Supporting information

S-doped hierarchical graphene decorated with Co-porphyrins as an efficient electrocatalyst for Zinc-Air Batteries

Zhi-Jie Peng,[‡] Jiao Zhao,[‡] Lei Gu, Xuan-Long Sun, Hai-Lang Jia,* Ming-Yun Guan and Shuai-Shuai Ma*

School of Chemical and Environmental Engineering, Institute of Advanced Functional Materials for Energy, Jiangsu University of Technology, Changzhou 213001, P. R. China.

Electrochemical measurements

A conventional three-electrode system was employed to evaluate the electro-catalytic performance of the obtained catalyst on a CHI 760E electrochemical workstation. A rotating disk electrode (RDE) with a glassy carbon (GC) disk (electrode area: 0.1256 cm^2) was used as the working electrode, Ag/AgCl was used as the reference electrode, and platinum wire was used as the counter electrode. The rotating ring disk electrode measurements for ORR were carried out on RRDE in a N$_2$ or O$_2$-saturated 0.1 M KOH electrolyte solution at a scan rate of 10 mV/s at various rotation rates of 400, 600, 900, 1200, 1600rpm. Linear sweep voltammetry (LSV) at a scan rate of 10 mV/s was conducted in 0.1 M KOH at room temperature. Before the electrochemical measurements, the electrolyte solution was purged with O$_2$ for 30 min to achieve an O$_2$-saturated solution, and stable polarization curves were recorded after 20 cycles. All the potentials were converted to the potential versus the reversible hydrogen electrode (RHE) according to $E_{vs}RHE = E_{vs}Ag/AgCl + E_{ø}Ag/AgCl + 0.059$ pH. The RDE measurements were performed at different rotating speeds from 400 to 1600 rpm at a scan rate of 10 mV s^{-1}. Koutecky-Levich plots were used to investigate the effective electron-transfer number and the mass-transport corrected current density for ORR at different potentials. According to the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_K} + \frac{1}{J_L} = \frac{1}{J_k} + \frac{1}{Bw^{1/2}} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6} \quad (2)$$

$$J_k = nFkC_0 \quad (3)$$

Where ω is the angular velocity, J is the measured current density, J_K and J_L are the kinetic and diffusion-limiting current densities. F is Faraday constant (96485 C mol^{-1}), D_0 is the diffusion coefficient of O$_2$ (1.9×10^{-5} cm^2 s^{-1}), v is the kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1}) and C_0 is the bulk concentration of O$_2$ (1.2×10^{-6} mol cm^{-3}), n is the electron transfer number. B can be determined from the slope of the K-

L plots, and then the electron transfer number n can be obtained.

Rotating ring-disk electrode (RRDE) measurements were recorded with catalyst inks and electrodes prepared by the same method as that for the RDE measurements. The H_2O_2 produced and the electron number (n) transferred during the ORR were calculated using the following equations:

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

$$H_2O_2\% = 100 \times \frac{4 - n}{2}$$

The rotating ring-disk electrode was employed to detect the H_2O_2 yield, where the ring potential was set to 1.3 V (vs. RHE). where I_D is the Faradaic current at the disk, I_R is the Faradaic current at the ring, and N= 0.37 is the collection efficiency of ring electrode.

The measurements of the zinc–air batteries were performed using home-built electrochemical cells. The electrolyte was 6.0 M KOH/0.2 M zinc acetate. Zinc foil was used as the anode and the catalyst of Por/S/rGO or Pt/C sprayed onto the foamed nickel (1 cm × 1 cm) with a loading of 2 mg cm^{-2} was used as the air-cathode, respectively. Cell guard 3501 membrane was used for a separator. The GDL had an effective area of 1 cm^2 and allows O_2 from ambient air to reach the catalyst sites. Measurements were carried out on the as-fabricated cell with a CHI 760E electrochemical workstation and a LAND CT2001A multichannel battery testing system at room temperature.
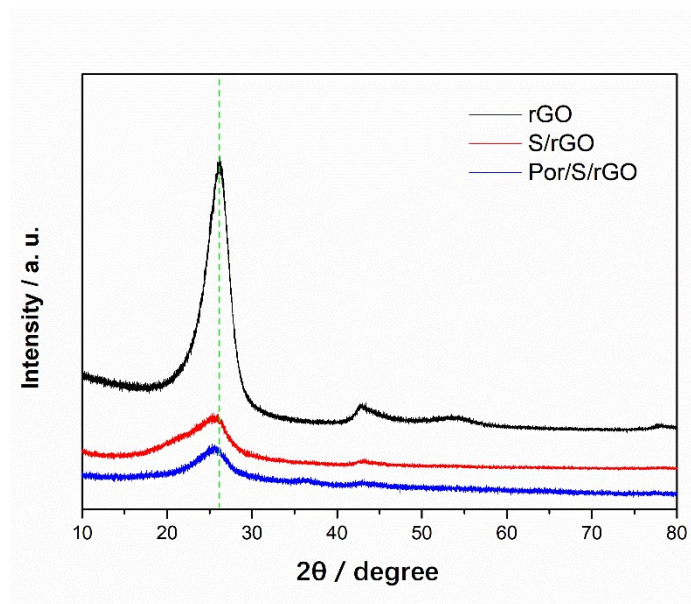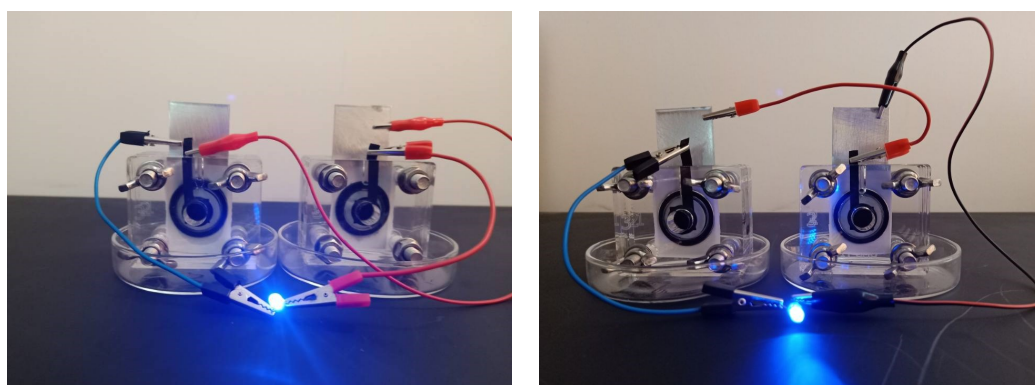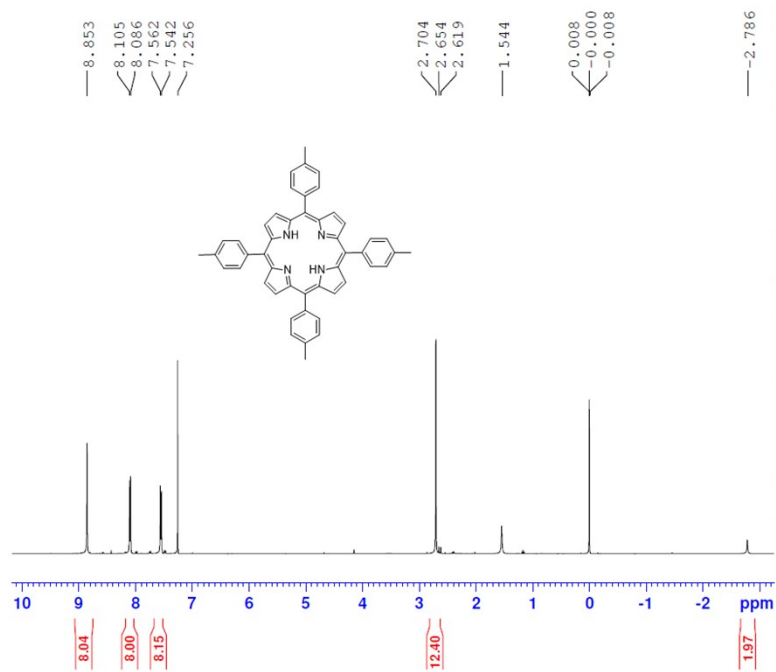
Fig. S1 XRD of rGO, S/rGO, and Por/S/rGO.
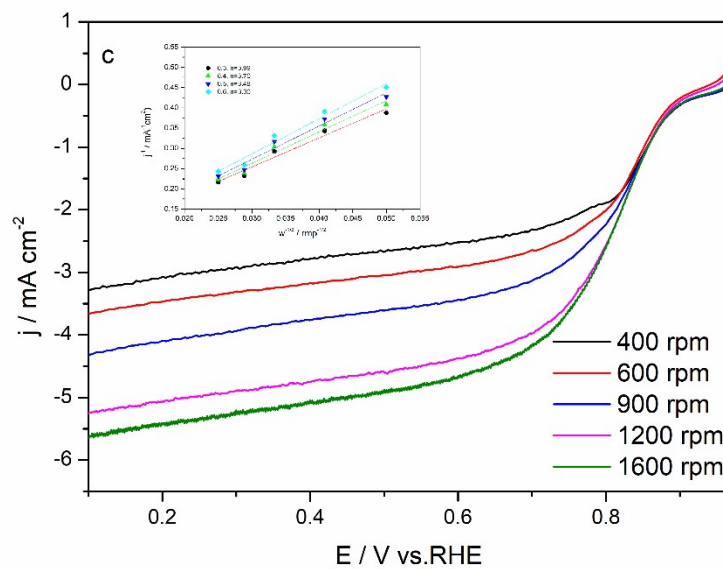
Fig. S2 LSV of Por/S/rGO in O_2-saturated 0.1 M KOH solution at different rotation rates, the illustration is corresponding K−L plots.
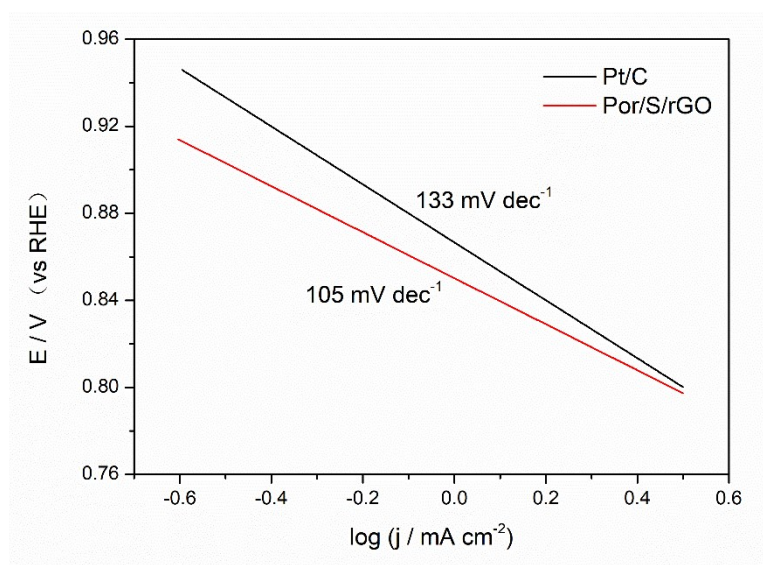
Fig. S3 Tafel plots of Por/S/rGO and Pt/C.

Fig. S4 Two Zn-air batteries were connected in series to supply adequate voltage to power the colored LEDs (2.5 V), Por/S/rGO (left), Pt/C (right).

Fig. S5 The ^{1}H NMR of 5,10,15,20-tetrakis(4-methylphenyl)-21,22-dihydroporphyrin