Exquisite regulated CeO$_2$/Co (OH)$_2$ electrocatalysts for enhanced oxygen evolution reaction

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1. Synthesis methods

1.1 Synthesis of $CeO_2/Co(OH)_2$ powder

A simple chemical disposition method was used to prepare $CeO_2/Co(OH)_2$ catalysts using solution with different pH values. 1.0 g NH_4Cl was dissolved into 200 ml deionized water. The pH value of the solution was adjusted to 8.5, 9, 9.5, 10, 10.5 and 11 by adding 5 mol / L NaOH solution, respectively. 1.0 g $Co(NO_3)_2 \cdot 6H_2O$ and 0.1g $Ce(NO_3)_3 \cdot 6H_2O$ were added into the above solution to gain hydroxide, and then the solution pH value was adjusted by NaOH solution again. Finally, it was precipitated for 24 hours at room temperature statically. Precipitation was achieved after washing the solution three times with deionized water and ethanol. After drying at 70 °C for 12 hours, $CeO_2/Co(OH)_2$ powder was gained by grinding the bulk sample. The samples prepared under different pH values were denoted by 8.5-$CeO_2/Co(OH)_2$, 9-$CeO_2/Co(OH)_2$, 9.5-$CeO_2/Co(OH)_2$, 10-$CeO_2/Co(OH)_2$, 10.5-$CeO_2/Co(OH)_2$ and 11-$CeO_2/Co(OH)_2$, respectively. The preparation process is shown in Fig.1.

1.2 Synthesis of $Co(OH)_2$ powder

The best pH value for preparing $CeO_2/Co(OH)_2$ sample was screened by electrochemical testing. Then, the same method was adopted to prepare $Co(OH)_2$ without Ce salt at this pH value. In brief, 1.0 g NH_4Cl was dissolved into 200 ml deionized water and NaOH solution was added to adjust the solution pH value to 9.5. Then, 1.0 g $Co(NO_3)_2 \cdot 6H_2O$ was added into the above solution to gain hydroxide and then NaOH solution was used to adjust the solution pH value again. Finally, it was precipitated for 24 hours at room temperature statically. Precipitation was achieved after washing the solution three times with deionized water and ethanol. After drying at 70 °C for 12 hours, $Co(OH)_2$ powder was gained by grinding the bulk sample.

1.3 Preparation of the working electrodes

The above prepared $CeO_2/Co(OH)_2$ or $Co(OH)_2$ catalyst (10 mg) was dispersed in 900 μL of ethanol and 100 μL of 5% Nafion, and then sonicated for 30 min. 100 μL catalyst ink was drop-casted on a carbon paper electrode area of 1 cm × 1 cm and dried at 70 °C.

1.4 Electrochemical tests

The OER activities were measured by a CHI 760D electrochemical workstation in a three electrodes method using sample as the working electrode, carbon bar as the counter electrode, and Ag/AgCl electrode as the reference electrode in 1 M KOH electrolytes. The OER activities were measured using the linear sweep voltammetry (LSV) technique. LSV curves were executed at the potential range between 0.3 to 1 V vs Ag/AgCl with a scan rate of 5 mV s^{-1}. Measured potentials were converted and presented as a reversible hydrogen electrode (RHE) by the equation of $E_{(RHE)} = E_{(Ag/AgCl)} + 0.197 \text{ V} + 0.059 \times pH$. And then, the potentials were referenced by iR correction. The overpotential (η) was calculated with the following equation: $\eta = E_{(RHE)} - 1.23 \text{ V}$. The electrochemical impedance spectroscopy (EIS) plots were collected at the potential of 0.5 V with a frequency range from 100 kHz to 0.01 Hz. Electrochemical surface area (ECSA) testing by cyclic voltammetry. Catalyst stability was determined using i-t curves at 20 mA cm^{-2} process potential.
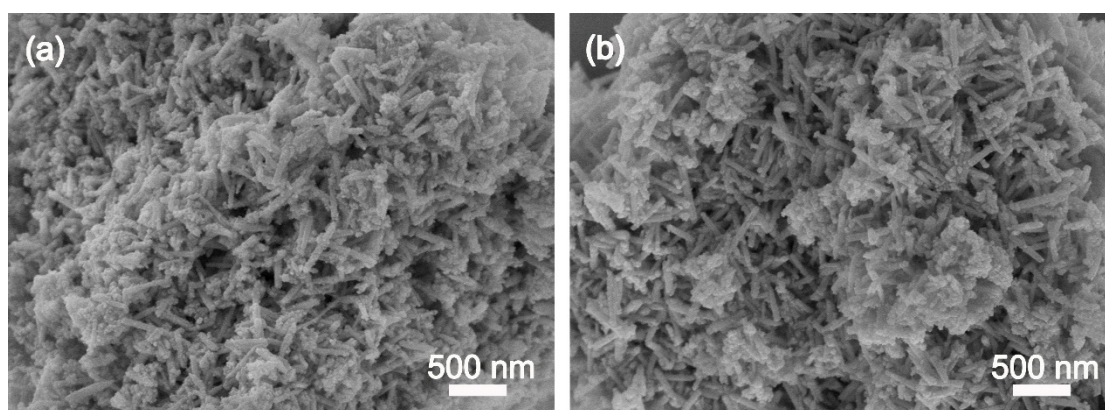

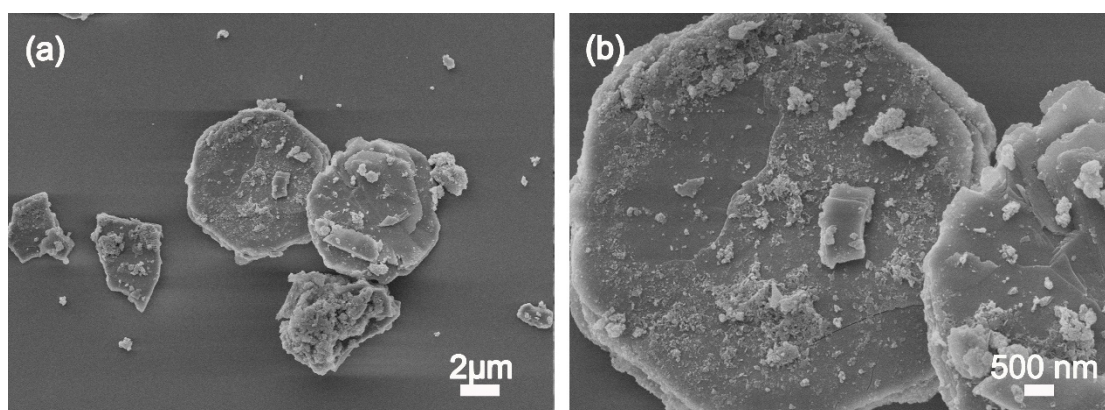Fig. S1. Morphology characterizations of CeO_2

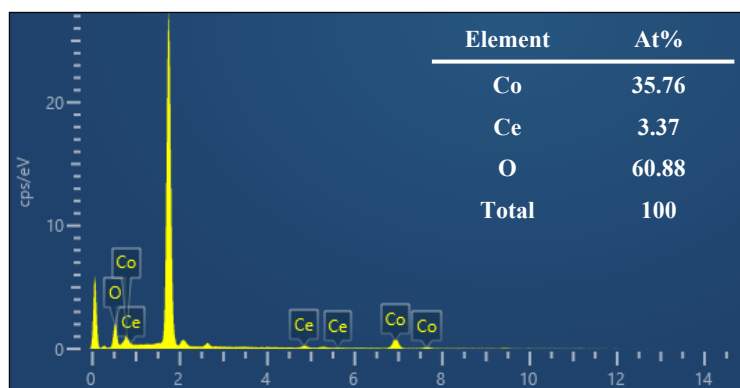Fig. S2. Morphology characterizations of Co $(OH)_2$
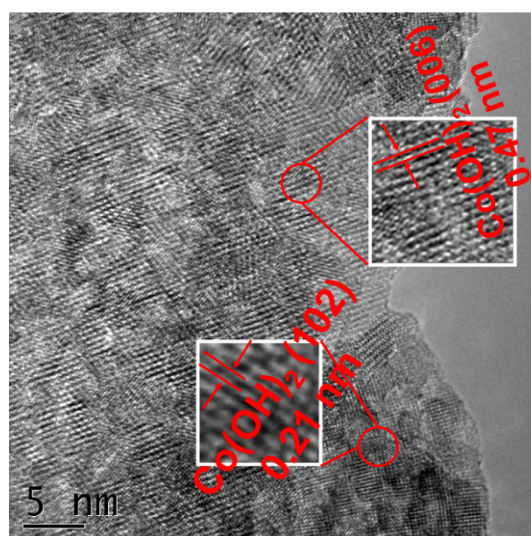
Fig. S3. Element distribution diagram

Fig. S4. Co(OH)$_2$ of TEM images

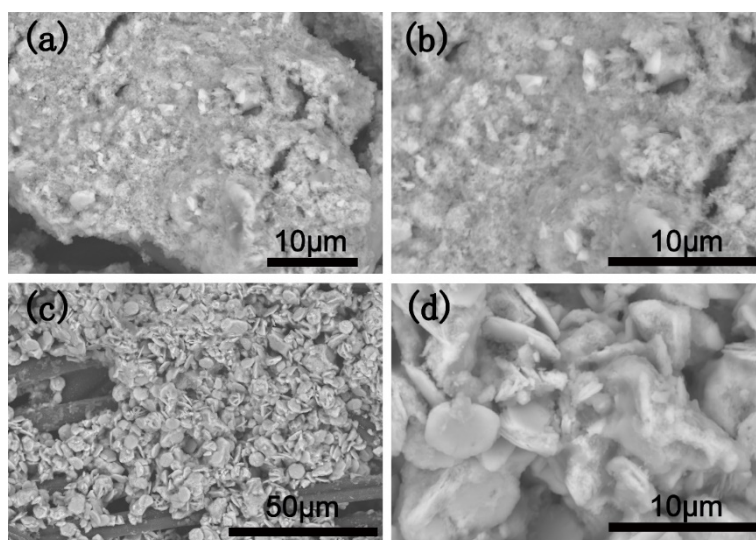
Fig. S5. SEM images of morphology characterizations of samples after accelerated stabilization; a, b) Co(OH)$_2$; c,d) pH-9.5-CeO$_2$/Co(OH)$_2$.
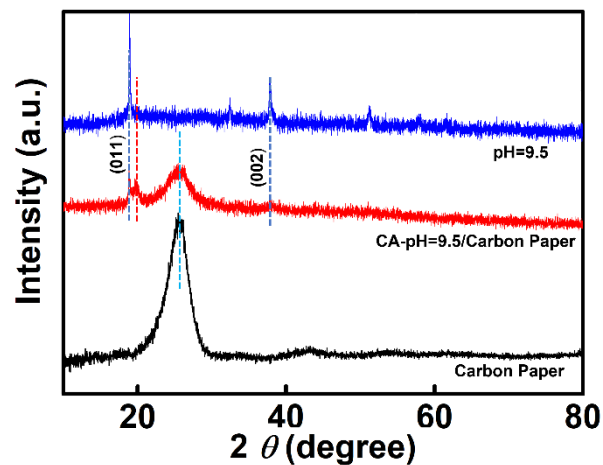
Fig. S6. XRD pattern of samples of 9.5-CeO_2/$Co(OH)_2$, after accelerated stabilization of 9.5-CeO_2/$Co(OH)_2$ in carbon paper; and carbon paper.
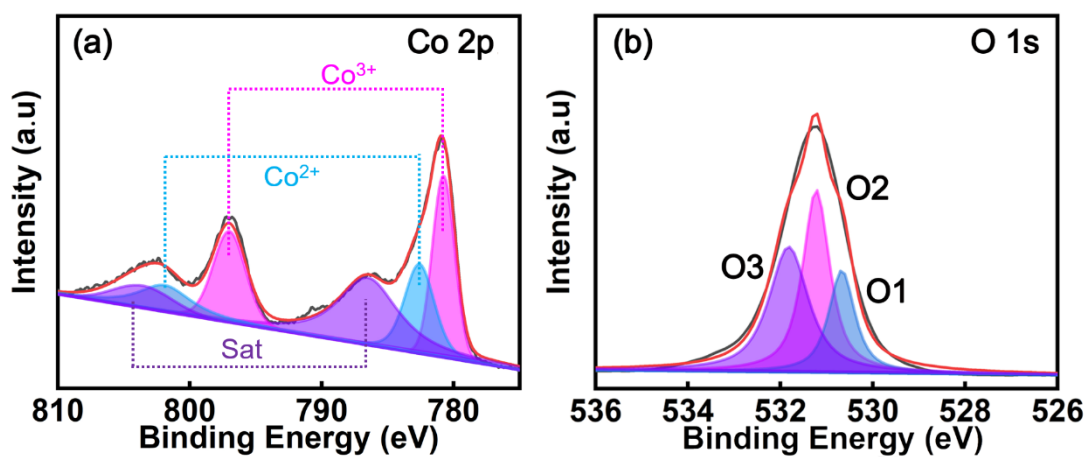

Fig. S7. XPS spectra of the $Co(OH)2$ electrode. High-resolution XPS spectra of a) Co 2p, b) O 1s, respectively.
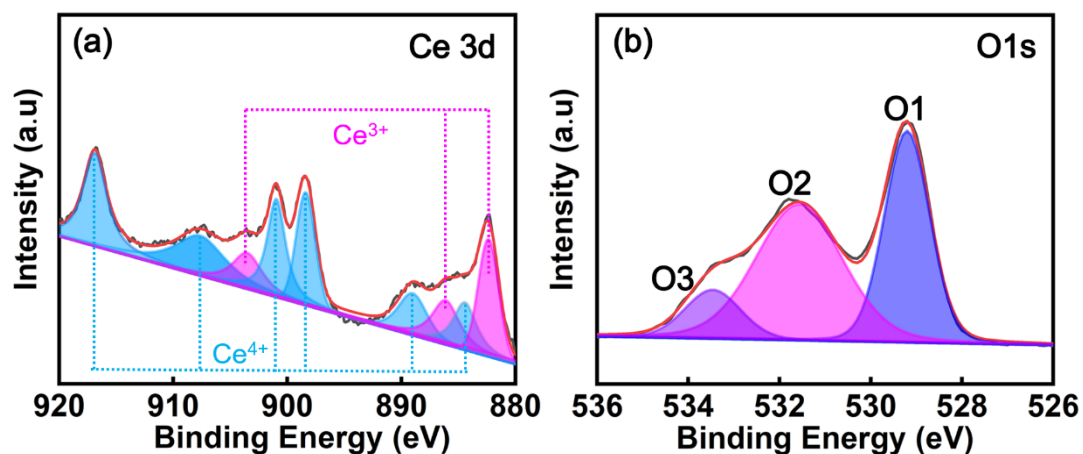

Fig. S8. XPS spectra of the CeO_2 electrode. High-resolution XPS spectra of a) Ce 3d, b) O 1s, respectively.
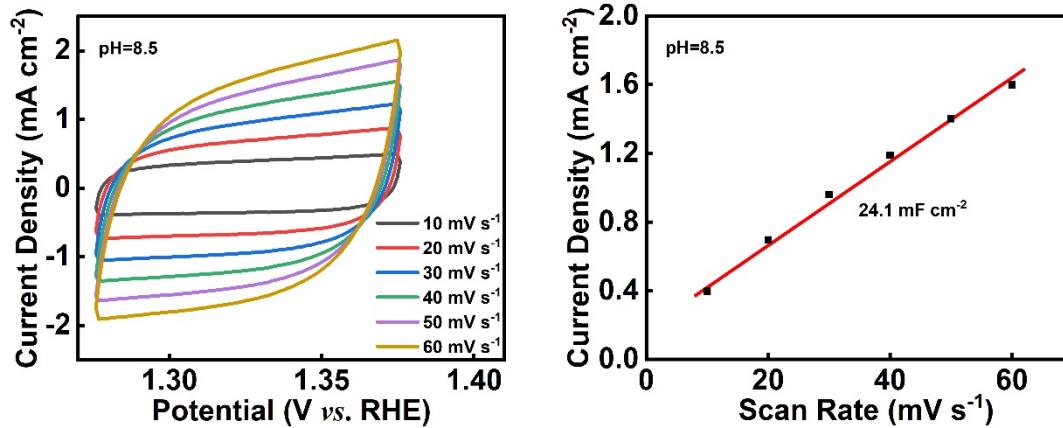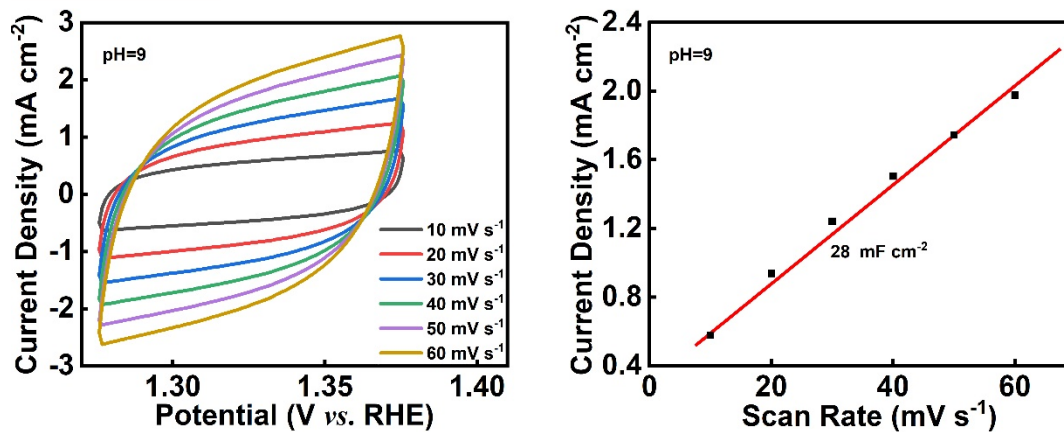
Fig. S9. Electrochemical double-layer capacitance measurements. CVs at different sweeping rates from 10 mV s^{-1} to 60 mV s^{-1} and Cdl value observed from CV plots at different scan rates of 8.5-CeO$_2$-Co (OH)$_2$.
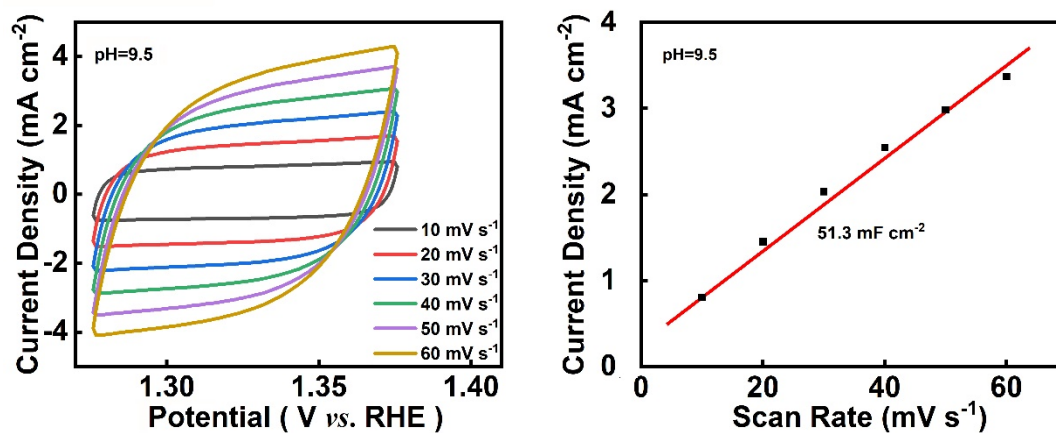

Fig. S10. Electrochemical double-layer capacitance measurements. CVs at different sweeping rates from 10 mV s^{-1} to 60 mV s^{-1} and Cdl value observed from CV plots at different scan rates of 9-CeO$_2$-Co (OH)$_2$.
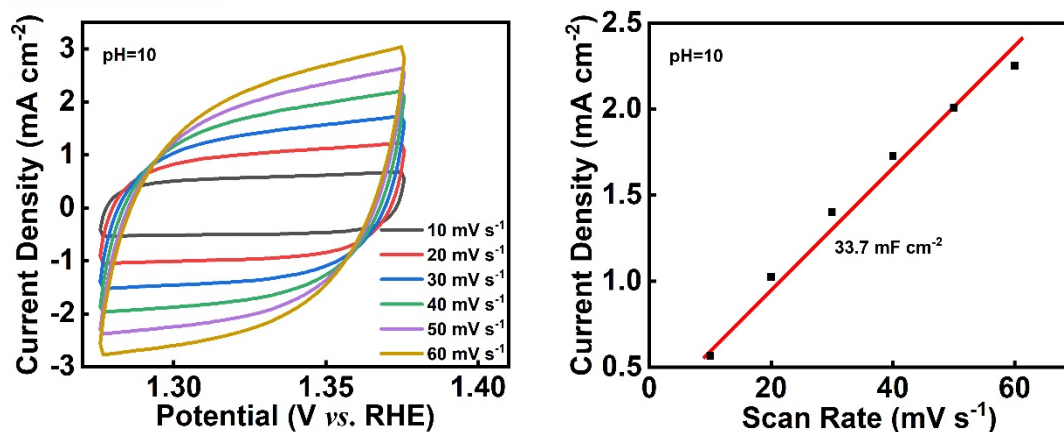

Fig. S11. Electrochemical double-layer capacitance measurements. CVs at different sweeping rates from 10 mV s^{-1} to 60 mV s^{-1} and Cdl value observed from CV plots at different scan rates of

9.5-CeO$_2$-Co (OH)$_2$.

Fig. S12. Electrochemical double-layer capacitance measurements. CVs at different sweeping rates from 10 mV s^{-1} to 60 mV s^{-1} and Cdl value observed from CV plots at different scan rates of 10-CeO$_2$-Co (OH)$_2$.

Fig. S13. Electrochemical double-layer capacitance measurements. CVs at different sweeping rates from 10 mV s^{-1} to 60 mV s^{-1} and Cdl value observed from CV plots at different scan rates of 10.5-CeO$_2$-Co (OH)$_2$.
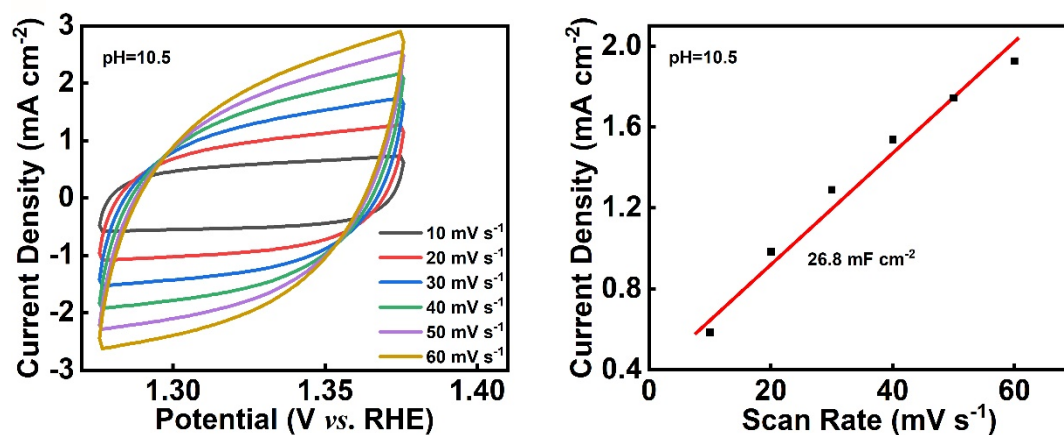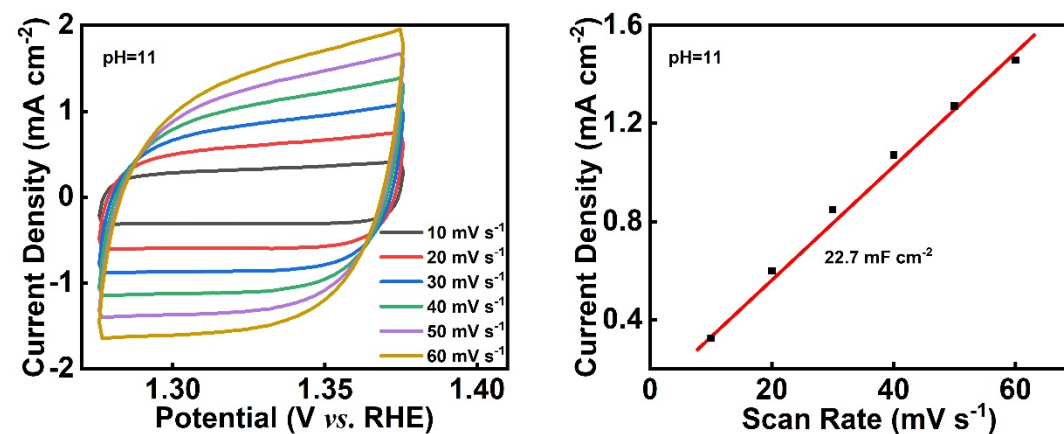

Fig. S14. Electrochemical double-layer capacitance measurements. CVs at different sweeping

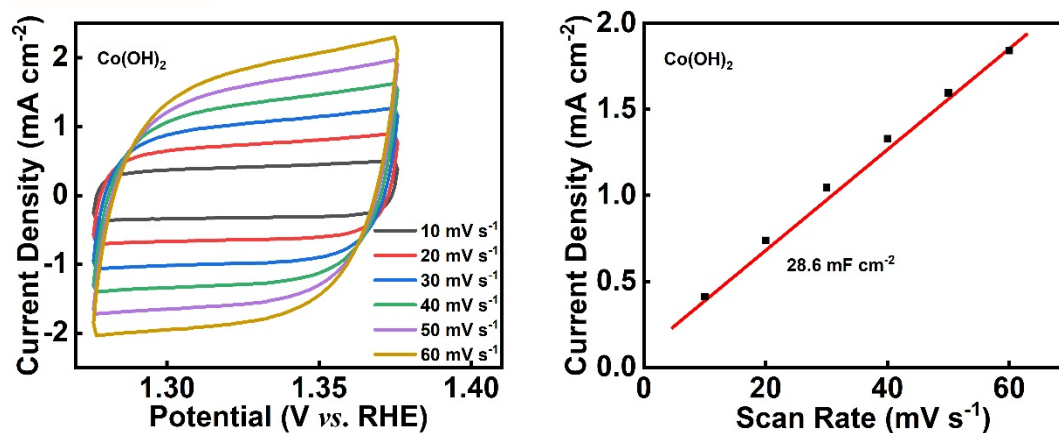rates from 10 mV s⁻¹ to 60 mV s⁻¹ and Cdl value observed from CV plots at different scan rates of 11-CeO$_2$-Co (OH)$_2$.

Fig. S15. Electrochemical double-layer capacitance measurements. CVs at different sweeping rates from 10 mV s⁻¹ to 60 mV s⁻¹ and Cdl value observed from CV plots at different scan rates of Co (OH)$_2$.
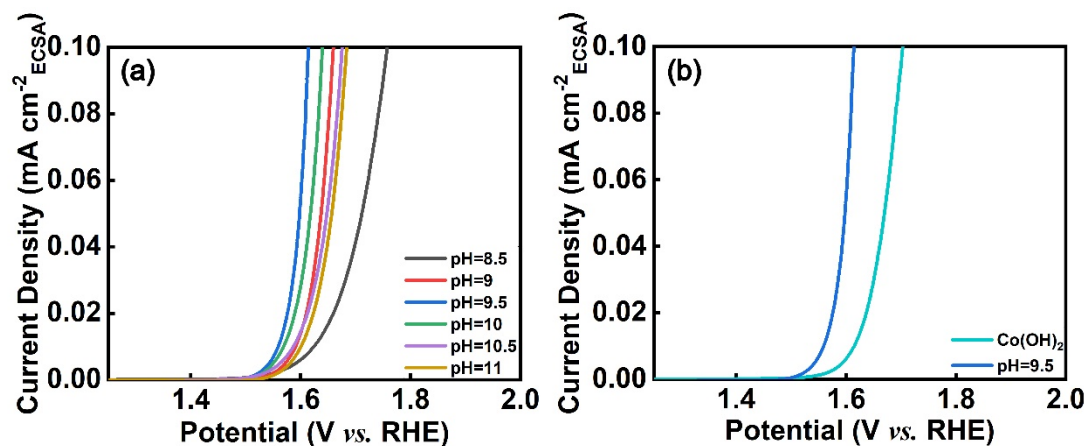

Fig. S16. ECSA-normalized LSV curves a) samples prepared from solutions of different pH values of CeO$_2$-Co (OH)$_2$; b) LSV curves of optimized by controlling solution pH value of 9.5-CeO$_2$-Co (OH)$_2$ and Co (OH)$_2$.