Supporting Information

Fluorine doped carbon aerogel prepared from spent cathode carbon of aluminum electrolysis towards electrocatalytic synthesis of H_2O_2

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Electrode preparation

For rotating ring disk electrode (RRDE). The catalyst inks were prepared as follows: 2 mg of prepared catalyst were dispersed in the mixture containing anhydrous ethanol (400 μl) and 5 wt.% Nafion (20 μl) solution by ultrasonic oscillation for at least 2 h to form a homogeneous suspension. Then, 5 μl of homogeneous ink was dropped on the RRDE, (disc area:0.1964 cm^2) and gently blow dried with a fan.

For carbon paper. The catalyst inks were prepared as follows: 2 mg of prepared catalyst was dispersed in the mixture containing anhydrous ethanol (400 μl) and 5 wt.% Nafion (20 μl) solution by ultrasonic oscillation for at least 2 h to form a homogeneous suspension. The catalyst loading mass is about 0.5 mg.

Electrochemical measurement

For RRDE. The catalyst-coated RRDE electrode is equipped as a working electrode, and then the electrochemical workstation performs cyclic voltammetry (CV) and linear sweep voltammetry (LSV), respectively. To evaluate the response to ORR of samples, the CV test was performed in Ar- and O_2-saturated electrolyte, respectively, at the scan rate of 10 mV/s, with ring voltage turned off. In addition, the LSV test was conducted in O_2-saturated electrolyte at the scan rate of 5 mV/s, with the ring voltage setting to 0.335 V (*vs.* Hg/HgO). The H_2O_2 selectivity (H_2O_2 %) and the electron transfer number (n) was calculated by Eq. 1 and 2.

$$H_2O_2\% = 200 \times \frac{I_R}{I_D + I_R/N} \tag{1}$$

$$n = 4 \times \frac{I_D/N}{I_D + I_R/N} \tag{2}$$

where I_R is the ring current, I_D is the disk current, and N is the collection efficiency.

For H-type cell. The H_2O_2 yield was tested in a H-cell with Nafion-N117 membrane as the separator, at each fixed potential for 1h. In this H-type cell, the cathodic chamber and anodic chamber were filled with 0.1 M KOH of 30 ml and 30 ml, respectively. Firstly, the prepared working electrode was equipped in the H-cell, and

the several cycles CV test was conducted to active the catalysts. Then, the voltage was fixed at certain value, and the run time was set to 1h, and 10 μl of solution was taken out to test H_2O_2 concentration. As for the durability test, stability was tested on RRDE by uniformly dropping 5 microliters of ink onto the disk electrode for 10 hours. The H_2O_2 yeild was calculated by Eq. 3.

$$Yeild = C_{H_2O_2} \times \frac{V}{m_{cat} \times t} \tag{3}$$

Where V (L) is the volume of the cathode electrolyte that's involved in the reaction, m_{cat} (g) is the amount of catalyst involved in the reaction and t (h) is the reaction time.

**Standard curve drawing.** The yellow Ce^{4+} solution can be reduced to colorless Ce^{3+} by H_2O_2 in the electrolyte. The absorbance of Ce^{4+} before and after the reaction can be determined by the UV−visible absorption spectrum (UV−Vis), and the measurement wavelength is about 318 nm. Firstly, different concentrations of Ce^{4+} solutions (0.1, 0.2, 0.3, 0.4 and 0.5 mmol L^{-1}) were configured and the corresponding absorption spectra and standard curves (Y=3.9649X+0.0294, R^2=0.9988) could be obtained by using UV−Vis to detect different concentrations of Ce^{4+} solutions, as shown in Fig. S6 (a). To quantify the generated H_2O_2 after electrolysis for 1 h, 10 μL of solution in catholde was added to 4 mL of 0.5 mmol L^{-1} standard $Ce(SO_4)_2$ solution. The mixture solution was measured by UV−Vis after standing for 2 h, and the yield of H_2O_2 was finally determined based on the reduced Ce^{4+} concentration.
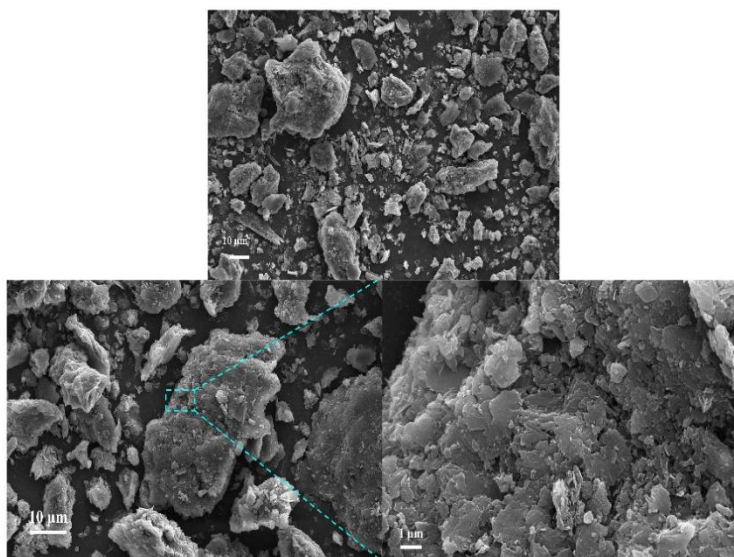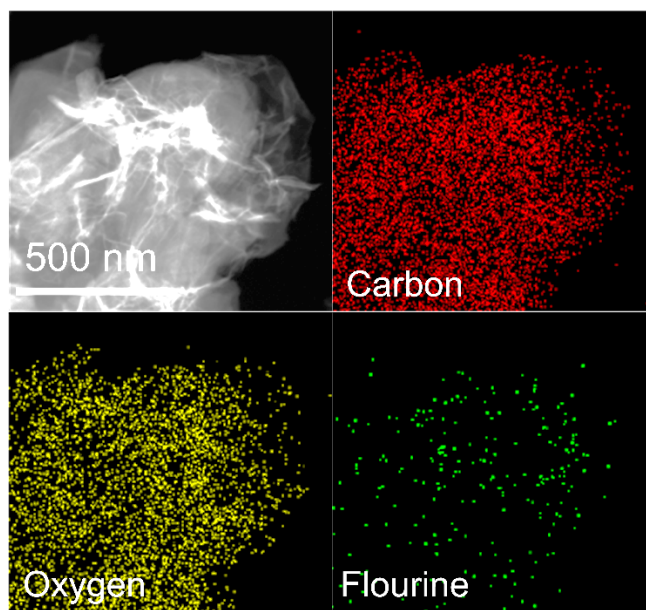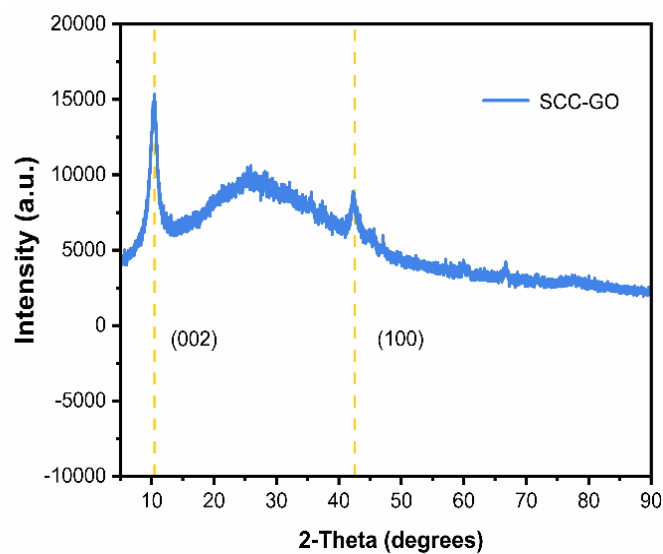
Fig. S1 SEM images of raw material SCC.
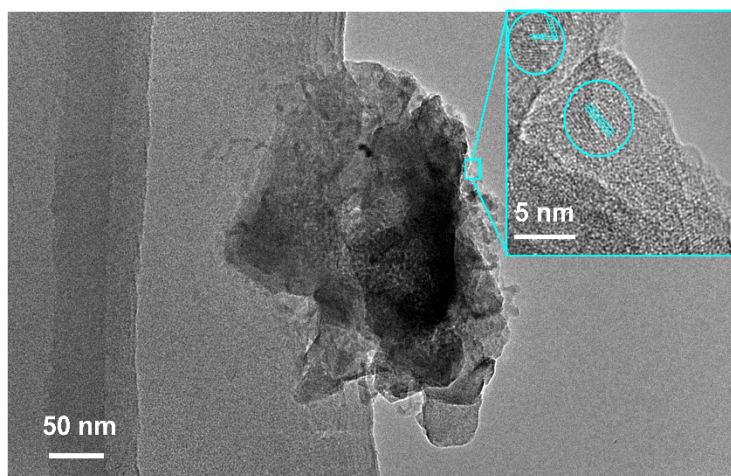
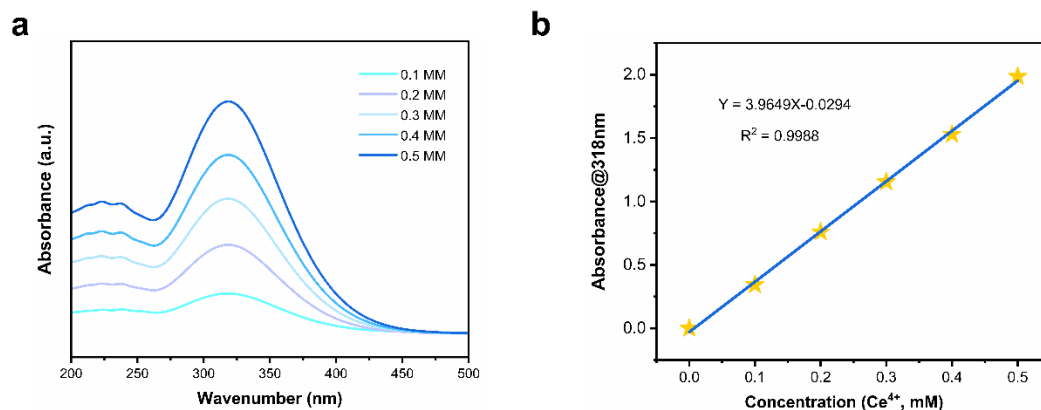

Fig. S2 TEM image of impurities in SCC-FCA-500*.
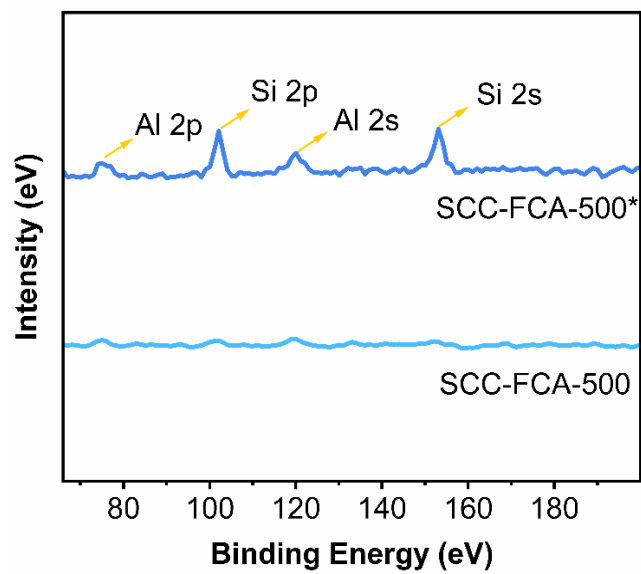
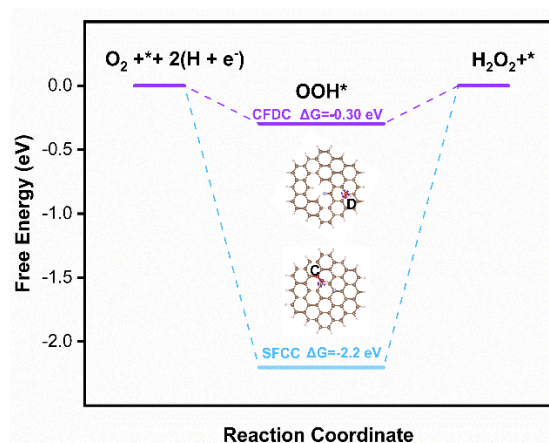**Fig. S3** XPS local spectra of SCC-FCA-500* and SCC-FCA-500.

Fig. S4 EDS element mapping images of SCC-FCA.

Fig. S5 XRD patterns of SCC-GO.

Fig. S6 (a) UV−Vis spectra of Ce^{4+} solution with various concentrations and (b) corresponding standard curve.

Fig. S7 Free energy of O_2 reduction pathway of CFDC and SFCC.

Table. S1 Types and proportions of elements contained in SCC in XRF.

Elements	Concentration ($w\%$)
F	32.716
Na	28.530
Al	8.737
K	8.162
Ca	6.866
Si	5.914
Fe	5.108

Table. S2 A comparison between CFDC and SFCC for free energy and bader charge of OOH*.

Active Site Model	Free Energy (ΔG)	Bader Charge (e)
CFDC	-0.30 eV	0.16
SFCC	-2.2 eV	0.23