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# Bifunctional carbon nanoplatelets as metal-free catalysts for direct conversion of fructose to 2,5-diformylfuran<sup>†</sup>

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Synthesis of 2,5-diformylfuran (DFF) using a carbohydrate as a raw material by dehydration to 5-hydroxymethylfurfural (HMF) and *in situ* selective oxidation of HMF is important for the direct preparation of high value chemicals from biomass materials, to avoid the energy consumption process of HMF separation and purification. In this study, carbon nanoplatelets were prepared by a facile molten-salt method and functionalized to be the bifunctional catalysts for the tandem reaction from fructose to DFF. The excellent catalytic performance of the catalysts was attributed to the rich oxygen-containing groups on the surface of the catalysts. A DFF yield of 70.3% can be achieved in a one-pot and one-step conversion of fructose to DFF with oxygen as the only oxidant at atmospheric pressure.

The development of green and efficient chemical technology using biomass materials instead of fossil fuels to produce bulk chemicals, organic intermediates and polymer materials has attracted wider attention around the world which is facing continuous consumption of fossil resources and increasing environmental problems. As one of the most important biomass platform compounds, 5-hydroxymethylfurfural (HMF) is an ideal intermediate for the synthesis of various chemicals due to its rich chemical properties.<sup>1</sup> The selective oxidation of HMF can produce several kinds of furan chemicals, such as 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 5-formyl-2-furancarboxylic acid (FFCA) and 2,5furandicarboxylic acid, as shown in Scheme S1.<sup>†2</sup>

DFF can be used to synthesize many useful chemicals and polymer materials, such as fluorescent agents,<sup>3</sup> macrocyclic ligands,<sup>4</sup> organic conductors<sup>5</sup> and pharmaceuticals<sup>6</sup> through hydrogenation, oxidation, polymerization, hydrolysis, etc.<sup>7</sup> It is generally prepared by the selective oxidation of the hydroxyl group in HMF. Traditional oxidants, such as NaOCl,<sup>8</sup> BaMnO<sub>4</sub> (ref. 9) and pyridinium chlorochromate,<sup>10</sup> have primarily been used in the oxidation process, resulting in a low atomic utilization rate and formation of toxic waste. In recent years, green oxidants, such as H<sub>2</sub>O<sub>2</sub>,<sup>11</sup> oxygen and air, have been used in the synthesis of DFF from HMF in the presence of various catalysts, such as Pt/C,<sup>12</sup> Ru/C,<sup>13</sup> Pd/C,<sup>14</sup> V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>,<sup>15</sup> Cs/MnO<sub>r</sub> (ref. 16) and OMS-2.<sup>17</sup> The DFF yield was greatly enhanced by the use of these noble metals or transition-metal based catalysts. However, the large-scale production of DFF was still limited by the high cost of HMF, which is typically obtained from the dehydration of fructose by an acid.<sup>18</sup> Integration of fructose dehydration with HMF oxidation in a one-pot reaction has gradually become an important research topic because it can dramatically reduce the production cost of DFF by avoiding the separation and purification of HMF. An acidic catalyst for fructose dehydration and an oxidative catalyst for HMF oxidation work synergistically in the one-pot reaction process. Amberlyst-15 and Ru/HT,<sup>19</sup> Fe<sub>3</sub>O<sub>4</sub>-SBA-SO<sub>3</sub> and K-OMS-2,<sup>20</sup> H-form cation-exchange resin and VOHPO<sub>4</sub> (ref. 21) are such types of catalyst couples used in the one-pot synthesis of DFF from fructose. However, the two catalysts should be added into the reaction system in phases in order to achieve a high DFF yield, which means that the oxidative catalyst should be added after most of the fructose is converted to HMF in the presence of acidic catalysts. Otherwise, premature addition of the oxidative catalyst will lead to the direct oxidation of fructose, resulting in a low DFF yield. Recently, bifunctional catalysts possessing both acidity and oxidability have been developed to achieve a one-pot and one-step conversion of fructose to DFF. MOF-derived Fe<sub>3</sub>O<sub>4</sub>,<sup>22</sup> sulfonated MoO<sub>3</sub>-



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 $ZrO_2$ <sup>23</sup> V-g-C<sub>3</sub>N<sub>4</sub> (H<sup>+</sup>)<sup>24</sup> and a series of Mo-containing Keggin heteropolyacids<sup>25-27</sup> were prepared and applied in the onepot and one-step synthesis of DFF from fructose. It can be seen that metal/metal oxides were used in all of these catalysts, whether in a two-step or one-step process. However, a recent study showed that graphene oxide can achieve metal-free catalytic conversion of fructose to DFF, avoiding metal leaching which may affect the product quality or make the product purification difficult.<sup>28</sup> Since graphene, carbon nanotubes and active carbon are well carbonized materials, a harsh treatment method can be applied in order to enrich the oxygen-containing functional groups, which are responsible for the catalytic activity.<sup>29</sup> Inspired by the acidic and oxidative properties of graphene oxide, we herein synthesized a low cost carbon-based catalyst bearing rich oxygen-containing groups under relatively mild conditions. The carbon nanoplatelets showed excellent performance in the one-pot and one-step synthesis of DFF from fructose.

Carbon nanoplatelets were synthesized by a modified molten salt method using glucose as a carbon source and functionalized with oxygen-containing groups, such as a carboxyl group, sulfonic acid group, or nitro group through nitric/sulfuric acid treatment. The FTIR spectra (Fig. S3<sup>†</sup>) and Table S2<sup>†</sup> show that GN-N treated with nitric acid has rich carboxyl groups. Sulfonic acid groups were introduced on GN-S by sulfuric acid treatment. GN-NS possessed nitro groups in addition to carboxyl groups and sulfonic acid groups (Fig. S6<sup>†</sup>). These differences are consistent with the element analysis results of the as-synthesized catalysts. In Table S1,† it can be seen that all the carbon materials contain rich oxygen-containing groups compared with CNT. The oxygen content of the carbon materials increased significantly after the acid treatment. Sulfur was detected in GN-S and GN-NS, while nitrogen was detected in GN-N and GN-S, indicating that the successful introduction of the nitrogen group and sulfonic acid group was attributed to the concentrated nitric acid and sulfuric acid treatment, respectively.<sup>30</sup> The increase of oxygen content was mainly attributed to the increase of the amount of carboxyl groups. The  $CO/CO_2$ -TPD-MS spectra (Fig. S5<sup>†</sup>) show that the sulphuric acid treatment could introduce anhydride, phenol, carbonyl, quinone and lactone groups, while the nitric acid treatment can introduce more carboxyl groups.

The dehydration of fructose to HMF was conducted in a 25 mL flask equipped with a reflux condenser. 200 mg fructose was dissolved in 5 mL DMSO to form the reaction solution. The reaction was ran at 110 °C in the presence of 10 mg catalyst. The product was analyzed by HPLC and the results are shown in Fig. 1. It has been demonstrated in many reports that DMSO can promote the dehydration of fructose and help to stabilize the produced HMF.<sup>31</sup> For example, 21.6% fructose conversion and 14.7% HMF yield were obtained in 2 h at 140 °C without any catalyst, as reported by G. Lv.<sup>28</sup> In Fig. 1a, a fructose conversion of 73.26% and a HMF yield of 52.14% were obtained at 110 °C in 2 h with GN as the catalyst. The higher fructose conversion



**Fig. 1** a) Dehydration of fructose to HMF over GN, GN-S, GN-N, GN-NS and CNT, b) oxidation of HMF to DFF over GN, GN-S, GN-N, and GN-NS, c) one-pot synthesis of DFF from fructose over GN, GN-S, GN-N, GN-NS and CNT, and d) reaction monitoring of one-pot synthesis of DFF from fructose over GN-NS.

and HMF yield at the relatively lower reaction temperature suggested that the oxygen-containing groups in GN can promote the dehydration of fructose to HMF. The fructose conversion and HMF yield increased to 85.7% and 65.34%, respectively, in the presence of GN-N. The increase can be attributed to the increase of the amount of carboxyl groups in GN-N by the HNO3 treatment. Further enhancement of fructose conversion and HMF yield can be achieved by the catalysts treated with H<sub>2</sub>SO<sub>4</sub>. All the fructose was converted and a HMF yield as high as 87.38% was obtained when GN-S was used as the catalyst, demonstrating the high activity of sulfonic acid groups towards fructose dehydration to HMF.<sup>32</sup> Comparable fructose conversion and HMF yield were obtained when GN-NS was used as the catalyst. The highest HMF yield was achieved by GN-S which contains the highest number of sulfonic acid groups but the lowest number of carboxyl groups (Table S2<sup>†</sup>), indicating that the sulfonic acid group is much more efficient than the carboxyl group in the fructose dehydration process.

The aerobic oxidation of HMF to DFF was conducted under similar reaction conditions to those for fructose dehydration to HMF. 0.5 mmol HMF was dissolved in 5 mL DMSO and heated to 140 °C in the presence of 10 mg catalysts. Oxygen was bubbled into the reaction systems at a flow rate of 20 mL min<sup>-1</sup>. Reaction results are summarized in Fig. 1b. It has been reported that the carboxyl group is active in the catalytic oxidation of HMF to DFF,<sup>33</sup> which can be proved through the comparison of the catalytic performance of GN and GN-N. A HMF conversion of 12.37% and a DFF yield of 9.83% were obtained after 19.5 h with GN as the catalyst. The HMF conversion and DFF yield increased significantly to 41.31% and 36.25%, respectively, when GN-N was used as the catalyst. Comparing the catalytic performance of GN-S and GN-N or GN, it can be found that sulfonic acid groups can also promote the conversion of HMF,<sup>34</sup> but the selectivity to DFF is not as high as that of carboxyl-catalyzed HMF oxidation. The highest HMF conversion and DFF yield were achieved by using GN-NS which bears the highest amount of carboxyl groups. Therefore, the carboxyl acid groups are more active than the sulfonic acid groups in promoting the conversion of HMF to DFF.

It is well known that the carboxyl group and sulfonic acid group can be introduced in carbon materials through nitric acid and sulfuric acid treatment, respectively, and the additional nitro group could be grafted on the carbon material when it is treated with the mixture of sulfuric acid and nitric acid. In order to confirm whether nitro groups contribute to the oxidation of HMF to DFF, a series of parallel experiments were conducted and the results are given in Table 1. CS (carbon sphere) and CNT (carbon nanotube) were used as catalysts, respectively, for HMF oxidation. NaNO2 was chosen as the additive to the reaction mixtures to mimic the nitro groups since nitrite can adsorb on the surface of carbon materials. Both CS and CNT showed low activity toward oxidation of HMF to DFF, and the addition of NaNO2 into the reaction system in the presence of CS showed no significant improvement, also ruling out the activity of NaNO2 dissolved in the solution. However, the HMF conversion and DFF yield increased dramatically when NaNO2 was added into the reaction mixture with CNT, possibly due to the conductivity difference in the two carbon materials and implying that the electron transfer in the carbon materials plays an important role in alcohol oxidation. A similar comparison experiment was reported by J. Luo et al. using CNT as the catalyst and NaNO<sub>2</sub> as the additive for benzyl alcohol aerobic oxidation.<sup>35</sup> The addition of NaNO<sub>2</sub> did not enhance the catalytic activity in the test. In the study, the CNT was treated with HCl, rather than HNO<sub>3</sub>. Thus, the amount of carboxyl groups may be limited. It can be speculated that the conductive graphene sheets bearing an adequate amount of carboxyl groups can activate the nitro groups for the catalytic oxidation of HMF to DFF.

The one-pot and one-step conversion of fructose to DFF was conducted with the same reflux setup in an oil bath. 200 mg fructose was dissolved in 5 mL DMSO and reacted at 150 °C with 10 mg catalyst for 19 h. The results are summarized in Fig. 1c. A DFF yield of 34.26% and a HMF yield of 12.77% were obtained when GN was used as the catalyst. In contrast,

Table 1	Effect of NaNO <sub>2</sub> on HMF oxidation	
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Entry	Catalyst	HMF conversion/%	DFF yield/%
1	CS	21.5	4.8
2	$CS + NaNO_2$	23.64	5.26
3	CNT	25.78	11.43
4	$CNT + NaNO_2$	72.67	44.93

Reaction conditions: HMF (63 mg), catalysts (10 mg), DMSO (5 mL),  $O_2$  (20 mL min  $^{-1})$ , 140 °C, and 18 h.

the increase in HMF yield and decrease in DFF yield, when GN-S was used as the catalyst, suggest that sulfonic acid groups can significantly promote the dehydration of fructose to HMF but have very limited catalytic activity in the oxidation of HMF to DFF. A DFF yield of 40.28% was achieved in the presence of GN-N, showing once again the high catalytic activity of carboxyl groups toward the aerobic oxidation of HMF to DFF. The DFF yield increased further to 51.36% using GN-NS as the catalyst. The above reaction results reveal that GN-NS with rich oxygen containing groups (carboxyl group, nitro group, and sulfonic acid group) is the best catalyst candidate for the one-pot and one-step conversion of fructose to DFF. The lowest DFF yield was obtained by CNT due to the limited amount of carboxyl groups on it, indicating that the as-synthesized carbon materials are more active than CNT during the acid treatment.

The one-pot and one-step reaction process was monitored by using HPLC to measure the product concentration during the reaction. It can be seen clearly that the reaction process can be divided into two phases in Fig. 1d. The dehydration of fructose to HMF is the main reaction within the first 2 hours, which is the first reaction phase. Almost all the fructose was converted to HMF after two hours and then the aerobic oxidation of HMF to DFF becomes the main reaction, which is the second reaction phase. The HMF yield peaked at 87.13% after 2 hours, and then decreased as the reaction progresses due to the oxidation of HMF to DFF. The DFF concentration in the reaction solution continuously increased until the DFF yield reached 70.26% after 25 hours. The long reaction process also led to the formation of FFCA as an overoxidized product. The dark brown reaction solution and relatively low carbon balance may be caused by the degradation of HMF and fructose, forming by-products, such as humic acid, levulinic acid, etc.36

Based on the analysis of the reaction results and the reported works on graphene oxide catalyzed alcohol oxidation,<sup>37–39</sup> we propose a mechanism for the direct synthesis of DFF by catalytic conversion of fructose in the presence of GN-NS in Fig. 2. The protons ionized from sulfonic acid groups catalyze the dehydration of fructose to



Fig. 2 Mechanism of GN-NS catalyzed fructose dehydration to HMF and HMF oxidation to DFF.



Fig. 3 Recycle use of GN-NS for the one-pot synthesis of fructose to DFF.

HMF. The unpaired electrons and carboxyl groups at the edges of graphene sheets activate the oxygen molecules to superoxide radicals; the latter can abstract the hydrogen atom from the hydroxyl group of HMF to produce DFF. Meanwhile, the activated nitro groups can promote the aerobic oxidation of HMF to DFF at the same time.<sup>40,41</sup>

The reusability and stability for GN-NS were investigated under the same reaction conditions and are shown in Fig. 3. The used catalyst was separated from the reaction solution by filtration and washed with deionized water and ethanol, followed by overnight drying in an oven at 65 °C. There is no significant loss in catalytic activity with GN-NS during the recycling test. The slight decrease of DFF yield and increase of residual HMF could be due to the partial reduction of oxygen-containing groups after the long time reaction.<sup>37</sup>

Carbon nanoplatelets bearing rich oxygen-containing groups were synthesized by a facile molten salt method followed by an acid treatment. The sulfonic acid groups can be introduced on the carbon nanoplatelets by a concentrated sulfuric acid treatment and carboxyl groups can be introduced by a concentrated nitric acid treatment. Treated with a mixture of concentrated sulfuric acid and nitric acid, nitro groups (except sulfonic acid groups and carboxyl groups) can be generated on the carbon nanoplatelets. These functional groups and the unpaired electrons at the edge of the graphene sheets in the carbon nanoplatelets work synergistically in the dehydration of fructose and aerobic oxidation of HMF, resulting in the excellent catalytic performance in the direct synthesis of DFF from fructose. A DFF yield of 70.26% can be achieved by GN-NS in a one-pot and one-step reaction system with atmospheric oxygen as the only oxidant. The used catalysts can be easily recycled from the reaction solution for reuse, showing good stability. The use of GN-NS as a metal-free catalyst for the DFF synthesis from fructose can effectively avoid the problem of metal leaching which exists in most reactions with metal/metal oxide-based catalysts. Thus, the as-synthesized green and low cost catalysts have great potential for industrial applications.

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#### Conflicts of interest

There are no conflicts of interest to declare.

### Notes and references

- 1 B. Liu and Z. Zhang, ChemSusChem, 2016, 9, 2015-2036.
- 2 Z. Zhang and G. W. Huber, *Chem. Soc. Rev.*, 2018, 47, 1351–1390.
- 3 J. Ma, Z. Du, J. Xu, Q. Chu and Y. Pang, *ChemSusChem*, 2011, 4, 51–54.
- 4 D. T. Richter and T. D. Lash, *Tetrahedron Lett.*, 1999, 40, 6735–6738.
- 5 A. S. Benahmed-Gasmi, P. Frere, M. Jubault, A. Gorgues, J. Cousseau and B. Garrigues, Synth. Met., 1993, 56, 1751–1755.
- 6 K. T. Hopkins, W. D. Wilson, B. C. Bender, D. R. McCurdy, J. E. Hall, R. R. Tidwell, A. Kumar, M. Bajic and D. W. Boykin, *J. Med. Chem.*, 1998, **41**, 3872–3878.
- 7 J. C. Serrano-Ruiz, R. Luque and A. Sepúlveda-Escribano, Chem. Soc. Rev., 2011, 40, 5266–5281.
- 8 A. S. Amarasekara, D. Green and E. McMillan, *Catal. Commun.*, 2008, **9**, 286–288.
- 9 T. El-Hajj, J. C. Martin and G. Descotes, J. Heterocycl. Chem., 1983, 20, 233–235.
- L. Cottier, G. Descotes, E. Viollet, J. Lewkowski and R. Skowroňski, J. Heterocycl. Chem., 1995, 32, 927–930.
- 11 C. T. Chen, C. V. Nguyen, Z. Y. Wang, Y. Bando, Y. Yamauchi, M. T. S. Bazziz, A. Fatehmulla, W. A. Farooq, T. Yoshikawa and T. Masuda, *ChemCatChem*, 2018, **10**, 361–365.
- 12 H. A. Rass, N. Essayem and M. Besson, *Green Chem.*, 2013, 15, 2240–2251.
- 13 N. I. E. Junfang, X. I. E. Jiahan and L. I. U. Haichao, *Chin. J. Catal.*, 2013, 34, 871–875.
- 14 S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye and R. J. Davis, *Catal. Today*, 2011, **160**, 55–60.
- 15 C. Moreau, R. Durand, C. Pourcheron and D. Tichit, *Stud. Surf. Sci. Catal.*, 1997, **108**, 399–406.
- 16 Z. Yuan, B. Liu, P. Zhou, Z. Zhang and Q. Chi, *Catal. Sci. Technol.*, 2018, 8, 4430–4439.
- 17 J. Nie and H. Liu, J. Catal., 2014, 316, 57-66.
- 18 K. Markwart, Stud. Plant Sci., 1993, 3, 149-160.
- 19 A. Takagaki, M. Takahashi, S. Nishimura and K. Ebitani, ACS Catal., 2011, 1, 1562–1565.
- 20 Z.-Z. Yang, J. Deng, T. Pan, Q.-X. Guo and Y. Fu, Green Chem., 2012, 14, 2986–2989.
- 21 G. A. Halliday, R. J. Young and V. V. Grushin, Org. Lett., 2003, 5, 2003–2005.
- 22 R. Fang, R. Luque and Y. Li, Green Chem., 2017, 19, 647-655.
- 23 J. Zhao, A. Jayakumar and J.-M. Lee, *ACS Sustainable Chem.* Eng., 2018, **6**, 2976–2982.

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- 24 J. Chen, Y. Guo, J. Chen, L. Song and L. Chen, *ChemCatChem*, 2014, 6, 3174–3181.
- 25 Y. Liu, L. Zhu, J. Tang, M. Liu, R. Cheng and C. Hu, ChemSusChem, 2014, 7, 3541–3547.
- 26 J. Zhao, J. Anjali, Y. Yan and J. M. Lee, *ChemCatChem*, 2017, 9, 1187-1191.
- 27 R. Liu, J. Chen, L. Chen, Y. Guo and J. Zhong, *ChemPlusChem*, 2014, **79**, 1448–1454.
- 28 G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu and X. Hou, *Green Chem.*, 2016, 18, 2302–2307.
- 29 D. Chen, H. Feng and J. Li, *Chem. Rev.*, 2012, **112**, 6027–6053.
- 30 G. Zhang, S. Sun, D. Yang, J.-P. Dodelet and E. Sacher, *Carbon*, 2008, 46, 196–205.
- 31 A. S. Amarasekara, L. D. Williams and C. C. Ebede, *Carbohydr. Res.*, 2008, **343**, 3021–3024.
- 32 J. Wang, W. Xu, J. Ren, X. Liu, G. Lu and Y. Wang, Green Chem., 2011, 13, 2678–2681.

- 33 G. Lv, H. Wang, Y. Yang, T. Deng, C. Chen, Y. Zhu and X. Hou, *ACS Catal.*, 2015, 5, 5636–5646.
- 34 O. C. Navarro and S. I. Chornet, *Top. Catal.*, 2009, 52, 304–314.
- 35 J. Luo, F. Peng, H. Yu and H. Wang, *Chem. Eng. J.*, 2012, **204**, 98–106.
- 36 F. S. Asghari and H. Yoshida, *Ind. Eng. Chem. Res.*, 2007, **46**, 7703-7710.
- 37 D. R. Dreyer, H. P. Jia and C. W. Bielawski, Angew. Chem., 2010, 122, 6965–6968.
- 38 C. Su, M. Acik, K. Takai, J. Lu, S.-j. Hao, Y. Zheng, P. Wu, Q. Bao, T. Enoki and Y. J. Chabal, *Nat. Commun.*, 2012, 3, 1298.
- 39 Y. Cui, Y. H. Lee and J. W. Yang, Sci. Rep., 2017, 7, 3146.
- 40 Y. Ren, Z. Yuan, K. Lv, J. Sun, Z. Zhang and Q. Chi, *Green Chem.*, 2018, 20, 4946–4956.
- 41 B. S. Tovrog, S. E. Diamond, F. Mares and A. Szalkiewicz, J. Am. Chem. Soc., 1981, 103, 3522–3526.