Supporting Information

Synthesis of ultrasmall and monodisperse sulfur nanoparticles intercalated CoAl layered double hydroxide and their electrocatalytic water oxidation reaction at neutral pH

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Experimental Section

Materials: Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), urea (CON_2H_4), sodium chloride (NaCl) sodium thiosulphate ($Na_2S_2O_3$), Phosphoric acid (H_3PO_4) and sodium perchlorates ($NaClO_4$) were purchased from Sigma-Aldrich. Polyvinyl pyrrolidone K_{90} (PVP), sodium hydroxide (NaOH) and hydrochloric acid (HCl) was obtained from SD Fine-Chem Limited. All the chemicals were analytical reagent grade. Ethanol was purchased from Sisco Research Laboratories (SRL) pvt. Ltd. India. Aqueous solution of phosphoric acid (H_3PO_4) and sodium perchlorates ($NaClO_4$) with 1:1 molar concentration were mixed to prepare an aliquot of 0.1 M phosphate buffer saline (PBS) and maintain the solution pH at 7.0 by the dropwise addition of aqueous NaOH. De-ionized water was used in all the experimental processes.

Preparation of CoAl-(CO_3^{2-}) LDH: Two dimensional CoAl-(CO_3^{2-}) LDH was synthesized by urea hydrolysis method of mixing of 3:1 molar ratio of bivalent and trivalent metal ions as a reported procedure.[1] In this reaction, $Co(NO_3)_2.6H_2O$ (0.43 g, 2.25 mmol), $Al(NO_3)_3.9H_2O$ (0.28 g, 0.75 mmol) and urea (0.315 g, 5.25 mmol) was dissolved in 150 mL deionized water and the resulting mixture was heated at 97 ^oC for 48 h. The pH of the reaction mixture was changed from 6.0 to 7.5. The pink product obtained was centrifuged and washed with distilled water and anhydrous ethanol for several times. Finally, the product was kept in a desiccator dried under reduced pressure at room temperature.

Decarbonation of CoAl-(CO_3^{2-}) LDH by Cl^- ion: The chloride ions intercalated CoAl-(Cl^-) LDH was prepared by anion exchange method. The de-intercalation of (CO_3^{2-}) ions from the as prepared CoAl-(CO_3^{2-}) LDH was carried out by treating it with a salt–acid mixed solution.[1] In a typical reaction, 0.15 g of the CoAl-(CO_3^{2-}) LDH sample was dispersed into 150 mL of an aqueous solution containing 1 M NaCl and 3.3 mM HCl and the resulting mixture was stirred for 12 h under nitrogen atmosphere at room temperature. The anion exchanged product washed with decarbonated water and anhydrous ethanol several times, and finally dried at room temperature.

Preparation of $S_2O_3^{2-}$ intercalated CoAl-LDH: The ($S_2O_3^{2-}$) intercalated CoAl-LDH was prepared through anion exchange method using CoAl-(Cl^-) LDH as precursors. In a typical procedure, 0.3 g of Co-Al Cl^- LDH was dispersed into 50 mL deionized water and 0.6 g of $Na_2S_2O_3$ was added to it. The resulting mixture was stirred for 48 h under nitrogen atmosphere at room temperature. The exchanged product was washed with distilled water and dry ethanol for several times and then dried at 65 ^0C in a hot air oven.

Preparation of S-NPs intercalated CoAl-(S-NPs)LDH: S-NPs deposited CoAl-(S-NPs) LDH was prepared by disproportionation method by treatment of CoAl ($S_2O_3^{2-}$) LDH with dilute HCl. In this reaction, 300 mg of Co-Al ($S_2O_3^{2-}$) LDH was taken in 10 mL of deionised water and 0.002 g of polyvinyl pyrrolidone K_{90} was added to it. 0.1 mL of concentrate HCl was added into the reaction mixture and stirred for 4 hours at room temperature. The CoAl-(S-NPs) LDH thus prepared was washed with deionised water three times and dried at room temperature.

Characterization techniques: The microscopic morphology were examined using a JEOL JEM-2100 transmission electron microscope (TEM) operated at an accelerating voltage of 200 kV. Energy dispersive X-ray (EDX) analysis was carried out using INCA Energy TEM 200 with X-ray detector. Powder X-ray diffraction (XRD) spectra were measured using a Bruker- D8 Advance X-ray diffractometer operating at a voltage of 40 kV and a current of 40 mA with Ni-filtered Cu K_α radiation ($\lambda = 1.5406 Å$). The data were collected in a 2θ range of 5^o–80^o at a scan rate of 3^o min^{-1} with a step size of 0.05^o. Fourier transform infrared (FTIR) spectra were recorded using a Perkin-Elmer L 120-000A spectrometer over the wavenumber range of 400–4000 cm^{-1} using the KBr disc method. Thermo-gravimetric analysis (TGA) was done using PerkinElmer STA 6000 thermal analyzer and the data were recorded in the temperature range of 30–770 ^oC with a N_2 flow rate of 20 mL/min and heating rate of 20 ^oC/min. X-ray photoelectron spectroscopy (XPS) measurement was performed by using PHI 5000 VersaProbe III spectrophotometer. Nitrogen (N_2) adsorption-desorption isotherms and pore size distribution were measured at 77 K using QUANTACHROME, NOVA 1000E specific surface area and pore size analyzer. The surface morphology and particle distribution of the material was observed by using JEOL, JSM 6390LV scanning electron microscope (SEM).

Electrochemical Tests: The electrocatalytic activity of as-synthesized materials for water oxidation reaction (WOR) were evaluated by performing electrochemical tests using three electrode glass cell systems controlled by a CHI-660C electrochemical workstation. A Pt wire was used as the auxiliary electrode and Ag/AgCl electrode (in 3.0 M KCl) as reference electrode. All the potential values referenced to RHE (Reversible hydrogen electrode) were calculated based on the equation, $E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + E^o_{Ag/AgCl}$, where $E^o_{Ag/AgCl} = 0.210$ at 25 ^oC. For all electrochemical studies, the CoAl-(S-NPs) LDH hybrids deposited glassy carbon (GC) was used as working electrode (electrode area 0.07 cm^2) in 0.1 M phosphate buffer solution (PBS) at pH 7.0. To prepare the CoAl-(S-NPs) LDH hybrids deposited GC electrode, the hybrid materials were dispersed in distilled water and drop casted on the surface of GC electrode and dried at room temperature under reduced pressure. The phosphate buffer saline (PBS) was prepared by mixing of equimolar quantity of aqueous solution of phosphoric acid and sodium perchlorate. The WOR activities of CoAl-(S-NPs) LDH hybrids were evaluated by linear sweep voltammetry (LSV) using GC and modified GC electrodes with a sweep rate of 100 mVs^{-1} in 0.1 M PBS at pH 7.0. Electrochemical impedance spectroscopy (EIS) was also performed in 0.1M

PBS at pH 7.0 (1.46 V vs RHE) using different electrode systems where the frequency range was 0.01 Hz to 100000 Hz and E_{ac}= 10 mV. The durability tests for the catalytic WORs were performed by chronoamperometry at applied potentials of 1.46 V vs RHE obtained the steady state current density of 8.0 mA cm^{-2} for 30 mins. During WOR catalysis, the generated oxygen was measured by using a calibrated Ocean Optics FOXY probe at a fixed potential. Faradaic efficiency (FE) was calculated using the following formula:

FE= (Amount of O_2 produced × number of electrons needed to produce O_2) /(Charge passed through the solution).

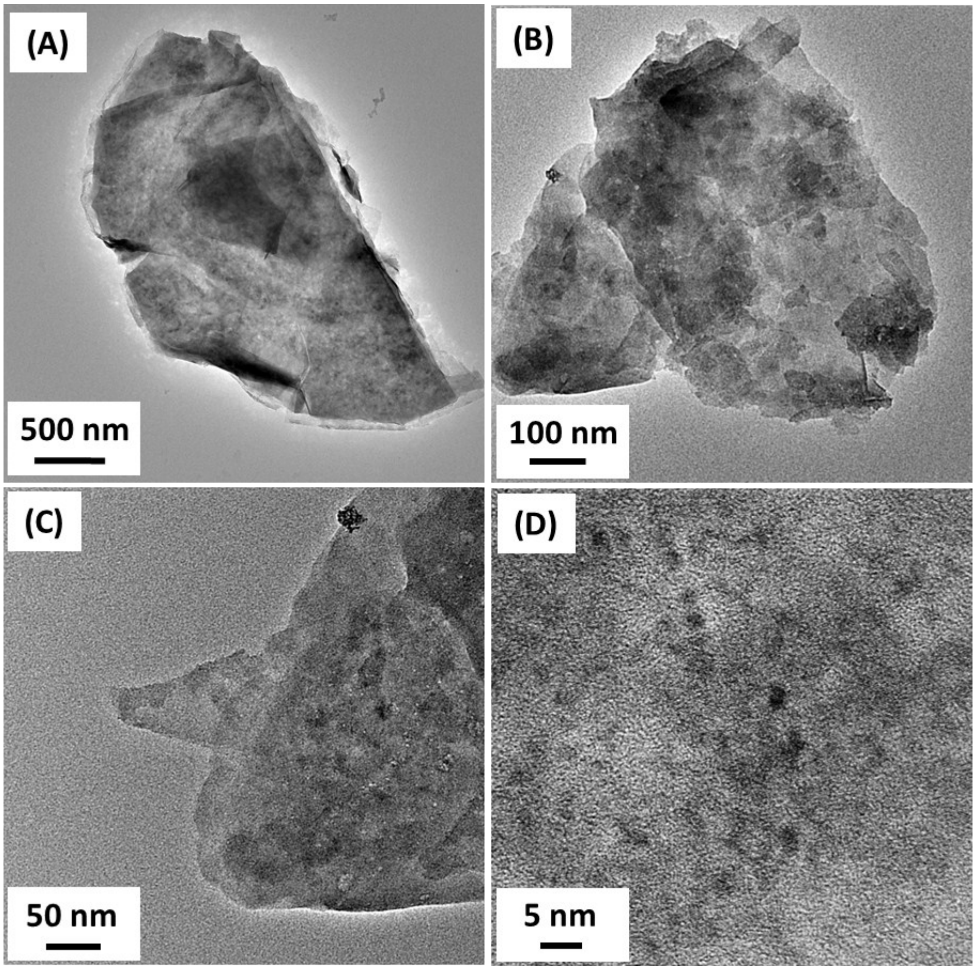

Fig. S1 Representative TEM images of CoAl-(S-NPs) LDH at different magnifications show irregular morphology of LDH sheets and dark spots indicates deposited S-NPs.

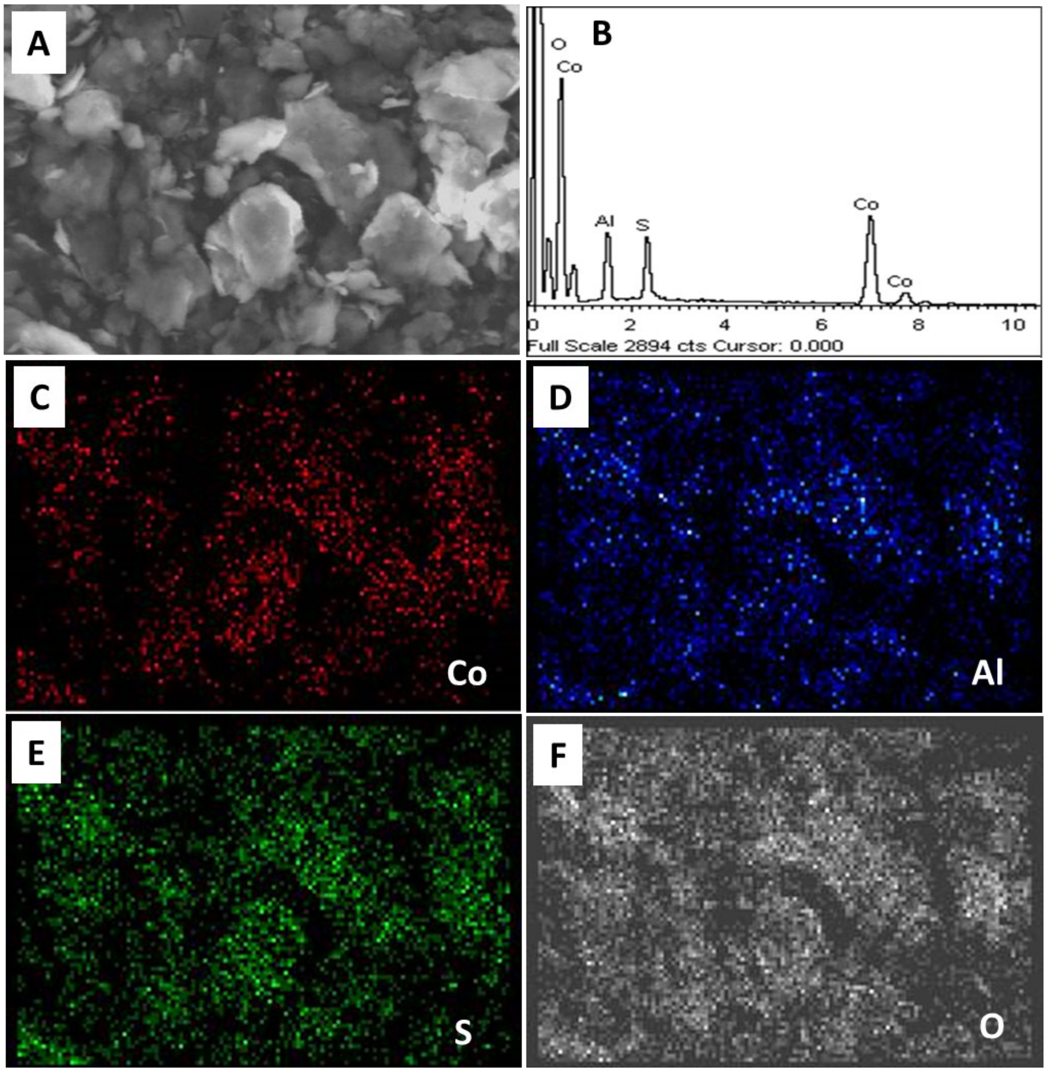

Fig. S2 (A) Scanning electron microscopy (SEM) image, (B) energy dispersive X-ray spectrum (EDX) and (C-F) corresponding elemental mapping images of Co, Al, S and O atoms present in CoAl-(S-NPs) LDH.

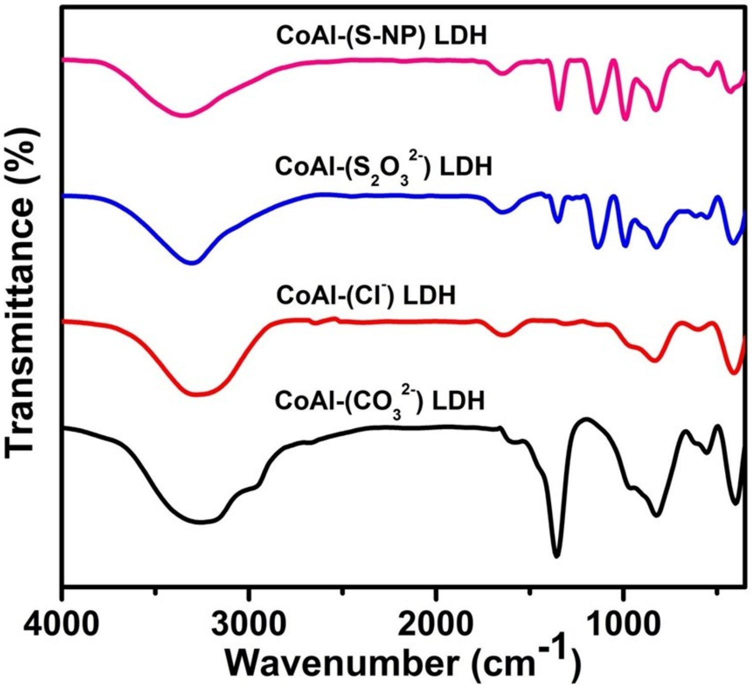

Fig. S3 FTIR spectra of CoAl-(CO_3^{2-}) LDH, CoAl-(Cl^-) LDH, CoAl-($S_2O_3^{2-}$) LDH and CoAl-(S-NPs) LDH.

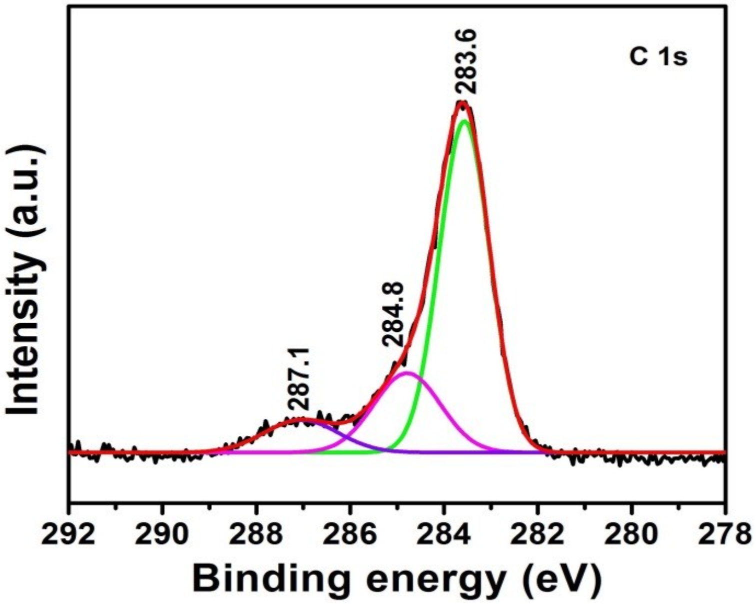

Fig. S4 XPS spectrum of C 1s of the CoAl-(S-NPs) LDH.

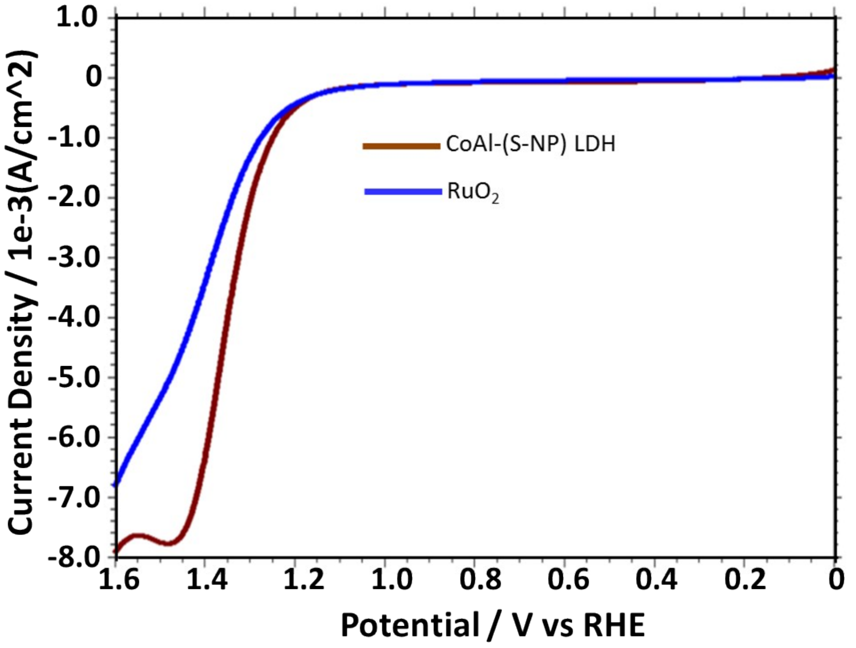

Fig. S5 LSVcurve in 0.1 M PBS using CoAl-(S-NPs) LDH and commercially available RuO_2 modified GC electrodes at pH 7.0

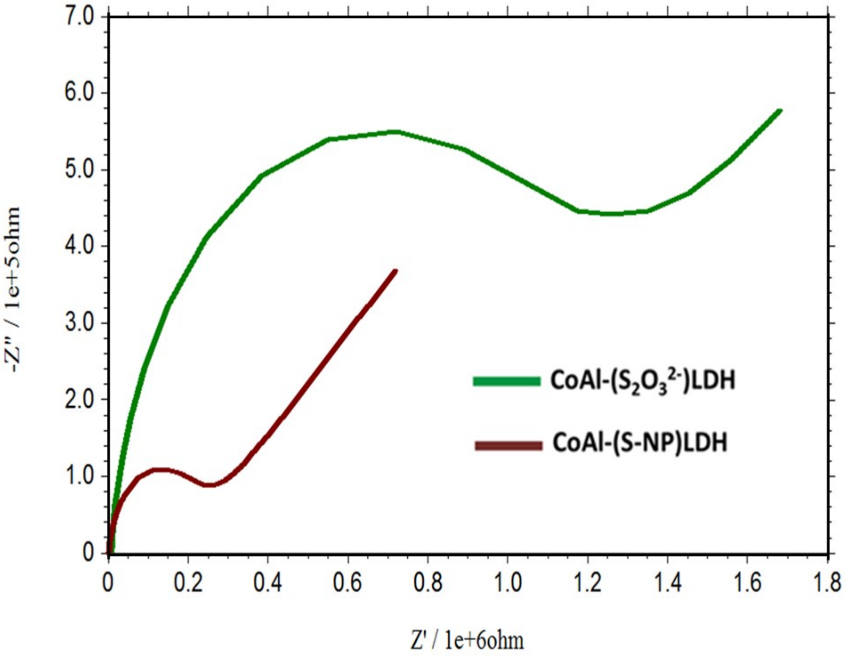

Fig. S6 Overlaid Nyquist plot obtained at $CoAl(S_2O_3^{2-})$ LDH and CoAl-(S-NPs) LDH modified GC Electrodes in 0.1 M PBS at pH 7.0.

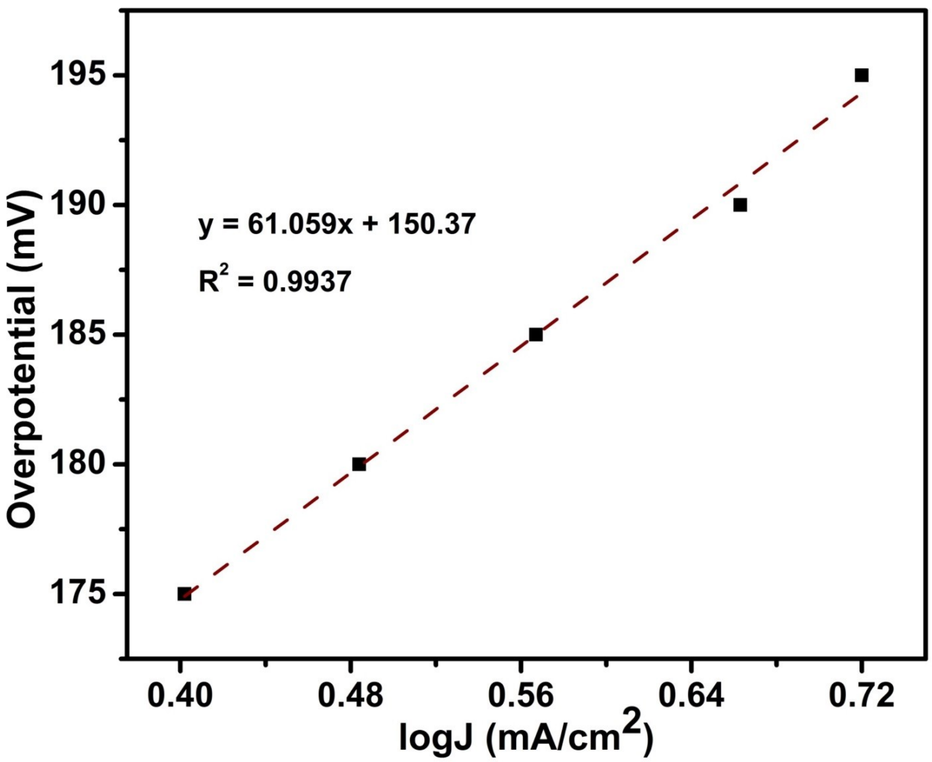

Fig. S7 Tafel plot obtained for CoAl-(S-NPs) LDH-GC electrode in 0.1 M PBS at pH 7.0.

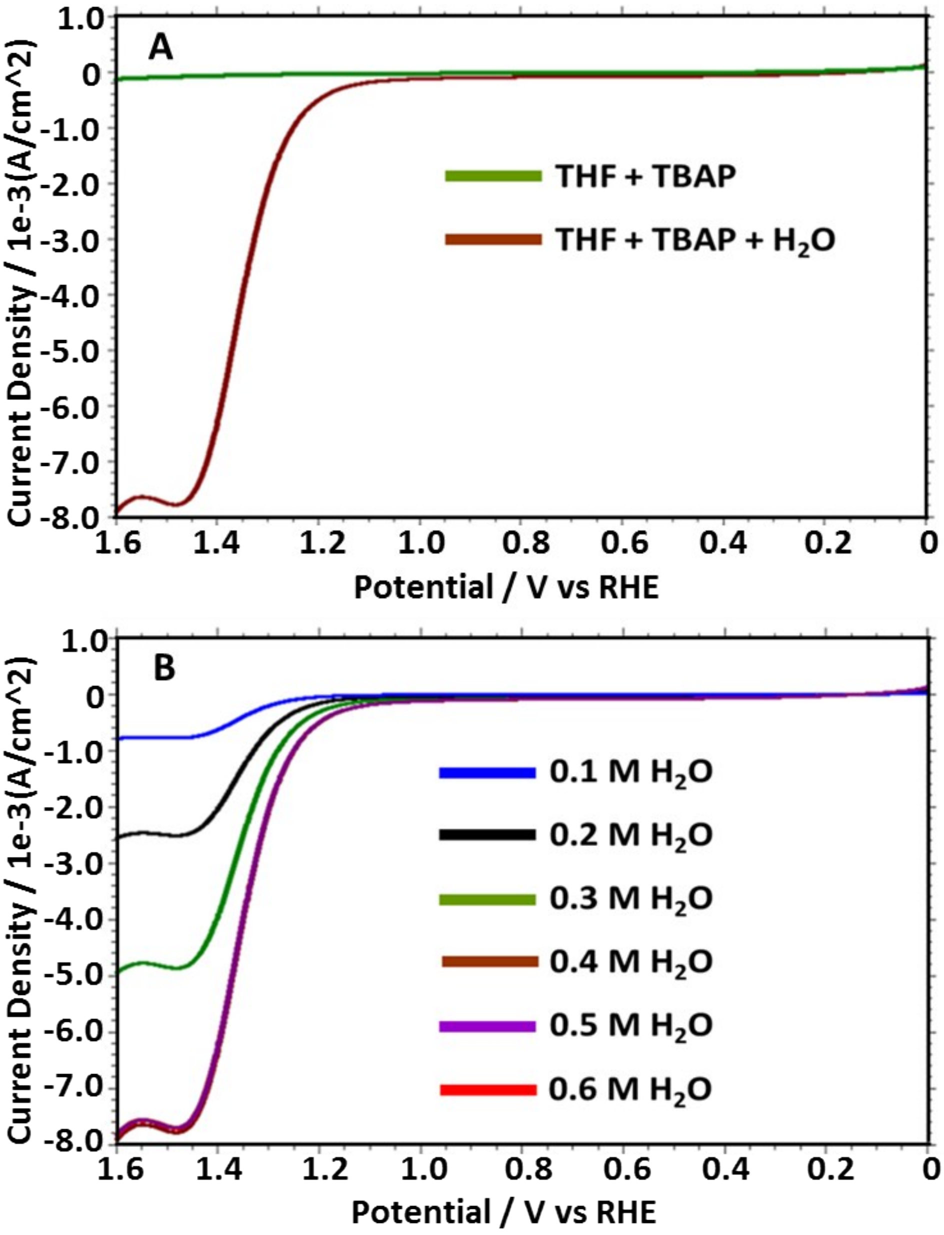

Fig. S8 LSV in absence and presence of H_2O in dry THF (A) and LSV plot with increasing concentration of water (0.1 -0.5 M) (B), using CoAl-(S-NPs) LDH-GC electrode.

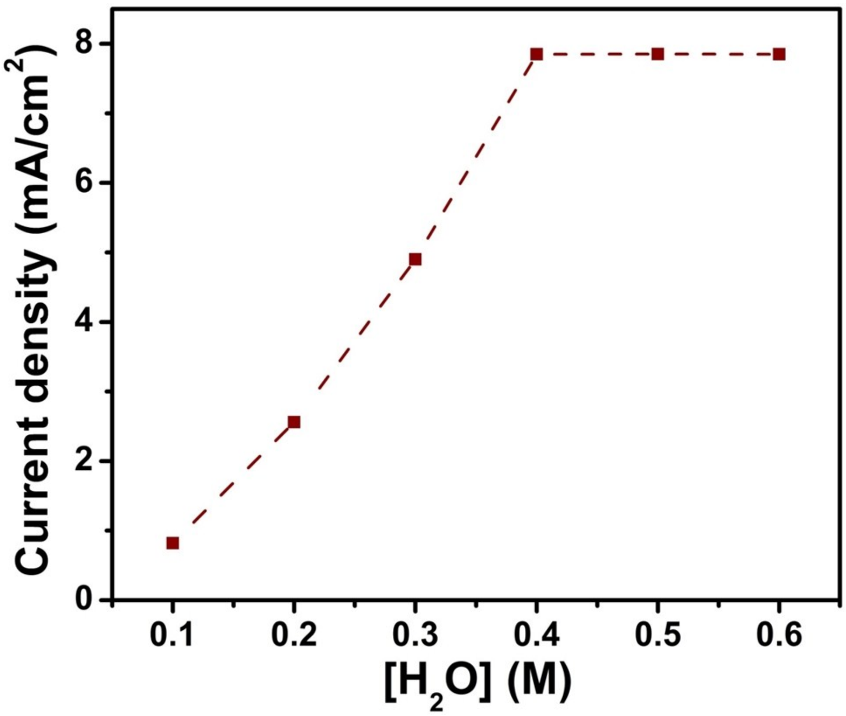

Fig. S9 A plot of anodic current (mAcm^{-2}) density *versus* [H_2O].

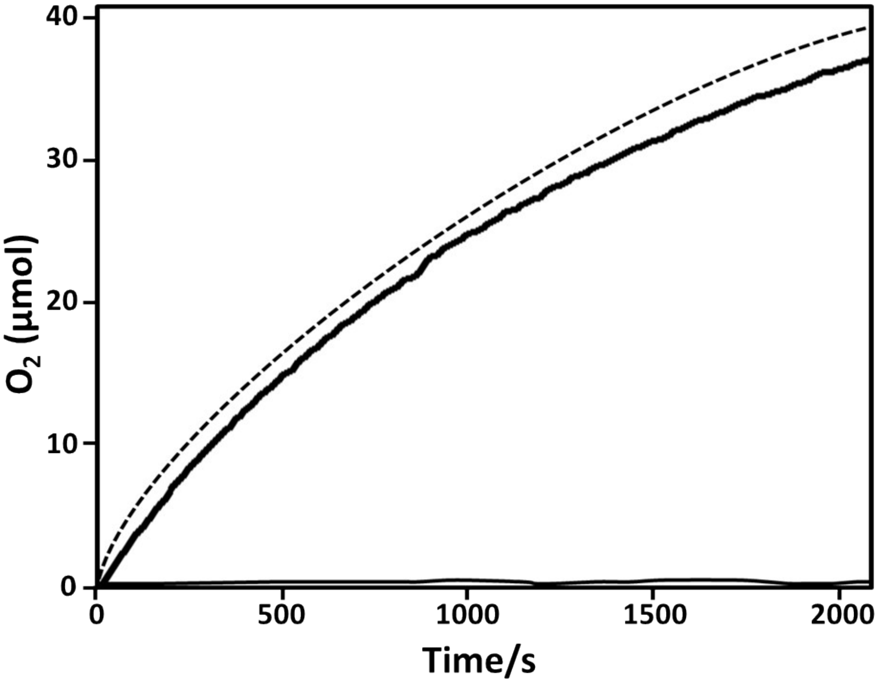

Fig. S10 Oxygen evolution recorded during controlled potential electrolysis at 1.45 V (vs RHE) using CoAl-(S-NPs) LDH modified (a) and bare (b) GC electrode in 0.1 M PBS at pH 7.0. Dotted line shows 100% efficiency.

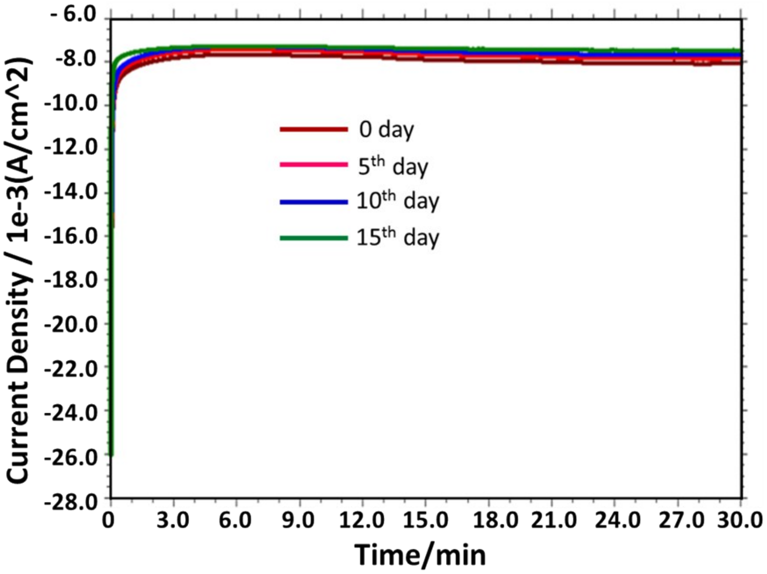

Fig. S11 Chronoamperogram obtained in 0.1 M PBS (pH 7.0) using CoAl-(S-NPs) LDH modified GC electrode at different intervals of time.

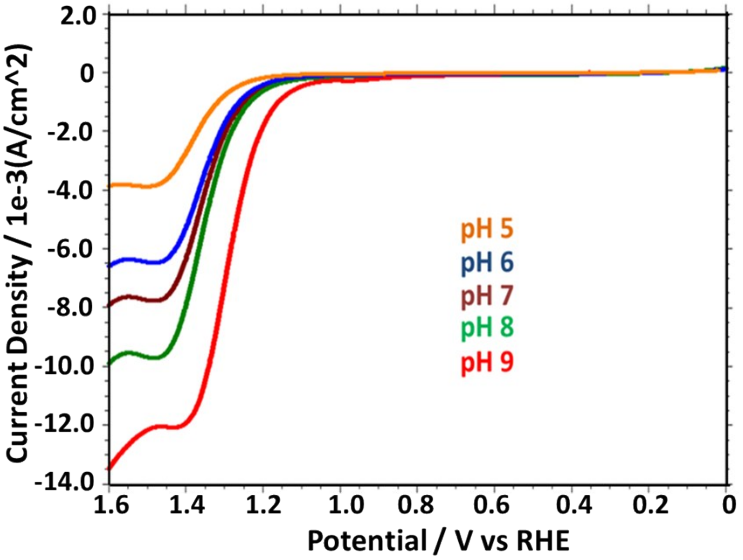

Fig. S12 Overlaid LSV obtained in 0.1 M PBS using CoAl-(S-NPs) LDH modified GC electrodes at different pH.

Reference

1. Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, and T. Sasaki, *J. Am. Chem. Soc.*, 2006, **128**, 4872-4880.