# Supporting information for

Graphene oxide: A Convenient Metal-free Carbocatalyst for Facilitating Aerobic Oxidation of 5-Hydroxymethylfurfural into 2,5-Diformylfuran

Guangqiang Lv <sup>a,b,</sup> Hongliang Wang <sup>a</sup>, Yongxing Yang <sup>a</sup>, Tiansheng Deng <sup>a</sup>, Chengmeng Chen <sup>c</sup>, Yulei Zhu <sup>d</sup>, Xianglin Hou <sup>a\*</sup>

<sup>a</sup> The Biorefinery Research and Engineering Center, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001,People's Republic of China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing, 100039 People's Republic of China

<sup>c</sup> Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan 030001,People's Republic of China

<sup>d</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 South Taoyuan Road, Taiyuan, People's Republic of China. 030001

*Fax:* +86 351 4041153; *Tel:* +86 351 4049501, *E-mail:* <u>houxianglin@sxicc.ac.cn</u> (Xianglin Hou)

## **Experimental section**

### 1. Chemicals

Graphite powder (Aladdin, Aladdin Chemistry Co., Ltd. Shanghai, China), H<sub>2</sub>SO<sub>4</sub> (98 wt.%, Xilong Chem. Co., Ltd, China), NaNO<sub>3</sub> (Kermel Chem. Reagent Co., Ltd. China), KMnO<sub>4</sub> (Kermel Chem. Reagent Co., Ltd. China), H<sub>2</sub>O<sub>2</sub> (30%, Dong Fang Chem. Co., Ltd. China), 5-Hydroxymethylfrufural (98%, DEMO Medical Tech Co., Ltd. China), 2,5-Diformylfuran (98%, TCI). Acetonitrile (Kermel Chem. Reagent Co., Ltd. China). All the regents were used as received without further purification.

### 2. Preparation of graphene oxide (GO)

GO was prepared by the Hummers' method. Typically, graphite powder (8000 meshes, 5 g) and NaNO<sub>3</sub> (2.5 g) were mixed with sulfuric acid (115 mL, 98 wt. %) under magnetic stirring for 0.5 h, then the mixture was put into an ice bath before KMnO<sub>4</sub> (15 g) was slowly added, during which the temperature was kept below 20 °C. Subsequently, the reaction system was transferred to a water bath of 35 °C and maintained for 0.5 h. After that, 230 mL water was slowly added to the system. The diluted suspension was then stirred at 98 °C for 15 min, followed by another 700 mL of water was added. And the reaction was terminated by the addition of  $H_2O_2$  (50 mL, 30 wt. %). The mixture was filtered and washed with HCl (1 L, 1 mol·L<sup>-1</sup>) and a large amount of distilled water in sequence. The resulting graphite oxide was separated from the colloid by spray drying method. The obtained graphite oxide (1.0 g) was placed into an Al<sub>2</sub>O<sub>3</sub> boat in the center of a tube furnace, and the tube was connected to a vacuum pump to maintain the pressure in tube at 25 Torr. The temperature of the furnace was raise to 200 °C in 10 min and remained for 4 hours. After that, the furnace was cooled down naturally to room temperature, and the graphite oxide was exfoliated to graphene oxide and partially reduced.

The procedure of thermal reducing GO materials under different temperature was described as follow: the GO sample (300 mg) was placed into the tube furnace center. After flowing with He (100 ml·min<sup>-1</sup>) for 20 min, the temperature of the furnace was raised to the indicated temperature at a heating rate of 10 °C · min<sup>-1</sup>. Three temperature temperatures of 400, 700, 1000 °C were chosen to obtain reduced samples at different degree. After 3 hours of thermal reducing at indicated temperature, the furnace was cooled down naturally to room temperature under flowing He atmosphere. The sample was named GO-400, GO-700 and GO-1000. After the sample was treated at 1000 °C in He atmosphere (100 mL·min<sup>-1</sup>) for 10 hours, the highly reduced GO sample was obtained, named GO-1000-H.

#### Ultrasonic exfoliated graphene oxide

The obtained grapheite oxide (0.5 g) was dispersed into 500 mL deionized water. The suspension was ultrasonicated under 40K Hz for 180 min and dried in a freeze dryer (-40 °C, 10-13 Pa), obtaining the stable and exfoliated GO.

#### 3. GO characterization

X-ray diffraction (XRD) patterns were conducted on a Rigaku MiniFlex II

desktop X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA with a scanning speed (2θ) of 4°/min. N<sub>2</sub> adsorption-desorption isotherms were exhibited at –196 °C on a Micromeritics TriStar 3000 instrument. The samples were first degassed under vacuum at 150 °C for 8 h. Scanning Electron Microscopy (SEM) was measured on a JSM-7001F microscope. TEM (Transmission electron microscope) was conducted on a JEM-2100F microscope. XPS were performed under an ultrahigh vacuum on a Kratos AXIS ULTRA DLD spectrometer with Al K radiation and a multichannel detector. The collected binding energies were calibrated by the C1s peak at 284.6 eV as reference. Raman spectroscopy was performed using a Raman Microprobe (HR-800 Jobin-Yvon) with a 532 nm Nd:YAG excitation source at room temperature. The amount of element was determined by elemental microanalysis (EA) (vario MICRO cube, Elemental).

#### 4. Acidimetric titration of GO material.

The acidic functional groups and the presences of such groups were determined by a neutralization adsorption experiment. Typically, Four GO samples (50 mg) were dispersed into 25 mL of 0.05 mol/L NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> aqueous solution and 0.05 mol/L NaOC<sub>2</sub>H<sub>5</sub> ethanol solutions. The resultant mixtures were allowed to equilibrate with magnetic stirring for 72 h without air. After that, the mixtures were filtered and the GO samples were washed with 75 mL deionized water. All of the filtrate was collected and 25 mL of the mixture was pipetted out and back titrated using 0.05 mol/L hydrochloric acid solutions (0.05 mol/L HCl solution in ethanol was used in titration of NaOC<sub>2</sub>H<sub>5</sub> filtrate). Bromocresol green - methyl red was used as the indicator.

The adsorbed base was calculated as follow equation (1-4):

$n_{NaOH} = c_{NaOH} V_{NaOH} - c_{HCI}$	V <sub>HCl</sub> (	(1)
--	--------------------	-----

$$n_{\text{Na2CO3}} = c_{\text{Na2CO3}} V_{\text{Na2CO3}} - c_{\text{HCl}} V_{\text{HCl}} / 2$$
(2)

$$n_{\text{NaHCO3}} = c_{\text{NaHCO3}} V_{\text{NaHCO3}} - c_{\text{HC1}} V_{\text{HC1}}$$
(3)

$$n_{\text{NaOC2H5}} = c_{\text{NaOC2H5}} V_{\text{NaOC2H5}} - c_{\text{HCl}} V_{\text{HCl}}$$
(4)

In the equations,

n  $_{\rm NaOH},$  n  $_{\rm Na2CO3},$  n  $_{\rm NaHCO3},$  n  $_{\rm NaOC2H5}$  : The adsorbed base quantity on GO samples.

 $c_{\text{NaOH}}$ ,  $c_{\text{Na2CO3}}$ ,  $c_{\text{NaHCO3}}$ ,  $c_{\text{NaOC2H5}}$ : The concentration of standard base solution.

 $V_{NaOH}$ ,  $V_{Na2CO3}$ ,  $V_{NaHCO3}$ ,  $V_{NaOC2H5}$ : The base solution volume used in GO

dispersion.

 $c_{\text{HCl}}$ : Standard HCl solution concentration.

V<sub>HCl</sub>: Standard HCl solution volume consumption in titration.

The surface oxygen groups on GO samples are determined as follow equations (5-8):

$$\eta (\text{RCOOH}) = n_{\text{NaHCO3}} / m_1$$
(5)

$$\eta (R_1 \text{COOCOR}_2) = 2 n_{\text{Na2CO3}} / m_2 - \eta (\text{RCOOH})$$
(6)

$$\eta (\text{ArOH}) = n_{\text{NaOH}} / m_3 - \eta (\text{RCOOH}) - \eta (R_1 \text{COOCOR}_2)$$
(7)

$$\eta (R_1 COR_2) = n_{NaOC2H5} / m_4 - \eta (RCOOH) - \eta (R_1 COOCOR_2) - \eta (ArOH) (8)$$

In the equations,

 $\eta$  (RCOOH),  $\eta$  (R<sub>1</sub>COOCOR<sub>2</sub>),  $\eta$  (ArOH),  $\eta$  (R<sub>1</sub>COR<sub>2</sub>): The oxygen group concentrations in GO-T materials.

m<sub>1</sub>, m<sub>2</sub>, m<sub>3</sub>, m<sub>4</sub>: The sample quantity used in different acid-base titrations.

### 5. Catalysts Reactivity tests

All the reactions were performed in a 100 mL Teflon-lined stainless steel autoclave with vigorous stirring. Typically, 100 mg GO, 1 mmol HMF, 1mmol TEMPO and 30 mL acetonitrile were added into the reactor. The reaction mixture was stirred and heated at 100 °C. After a fixed reaction time, the reactor system was quickly cooled to room temperature in an ice-water bath. For reusability tests, the GO was filtrated, washed in acetonitrile and dried at 80 °C in an oven.



The schematic diagram of experimental set-up as following:

### 6. Analytical methods

The products were separated by a reversed-phased C18 column (200 × 4.6 mm) at 25 °C with a detection wavelength of 280 nm. The mobile phase was acetonitrile and 0.1 wt.% acetic acid aqueous solution (30:70 v/v) at 0.5 mL/min. The HMF conversion and DFF yield were expressed in mol.%, based on the total

HMF amount. The product was identified by NMR.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ /ppm 7.34 (s, 2H), 9.86 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ /ppm 119.23 (2C), 154.23 (2C), 179.24 (2C).

## 7. Figures S1-9



Figure S1. Comparing of XRD patterns of fresh GO and used GO in reaction under  $N_2$  atmosphere.



Figure S2. SEM and TEM of fresh GO (up) and used GO (down, in  $N_2$  atmosphere) in oxidation reaction



Figure S3. XPS patterns of fresh GO and used GO in oxidation reaction in  $N_2$  atmosphere



Figure S4. Visible-Raman sepctra of fresh GO and used GO in oxidation reaction under  $N_2$  atmosphere.



Figure S5. XPS pattern of Ultrasonic exfoliated GO in water (1 mg/mL).



**Figure S6.** SEM and TEM of GO samples thermal annealed at 400  $^{\circ}$ C (a), 700 $^{\circ}$ C (b), 1000  $^{\circ}$ C (c) and 1000-H (d) in He atmosphere.



**Figure S7.** High-resolution C1s XPS spectra of the thermal treated GO material under different temperature or time.





**Figure S8.** Relationship between HMF initial reaction rate and total HMF conversion aftre 12 h with different oxygen groups in GO samples.



Figure S9. ESR measurement of thermal reduced GO materials.

#### 8. Tables S1-4

Cycles	HMF conversion (%)	DFF selectivity (%)
1	98.8	98.8
2	91.2	98.5
3	85.2	98.5
4	81.6	99.5
5	77.5	99.6
6	77.6	99.4
7	75.6	99.2
8	71.2	99.1
9	48.5	95.5
10	42.1	96.4

**Table S1** Recyclability of GO in aerobic oxidation of HMF<sup>*a*</sup>

<sup>a</sup> Reaction conditions: HMF, 1mmol, 126 mg; acetonitrile, 30 mL; TEMPO, 1mmol, 155 mg; GO, 100 mg. reaction temperature, 100 °C; reaction time, 24 h; stirring speed, 800 rpm; 0.1 MPa N<sub>2</sub> atmosphere in 100 mL autoclave.

Table S2. Elements content by EA and intensity ratio of  $I_D/I_G$  and  $I_{2D}/I_{2G}$  for GO,

thermal reduced GO and used GO by Raman

Samples	EA	Ra	man
	C/O ratio	$I_D/I_G$	$I_{2D}/I_{2G}$
GO	4.68	0.92	0.91
GO-used	4.71	0.93	0.92

GO-400	6.82	0.94	0.93
GO-700	13.47	0.95	0.96
GO-1000	20.64	1.19	0.97
GO-1000-Н	40.36	1.40	1.01

**Table S3.** BET analysis of GO and GO-T

Sample	$S_{BET}$	$PV (cm^3 g^{-1})$	Average PD (nm)
GO	340.6	1.22	14.3
GO-400	345.8	1.23	14.2
GO-700	347.3	1.25	14.5
GO-1000	346.1	1.24	14.8
GO-1000-Н	344.2	1.27	17.6

Table S4. Mn and oxygen content in GO-T and catalytic activity of GO materials with

Entry	Samples	Mn (ppm) <sup>b</sup>	$O(wt.\%)^c$	HMF conv.%	DFF Yield %
1	GO	250	18.64	89.4	88.3
2	GO-400	240	13.84	71.4	69.7
3	GO-700	250	7.52	39	37.2
4	GO-1000	258	5.86	23.2	17.15
5	GO-1000-Н	272	4.37	15.03	5.05
6 <sup><i>d</i></sup>	GO-washed	45	18.64	91.2	89.7
7 <sup>e</sup>	Mn/GO-1000-H-1	2700	4.37	17.1	6.56

different level of Mn on the aerobic oxidation of HMF  $^a$ 

8 <sup>e</sup>	Mn/GO-1000-H-2	5400	4.37	16.8	6.25
9 <sup>e</sup>	Mn/GO-1000-H-3	8100	4.37	15.4	7.13

<sup>a</sup> Reaction conditions: Reaction conditions: HMF (1 mmol, 126 mg), acetonitrile (30 mL), TEMPO (1 mmol, 155 mg), reaction time (3 h), reaction temperature (100 oC), catalyst (100 mg), 1 atm air pressure in 100 mL autoclave; stirring speed, 800 rpm.
<sup>b</sup> Determined by ICP.

<sup>*c*</sup> Determined by elemental analysis.

<sup>*d*</sup> The as-made GO was dispersed in 500 mL DI water at a concentration of 0.5 mg  $mL^{-1}$ . 5 mL HCl (37%) was added into the solution slowly. The mixture was kept in room temperature for 12 h with stirring. The final GO were filtered and washed by DI and acetone.

 $^{e}$  Mn/GO-1000-H were prepared by impregnation method. The GO-1000-H was dipped into a certain amount of KMnO<sub>4</sub> aqueous solution, stirred for 30 min. Dried in oven and followed by thermal treatment at 200 °C in vacuum condition (25 Torr) for 4 h.

### 9. Effect of solvents on HMF selective oxidation.

Table S5. Results of the aerobic oxidation of HMF into DFF in GO/TEMPO catalytic

Entry	Solvent	HMF conversion (%)	DFF selectivity (%)
1	Acetonitrile	89.4	98.7
2	Water	84.2	70.7
3	Methanol	26.0	98.1

system in various solvents <sup>a</sup>

4	Acetone	30.8	81.5
5	DMSO	49.0	99.8
6	DMF	69.8	61.3
7	MIBK	80.0	92.1
8	Toluene	100	93.6
9	Dichloromethane	38.6	65.5

<sup>*a*</sup> Reaction condition: HMF, 1 mmol, 126 mg; GO, 100 mg; TEMPO, 1 mmol, 155 mg; solvent, 30 mL; reaction time, 12 h; reaction temperature, 100 °C; 1 atm air pressure in 100 mL autoclave; stirring speed, 800 rpm.

The effect of different solvents on the oxidation of HMF into DFF was summarized in Table S5. HMF conversion and DFF selectivity were affected greatly by the solvent. Generally, the nature of these solvent effect is complicated because of their dependence on the catalyst properties and reaction condition and their origin remains unclear.<sup>1</sup> In addition, the properties of the solvent, such as polarity, dielectric property, steric hindrance, and acid-base properties, also have great effect on the chemical reaction. In polar solvents, different HMF transformation behaviors were observed (Table S5, entry 1-6). Water – which from a sustainability viewpoint would be preferred- also showed a relative high HMF conversion and DFF selectivity. Methanol and acetone gave the lowest HMF conversion in all investigated solvents. Although both DMSO and DMF are strongly polar solvents with high boiling points, compared with DMF, a relative low HMF conversion in DMSO was obtained. The DFF selectivity up to 99.8 % in DMSO was obtained. In a longer reaction time, nearly full HMF conversion and nearly 100 % DFF selectivity in DMSO can be got (32 h). In non-polar solvents, MIBK gave a moderate HMF conversion and DFF selectivity (entry 7). As MIBK was usually used as an organic extractant in biphasic systems (MIBK/water) for the conversion of fructose into HMF, graphene with strong acid and redox catalytic properties showed the potential as the metal-free catalyst for the synthesis of DFF from fructose by two consequence steps, which compromised the production of HMF from fructose in a biphasic system (MIBK/water) and the subsequent oxidation of HMF in MIBK. A full HMF conversion and 93.6% DFF selectivity was obtained in toluene (entry 8), similar results also were observed with metal catalysis system.<sup>1, 2</sup> A poor catalytic performance was observed if the oxidation of HMF was conducted in dichloromethane (entry 9).

10. Reaction pathway in anaerobic oxidation of HMF into DFF with GO as a direct oxidant.



**Figure S10.** Proposed reaction pathway of GO material functioned as a direct oxidant in oxidation of HMF into DFF.

In anaerobic oxidation of HMF, GO functioned as an oxidant, part of carboxylic acid groups were reduced into carbonyl group, hydroxyl or epoxy groups. The possible reaction pathway was shown in Figure S10 as following: (*a*) The TEMPO molecular was oxidized by GO material to form the oxoammonium cation (1). (*b*) HMF was oxidized by oxoammonium cation with DFF was produced, and (*c*) the produced hydroxylamine (2) was re-oxidized by GO to reproduce the TEMPO. These results suggested that the GO catalyst underwent partial reduction during the conversion of HMF into DFF and afforded a carbon product that was similar to the r-GOs and CMGs that had been previously reduced by low concentration of sodium borohydride solution.<sup>3</sup> However, the mechanism of how GO worked in oxidative

reaction (a) and (c) was still unclear. Besides, the aerobic catalytic contribution from dissolved molecular oxygen in solvent and adsorbed molecular oxygen on GO material cannot be excluded completely for the oxidation of HMF into DFF.

# **References:**

- 1. Zhang, Z.; Yuan, Z.; Tang, D.; Ren, Y.; Lv, K.; Liu, B. ChemSusChem 2014, 7, 3496-3504.
- 2. Nie, J.; Xie, J.; Liu, H. J. Catal. 2013, 301, 83-91.
- Shin, H.-J.; Kim, K. K.; Benayad, A.; Yoon, S.-M.; Park, H. K.; Jung, I.-S.; Jin, M. H.; Jeong, H.-K.; Kim, J. M.; Choi, J.-Y.; Lee, Y. H. Adv. Funct. Mater. 2009, 19, 1987-1992.