

## Supporting Information for

# Direct Synthesis of 2,5-Diformylfuran from Fructose with Graphene Oxide as Bifunctional and Metal-free Catalyst

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## **1. Experimental Materials**

Fructose (99%), HMF (99%) and DMSO were purchased from Amresco and J&K Scientific Company, respectively. Graphite powder was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). All reagents were used as received without further purification.

## **2. Preparation and Characterization of GO**

### **2.1. Preparation of GO**

GO was prepared by the Hummers' method. Typically, graphite powder (8000 meshes, 5 g) and  $\text{NaNO}_3$  (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  $\text{KMnO}_4$  (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 addition of 700 mL water. And the reaction was terminated by the addition of  $\text{H}_2\text{O}_2$  (50 mL, 30 wt %). The mixture was filtered and washed with  $\text{HCl}$  (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.

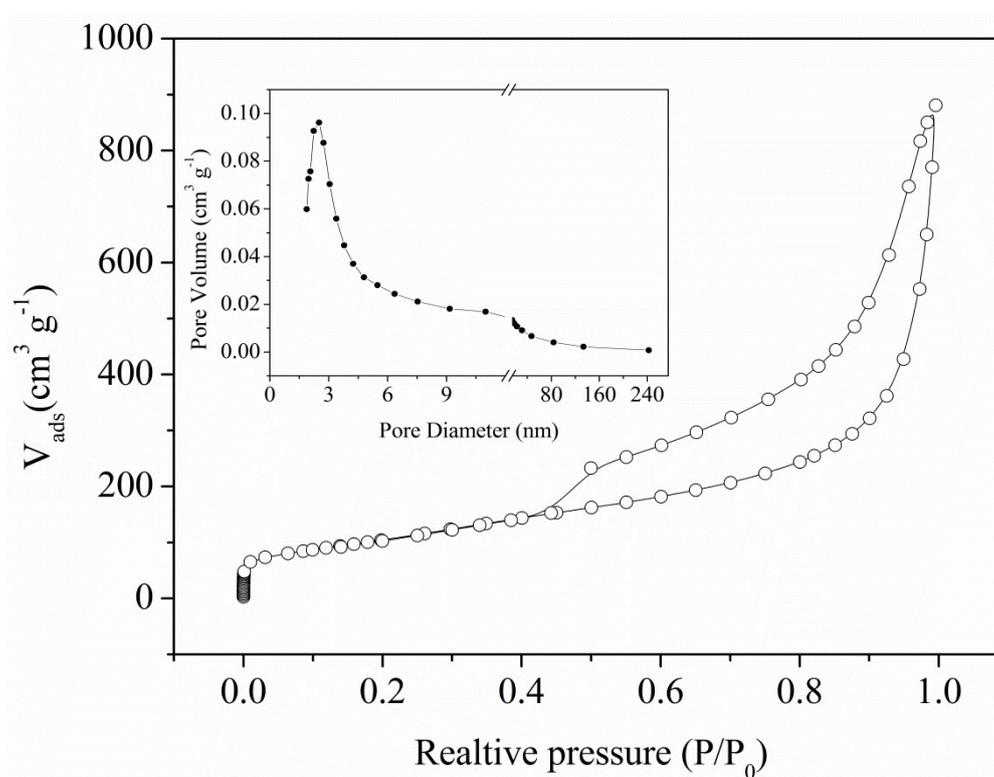
### **2.2. Ultrasonic Exfoliated GO**

The obtained graphite oxide (0.5 g) was dispersed into 500 mL deionized water. The graphene oxide suspension was exfoliated by ultrasonic under 40 KHz for 180 min and dried in a freeze dryer (-70 °C, 10-13 Pa), obtaining the stable and exfoliated

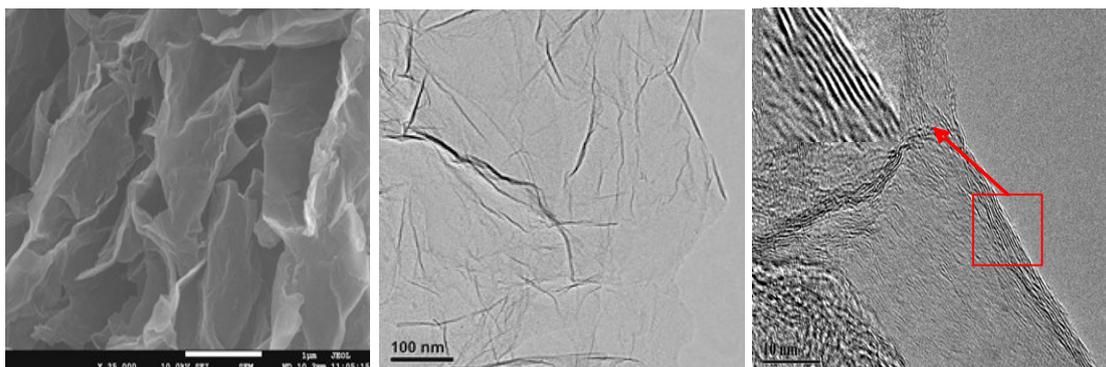
GO material.

### 2.3. BET, SEM and TEM Analysis of GO

The specific surface area ( $S_{\text{BET}}$ ) was measured by  $\text{N}_2$  adsorption/desorption at liquid nitrogen temperature using a Micromeritics ASAP2020HD88 apparatus after outgassing under vacuum at 150 °C for 3 h, the area was calculated by the Brunauer-Emmett-Teller (BET) model (Figure S1). The obtained graphene oxide has a BET surface area of 379.0  $\text{m}^2/\text{g}$  with an average pore diameter of 14.4 nm.



**Figure S1.**  $\text{N}_2$  sorption and pore distribution of graphene oxide material



**Figure S2.** SEM and TEM images of fresh GO

The morphology and structure of the prepared graphene oxide were studied by SEM, TEM and HRTEM analysis. As shown in Figure S2, the sample exhibits the typical nanosheet structure of graphene. The morphology of graphene oxide showed randomly aggregated, crumpled nanosheet under SEM and TEM observation. HRTEM characterization further indicates that these nanosheets consist of 1-10 layer graphenes.

#### 2.4 Boehm titration

The acidic functional groups (assigned as the acidity density roughly) were determined by a neutralization adsorption experiment. Typically, GO samples (50 mg) were dispersed into 25 mL of 0.05 mol/L NaOH aqueous solution. 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. Bromocresol green - methyl red was used as the indicator.

The adsorbed base was calculated as follow equation:

$$n_{\text{NaOH}} = c_{\text{NaOH}} V_{\text{NaOH}} - c_{\text{HCl}} V_{\text{HCl}}$$

In the equations,

$n_{\text{NaOH}}$ , The adsorbed base quantity on GO samples.

$c_{\text{NaOH}}$ , The concentration of standard base solution.

$V_{\text{NaOH}}$ , The base solution volume used in GO dispersion.

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

$V_{\text{HCl}}$ : Standard HCl solution volume consumption in titration.

### **3. Experimental Procedure for Reactions**

#### **3.1 Fructose Conversion into HMF**

In a typical run, the procedure for fructose dehydration into HMF was as follow: fructose (2 mmol, 360 mg), GO (20 mg), and DMSO (4 mL) were added into a 25 mL three-necked round bottom flask. The reactor was equipped with a total reflux condenser to avoid solvent evaporation. A thermostatic oil bath was used as the heating source. The reaction was performed under a constant nitrogen flow (20 mL min<sup>-1</sup>) and maintained at the reaction temperature for a specific time under vigorous stirring (600 rpm). Samples were taken from the reaction mixture at specified time for products analysis.

#### **3.2 HMF Conversion into DFF**

In a typical run, the procedure for the HMF oxidation was as follow: HMF (2 mmol, 252 mg), GO (20 mg) and DMSO (4 mL) were added into a 25 mL three-necked round bottom flask. A thermostatic oil bath was used as the heating source. The reaction was performed under a constant oxygen flow (20 mL min<sup>-1</sup>) and maintained

at the reaction temperature for a specific time under vigorous stirring. Samples were taken from the reaction mixture at specified time for products analysis.

### **3.3 One Pot Synthesis of DFF from Fructose**

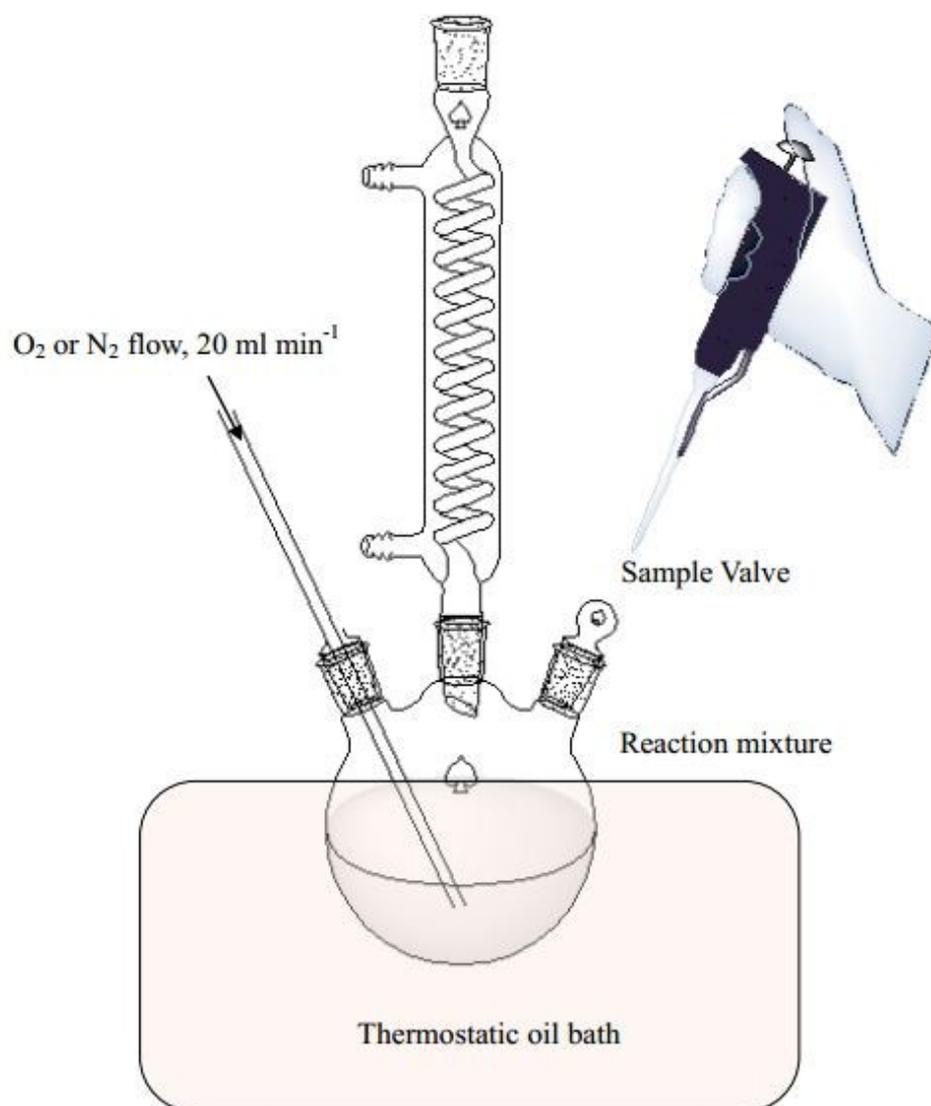
#### **3.3.1 One-pot, One step**

In a typical run, the procedure for the one pot synthesis of DFF from fructose was as follow: fructose (2 mmol, 360 mg), GO (20 mg), and DMSO (4 mL) were added into a 25 mL three-necked round bottom flask. A thermostatic oil bath was used as the heating source. The reaction was performed under a constant oxygen flow (20 mL min<sup>-1</sup>) and maintained at the reaction temperature for a specific time under vigorous stirring. Samples were taken from the reaction mixture at specified time for products analysis.

#### **3.3.2 One-pot, Two-step**

In a typical run, the procedure for the one pot synthesis of DFF from fructose was as follow: fructose (2 mmol, 360 mg), GO (20 mg), and DMSO (4 mL) were added into a 25 mL three-necked round bottom flask. A thermostatic oil bath was used as the heating source. The reaction mixture was maintained at indicated reaction temperature under vigorous stirring. The reaction was performed under a constant nitrogen flow (20 mL min<sup>-1</sup>) for 2 h. Then the oxidation was performed under oxygen flow (20 mL min<sup>-1</sup>) for another 22 h. Samples were taken from the reaction mixture at specified time for products analysis.

The Schematic diagram of experimental set-up as following:

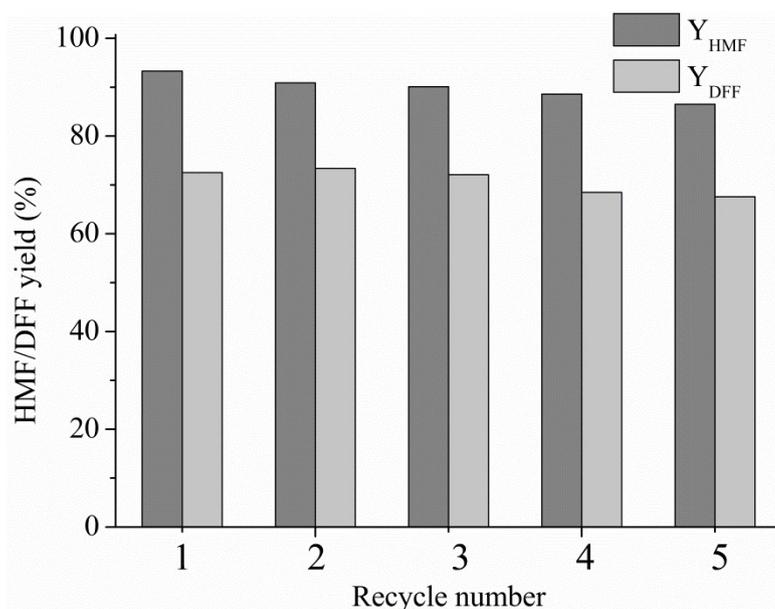


#### 4. Analysis of the Products

The reaction mixture was diluted with deionized water and filtered with a 0.45  $\mu\text{m}$  syringe filter prior to analysis. The yield of HMF was determined by using a Shimadzu high-pressure liquid chromatograph (LC-10AT) equipped with a UV-VIS detector (SPD-10A). A 4.6 mm id  $\times$  250 mm Kromstar C 18 reverse-phase column was used. The mobile phase was acetonitrile and 0.1 wt % acetic acid aqueous solution (30:70 v/v) at 0.3 mL  $\text{min}^{-1}$ . For the analysis of fructose, a 4.6 mm  $\times$  250 mm

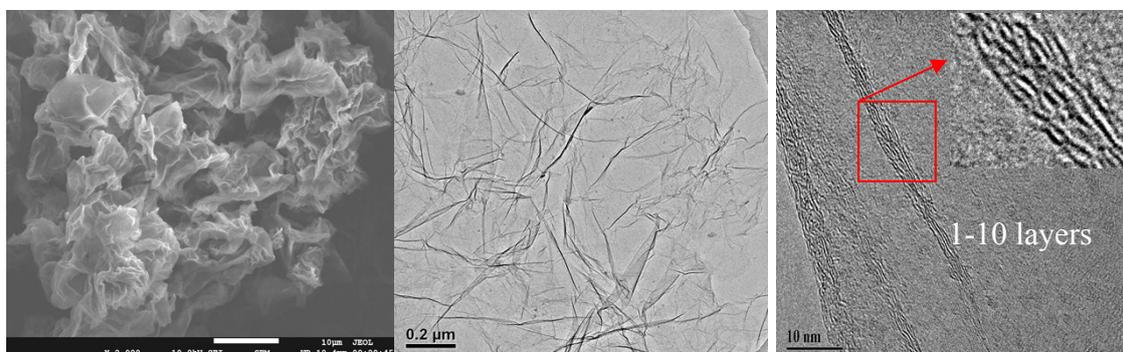
Shodex sugar column (SC1011) and a refractive index detector (RID-10A) was used, distilled water was used as the mobile phase at a flow rate of 1.0 mL min<sup>-1</sup>. The column temperature was maintained at 35 °C. The fructose conversion and HMF, DFF yield were calculated on the basis of external standard curves constructed with authentic standards.

## 5. Reusability Study of GO as a Bifunctional Catalyst

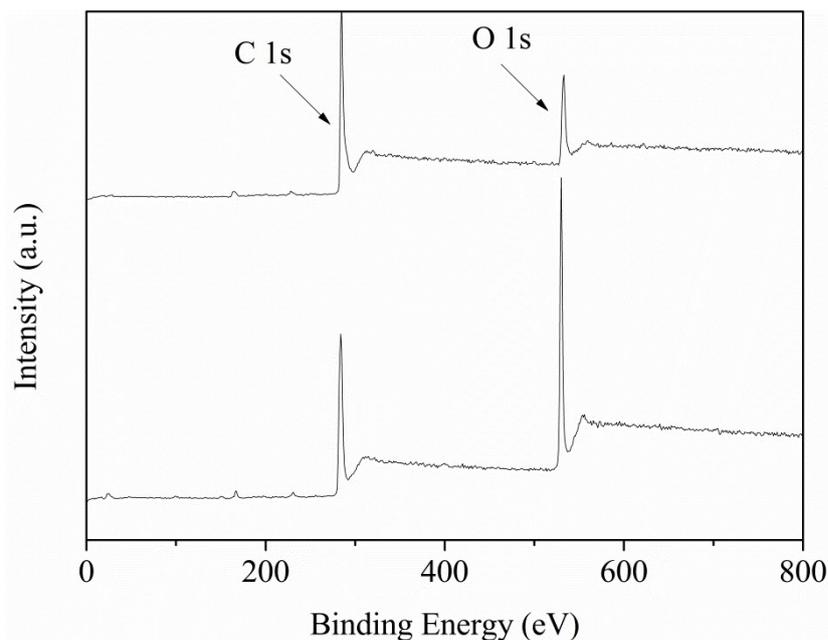


**Figure S3.** Reusability study of GO as bifunctional catalyst in one-pot synthesis of DFF from fructose. Reaction condition: fructose, 2 mmol, 360 mg; GO, 20 mg; DMSO, 4 mL; T, 140 °C; N<sub>2</sub> or O<sub>2</sub>, 20 mL min<sup>-1</sup>. Y<sub>HMF</sub>: the HMF yield was obtained from fructose dehydration reaction under N<sub>2</sub> flow atmosphere after 2 h. Y<sub>DFF</sub>: the DFF yield was obtained after the reaction performed under O<sub>2</sub> flow atmosphere for another 22 h.

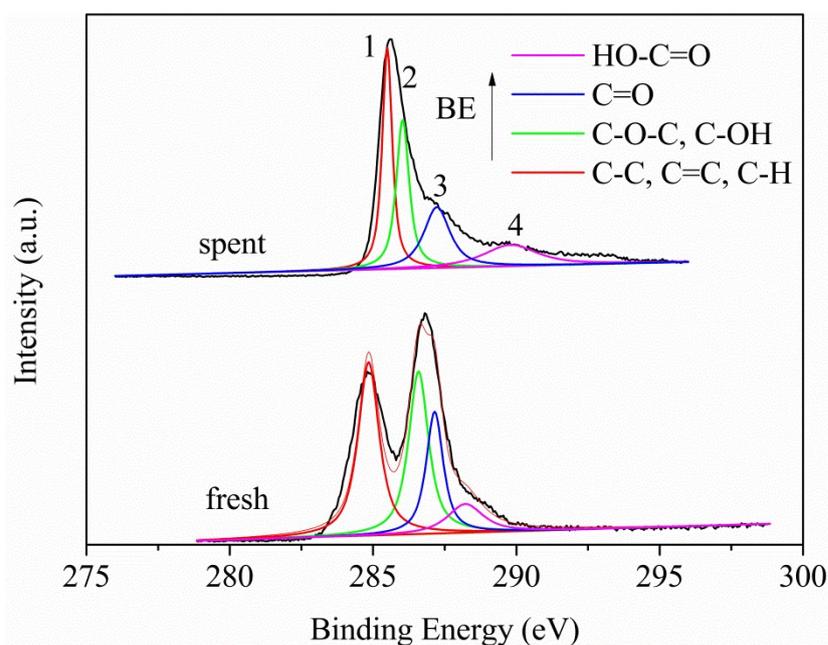
## 6. Characterization of Fresh and Spent GO



**Figure S4.** SEM and TEM image of spent GO after five catalytic cycles



**Figure S5.** XPS pattern of fresh and spent GO after 5 cycles.



**Figure S6.** C 1s peak in the XPS spectra of fresh (down) and spent GO after 5 cycles (up). The curve was fitted considering the following contributions: C-C, C=C, C-H (peak 1), C-O/C-O-C (hydroxyl and epoxy groups; peak 2), C=O (carbonyl groups; peak 3), and O=C-OH (carboxyl groups; peak 4).

**Table S 1.** Ratio of C/O and Oxygen Species Distribution in Fresh and Spent GO

Calculated from XPS Results

Samples	C/O	Oxygen content (atom %)		
		C-OH/C-O-C	C=O	HO-C=O
Fresh GO	1.49	0.20	0.13	0.09
Spent GO	2.39	0.12	0.10	0.06

**Table S2.** Elemental Analysis of Fresh and Spent GO Catalyst in DMSO Solvent

Samples	Elemental content (wt %)			
	C	H	O	S
Fresh GO	49.6	2.4	46.8	1.2
Spent GO	65.8	3.7	27.3	3.2

## 7. Effect of the Solvents on the Direct Synthesis of DFF from Fructose with GO as Bifunctional Catalyst

**Table S3.** One-pot and Two Step synthesis of DFF from Fructose in other Solvents Catalyzed by GO <sup>a</sup>

Entry	Solvent	In N <sub>2</sub>			In O <sub>2</sub>		
		Time (h)	Y <sub>HMF</sub> (%)	Y <sub>DFF</sub> (%)	Time (h)	Y <sub>HMF</sub> (%)	Y <sub>DFF</sub> (%)
1	DMSO	2	93.3	0	22	0	72.5
2	DMF	5	9.7	0	22	0	0
3	DMAC	5	40.5	0	22	20.9	4.5
4	NMP	5	79.1	0	22	0.5	0.6
5	acetonitrile	5	11.9	0	22	19.6	0
6	water	5	10.2	0	22	0.6	0
7	water/MIBK (V ratio=1:3)	5	32.3	0	22	2.3	0

<sup>a</sup> Reaction condition: fructose, 2 mmol, 360 mg; Total solvent, 4 mL; GO, 20 mg;

T, 140 °C; The reaction was conducted in N<sub>2</sub> for a certain time and then the atmosphere was converted to O<sub>2</sub> (as stated in Table ), 20 mL min<sup>-1</sup>.

The bifunctional catalytic ability of GO was tested in other polarity solvents, such as DMF, DMCA, NMP, acetonitrile, water, and a mixed solvent with water and MIBK volume ratio 1:3. Compared with DMSO, as listed in Table S3, the highest HMF yield was obtained in 5 h in the studied solvents, but they all led to inferior

results, (Table S3, entries 1-7) and much insoluble humus was observed in reaction. After the atmosphere converted to O<sub>2</sub>, no or only trace amount of DFF was observed (entries 2-7). Above results demonstrated that DMSO has the unique advantages in suppressing undesired side reactions, such as the formation of humus from fructose and the degradation of HMF in the presence of acid catalyst and facilitating the transformation of fructose.