Electrosynthesized CuO_x/graphene by a four-electrode electrolysis system for oxygen reduction reaction to hydrogen peroxide

Experimental

Chemicals and materials

Graphite powder was bought from Qingdao Graphite Company. Copper wire was purchased from Runde Metal Material Company. Anhydrous ethanol (99.5%) was purchased from Woke Company. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, 98%, powder) and proprylene carbonate (PC, ≥99.9%) were bought from Aladdin.

Characterization

X-ray diffraction (XRD) analysis was applied to analysis the crystalline of as-prepared samples on an X-ray diffractometer (Ultima IV-185) using Cu Ka radiation. Raman spectra were applied to test the defective properties of sample on a JobinYvon LabRAM HR800 micro-Raman spectrometer. X-ray photoelectron spectroscopy (XPS) was operated to detect the chemical compositions of the materials on Thermo Fisher SCIENTIFIC with Al Ka X-ray source. Scanning electron microscopy (SEM, JSM-7001F) and transmission electron microscopy (TEM, FEI Tecnai F20) were used to study the morphologies of the samples. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was measured to analyze the chemical composition (Cu) of the obtained samples.

Preparation of CuO_x/graphene

A facile four-electrode electrolysis system is first designed to synthesize the CuO_x/graphene composites as shown in Fig. 1. 50 mg of graphite was put in a porous plastic tube with a platinum plate inserted and served as negative electrode and positive electrode respectively. These two electrodes were put in proprylene carbonate (PC) solvent containing 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$). Copper wire bipolar electrodes were put in both sides of graphite electrode respectively. A voltage (30 V, 20 V or 10 V) was applied for 4 h. After the electrochemical expansion step, the exfoliated graphite was taken out from the cathode and dispersed in the electrolyte solution. This mixture was stirred for 12 h and then transferred into 100 ml Teflon cup inserted in a stainless steel autoclave. After continuous Ar gas (0.5 h) flowed through the Teflon cup to completely remove the air, the solution was treated at 160 ^{o}C under stirring (500 round min^{-1}) for 12 h. Finally the samples were filter washed with PC solution for three times and ethanol for three times, then dried in a vacuum oven at 80 ^{o}C for 8 h.

Electrochemical tests

Electrochemical properties of CuO_x/graphene catalysts were tested in 1 M KOH solution by a CHI Instruments 760E electrochemical workstation using a standard three-electrode setup. A graphite rod, a modified glassy carbon electrode (GCE), and Hg/HgO (dipped in 1M KOH) were used as the counter, working, and reference electrodes, respectively. The rotating disk electrode (RDE, diameter = 3mm) is used as the working electrode on which deposited with the catalysts ink. The catalyst ink was prepared by dispersing 5.0 mg of catalyst into 0.75ml of anhydrous ethanol and 0.25ml of ultrapure water with 0.03ml of Nafion solution (5 wt%), then treated with ultra-sonication for 30 min. Rotating ring disk electrode (RRDE, diameter = 4 mm) was also used as a working electrode to detect hydrogen peroxide.

Pior to each measurement, N_2 gas was bubbled through the electrolyte for 30 min in order to expel O_2. Furthermore, to remove any organic species, cyclic voltammograms (CVs) were measured in a 1M KOH aqueous solution at a scan rate of 50 mVs^{-1} under N_2 ambient. Then repeat the above CV test with oxygen saturation for 30 min. The electrocatalytic activity for ORR was investigated by linear sweep voltammograms (LSVs), with scan rate of 5mV/s at different rotational speeds. All electrochemical measurement was performed at room temperature. All potentials were converted to reversible hydrogen electrode (RHE) according to the following equation:

$E(RHE) = E(Hg/HgO)+0.0591*pH+0.098$

The kinetic current (j_k) value can be analyzed on the basis of koutecky-levich(K-L) equation.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f}$$

J_f^{-1} is very small and negligible

$J_d=0.620nFAC_oD^{2/3}\omega^{1/2}\upsilon^{-1/6}$

J is the measured current density, j_k and j_d are the kinetic and diffusion-limiting current densities, n is the overall number of electrons transferred in O_2 reduction, F is Faraday constant(F=96485C/mol), A is area of electrode, C_o is the concentration of oxygen in solution,($Co=1.21*10^{\wedge(-6)}$) D is the rate of diffusion of oxygen molecules(D=1.65*10^(-5)), ω is the angular velocity of the disk (ω=2πN, N is the linear rotation speed), υ is the kinetic viscosity of the solution($0.01 cm^2/s$). The n value and j_k can be obtained from the slope and intercept of the K-L plots, respectively.

RRDE measurements were performed to calculate the electron transfer number (n) and hydrogen peroxide selectivity (%H_2O_2) of catalysts during ORR from the following equation. I_d and I_r represent the disk and ring current respectively, N refers to the collection efficiency of Pt ring, which is (N=0.49) in this study.

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

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

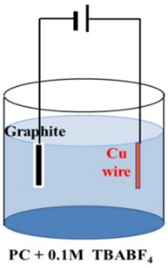

Fig. S1 The initial electrochemical synthesis device of CuO$_x$/G.

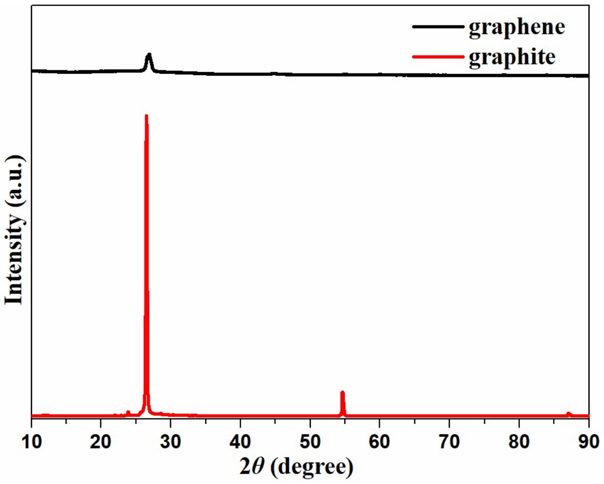

Fig. S2 The XRD spectra of graphene and graphite

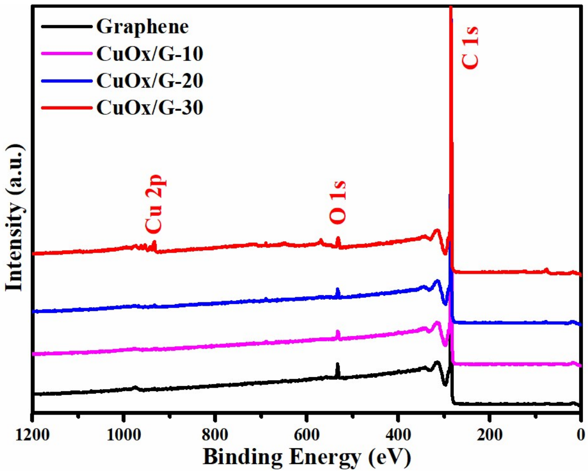

Fig. S3 The XPS survey spectra of these as-prepared samples

Table S1 The content of Cu with different oxidation states calculated based on the ICP-OES results and XPS results.

Voltage (V)	Cu^+ mol% (XPS)	Cu^{2+} mol% (XPS)	Cu^{2+}/Cu^+ ratio (XPS)	Cu wt% (ICP-OES)	Cu_2O wt% (Cal.)	CuO wt% (Cal.)
10	57.5	42.5	0.74	0.85	0.55	0.45
20	48.0	52.0	1.08	2.18	1.18	1.42
30	35.8	64.2	1.79	11.71	4.71	9.40

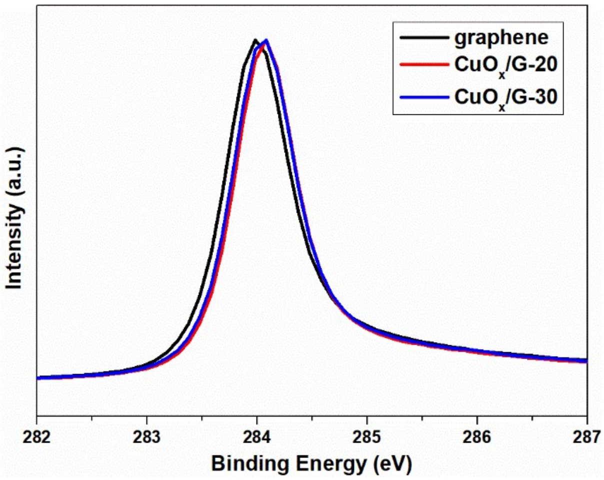

Fig. S4 The XPS C1s spectra of these as-prepared samples

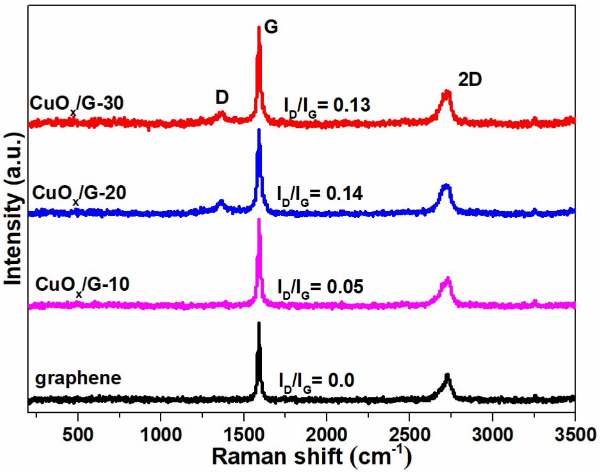

Fig. S5 Raman spectra of the samples prepared at different electrolytic voltages and graphene prepared at 30 V.

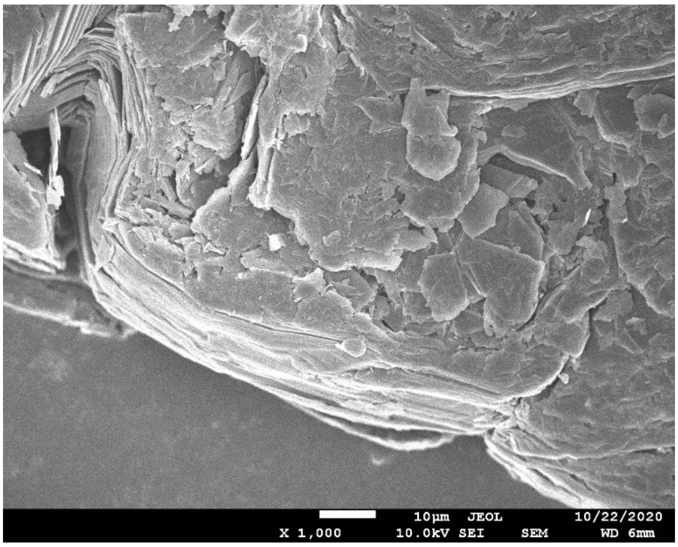

Fig. S6 Representative SEM micrograph of graphite powder;

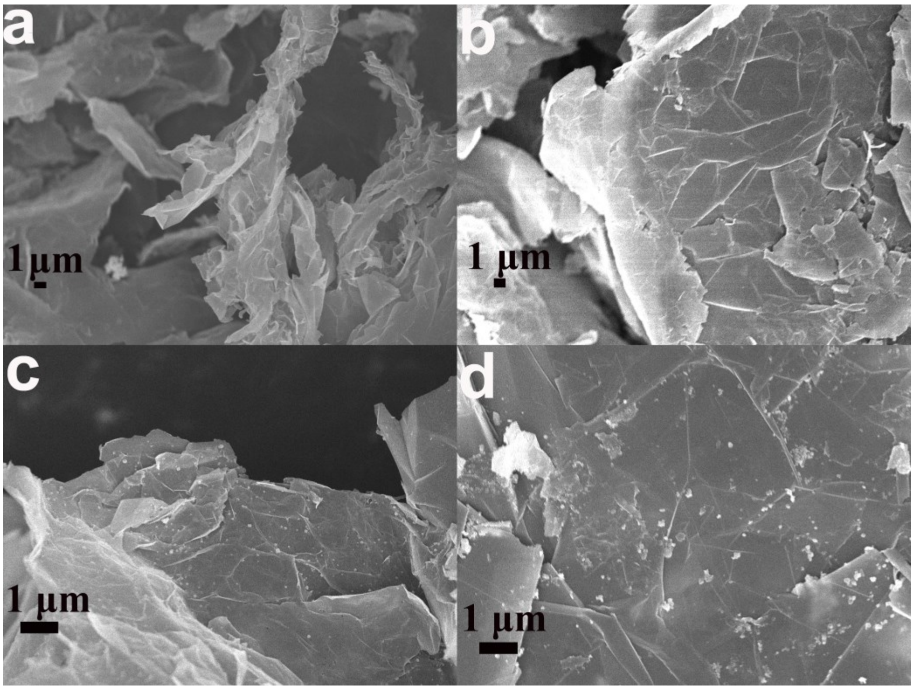

Fig. S7 (a) Representative SEM micrograph of obtained graphene prepared at 30 V via electrochemical exfoliation; (b) Representative SEM micrograph of CuO_x/G-10 prepared at 10 V; (c) Representative SEM micrograph of CuO_x/G-20 prepared at 20 V; (d) Representative SEM micrograph of CuO_x/G-30 prepared at 30 V.

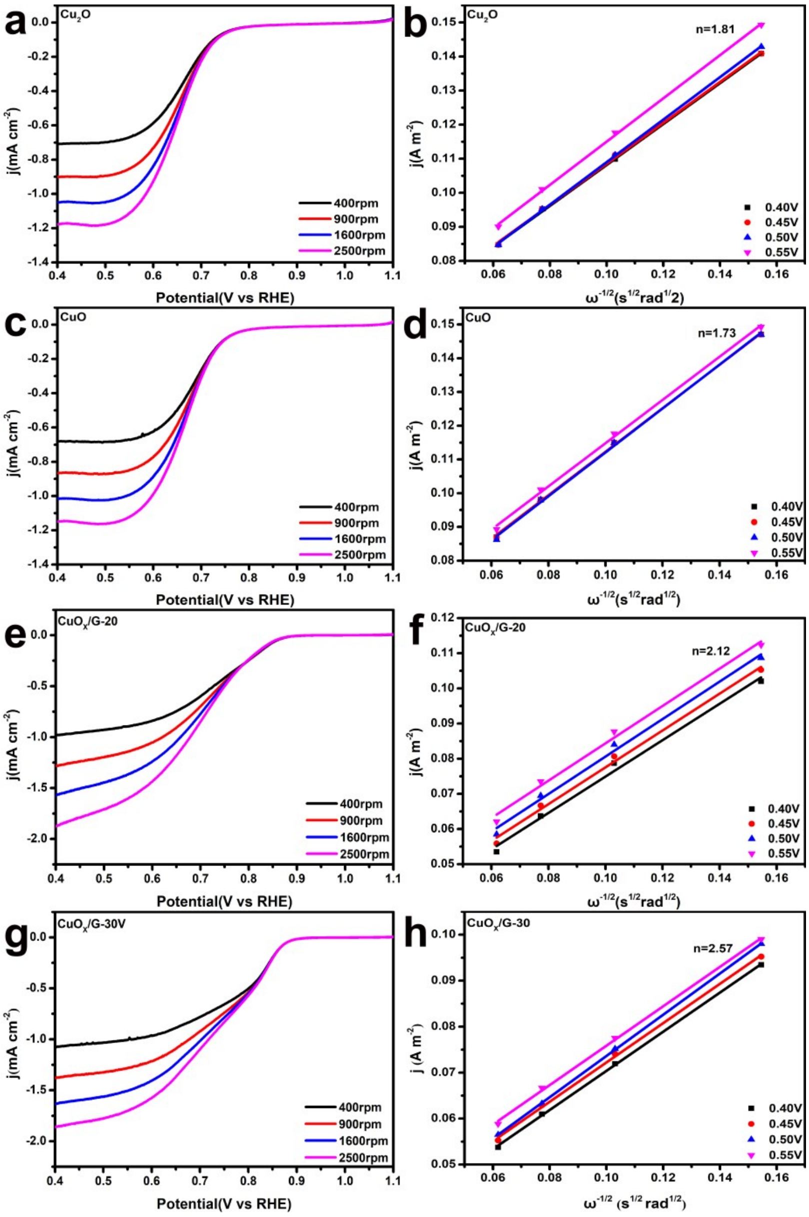

Fig. S8 (a) Rotating-disk voltammograms of CuO in O_2-saturated 1.0 M KOH with a sweep rate of 5 mVs^{-1} at different rotation rates; (b) Koutecky–Levich plots (J^{-1} versus $\omega^{-0.5}$) at different potentials corresponding to (a); (c) Rotating-disk voltammograms of Cu_2O in O_2-saturated 1.0 M KOH with a sweep rate of 5mVs^{-1} at different rotation rates; (d) Koutecky–Levich plots (J^{-1} versus $\omega^{-0.5}$) at different potentials corresponding to (c); (e) Rotating-disk voltammograms of CuO_x/G-20 V in O_2-saturated 1.0 M KOH with a sweep rate of 5 mVs^{-1} at different rotation rates; (f) Koutecky–Levich plots (J^{-1} versus $\omega^{-0.5}$) at different potentials corresponding to (e); (g) Rotating-disk voltammograms of CuO_x/G-30 V in O_2-saturated 1.0 M KOH with a sweep rate of 5 mVs^{-1} at different rotation rates; (h) Koutecky–Levich plots (J^{-1} versus $\omega^{-0.5}$) at different potentials corresponding to (g);

H_2O_2 generation was performed in a H-type electrolytic cell separated by Nafion 115 membrane using chronoamperometry at 0.5 V vs. RHE for 120 min. Both compartments were filled with 40 mL of the same electrolyte. The catalyst suspension (50 µL) was loaded onto 1.2 cm × 1 cm carbon fiber paper to prepare the working electrode. The H_2O_2 (HO_2^-) produced was quantified by $Ce(SO_4)_2$ titration method[1]. The yellow transparent $Ce(SO_4)_2$ solution (1mM) was prepared by dissolving 33.2 mg $Ce(SO_4)_2$ in 100 ml 0.5 M sulfuric acid solution. To obtain the calibration curve, H_2O_2 with known concentration was added to $Ce(SO_4)_2$ solution and measured by ultraviolet-visible spectroscopy. Based on the linear relationship between the signal intensity and Ce^{4+} concentration (~0.2–1.0 mM), the H_2O_2 concentration of the sample could be obtained.

The faradaic efficiency of H_2O_2 production was calculated as follows:

$$FE(H_2O_2\%) = \frac{2CVF}{Q}$$

where C is the concentration of H_2O_2 (M), V is the volume of electrolyte (L), F is the Faraday constant (C mol^{-1}), and Q is the quantity of charge passed through the cell.

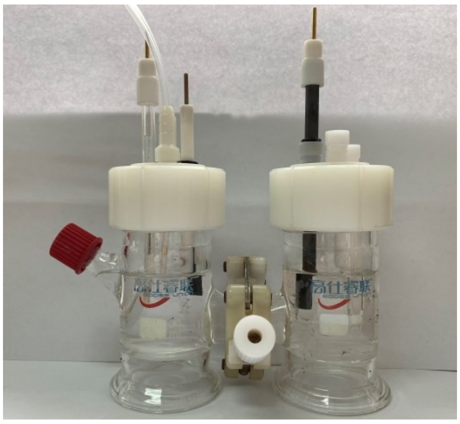

Fig. S9 H-shaped electrochemical cell.

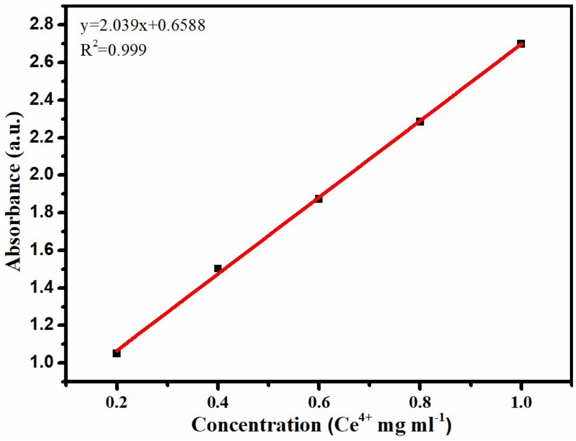

Fig. S10 The calibration curve of Ce^{4+} concentration with absorbance tested by ultraviolet-visible spectroscopy.