Supporting Information

Reduced graphene oxide intercalated ZnS nanoparticles as an efficient and durable electrocatalyst for oxygen reduction reaction

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Instrumentation and Measurements

The prepared catalysts were structurally characterized by using X-ray diffraction (XRD). XRD patterns were recorded on a glass wafer by a Rigaku MiniFlex II diffractometer with a slit of 1.25 at a scanning rate of 10°/min using Cu-Kαradiation (λ = 1.5406 Å). The morphology of the prepared catalysts was studied using scanning electron microscopy (SEM, JEOL JSM-6701F electron microscope operating at 5 KV). Transmission electron microscopy (TEM) images were examined according to a Philips Tecnai 20U-TWIN transmission electron microscope with linear resolution of 0.14 nm and dot resolution of 0.19 nm.

X-ray photoelectron spectroscopy (XPS) measurements were taken with an ESCALABMKII X-ray photoelectron spectrometer (VG Scienta, USA) equipped with a monochromatic Al Kα X-ray source (1486.6 eV). The pressure in the chamber during the measurements was kept at 1×10^{-7} Pa. The analyzer was operated at a pass energy of 50 eV for high resolution scans. The binding energy of the C 1s peak at 284.6 eV was taken as a reference for the binding energy calibration. A background subtraction and peak fitting were deconvolved using the XPS peak fitting software (XPSPEAK41 by Prof. R. W. M. Kwok).

Electrode preparation and electrochemical tests

The electrochemical characterization were tested according to a CHI 760D electrochemical workstation. In the electrochemical testing system, a saturated calomel electrode (Hg/Hg_2Cl_2) was the reference electrode, a platinum wire was the counter-electrode and glassy carbon (GC) electrode with catalysts was the working electrode. The electrolyte solution was 0.1 mol/L KOH. The working electrode was prepared by the following: 5.0 mg catalyst was dispersed in the mixture of 50 μl Nafion solution and 450 μl DI water. The mixture was sonicated for at least 40 min to form a homogeneous ink. Then 5.0 μl of the ink was dropped onto a polished glassy-carbon electrode (GCE, 3 mm in diameter) and fully dried. Before electrochemical tests, the working electrode was conducted at a sweeping rate of 100 mV/s between 0.2 and -0.8 V versus Hg/Hg_2Cl_2 until reproducible results were obtained. Thereafter, the electrolyte was saturated with oxygen and cyclic voltammogram tests were conducted for oxygen reduction from 0.2 to -0.8 V versus Hg/Hg_2Cl_2 at sweeping rates of 5, 10, 20, 50 and 100 mV s^{-1}, respectively. The linearly sweeping voltammetry (LSV) and Tafel tests were conducted at the sweeping rate of 5 mV/s. The electrochemical impedance spectroscopy (EIS) tests were carried out at a half wave potential from 1 to 10^5 Hz. The long-time running stability test was recorded for 16000 s at the potential of -0.2 V versus Hg/Hg_2Cl_2.

The rotating disc electrode (RDE) and rotating ring disc electrode (RRDE) tests were carried out on a RRDE-3A rotating ring disc electrode combined with CHI 760D. The RDE tests were conducted with the sweeping rate of 5 mV/s at different rotating speed. RRDE tests were carried out on a rotating speed of 1600 rpm with the sweeping rate of 5 mV/s.

The *Koutechy–Levich* plots can be analyzed for determining the electron transfer number (n) at various electrode potentials.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{Bw^{0.5}} \quad (1)$$

$$B = 0.62nF(D_{O_2})^{2/3} v^{-1/6} C_{O_2} \quad (2)$$

Where j_k is the kinetic current and w is the angular velocity ($w = 2\pi N$, N is the linear rotation speed). B could be determined from the slope of the K–L plots based on the *Koutechy–Levich* equation. n represents the transferred electron number, F is the Faraday constant (F = 96485 C mol^{-1}), D_{O_2} is the diffusion coefficient of O_2 in 0.1 mol L^{-1} KOH (1.9×10^{-5} cm^2 s^{-1}), v is the kinetic viscosity (0.01 cm^2 s^{-1}), and C_{O_2} is the bulk concentration of O_2 (1.2×10^{-7} mol $(cm^3)^{-1}$).

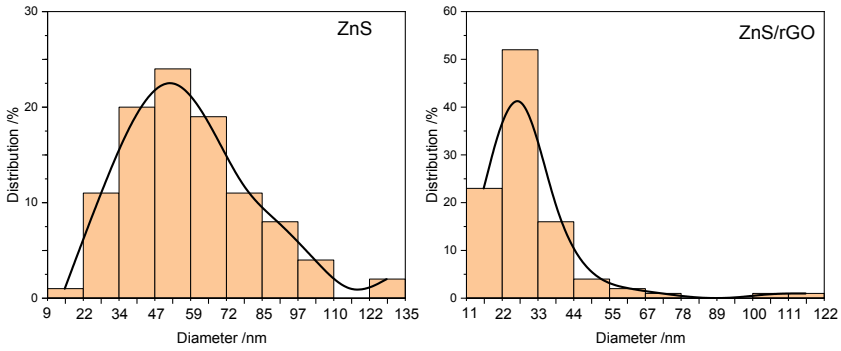

Fig. S1 The size distributions estimated from TEM graph.