Metal-free bifunctional graphene oxide-based carbocatalysts toward reforming biomass from glucose to 5-hydroxymethylfurfural

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Table S1. Comparison of HMF yields from glucose with relevant literatures.

	Catalyst	Solvent	Catalyst conc. (wt. %)	Temp. (°C)	Time (h)	HMF Yield (%)	Ref
Metal	$CrCl_2$	DMA[a]-NaBr	6	100	5	81	[S1]
	$CrCl_2$	[EMIM]Cl	6	100	3	62	[S2]
	$YbCl_3$	[BMIM]Cl[b]	10	140	6	24	[S3]
	$SO_4^{2-}/ZrO_2–Al_2O_3$	DMSO	7.6	130	4	48	[S4]
	$CrCl_2$	[EMIM]Cl	0.4	100	3	70	[S5]
	Nb_2O_5-WO_3	2-BuOH, Water	1000	140	2	52	[S6]
	Sulfated zirconia catalyst	Water	0.5	100	6	3.9	[S7]
	$MgCl_2$, boronic acid	DMA[a]	20	120	4	57	[S8]
	ZrPO	Water	2.5	155	6	46.6	[S9]
	SnPO	[EMIM]Br	10	120	3	58.3	[S10]
	$AlPW_{12}O_{40}$	DMSO, Water	25	170	4	61.7	[S11]
	Zeolite	Water, DMSO, THF[c]	0.5	180	3	43	[S12]
Non-metal	Sulfonated graphene quantum dots	DMSO, Water, MIBK[d], butanol	0.4	170	2	19	[S13]
	Functionalized silica nanoparticles	[EMIM]Cl	2.7	120	3	13	[S14]
	Sulfonated silica particles	Water, γ-valerolactone	0.5	180	4	52.9	[S15]
	Functionalized GO	[EMIM]Cl	0.25	130	3	36.5	**this study**
Homo-geneous	Boric acid	[EMIM]Cl	2.7	120	3	41	[S16]
	H_2SO_4	γ-valerolactone	6.4	130	1	13	[S17]
	H_2SO_4	[BMIM]Cl	1	120	3	66	[S18]

[a]DMA: Dimethylacetamide, [b][BMIM]Cl: 1-Butyl-3-methylimidazolium Chloride, [c]THF: Tetrahydrofuran, [d]MIBK: Methyl isobutyl ketone.

Table S2. Relative atomic compositions based on XPS measurements.

Catalyst	Atomic ratio (at. %)				
	C1s	O1s	B1s	S2p	C/O ratio
GO	71.1	27.4	ND	0.7	2.59
S-GO	66.7	30.9	ND	1.00	2.16
B-GO	84.8	8.71	4.78	ND	9.73
BS-GO	78.2	14.8	4.15	1.67	5.29

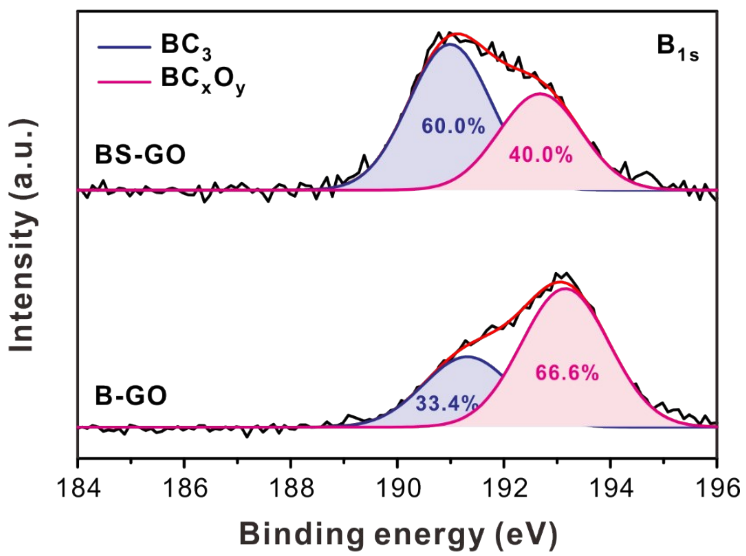


Fig. S1 Deconvoluted high-resolution XPS B1s spectra of B-GO and BS-GO.

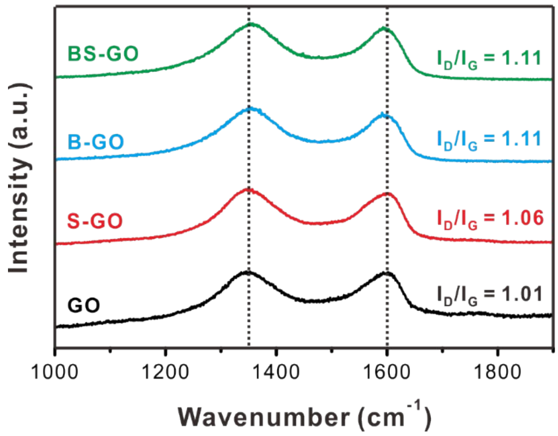


Fig. S2 Raman spectra of GO and GO-derivatives. An argon ion laser, with a wavelength of 532 nm, was used as an excitation source. The D and G bands appear at 1346 cm^{-1} and 1600 cm^{-1}, respectively.

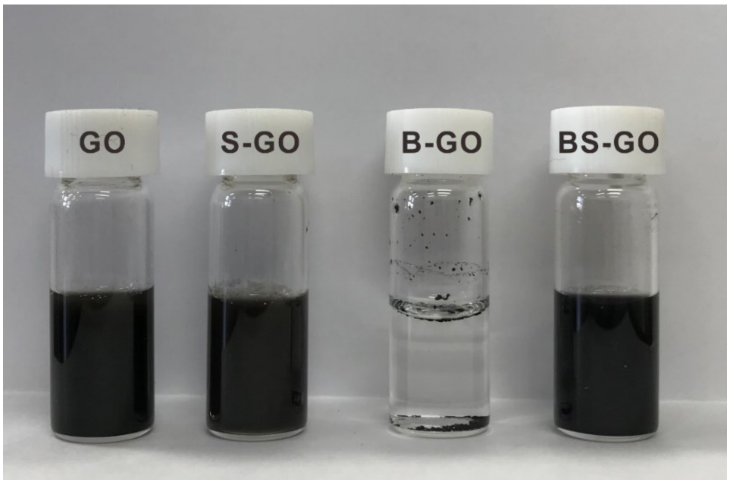


Fig. S3 Photograph of GO-based catalysts suspensions in water (conc. of 0.5 mg mL^{-1}).

Table S3. HMF yields from fructose under various reaction conditions.

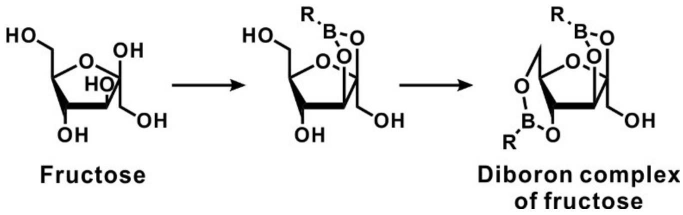
Entry	Temperature (°C)	Time (h)	Atmosphere	Pressure (MPa)	HMF yield (%)
1	130	1	N_2	0.4	0.02
2	130	2	N_2	0.4	0.06
3	130	3	N_2	0.4	0.05
4	140	1	N_2	0.4	0.02
5	140	2	N_2	0.4	0.07
6	140	3	N_2	0.4	0.1
7	150	1	N_2	0.4	0.04
8	150	2	N_2	0.4	0.3
9	140	1	N_2	0.2	3.7
10	140	2	N_2	0.2	2.6
11	140	3	N_2	0.2	7.3
12	140	4	N_2	0.2	8.1
13	140	0.5	Air	0.1	42.3
14	140	1	Air	0.1	62.1
15	140	2	Air	0.1	56.3
16	140	3	Air	0.1	57.5
17	150	1	Air	0.1	73.4
18	150	2	Air	0.1	78.9

Reaction conditions: Fructose 1.0 g, DMSO 10 mL, without catalyst.

Table S4. HMF yields from fructose with the GO-based carbocatalysts prepared in this study.

Entry	Catalyst	Time (h)	HMF yield (%)
1	No catalyst	1	73.4
2	No catalyst	2	78.9
3	GO	1	88.0
4	GO	2	87.9
5	S-GO	1	88.0
6	S-GO	2	89.2
7	B-GO	1	77.5
8	B-GO	2	81.7
9	BS-GO	1	81.4
10	BS-GO	2	84.3

Reaction conditions: Fructose 1.0 g, catalyst 10 mg, DMSO 10 mL, at 150 °C, under an air atmosphere.



Scheme S1. Schematic representation of diboron complex formation at high catalyst concentrations.

Table S5. HMF yields from glucose in DMSO.

Entry	Catalyst	Time (h)	HMF yield (%)
1	GO	4	4.6
2	GO	8	7.3
3	GO	12	7.8
4	BS-GO	4	1.4
5	BS-GO	8	2.4
6	BS-GO	12	3.3

Reaction conditions: Glucose 1.0 g, catalyst 10 mg, DMSO 10 mL, at 140 °C, under an air atmosphere.

Table S6. Changes in HMF yields depending on the temperature and reaction time.

	Yield (%)			
Reaction time (h)	100 °C	120 °C	130 °C	140 °C
1	5.5	16.0	19.1	18.7
2	8.0	17.0	20.5	14.5
3	7.8	18.2	21.0	12.2
4	8.8	16.7	18.9	11.2
5	8.9	15.7	15.2	8.4
6	9.7	17.2	14.8	6.4

Reaction conditions: Glucose 1.0 g, catalyst 10 mg, EMIM[Cl] 10 mL, at 140 °C, under an air atmosphere.

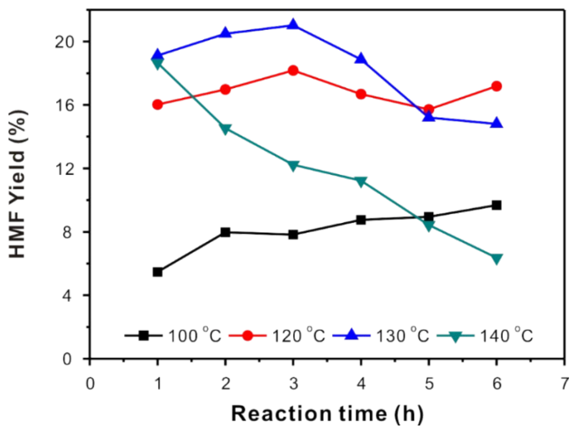


Fig. S4 Changes in HMF yields from glucose over BS-GO depending on the temperature and reaction time shown in Table S6.

Table S7. HMF yields and conversion of glucose with the GO-based carbocatalysts.

Entry	Catalyst	HMF yield (%)	Conversion of glucose (%)
1	GO	13.2	38.2
2	S-GO	15.1	39.5
3	B-GO	31.4	87.4
4	BS-GO	36.0	95.2

Reaction conditions: Glucose 0.5 g, catalyst 12.5 mg, solvent 5.0 mL, at 130 °C, under an air atmosphere.

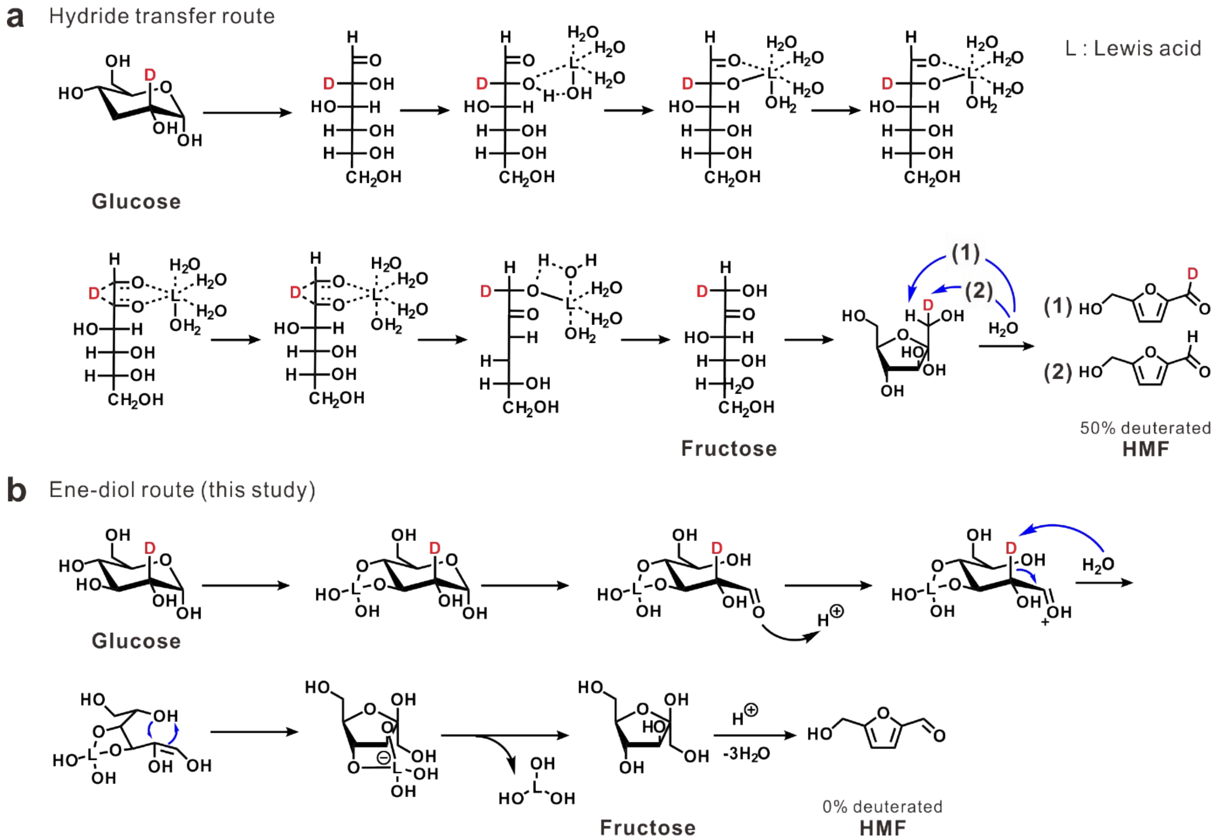


Fig. S5 Reaction pathways from *D*-Glucose-2-d_1 to HMF with (a) the hydride transfer route and (b) the ene-diol route.

Table S8. Relative atomic compositions before and after the catalytic reaction based on XPS measurements.

Catalyst	Atomic ratio measured by XPS (at. %)				
	C1s	O1s	B1s	S2p	C/O ratio
B-GO	84.8	8.71	4.78	ND	9.73
BS-GO	78.2	14.8	4.15	1.67	5.29
Post BS-GO	81.0	14.0	4.93	0.13	2.21

Post BS-GO was collected after 5th cycle.

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