Supplementary Information

Synthesis and characterizations of zinc oxide on reduced graphene oxide for high performance electrocatalytic reduction of oxygen

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Instrumentation and Measurements

The products were characterized by powder X-ray diffraction (XRD, Cu Ka irradiation; λ = 0.154 nm) with a SIEMENS D5000 X-ray diffractometer. The morphology of the synthesized samples was tested by scanning electron microscopy (SEM, JEOL JSM-6701F electron microscope operating at 5 KV). Transmission electron microscopy (TEM) images were examined by a Philips Tecnai 20U-TWIN transmission electron microscope with linear resolution of 0.14 nm and dot resolution of 0.19 nm. Raman spectra tests were conducted by a TriVista™ 555CRS Raman spectrometer at 785 nm. X-ray photoelectron spectroscopy (XPS) data was collected by 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 and at a pass energy of 100 eV for survey 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

5 mg of the prepared catalyst powder was dispersed in the mixture of 450 µL of deionized water and 50 µL of Nafion (5 wt% solution alcohols, DuPont). The mixture was fully sonicated to form a homogeneous ink. Then 5 µL of the ink was dropped onto a glassy carbon (GC) electrode of 3 mm in diameter and fully dried. Cyclic voltammetry measurements were performed using a CHI 760E electrochemical workstation (CH Instrument, USA) by conventional three-electrode cell. The coated glass carbon (GC) electrode is employed as the working electrode, graphite as the counter-electrode, and a saturated calomel electrode (Hg/Hg₂Cl₂) (SCE) as the reference electrode.

Before the ORR tests, cyclic voltammetry (CV) tests were performed from 0.2 to -0.8 V at 5 mV/s in Ar-saturated electrolyte to clean the electrode surface. 20 cycles were carried out to stabilize the current-potential signal. Thereafter, the electrolyte was saturated with oxygen before the start of every experiment by bubbling O₂ at least 30 min, which was maintained over the electrolyte in order to ensure its continued O₂ saturation during the recording. The working electrode was cycled at least 20 cycles before data were recorded at a scan rate of 5 mV/s from 0.2 to -0.8 V vs. Hg/Hg₂Cl₂ in O₂-saturated 0.1 mol/L KOH electrolytes.

The Tafel tests were also conducted at a sweeping rate of 5 mV/s. Rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) tests were performed using a RRDE-3A electrode at the same sweeping rate. For RRDE tests, the working electrode was a glassy carbon disk (5.61 mm in diameter) and a platinum ring leading to a collection efficiency of the ring disk electrode. The RRDE tests were performed at 1600 rpm in O₂-saturated solution. The Pt ring electrode was polarized at -0.3 V vs. Hg/Hg₂Cl₂ for oxidizing the hydrogen peroxide ion during oxygen reduction at the modified GC disk electrode. All the experiments were carried out in 0.1 mol/L KOH solution at room temperature.
The Tafel tests were also conducted at a sweeping rate of 5 mV/s. The exchange current density was derived from the mass-transport correction using Eq. (1):

$$E = E_0 + \frac{2.303RT}{n_\text{a}F}\log i_\text{a} - \frac{2.303RT}{n_\text{a}F}\log i_\text{d}$$

(1)

Where $E$ represents the tested electrode potential, $E_0$ is the thermodynamics electrode potential, $F$ is the Faraday constant, $R$ is the ideal gas constant, $T$ is the thermodynamic temperature, $i_d$ is the measured current density, and $i_0$ is the exchange current density.

Rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) tests were performed using a RRDE-3A electrode at the same sweeping rate. For RRDE tests, the working electrode was a glassy carbon disk (5.61 mm in diameter) and a platinum ring leading to a collection efficiency of the ring disk electrode. The RRDE tests were performed at 1600 rpm in O$_2$-saturated solution. The Pt ring electrode was polarized at -0.3 V vs. Hg/Hg$_2$Cl$_2$ for oxidizing the hydrogen peroxide ion during oxygen reduction at the modified GC disk electrode. All the experiments were carried out in 0.1 M KOH solution at room temperature.

For RDE test, the transferred electron numbers of oxygen reduction could be calculated according to the following Koutechy–Levich equation (Kakaei and Hasanpour, 2014):

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{Bw^{0.6}}$$

(2)

Where $I_k$ 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 as follows:

$$B = 0.62nF(D_{o2})^{2/3}v^{-1/6}C_{o2}$$

(3)

Where $n$ represents the transferred electron number, $F$ is the Faraday constant ($F = 96485$ C/mol), $D_{o2}$ is the diffusion coefficient of O$_2$ in 0.1 M KOH (1.9×10$^{-5}$ cm$^2$/s), $v$ is the kinetic viscosity (0.01 cm$^2$/s), and $C_{o2}$ is the bulk concentration of O$_2$ (1.2×10$^{-7}$ mol/cm$^3$).
For RRDE test, the ORR percentage of peroxide species and electron transfer numbers with respect to total ORR products on CuO/rGO were calculated from the following equations:

\[
\%H_2O_2 = 200 \times \frac{I_r/N}{I_d + I_r/N} \tag{4}
\]

\[
n = 4 \times \frac{I_d}{I_d + I_r/N} \tag{5}
\]

Where \(I_d\) is the disk current, \(I_r\) is the ring current, and \(N\) is the current collection efficiency of the Pt ring 0.39.