

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 K α 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:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where D is the average crystalline size, K is the shape factor being 0.890, λ is the wavelength of X-ray being 0.154 nm for Cu K α radiation, β is the full width at half maximum of the peak, θ 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 TriVistaTM 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 K α 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 μ L of deionized water and 50 μ L of Nafion (5 wt% solution alcohols, DuPont). The mixture was fully sonicated to form a homogeneous ink. Then 5 μ L 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. (2):

$$E = E_0 + \frac{2.303RT}{an_aF} \log i_0 - \frac{2.303RT}{an_aF} \log i_d \quad (2)$$

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.

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

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{Bw^{0.5}} \quad (3)$$

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:

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

Where n represents the transferred electron number, F is the Faraday constant ($F = 96485$ C/mol), D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH (1.9×10^{-5} cm²/s), ν is the kinetic viscosity (0.01 cm²/s), and C_{O_2} is the bulk concentration of O_2 (1.2×10^{-6} mol/cm³).

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:

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

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

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-H₂O

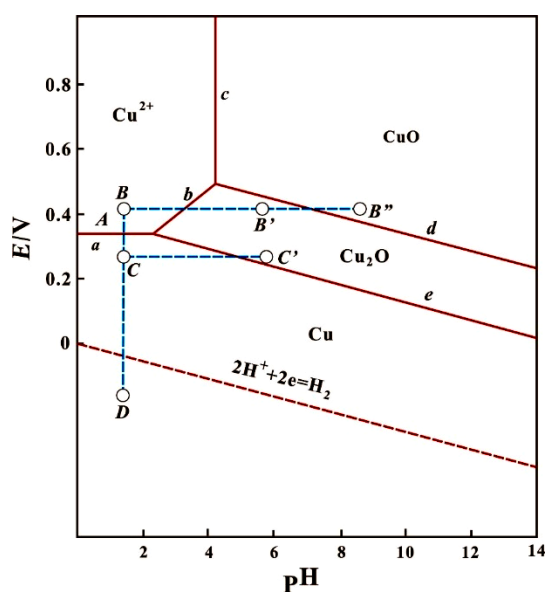


Fig.S1. Pourbaix Diagrams of Cu-H₂O

Reactions on the electrodes:

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

Anode: (B): $Cu - 2e^- = Cu^{2+}$

- a. $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ $E_a = 0.34 \text{ V}$
- b. $2 \text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e}^- = \text{Cu}_2\text{O} + 2\text{H}^+$ $E_b = 0.20 + 0.059 \text{ pH}$
- c. $\text{Cu}^{2+} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+$ $\text{pH} = 4.7$
- d. $\text{CuO} + 2\text{H}^+ + 2\text{e}^- = \text{Cu}_2\text{O} + \text{H}_2\text{O}$ $E_d = 0.75 - 0.059 \text{ pH}$
- e. $\text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^- = 2\text{Cu} + \text{H}_2\text{O}$ $E_e = 0.47 - 0.059 \text{ pH}$