

## Electronic Supporting Information

# Enhanced Electrochemical Catalytic Activity by Copper Oxide Grown on Nitrogen-doped Reduced Graphene Oxide

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## Chemicals

All chemicals are purchased from Sigma-Aldrich and used without further treatment. Pt/C used is 20% Platinum on Vulcan XC-72, purchased from Fuel Cell Store.

## 15 Synthesis of GO

Graphite flake (3 g) was put into concentrated H<sub>2</sub>SO<sub>4</sub> (12 ml), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.5 g), and P<sub>2</sub>O<sub>5</sub> (2.5 g). The mixture was kept at 80 °C for 4.5 h, then cooled to room temperature and diluted with 0.5 L of DI water. The mixture was filtered and washed with DI water. The product was dried in vacuum at 50 °C overnight.

20 The pretreated graphite was put into cold (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub> (120 mL). Then, KMnO<sub>4</sub> (15 g) was added gradually under stirring and the temperature of the mixture was kept to be below 20 °C by ice cooling. Successively, the mixture was stirred at 35 °C for 2 h, and then diluted with DI water (250 mL) using ice bath cooling. The mixture was then stirred for 2 h, and then additional 0.7 L of DI water was added. 20 mL of 30% H<sub>2</sub>O<sub>2</sub> was added to the mixture. The mixture was washed with 1:10  
25 HCl aqueous solution (1 L) and DI water. The resulting paste-like product was diluted to make a graphite oxide dispersion. Exfoliation was carried out by sonicating graphite oxide dispersion under ambient condition for 30 min, followed with centrifuging at 3000 rpm for 30 min to eliminate unexfoliated graphite.

For measurement of N<sub>2</sub> adsorption-desorption isotherms, the GO is thermally reduced under 200 °C  
30 in vacuum to form rGO.

## Synthesis of CuO

0.25 ml of 0.1 M CuCl<sub>2</sub> was added to 16 ml ethanol and stirred for 5 min at 25°C. Then, 0.75 ml of 0.1 M NaOH was added to the suspension and stirred for another 1 hour. The suspension was then centrifuged, washed and dispersed in ethanol.

## 35 Synthesis of CuO/GO.

0.25 ml of 0.1 M CuCl<sub>2</sub> was added to 8 ml of GO solution (1 mg ml<sup>-1</sup> in water) and was stirred for 5 min. Then 0.75 ml of 0.1 M NaOH was added to the suspension and stirred for another 1 hour at 60°C. The suspension was then centrifuged, washed with water and dispersed in ethanol. For measurement of N<sub>2</sub> adsorption-desorption isotherms, the sample is degassed under 200 °C in vacuum where GO is

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thermally reduced to reduced GO (rGO).

## Characterization

SEM images were taken with Philips XL30 FEG SEM. TEM images were collected with Tecnai F20. XRD spectrums were measured with Rigaku Miniflex benchtop XRD with Cu K $\alpha$  line. N<sub>2</sub> adsorption/desorption measurement was carried out with Micromeritics Tristar II. Surface area is calculated by the multipoint BET method on basis of adsorption curve data. XPS were taken by KRATOS Axis Ultra DLD with Al K $\alpha$  line. FTIR were collected with Nicolet 6700 FTIR. TGA were measured with SETARAM ABSYSTEM Thermogravimetric Analysis.

## Formulae

### 10 Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K}$$

J is the measured current density. J<sub>L</sub> is the diffusion-limiting current density. J<sub>K</sub> is the kinetic-limiting current density.

$$J_L = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6}\omega^{1/2}$$

Where n is the electron transfer number, F = 96485 C mol<sup>-1</sup> is Faraday constant, C<sub>0</sub> = 1.2 mol m<sup>-3</sup> is the concentration of O<sub>2</sub>, D<sub>0</sub> = 1.97 × 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup> is the diffusion coefficient of O<sub>2</sub> in water,  $\nu$  = 1.004 × 10<sup>-6</sup> m<sup>2</sup> s<sup>-1</sup> is the kinematic viscosity of water, and  $\omega$  is the angular velocity of the electrode.

J<sub>K</sub> and n are derived from the slope and intercept of KL plot.

### Equation in RRDE Measurement:

$$\%HOO^- = 200 \times \frac{I_r/N}{I_d + I_r/N}$$

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

I<sub>r</sub> is the ring current and I<sub>d</sub> is the disk current. N = 0.37 is the current collection efficiency of the RRDE.

### 20 Calculation of equilibrium electrode potential of reaction (3) and (2\*)

All the equations and data from Ref. 1.

### Estimation of ionic activity coefficient

In electrolyte of 0.1 M KOH and 0.01 M H<sub>2</sub>O<sub>2</sub>, the concentrations of each kind of ions are:

K<sup>+</sup>: 0.1 M, OH<sup>-</sup>: 0.09M, HOO<sup>-</sup>: 0.01M.

25 The ionic strength (I) is estimated using equation:

$$I = \frac{1}{2} \sum c_i z_i^2$$

Where  $c_i$  and  $z_i$  are the concentration and ionic charge of each ions.  $z_i=1$  for all ions so that  $I=0.1$  for our electrolyte.

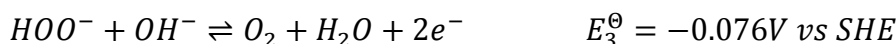
Ionic activity coefficient of each ion ( $f_i$ ) is calculated using Debye-Hückel equation:

$$-\log f_i = \frac{Az_i^2\sqrt{I}}{1 + B\tilde{a}_i\sqrt{I}}$$

Where A and B are constants. At 25°C,  $A=0.5115$  and  $B=0.3291$ .  $\tilde{a}_i$  is the effective radius of each ion in angstrom. For  $\text{OH}^-$  and  $\text{HOO}^-$ ,  $\tilde{a}$  is taken 3.5.

As a result,  $f=0.761$ .

### Estimation of equilibrium electrode potential



The equilibrium electrode potential of reaction is calculated by Nernst equation:

$$E = E^\ominus + \frac{RT}{ZF} \ln Q$$

$R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  is the universal gas constant.  $T=298\text{K}$  is the absolute temperature.  $Z$  is the number of electrons involved in the electrode reaction.  $Z=2$  for both reactions.  $F=96485 \text{ C mol}^{-1}$  is the Faraday constant.  $Q$  is the reaction quotient.

For reaction (3), pressure of  $\text{O}_2$  is 1 atm. Thus  $[\text{O}_2]$  is 1.

$$E_3 = E_3^\ominus + \frac{RT}{ZF} \ln \frac{[\text{O}_2]}{[\text{HO}_2^-][\text{OH}^-]} = 0.021V \text{ vs SHE}$$

For reaction (2\*):

$$E_{2*} = E_{2*}^\ominus + \frac{RT}{ZF} \ln \frac{[\text{HO}_2^-]}{[\text{OH}^-]^3} = 0.908V \text{ vs SHE}$$

The reference electrode used has potential 0.2 V vs SHE. Thus,

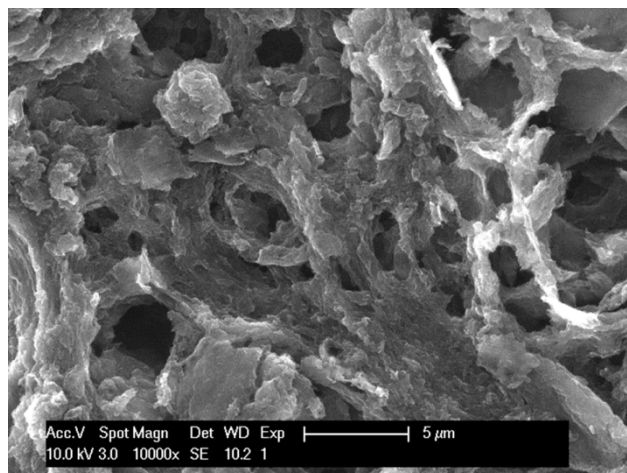
$$E_3 = -0.179V$$

$$E_{2*} = 0.708V$$

### Reference

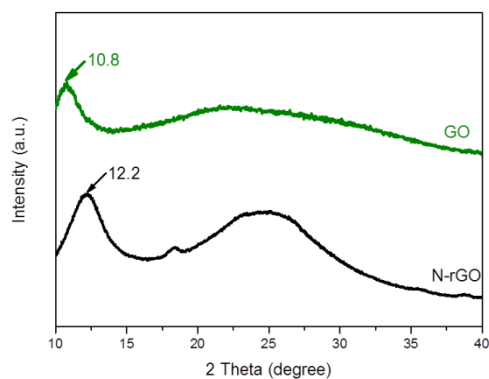
1. *Lange's Handbook of Chemistry*, J. A. Dean, McGraw-Hill, Columbus, 15th edn., 1999, vol. 8, pp. 8.2 - 8.5, 8.132.

## Supporting figures

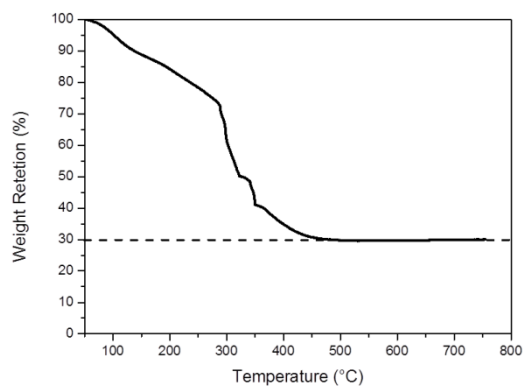


**Fig. S1** SEM image of CuO/N-rGO. Micrometer-scale pores are shown.

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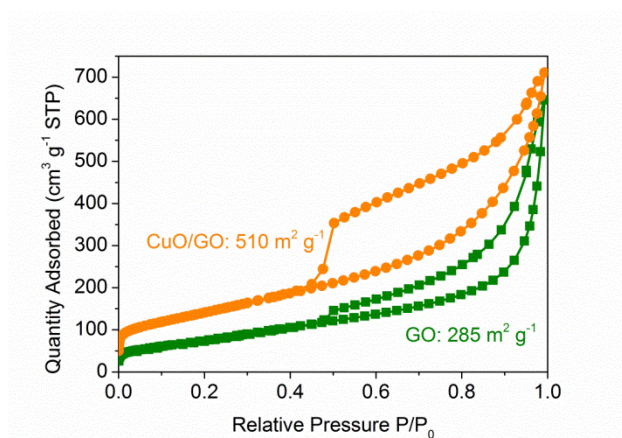


**Fig. S2** XRD pattern of GO and N-rGO. High-shifted interplanar diffraction of N-rGO is attributed to decreased interplanar displacement by elimination of functional groups during reduction.



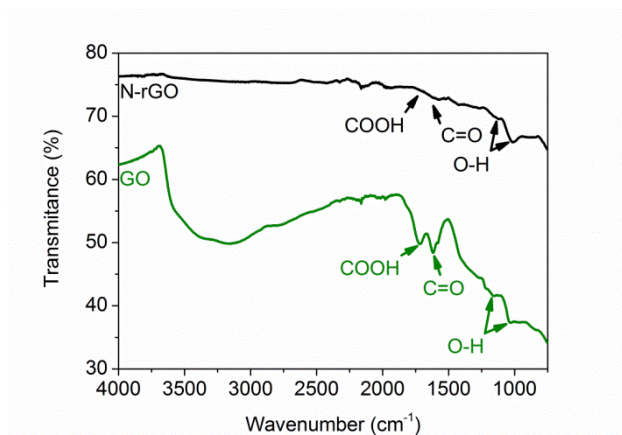
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**Fig. S3** TGA of CuO/N-rGO in air. N-rGO is burnt out and CuO is remained.



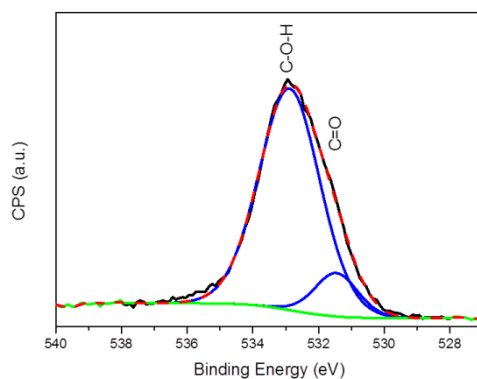
**Fig. S4** N<sub>2</sub> adsorption-desorption isotherms of GO and CuO/GO. Specific surface increases by CuO intercorporation.

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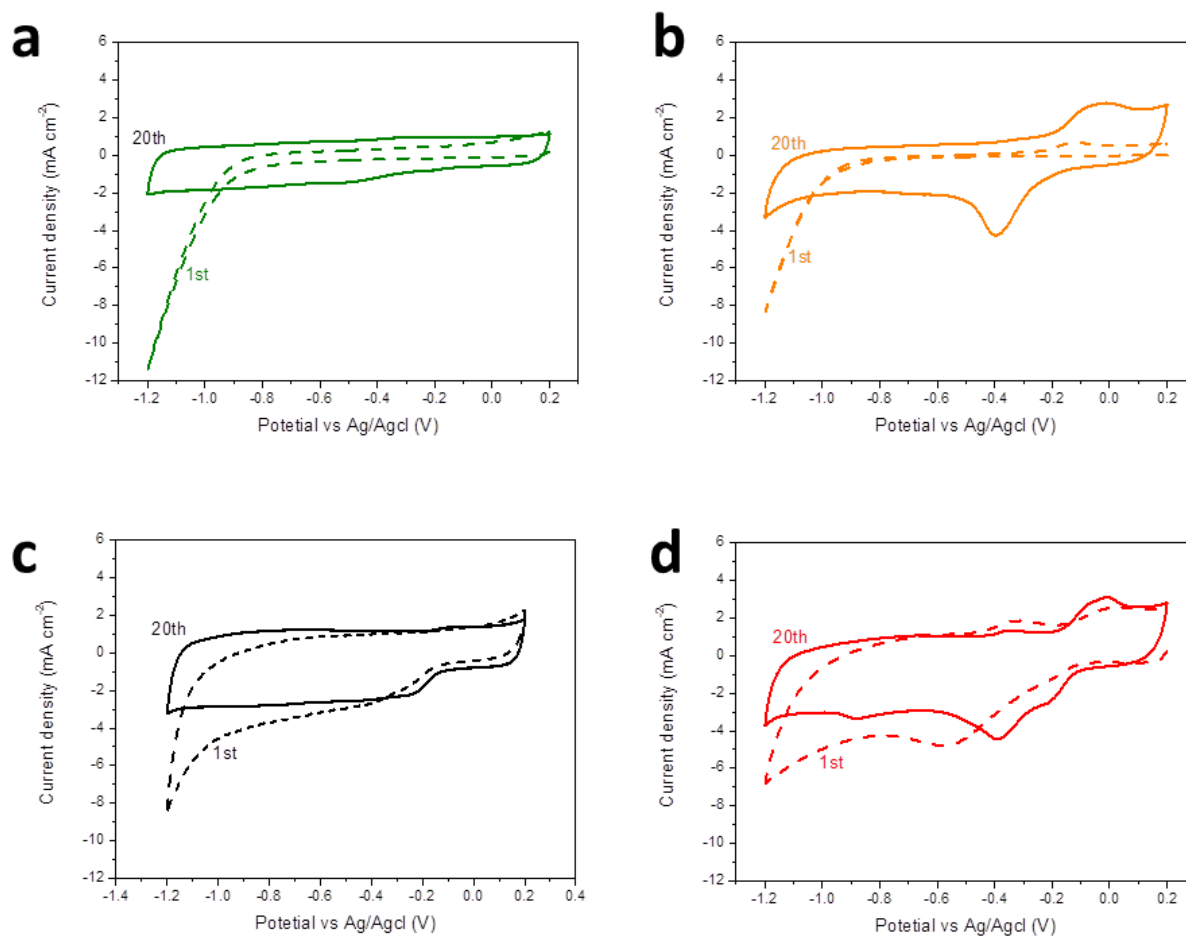


**Fig. S5** FTIR of GO and N-rGO. Carboxyl groups are eliminated after reduction while hydroxyl groups remain.

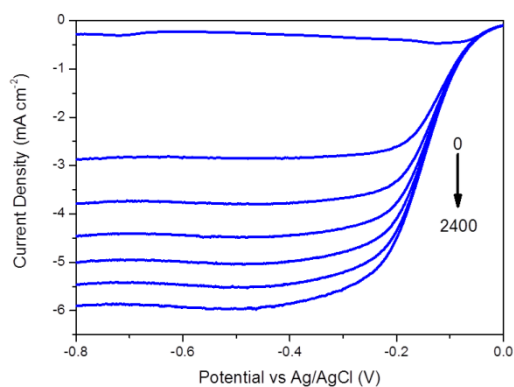
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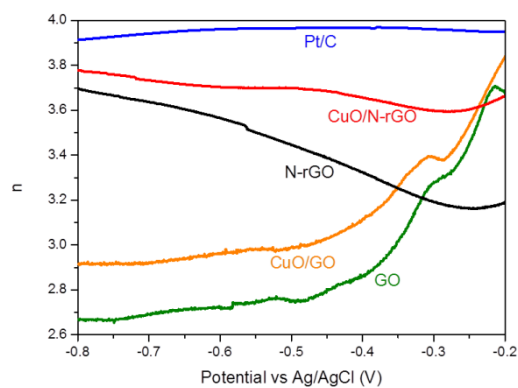
**Fig. S6** High resolution XPS of O 1s of N-rGO. Carbonyl groups are of low amount after reduction.



**Fig. S7** 1st (solid) and 20<sup>th</sup> (dash) CV of GO (a), CuO/GO (b), N-rGO (c) and CuO/N-rGO (d). GO is a poor in conductivity so that it shows very low capacitance. It is reduced at low potential and achieves high conductivity after 20 cycles of CV. N-rGO already has good conductivity but can still be reduced a bit.

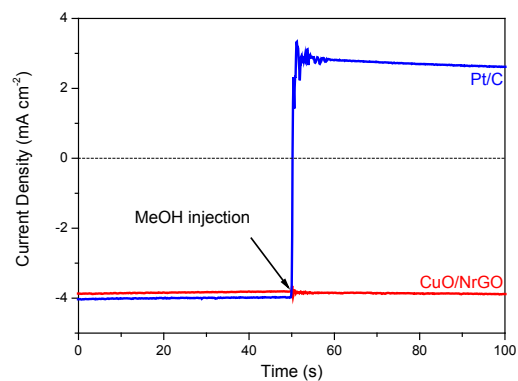


**Fig. S8** LSV of Pt/C at different rotation rate (rpm).



**Fig. S9** Electron transfer number of different catalysts calculated from RRDE test. The n is in accordance with that calculated from KL plot.

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**Fig. S10** MeOH tolerance test of CuO/N-rGO and Pt/C under -0.3 V and 1600 rpm.