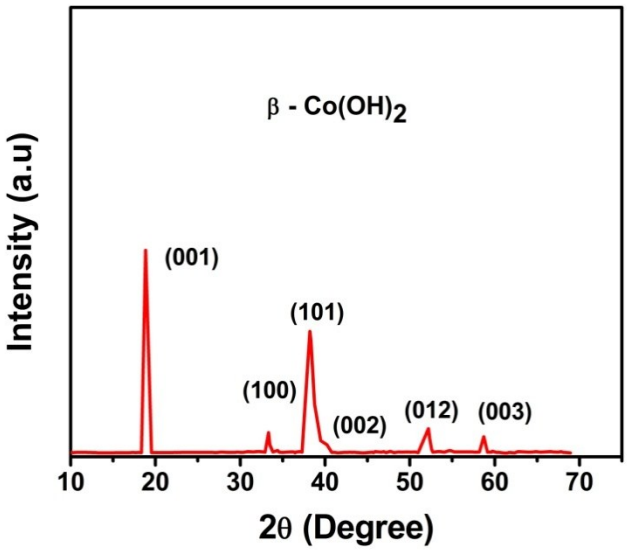

Figure S2: Powder XRD pattern of β-$Co(OH)_2$

Electrochemical Characterization:

For the preparation of the catalyst ink, 3 mg of the material was dispersed ultrasonically for 30 minutes in a mixture of 750 µl of DI H_2O, 250 µl of isopropanol and 30 µl of 5% nafion. After homogenization, 10 µl of this ink was drop-casted on the Glassy carbon electrode (GCE) of 0.196 cm^2 area.

Electrochemical experiments were performed using an Autolab PGSTAT302N electrochemical work station with the help of a three electrode system having a GCE (0.196 cm^2), mercury/mercuric oxide (Hg/HgO) and Pt foil electrodes as the working, reference and counter electrodes respectively.The potential scale was converted according to the reversible hydrogen electrode (RHE). All the LSV, chrono-amperometric and impedance measurements were carried out in a O_2 saturated 1M KOH. LSV of the material and standard were recorded at 2 mV/s and the polarization plots were iR corrected. Before recording

the data, the material as well standards ($Co(OH)_2$ and RuO_2) were subjected to 20 CV cycles at 10 mV/s in order to attain stability of the current-voltage curve. The EIS was performed at (1 Hz-100 KHz) using an amplitude of 10 mV.

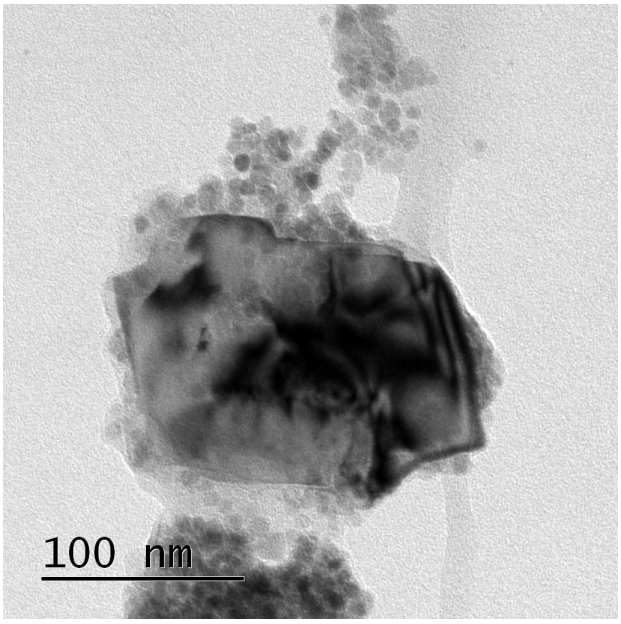

Figure S3: TEM image of post OER treated (after longterm cycling) β-$Co(OH)_2$-CoO showing the slight stacking of sheets with visible wrinkles on it and particle morphology.

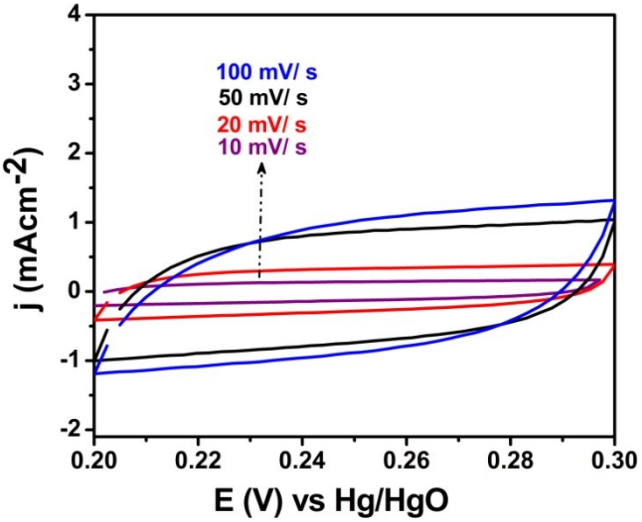

Figure S4: Cyclic voltammograms at different scan rates for the estimation of electrochemical active surface area (ECSA) for β-$Co(OH)_2$