Electronic Supplementary Information

Holey cobalt oxyhydroxides nanosheets towards oxygen evolution reaction†

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Experimental section

Reagents and chemicals. Ethylenediamine tetraacetic acid disodium salt (Na_2EDTA), hydrogen peroxide (H_2O_2, 30%), and cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Sodium hydroxide (NaOH, 97%) and potassium hydroxide (KOH, 85%) were provided by Alfa Aesar (China). Commercial RuO_2 nanoparticles (RuO_2 CNPs) were obtained from Aladdin Industrial Corporation.

Synthesis of CoOOH HNSs. CoOOH HNSs were synthesized by a simple coordination-oxidation-hydrolysis method. In a typical procedure, 20 mL aqueous solution of the mixture $CoCl_2$ (0.2 mmol) and Na_2EDTA (0.2 mmol) were stirred for 10 min at room temperature. Then NaOH solution (5 M) was added into the above solution until pH 13. The color of the solution changed from pink to purple. Next, H_2O_2 (30 μL 30%) was added dropwise and the color of the solution becomes blue. After continually stirring for 10 hours at room temperature, the dark brown precipitate can be clearly seen with the vanish of the blue color of the solution. The precipitates were collected by centrifugation and washed with water until pH 7. Finally, it was dried in a vacuum at 60 ℃. For comparison, CoOOH INPs were synthesized without Na_2EDTA.

Synthesis of CoOOH INPs. In a typical procedure, 30 μL H_2O_2 was added into 20 mL $CoCl_2$ (0.2 mmol) aqueous solution. Then pH of the solution was adjusted to 13 by NaOH. After continually stirring for 1 hour at room temperature, the precipitates were collected by centrifugation and washed with water until pH 7. Finally, it was dried in a vacuum at 60 ℃.

In the preparation process of CoOOH INPs, $Co(OH)_2$ can be oxidized immediately to CoOOH in the presence of H_2O_2, which is similar to the preparation mechanism of CoOOH HNSs.

Physical characterization. The morphology and composition of the samples were characterized by SU-8020 scanning electron microscopy (SEM) equipped with energy

dispersive X-ray spectroscopy (EDX). Transmission electron microscope (TEM) and selected area electron diffraction (SAED) were tested with TECNAI G2 F20 instrument. Powder X-ray diffraction (XRD) pattern was obtained by DX-2700 power X-ray diffractometer using silicon wafer as measuring substrate. X-ray photoelectron spectroscopy (XPS) was conducted on AXIS ULTRA spectrometer. The binding energies achieved in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.5 eV. The atomic force microscope (AFM) was performed on the Dimension Icon instrument. The ASAP 2460 surface area and porosimetry analyzer were used to analyze the specific surface area and pore size distribution of samples. UV-2600 ultraviolet-visible (UV-vis) was used to monitor the interaction between Na_2EDTA and $CoCl_2$ under different conditions.

Electrochemical measurements. Electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), cyclic voltammetry (CV), and chronopotentiometry tests were used on a CHI 660E electrochemical analyzer in 1 M KOH electrolyte saturated with O_2, using a three-electrode system at room temperature. The electrocatalyst modified glassy carbon electrode was used as the working electrode and carbon rod was used as the auxiliary electrode. It should be noted that the saturated calomel electrode (SCE) protected by Luggin capillary with KCI solutions was served as reference electrode. All LSV curves in the electrochemical test were compensated for 95% *iR*. All potentials mentioned in the article correspond to the reversible hydrogen electrode potential (RHE), where $E_{RHE} = E_{SCE} + 0.242\ V + 0.0591\ pH$. The saturated calomel electrode (SCE) is used as the reference electrode, the carbon rod is used as the auxiliary electrode, and the electrocatalyst modified glassy carbon electrode as the working electrode.

Preparation of working electrode. Under strong ultrasonic vibration, 2 mg of catalyst was dispersed into a solution of 800 μL of water, 5 μL of 5 wt% Nafion and 200 μL of isopropyl alcohol. Then 4 μL of the mixed solution was dropped on the surface of the glassy carbon electrode and dried at room temperature for the electrochemical test.

Figure

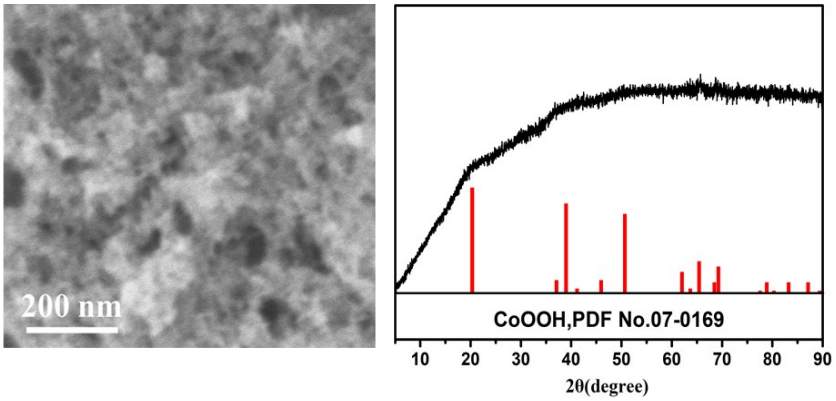

Fig. S1 SEM and XRD of CoOOH INPs

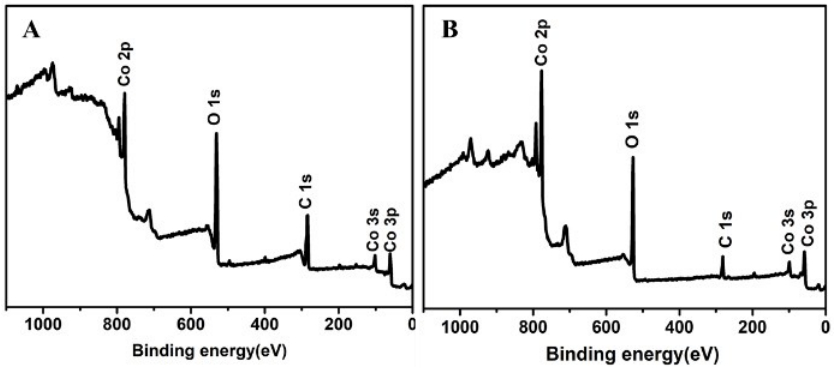

Fig. S2 XPS survey spectra of (A) CoOOH HNSs and (B) CoOOH INPs

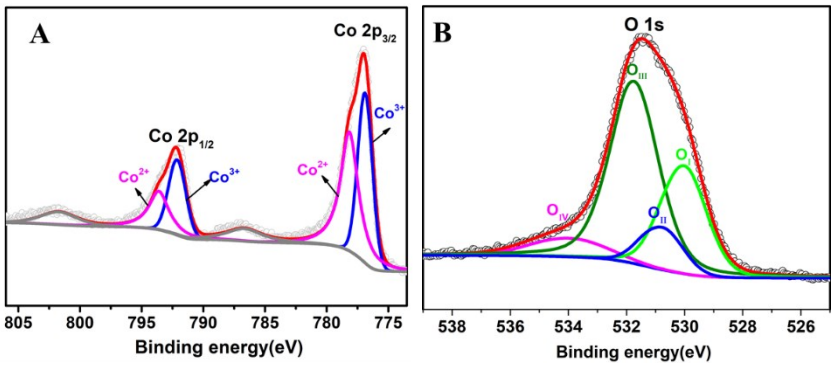

Fig. S3 (A) Co 2p XPS and (B) O 1s XPS spectra of CoOOH INPs.

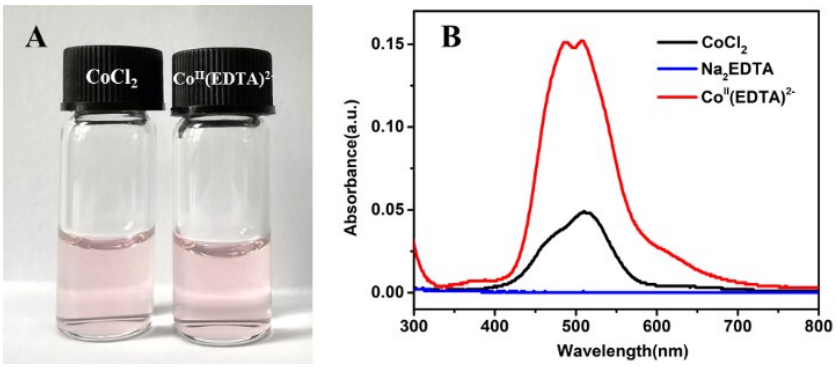

Fig. S4 (A) The photographs of $CoCl_2$ and $Co^{II}(EDTA)^{2-}$ complex aqueous solution at pH=2. (B) UV-Vis spectra of $CoCl_2$, Na_2EDTA, and $Co^{II}(EDTA)^{2-}$ complex aqueous solution.

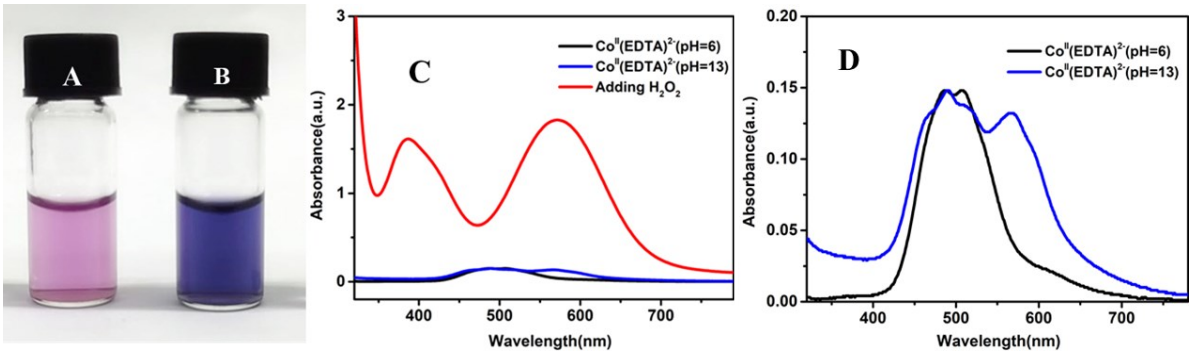

Fig. S5 The photographs of $Co^{II}(EDTA)^{2-}$ complex aqueous solution (A) before and (B) after addition of H_2O_2 at pH=13. (C) UV-Vis spectra of $Co^{II}(EDTA)^{2-}$ complex aqueous solution before and after adding H_2O_2 at pH 13. (D) the enlarged picture of (C).

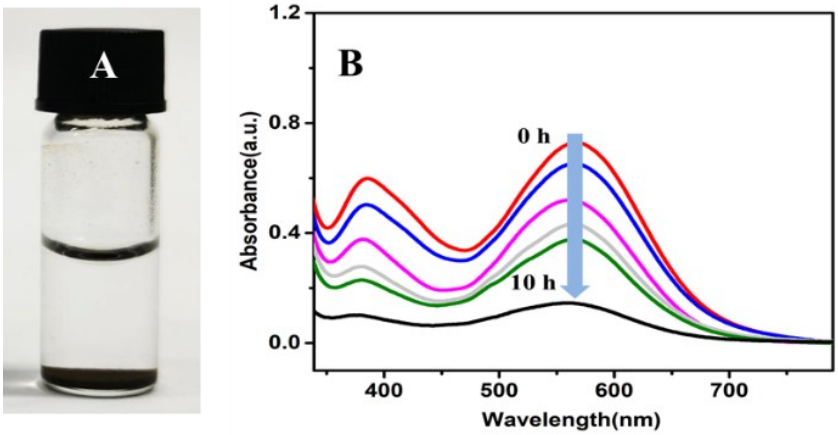

Fig. S6 (A) The photograph of $Co^{II}(EDTA)^{2-}$ complex aqueous solution after adding H_2O_2 for 10 h at pH=13. (B) UV-Vis spectra of $Co^{II}(EDTA)^{2-}$ complex aqueous solution after adding H_2O_2.

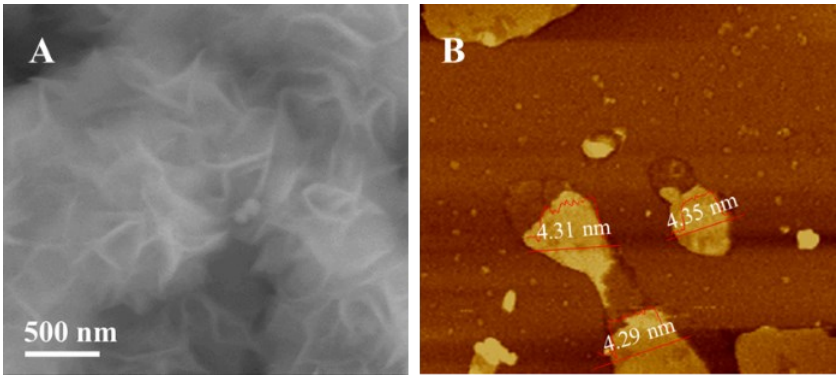

Fig. S7 (A) SEM image and AFM image of obtained CoOOH HNSs after increasing reaction temperature to 90 ºC.

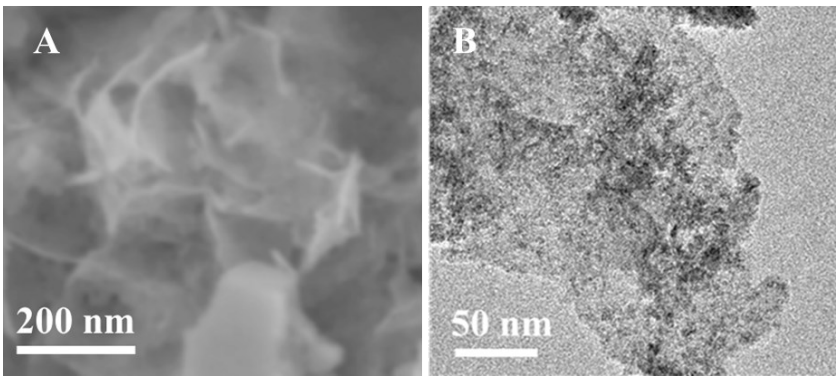

Fig. S8 (A) SEM and (B) TEM image of CoOOH HNSs after durability test.