Supplementary Information

A hybrid material combined copper oxide with graphene for oxygen reduction reaction in alkaline medium

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1. Experimental Details

1.1 Instrumentation and Measurements

The products were characterized by powder X-ray diffraction (XRD, Cu Ka irradiation; \( \lambda = 0.154 \) nm) with a SIEMENS D5000 X-ray diffractometer. The crystallite sizes of copper oxide can be calculated by the Scherrer's formula:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]  
(1)

Where \( D \) is the average crystalline size, \( K \) is the shape factor being 0.890, \( \lambda \) is the wavelength of X-ray being 0.154 nm for Cu Kα radiation, \( \beta \) is the full width at half maximum of the peak, \( \theta \) is the diffraction angle of the peak.

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

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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).

1.2 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 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 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. (2):

$$E = E_0 + \frac{2.303RT}{an_\text{F}} \log i_0 - \frac{2.303RT}{an_\text{F}} \log i_d$$

(2)

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):

$$\frac{1}{I} = \frac{1}{I_i} + \frac{1}{Bw^{0.5}}$$

(3)

Where $I_i$ 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:

$$B = 0.62nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2} \quad (4)$$

Where $n$ represents the transferred electron number, $F$ is the Faraday constant ($F = 96485 \text{ C/mol}$), $D_{O_2}$ is the diffusion coefficient of $O_2$ in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2/\text{s}$), $v$ is the kinetic viscosity ($0.01 \text{ cm}^2/\text{s}$), and $C_{O_2}$ is the bulk concentration of $O_2$ ($1.2 \times 10^{-6} \text{ mol/cm}^3$).

For RRDE test, the ORR percentage of peroxide species and electron transfer numbers with respect to total ORR products on our samples were calculated from the following equations:

$$\%H_2O_2 = 200 \times \frac{I_d/N}{I_d + I_r/N} \quad (5)$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \quad (6)$$

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.

2. Pourbaix Diagrams of Cu-H$_2$O

![Pourbaix Diagrams of Cu-H$_2$O](image)

Fig S1. Pourbaix Diagrams of Cu-H$_2$O

Reactions on the electrodes:

Cathode: $(C)$: $Cu^{2+} + 2e^- \rightarrow Cu$

Anode: $(B)$: $Cu - 2e^- \rightarrow Cu^{2+}$
a. \( \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu} \quad E_a = 0.34 \text{ V} \)

b. \( 2 \text{Cu}^{2+} + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{Cu}_2\text{O} + 2\text{H}^+ \quad E_b = 0.20 + 0.059 \text{ pH} \)

c. \( \text{Cu}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CuO} + 2\text{H}^+ \quad \text{pH} = 4.7 \)

d. \( \text{CuO} + 2\text{H}^+ + 2e^- \rightleftharpoons \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad E_d = 0.75 - 0.059 \text{ pH} \)

e. \( \text{Cu}_2\text{O} + 2\text{H}^+ + 2e^- \rightleftharpoons 2\text{Cu} + \text{H}_2\text{O} \quad E_e = 0.47 - 0.059 \text{ pH} \)