# **Supporting Information Available**

# Direct Catalytic Oxidation of Benzene to Phenol over Metal-free Graphene-based Catalysts

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# **Experimental**

#### Materials

The GO was synthesized by oxidation of purified natural small graphite and graphite flakes according to a modified Hummer's method. <sup>1</sup> Typically, the mixture of graphite (10 g) and sodium nitrate (5 g) was stirred by mechanical agitator in the concentrated sulfuric acid (230 ml) in the ice bath, and then 30 g of potassium permanganate was slowly put into the system within 10 minutes. After 3 h, the mixture was heated to 35 °C for 4 h, and then the deionized water (460 ml) was added to the mixture slowly (< 90 °C). After the water was added completely, the temperature of the slurry was increased until 98 °C and it was kept at that temperature for 3 h. The batch was poured into a 3 L beaker filled with 2 L deionized water. Immediately, the hydrogen peroxide (100 ml, 30%) and hydrochloric acid (300 ml, 37%) was added into the

mixture. Remove that supernatant twice a day until it did not show any precipitation with AgNO<sub>3</sub> solution. The mixture was filtered and the cake was put into oven (60 °C) for 2 weeks and then carefully powdered to get GO.

Graphene sheets were achieved by modified Li's method.<sup>2</sup> 0.4 g of GO was dispersed in 400 ml water by sonication for 30 min and then 4.12 mL of hydrazine hydrate (85%) and 70 mL of ammonia solution were added into the suspension. The solution was placed in an oil bath at 95 °C for 3 h and the color of the solution changed from yellow-brown to black. Solid graphene sheets (CCG) were obtained by filtration over a membrane filter and dried in an air oven at 60°C.

#### **Catalytic evaluation**

Benzene oxidation reaction rates and selectivities were measured at the sealed pressure tube at 333K. Catalyst samples 20 mg (50mg) with 2.4ml H<sub>2</sub>O<sub>2</sub> (30%) as oxidant and 130 mg benzene as substrate in 1.2 ml acetonitrile for different time. Upon completion of the reaction, 5 ml of ethanol was added through the condenser and a homogeneous solution was obtained. After removal of the catalyst, the solution was diluted to exactly 25 ml in a volumetric flask. 80  $\mu$ l of reaction mixture was diluted to 1 ml by acetonitrile/water (volume ratio 40:60) and analyzed by Agilent HPLC 1200 using a C-18 column.

### Characterization

Powder X-ray diffraction (XRD) performing on a RINTD/MAX-2500 X-ray diffractometer using Cu-K $\alpha$  radiation (l = 1.5406 Ű) was used for determining the crystal structure of the samples.

Raman spectroscopy was obtained using a Horiba HR800 Raman spectroscopy with a 632.8 nm line from He-Ne laser.

XPS spectra were obtained using an Axis Ultra spectrometer (Kratos, UK). A mono Al-K $\alpha$  (1486.6 eV) X-ray source was used at a power of 225 W (15 kV, 15 mA). To compensate for surface charge effects, binding energies were calibrated using the C 1s hydrocarbon peak at 284.8 eV.

For TEM analysis, samples were dissolved in ethanol under ultrasonic treatment and then put a drop of the solution on a Cu grid. TEM images were taken with a FEI Tecnai G2 T20

The zeta potential of the CCG and the GO was determined using the Zetaplus analyzer (Brookhaven Instruments Corporation) in water at PH=7.

BET of the CCG and graphite was determined using the Micromeritics TriStar 3000 V6.08 A (Analysis Adsorptive: N<sub>2</sub>. Analysis Bath Temp.: -195.8).

 $H_2O_2$  decomposition rate in different catalysts was determined by Gasometric Method.<sup>3</sup> The amount of catalysts was 6 mg and the volume of  $H_2O_2$  (30%) was 0.6 ml.

TPD-benzene of the catalysts was tested by chem-BET Plulsar TPD/TPR (quantachrome). First, the catalyst 40 mg was purged with nitrogen and then nitrogen containing benzene was introduced into the system until the saturated adsorption of benzene. And then the steam has been changed back to nitrogen

(30ml/min) and after flashing at room temperature for 30 min, the reactor was heated

with the rate of 10 K/min, the signal of benzene desorption was detected.



Figure S1: TEM images of graphite and CCG. small graphite with the diameter is about 25  $\mu$  m(A, B) and CCG (C, D). There are some dispersed small graphite fragments about 150 nm in small graphite. While, there are a lot of folds among the small flakes in the CCG.



Figure S2 (A): XRD pattern of graphite (a), the reacted CCG (b), fresh CCG (c) and CCG-H (d).



Figure S3: Benzene–TPD spectra of chemically converted graphene CCG, graphene oxide (GO) and graphite. The benzene desorption temperature in CCG is up to 158 °C because of the  $\pi$ - $\pi$  interaction which is much stronger than in GO nearly 90 °C which is a little higher than the boiling point of benzene (80 °C) but the graphite hardly can adsorb benzene.



Figure S4: Released oxygen volume as a function of reaction time at different temperatures. CCG (A); GO (B); graphite (C) and CCG-Mn (D). Condition: 6 mg catalysts and 0.6 ml hydrogen peroxide (30%). From the graphic we can see that it is better for graphite to catalyse decomposition of hydrogen peroxide than GO in 60 and 70°C. The CCG-Mn containing a mass fraction of Mn of 1.2 % because of not being washed clean enough deliberately could catalyse rapid decomposition of hydrogen peroxide.



Figure S5: Raman spectra of the CCG (a) and recycled CCG after 6 cycles (b) and 8 cycles (c).



Figure S6: The C 1s XPS spectra of: (A) CCG, (B) GO.

Material	GO	CCG
C/O ratio (atom)	3.0	9.4
zeta potential (mV)	-37.8	-24.6

Table S1: The C/O ratio based on XPS and the zeta potential of GO and CCG.

Table S2: Direct oxidation of benzene to phenol with TS-1 as catalyst at identical experimental conditions for the reaction with CCG.<sup>a</sup>

Entry	Catalyst	Particle size (µm)	Si/Ti (mol)	Conv. (%)	Phenol sel. (%)
1	TS-1	0.1-0.2	40	8.8	26.4
2	TS-1 <sup>b</sup>	1	50	4.4	14.3

<sup>a</sup> Reaction conditions: 130 mg benzene, 2.4 ml hydrogen peroxide (30%), 1.2 ml acetonitrile, 20 mg catalyst, in pressure vessel at 333 K 16h. <sup>b</sup> handle by tetrapropyl ammonium hydroxide (TPAOH). The TS-1 was obtained from Dr. Juan Tan's group of State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 16012, China.

Table S3: The specific surface area of CCG and graphite.

Material	Surface Area (BET m <sup>3</sup> g <sup>-1</sup> )
CCG	446.5
graphite	0.9



Figure S7: The conversion ratio of  $H_2O_2$  to  $O_2$  when benzene was catalytically oxidized with the assistance of CCG, GO and TS-1.

Note S1.

The decomposition of  $H_2O_2$  in solid catalysts follows a pseudo-first-order kinietic as long as an excess of solid catalyst is used. <sup>3, 4</sup> Following first-order reaction kinetics, overall kinetics of  $H_2O_2$  decomposition follow the formula

$$\frac{-dc_{H_2O_2}}{dt} = k_1 c_{H_2O_2}$$
(1)

and its integrated form

$$\ln \frac{c_t}{c_0} = -k_l t \tag{2}$$

where  $c_{\text{H2O2}}$  is the hydrogen peroxide molar concentration,  $k_1$  is the global H<sub>2</sub>O<sub>2</sub> decomposition rate constant at a specific temperature, and *t* represents the reaction time.  $c_t$  and  $c_o$  are the concentration of H<sub>2</sub>O<sub>2</sub> at a time and t=0, respectively. In the decomposition reaction, the concentration of hydrogen peroxide is proportional to the released volume of oxygen and proportionality constant is the constant, so it could be written as

$$-k_{1}t = \ln(\frac{V_{0} - V_{t}}{V_{0}})$$
(3)

$$k = A e^{-E_a/RT}$$
(4)

Where  $V_t$  and  $V_0$  represent the released oxygen volume at a time t and total oxygen released with the decomposition of all of hydrogen peroxide,  $E_a$  is the activation energy for the reaction, A is the frequency factor and R is the gas constant.

## Reference

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