Supporting Information

Carbothermal redox reaction in constructing defective carbon as superior oxygen reduction catalysts

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Materials and methods

Material Preparation: 0.75 g 1-Phenyl-1H-tetrazole-5-thiol (hptt) and 1.73g $Zn(NO_3)_2 \cdot 6H_2O$ have been ultrasonically dissolved in 65 ml DMF solution, and stirred at room temperature for 6 h to obtain white precursor powder $[Zn(ptt)_2]$. Then with the precursor pyrolysis at a temperature of 800 °C, 900 °C, 1000 °C, 1100 °C for 2 h in an inert N_2 atmosphere, the heating rate is kept at $10°Cmin^{-1}$, carbon materials ZnS/C-X (X = 800, 900 ,1000, 1100) are obtained. And then as-obtained samples are washed successively by hydrochloric acid, deionized water, absolute ethanol, and acetone to obtain sample C-X (X=800, 900, 1000 and 1100). ZnS/C-X (X = 800 and 900) are secondary carbonized at 1100 °C in the same heating process. Then it has been washed in accordance with the above method. The obtained carbon materials are denoted as $C800_{ZnS}$-1100, $C900_{ZnS}$-1100. For comparison, samples (C-800 and C-900) are carbonized and treated to produce C800-1100 and C900-1100.

Caution: Tetrazoles are potentially explosive and should be used in small quantities and handled with care.

Zn-air batteries preparation and performance measurements

The KOH solution (6 M) is invoked as the electrolyte used in the primary zinc–air battery. The polished Zinc plate and air electrode are used as the anode and cathode, respectively. The cathode consists of three parts: an active layer, current collector, and gas diffusion layer. 4 mg of ZnS/C-1100 or 20% Pt/C is mixed with 2 mg of acetylene black and 80 μL of Nafion solution (5 wt%) are ultrasonically suspended in 1 mL ethanol and 1 mL distilled water, and then the electrocatalyst ink is uniformly brushed onto 4 cm^2 of hydrophobic carbon paper acted as an active layer, in which the loading mass is 1 mg cm^{-2}. The nickel foam is used as current a collector. A home-made zinc–air battery device is performed for battery performance and long-term stability test. Polarization data (V-i) are collected by using linear sweep voltammetry at a scan rate of 10 mV s^{-1} with its impedance corrected to R = 1 Ω for consistency throughout the experiment. Chronopotentiometry (i-t) data is manually corrected to R = 1 Ω.

Material characterization

X-Ray diffraction data is measured with Rigaku Ultima IV instrument. The morphologies and microstructures of the materials have been observed by scanning electron microscopy (SEM, Germany MERLIN) and transmission electron microscopy (TEM). The elements and their chemical states in the materials are examined by using a ThermoFisher X-ray

photoelectron spectroscopy (XPS). N_2 sorption curves are collected by a Micromeritics ASAP 2020 instruments at 77 K and the Brunauer-Emmett-Teller (BET) multipoint adsorption theory is used to calculate the specific surface area. The electro-catalysis reactions have been tested by a Model CHI 760e workstation (CH Instruments, Chenhua, Shanghai, China)

Electrochemical test

Electrochemical measurements for ORR are conducted at room temperature in a CHI 760E electrochemical workstation integrated with a RRDE rotating ring-disk electrode apparatus in a typical 3-eletrode system, in which a glassy carbon electrode (GCE, 5.5mm in diameter) loaded with different catalysts is used as working electrode, with an Ag/AgCl (in 3 M KCl) electrode and graphite rod as reference and counter electrode, respectively. The recorded potential is converted to a reversible hydrogen electrode (RHE) using the formula E(RHE) = E(Ag/AgCl) + 0.0591*pH +0.197, where the 0.1 M KOH (pH=13) solution served as the electrolyte for ORR measurements. 6 mg catalyst is dispersed into the mixed solution of absolute ethanol (500 μL), deionized water (500 μL), and Nafion solution (50 μL, 5wt%), and sonicate it for 2 h until the solution forming a homogeneous ink. The loading masses for catalysts are 360 μg cm^{-2} for alkaline solution. Cyclic voltammetry (CV) is evaluated with 10 mV s^{-1}. Linear sweep voltammetry (LSV) is measured with 10 mV s^{-1} ranging from 400 to 2500 rpm. Electrochemical stability is evaluated using I-T test at 0.5 V RHE in alkaline medium. All the electrochemistry measurements are represented with iR compensation. Each catalyst is repeated at least 3 times for the above measurements to exclude possible incidental errors.

The number of electron transfer (n) can be measured with rotating ring-disk electrode technology (RRDE). For the RRDE measurements, the catalyst inks and electrodes are set by the same method as for RDE tests. The H_2O_2% and transferred electron number(n) per oxygen molecule were determined according to the following formulas:

$$H_2O_2\% = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$

where Id is disk current, Ir is ring current, and N is current collection efficiency of the Pt ring. N is determined to be 0.38.
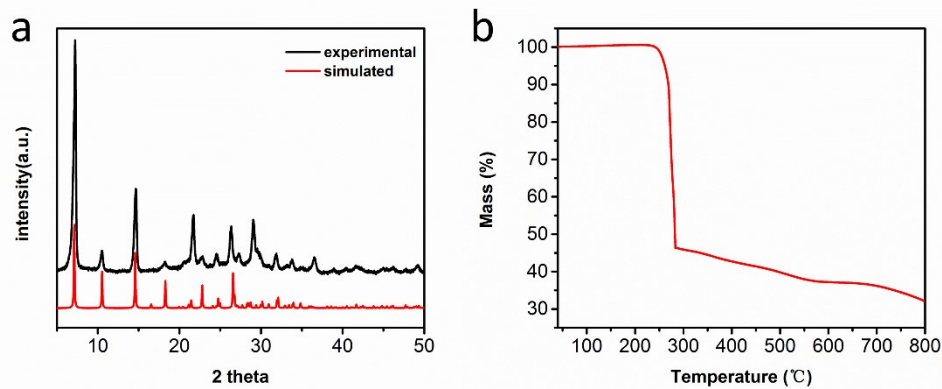
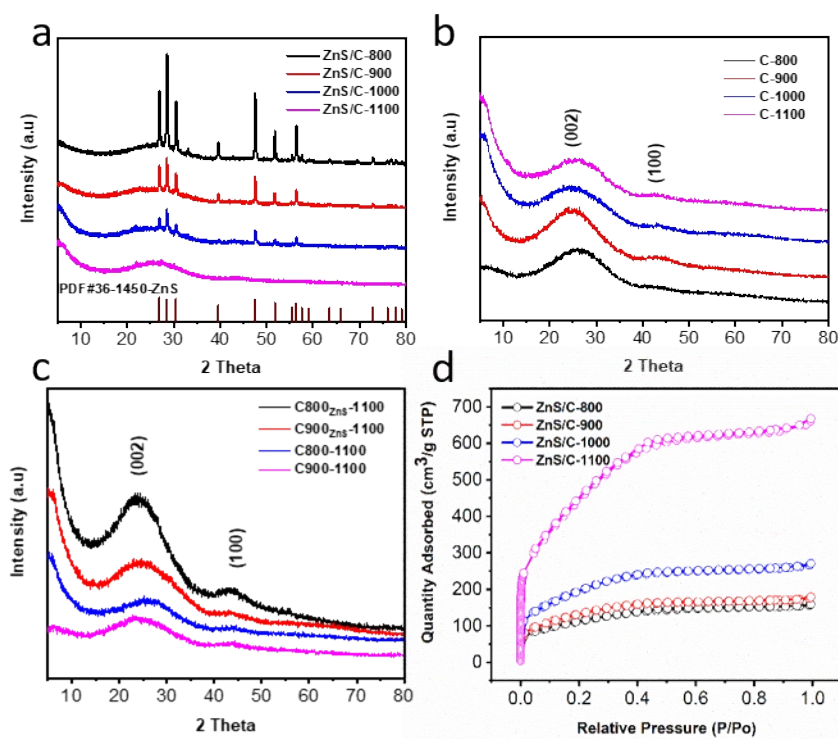**Fig. S1** a) Simulated and experimental XRD of the precursor [Zn(ptt)$_2$]. b) Thermogravimetric curve of the [Zn(ptt)$_2$].

Fig. S2 a) PXRD of ZnS/C800, ZnS/C900, ZnS/C1000 and ZnS/C1100. b) PXRD of C-800, C-900, C-1000, C-1100. c) PXRD of C800$_{ZnS}$-C1100, C900$_{ZnS}$-C1100, C800-C1100, C900-C1100. d) N$_2$ sorption isotherms of the ZnS/C-X.
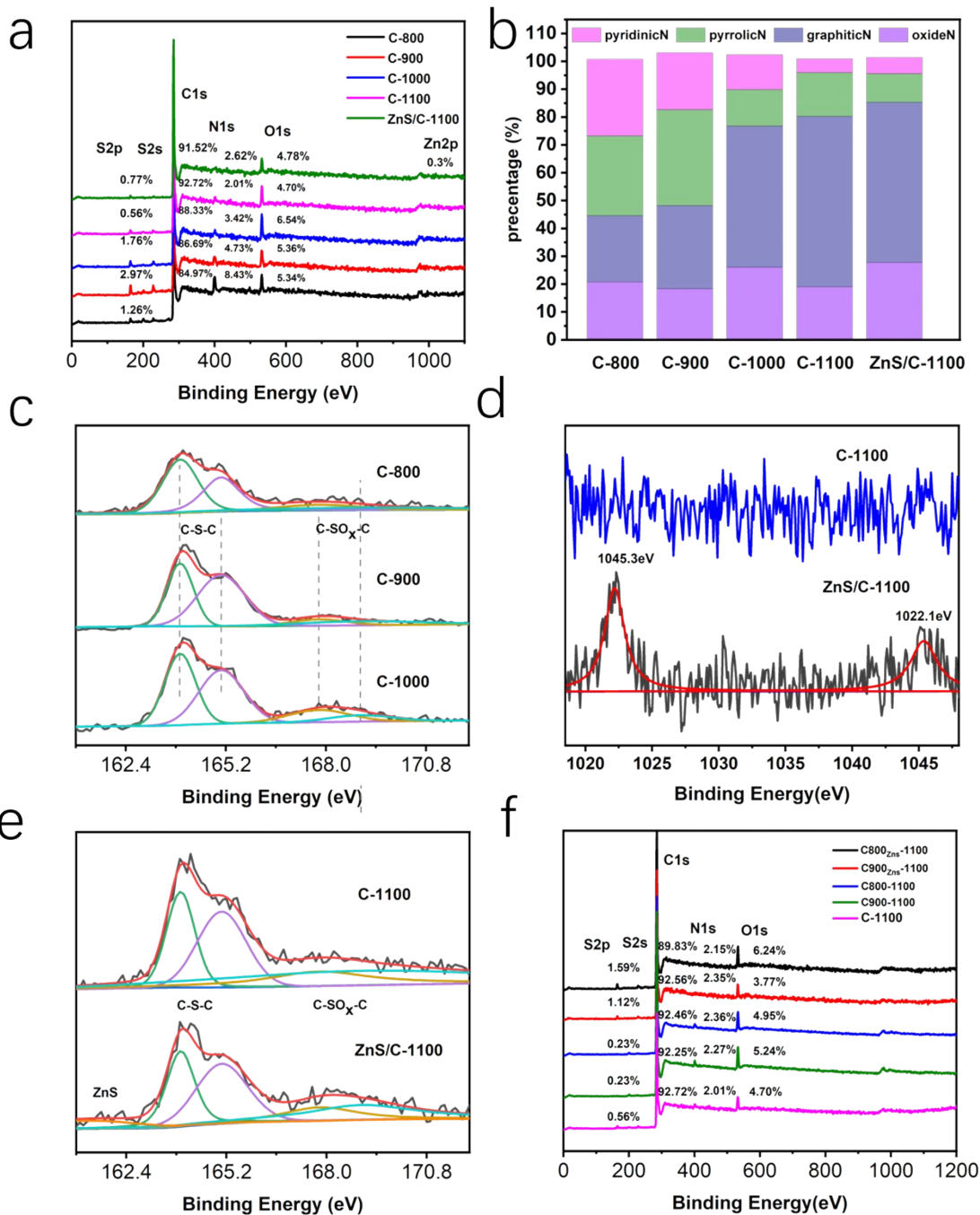
Figure S3. a) Survey XPS spectra of C-800, C-900, C-1000, C-1100 and ZnS/C-1100. b) Relative atomic percentage of different nitrogen bonding states of C-800, C-900, C-1000, C-1100 and ZnS/C-1100. c, e) S 2p spectra of C-800, C-900, C-1000, C-1100 and ZnS/C-1100. d) Zn 2p XPS spectra of C-1100 and ZnS/C-1100. f) Survey XPS spectra of C800$_{ZnS}$-1100, C900$_{ZnS}$-1100, C800-1100, C900-1100 and C-1100.
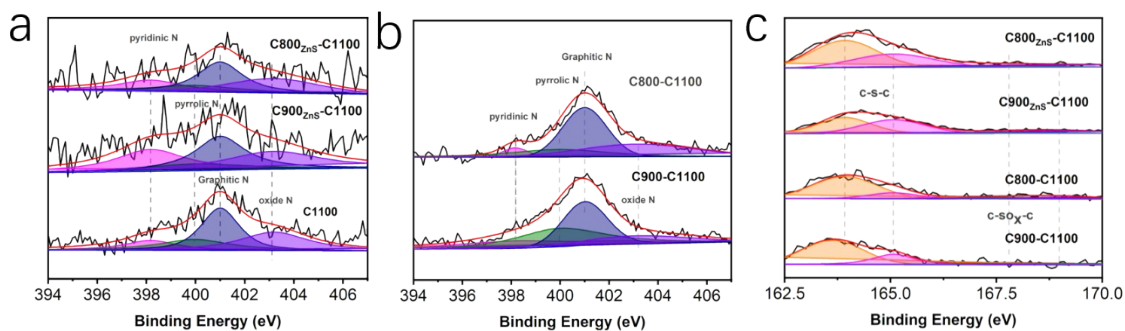
Figure S4. a) N 1s spectra of C800$_{ZnS}$-1100, C900$_{ZnS}$-1100 and C-1100. b) N 1s spectra of C800-1100 and C900-1100. d) S 2p spectra of C800$_{ZnS}$-1100, C900$_{ZnS}$-1100, C800-1100 and C900-1100.
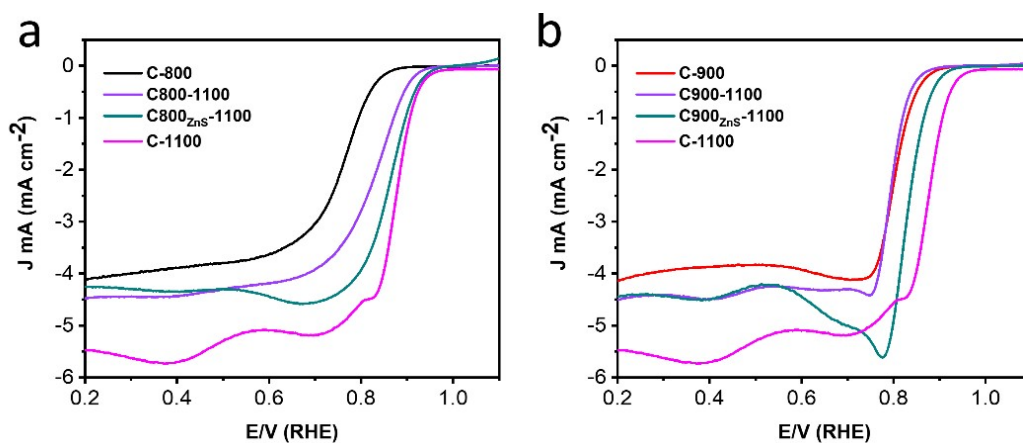

Figure S5. (a) LSV curves of C-800, C800-1100, C800$_{ZnS}$-1100 and C-1100 at 1600 rpm and 1 mV s^{-1}; (b) LSV curves of C-900, C900-1100, C800$_{ZnS}$-1100 and C-1100 at 1600 rpm and 1 mV s^{-1}.
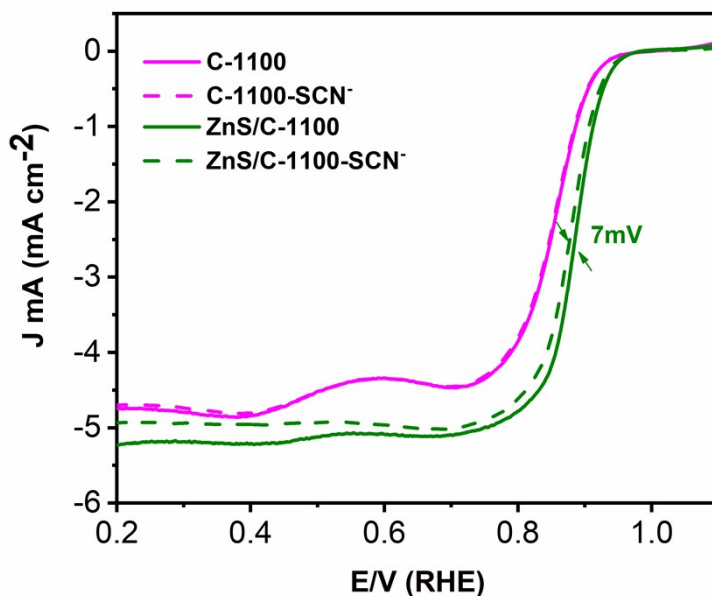
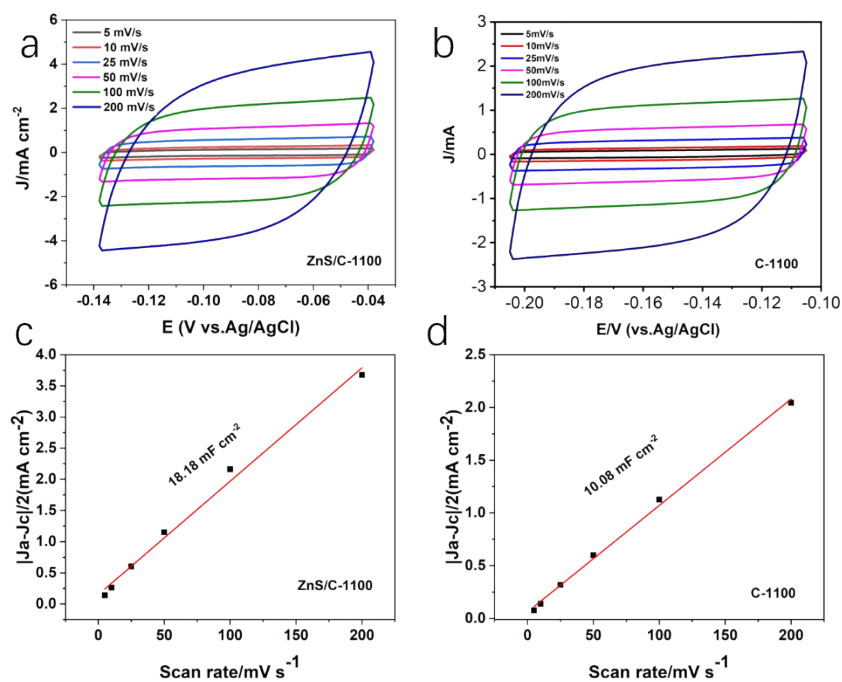**Figure S6.** LSV curves of C-1100, ZnS/C-1100 with and without of 10 mM SCN⁻ recorded at 1600 rpm and 1 mV s⁻¹.

Figure S7. (a, c) CV of ZnS/C-1100 and C-1100 in 5 M KOH. (5mV/s, 10mV/s, 25mV/s, 50mV/s, 100mV/s, 200mV/s) (b, d) Fitting curves of current densities of catalyst at different speeds.
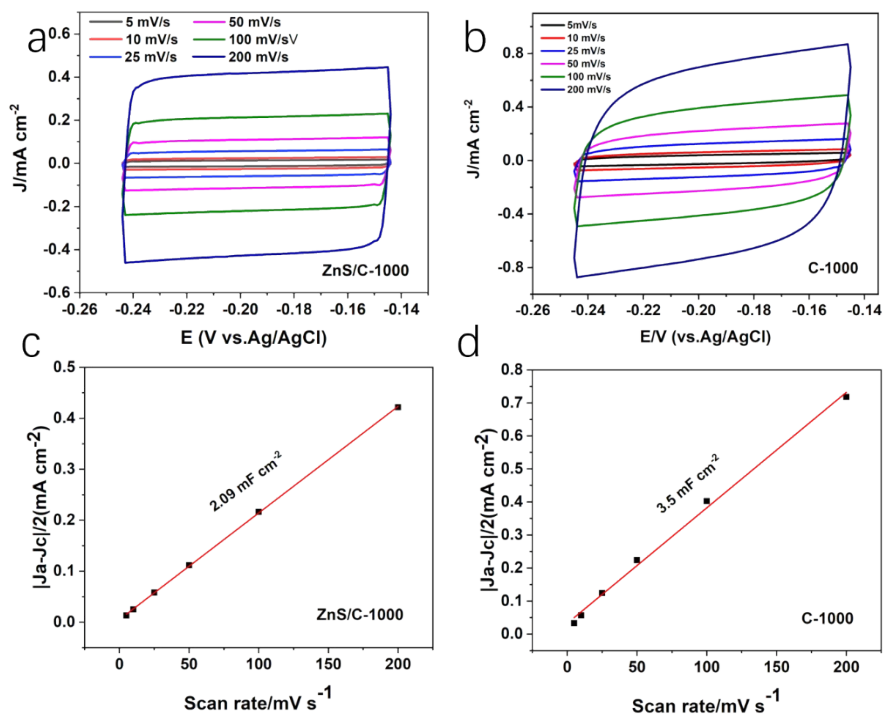
Figure S8. (a, c) CV of ZnS/C-1000 and C-1000 in 5 M KOH. (5mV/s, 10mV/s, 25mV/s, 50mV/s, 100mV/s, 200mV/s) (b, d) Fitting curves of current densities of catalyst at different speeds.
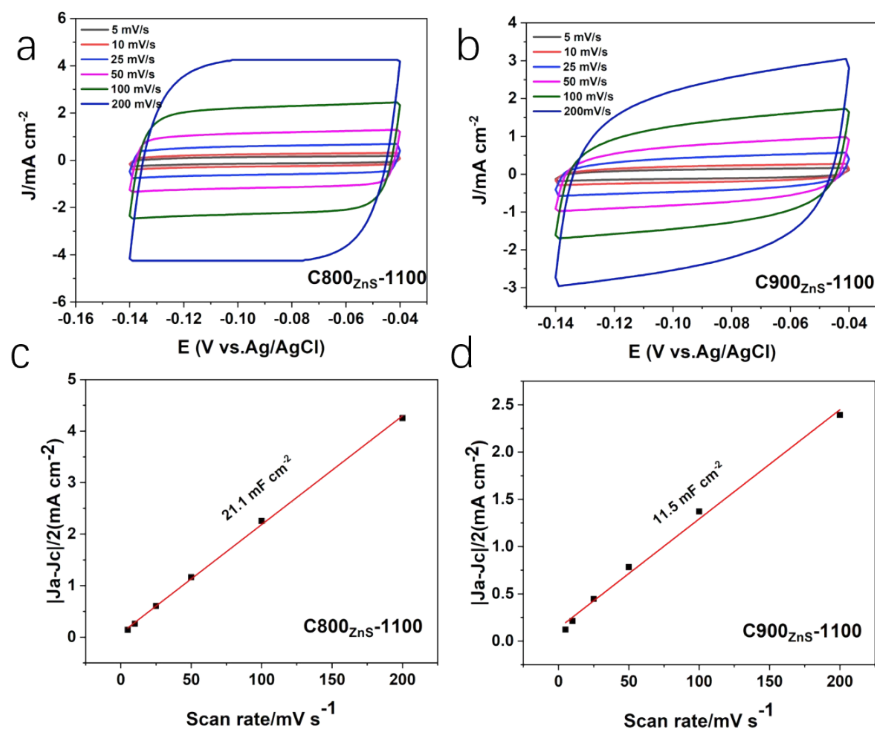

Figure S9. (a, c) CV of C800$_{ZnS}$-1100 and C900$_{ZnS}$-1100 in 5 M KOH. (5mV/s, 10mV/s, 25mV/s, 50mV/s, 100mV/s, 200mV/s) (b, d) Fitting curves of current densities of catalyst at different speeds.
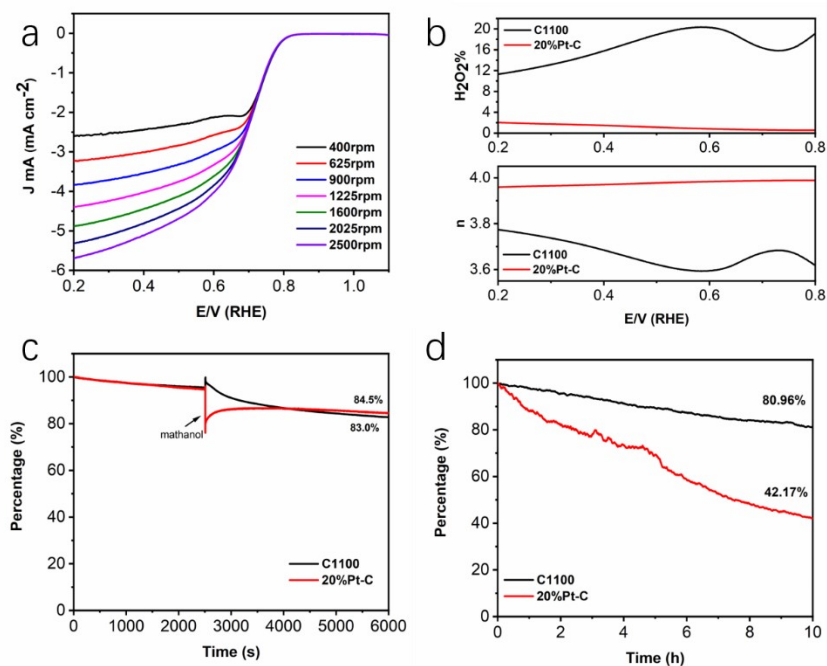
Figure S10. a) LSV curves at various rotating speeds of C-1100 in 0.1 M HClO$_4$ solution.
b) Electron transfer number (n) and a H$_2$O$_2$ yield of C-1100 and 20% Pt/C in 0.1 M HClO$_4$.
c) The *I-T* curves of C-1100 and 20% Pt/C by adding 1 M MeOH at 2500 s in 0.1 M HClO$_4$.
d) The durability testing of C-1100 and 20% Pt/C in 0.1 M HClO$_4$.
The C-1100 have a decent ORR property with a half-wave potential 0.69 V in 0.1 M HClO$_4$
solution. Compared with that of the 20% Pt/C, the C-1100 has the better durability, higher
H$_2$O$_2$ yield and comparable methanol tolerance in 0.1 M HClO$_4$ solution.