Supporting Information

Bifunctional carbon nanoplatelets as metal-free catalysts for direct conversion of fructose to 2,5-diformylfuran

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Experiment

Catalysts synthesis

The chemicals used in the experiment were purchased from Sigma-Aldrich and used directly without purification. Glucose was used as the carbon precursor for the synthesis of carbon nanoplatelets. For a typical process, 0.5g glucose was dissolved in a mixed solution of lithium chloride and potassium chloride at a ratio of 45/55 by weight. The mixed solution was heated at 80 ^{o}C and stirred until it was evaporated. The resulting mixture was then transferred to a crucible with a lid and calcinated at 800 ^{o}C for 5h. After cooling, the black product was dissolved in deionized water with the assistance of sonication. Black carbon materials can be collected after filtrating, washing and drying at a 65 ^{o}C oven for 12 hours, denoted as GN. Then GN was treated with a concentrated nitric acid for 3 hours at 110 ^{o}C, filtering and washing with sufficient deionized water to remove the redundant nitric acid, the resulting product obtained after overnight dry in an oven was denoted as GN-N. Using the same treatment method, GN-S was obtained after GN was treated with a concentrated sulfuric acid, and GN-NS was the product of GN treated with mixture of concentrated nitric acid and sulfuric acid at a volume ratio of 3:1. The carbon nanotubes (CNT) used in comparison experiments were treated with concentration nitric acid for 12h, and the carbon spheres (CS) were synthesized by a glucose hydrothermal method.

Catalyst characterizations

The morphology of the catalysts were investigated by field-emission scanning electron microscopy (FESEM; JEOL, JSM-6700F, 5 kV) and transmission electron microscopy (TEM; JEOL, JEM-2100F, 200 kV). Fourier transform infrared (FTIR) spectra were recorded on Digilab FTS 3100 FTIR with a 4 cm-1 resolution using a standard KBr disk technique. Raman tests were carried out on a Renishaw 1000 Raman spectrometer equipped with a 514 nm excitation from HeNe laser. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker Advance 8 X-ray diffractometer using a Ni filtered Cu Kα radiation (λ=0.154nm), operated at 40 kV and 40 mA. Surface element analysis of nitrogen and sulfur were performed by X-ray photoelectron spectroscopy (XPS) on SKL-12 spectrometer with Al X-ray source. The element composition of the catalyst was estimated by a CHNS Elemental Analyzer. Temperature-programmed desorption (TPD) was performed on a Micromeritics AutoChem II 2910 instrument connected with QMS 200 (Qmnistar) in flowing helium to study the surface groups. Nitrogen adsorption/desorption was

performed on Autosorb-6B to study the surface area of the catalysts. The surface acid groups was determined by titration, for the determination of the sulfuric acid groups, the catalyst was first suspended in a solution of NaCl which can substitute the protons of sulfuric acid groups, and then the content of sulfuric acid groups were determined by neutralization titration with sodium hydroxide. Carboxyl groups were measured following Boehm titration, sodium bicarbonate was neutralized by carboxyl groups.

Catalytic Reaction

Dehydration of fructose to HMF

In a typical run, the procedure for the fructose dehydration into HMF was as follows: fructose (200 mg), catalyst (10 mg), and DMSO (5 mL) were added into a 25 mL three-necked, round-bottomed flask equipped with a reflux condenser. The reaction was heated in a thermostatic oil bath with magnetic stirring and maintained at the reaction temperature for a specific time. After the reaction, the mixture was filtered and diluted with DI water prior to the analysis by HPLC.

Aerobic oxidation of HMF to DFF

In a typical run, the procedure for the aerobic oxidation of HMF was as follows: HMF (63 mg, 0.5 mmol), catalyst (10 mg), and DMSO (5 mL) were added to a 25 mL three-necked round-bottomed flask equipped with a reflux condenser and magnetic stirring. The reaction was heated in a thermostatic oil bath to a target temperature. The reaction was performed under a constant oxygen flow (20mL min^{-1}). After the reaction, the mixture was filtered and diluted with DI water and then analyzed by HPLC.

One-pot and one step synthesis of DFF from fructose

In a typical run, the direct conversion of fructose to DFF was as follows: fructose (200 mg), catalyst (10 mg), and DMSO (5 mL) were added into a 25 mL three-necked, round-bottomed flask equipped with a reflux condenser. The reaction was heated in an oil bath and oxygen was bubbled through the reaction mixture at a flow rate of 20 mL/min. After the reaction, the catalyst was separated from the reaction mixture by filtration and products were diluted with DI water prior to the analysis by HPLC.

Products analysis

Analyses of fructose, HMF and DFF were conducted on an Agilent 1260 HPLC with a Bio-rad aminex 87H column (300 mm×7.8 mm pre-packed column). The mobile phase was constituted of

5 mM H_2SO_4 solution at 0.6 mL/min. The column oven temperature was kept at 60 ^oC. The amount of each compound was quantified by an external standard calibration curve method, which was constructed based on the pure compound.

Characterizations of catalysts

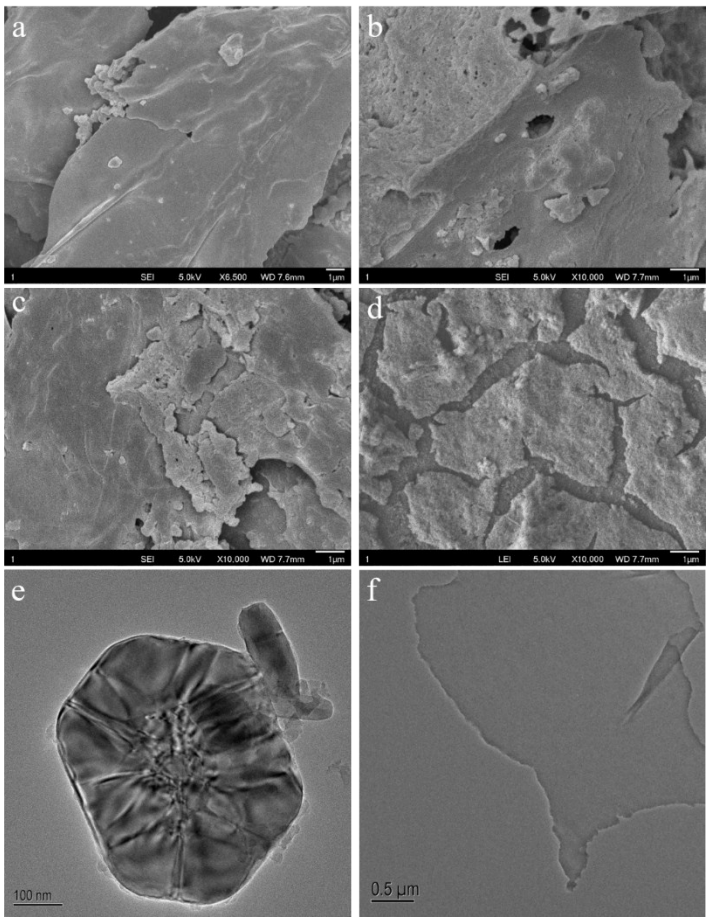


Fig.S1 FESEM of (a)GN, (b) GN-N, (c)GN-S, (d) GN-NS and TEM of (e) GN, (f) GN-NS.

The samples showed the typical nanosheet structure of graphene in Fig.S1.

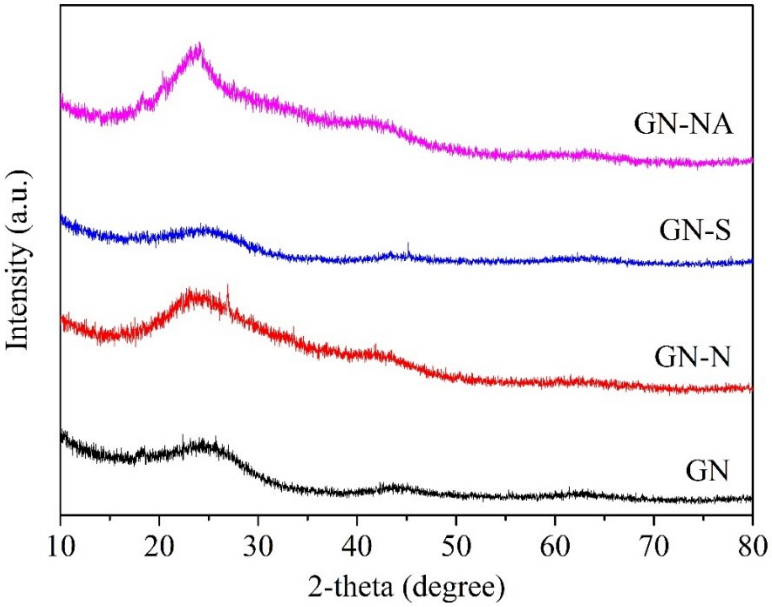


Fig.S2 XRD patters of GN, GN-N, GN-S and GN-NS.

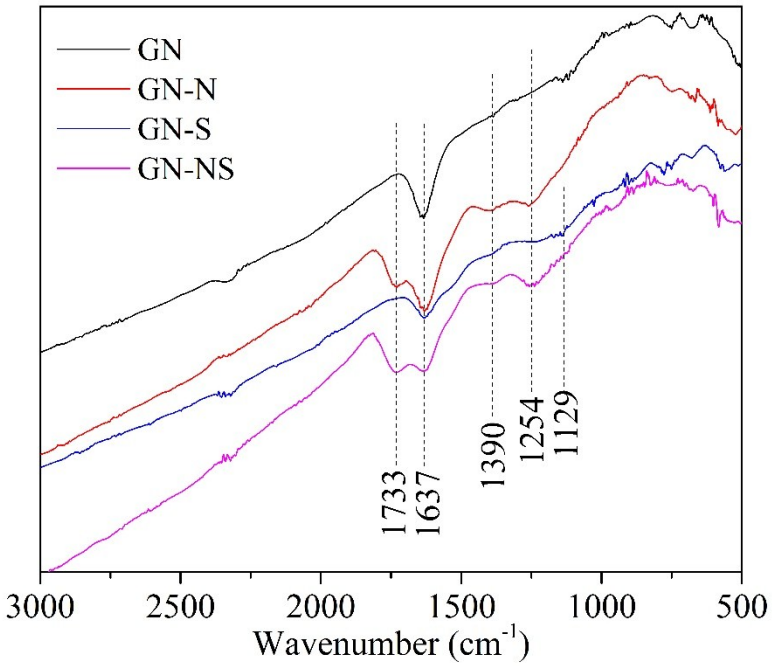


Fig.S3 FTIR spectra of GN, GN-N, GN-S and GN-NS.

C=O (1733 and 1390 cm-1), C=C (1637 cm-1); C-O (1254 cm-1); SO3H (1129 cm-1); NO2 (1390 cm-1)

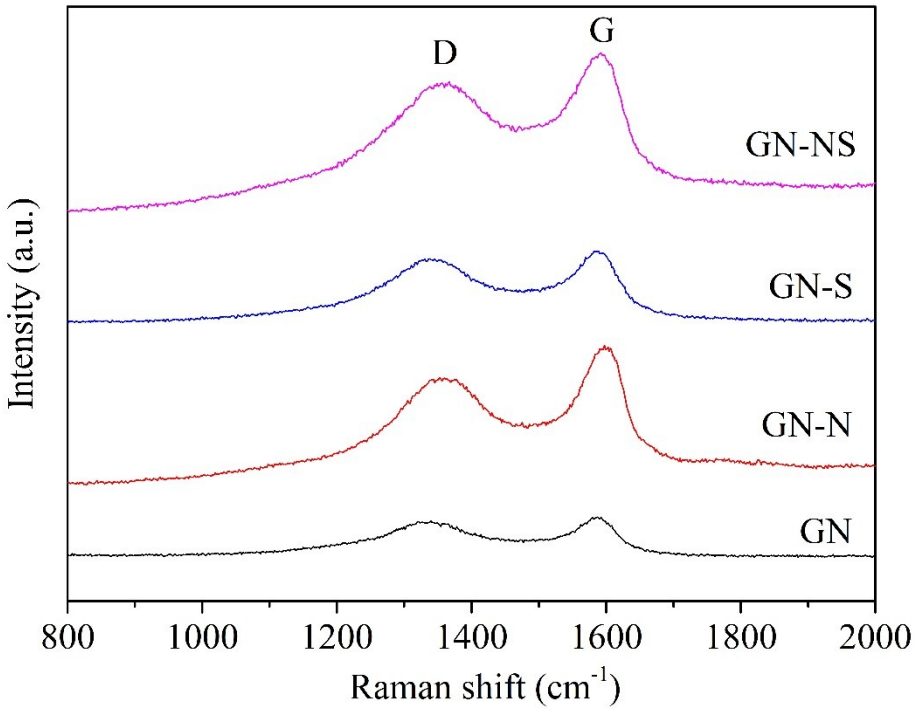


Fig.S4 Raman spectra of GN, GN-N, GN-S and GN-NS.

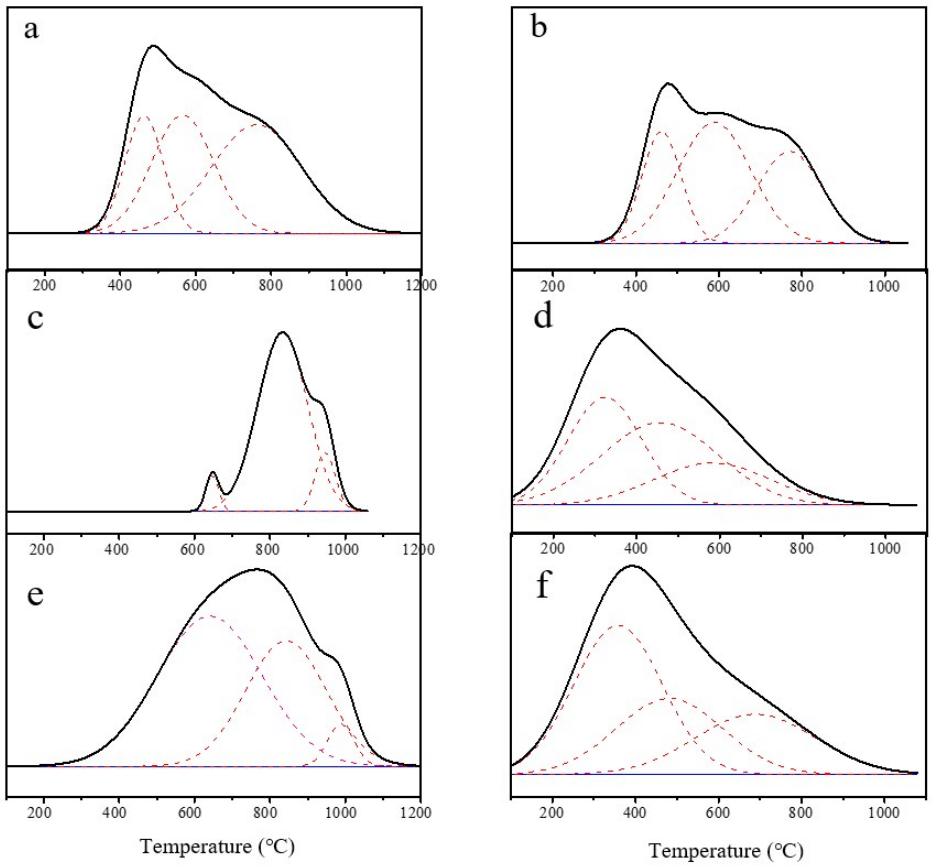


Fig.S5 CO (a,c,e) and CO_2 (b,d,f) TPD spectra of GN-S (a, b), GN-N (c,d) and GN-NS (e,f)

CO-TPD-MS: anhydride (480℃), phenol (635℃), carbony/quinone (870℃, 950℃),

CO_2-TPD-MS: carboxylic acid (350℃), anhydride (480℃), lactone (610℃, 750℃)

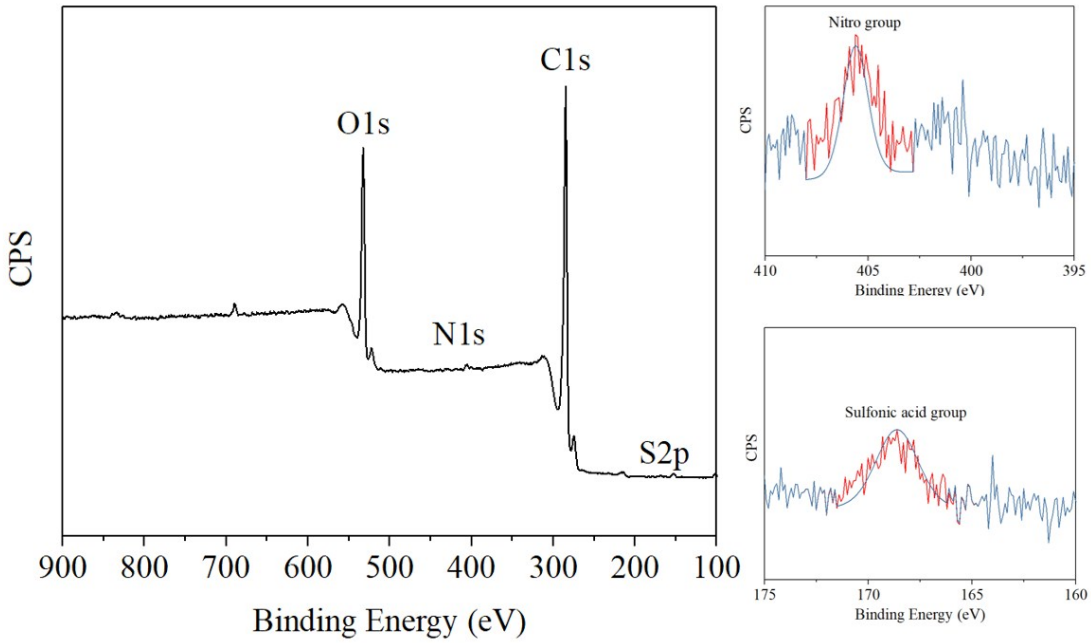


Fig.S6 XPS full spectra of GN-NS, N1s and S2p narrow spectra.

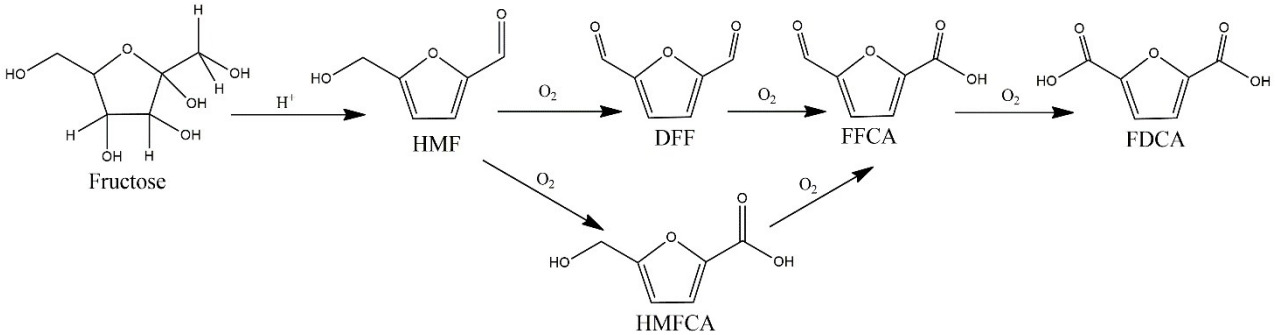
The XPS peaks at 405.5ev (N1s) and 169 ev (S2p) were attributed to the nitro groups and sulfonic acid groups respectively.

Table S1 Element analysis of GN, GN-N, GN-S, GN-NS and CNT

Catalyst	C/%	H/%	N/%	S/%	O/%
GN	81.60	2.23	0.00	0.00	16.17
GN-S	70.96	1.95	0.00	0.50	26.59
GN-N	61.05	2.12	0.69	0.00	36.14
GN-NS	45.26	2.55	1.13	0.45	50.61
CNT	91.76	0.27	0.11	0.00	7.86

Table S2 Surface properties of GN, GN-N, GN-S and GN-NS

Catalyst	BET surface area (m^2/g)	-SO_3H amount (mmol/g)	-COOH amount(mmol/g)



GN	473	--	--
GN-S	459	0.15	0.04
GN-N	394	--	0.56
GN-NS	335	0.14	1.08

Scheme S1 Conversion of fructose and HMF to valuable chemicals