

Supporting Information

In-situ bifunctional solid acid bearing B-OH and -COOH groups for efficient hydrolysis of cellulose to sugar in pure aqueous phase

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Figure S1. XRD (a) and FT-IR (b) spectra before and after pretreatment of cellulose.

Figure S2. SEM images of P160-6 (a), P160-8 (b), P160-10 (c), BP160-6 (d), BP160-8 (e), BP160-10 (f), BP180-6 (g), BP180-8 (h), and BP180-10 (i).

Figure S3. N₂ adsorption-desorption isotherms curve of BP160-10.

Figure S4. B element average mass concentration image of BP catalysts obtained at different hydrothermal conditions by ICP-OES.

Figure S5. NH₃-TPD image of BP catalysts (a) and the area diagram of peak integration (b).

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Figure S7. FT-IR (a), Raman (b) spectra and XPS survey spectra of C 1s (c) and O 1s (d) of BP160-10 before hydrolysis and after hydrolysis at 180 °C and 200 °C.

Table S1. Some solid acid-catalyzed hydrolysis reactions of cellulose to glucose.

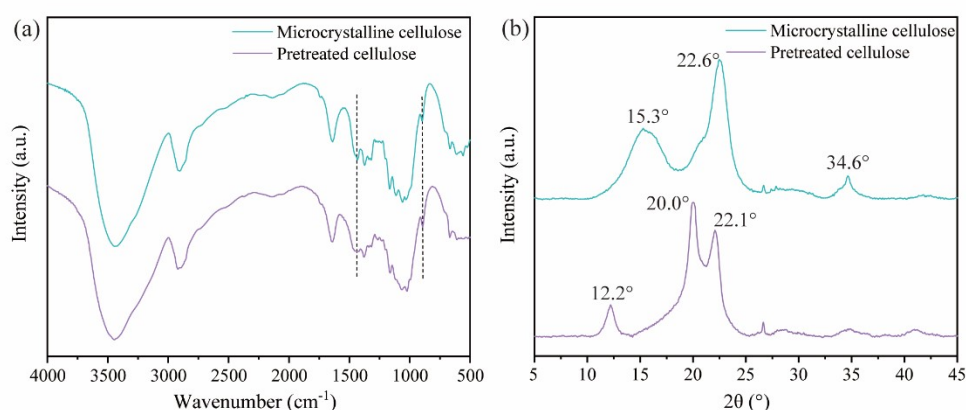


Figure S1. XRD (a) and FT-IR (b) spectra before and after pretreatment of cellulose.

After pretreatment of cellulose with phosphoric acid, the crystalline structure of cellulose transforms from natural cellulose I to cellulose II, and its crystallinity also decreases. This crystalline structure transformation is conducive to the catalytic hydrolysis of cellulose by the catalyst. Fig. S1(a) shows the infrared absorption spectra of MCC and pretreated cellulose. Both MCC and pretreated cellulose have the same infrared absorption characteristics, indicating that phosphoric acid pretreatment did not alter the chemical structure of cellulose. The absorption intensity of both slightly changes at 1430cm^{-1} and 895cm^{-1} , indicating that the crystal form of cellulose transforms phosphoric acid pretreatment.¹ Fig. S1(b) shows the X-ray diffraction spectra of MCC and pretreated cellulose. The MCC exhibits three distinct diffraction peaks at 15.3° , 22.6° and 34.6° , which are characteristic of cellulose I structure.²⁻⁴ The crystallinity of MCC is calculated to be 79.97% through peak fitting analysis by using Jade6.5 software. The spectrum of pretreated cellulose shows three diffraction peaks at 12.2° , 20.0° and 22.1° , belonging to the cellulose II structure.^{2,5} The crystallinity of pretreated cellulose is calculated to be 54.35% by Jade6.5 software. Based on the information provided, it can be observed that after phosphoric acid pretreatment, the crystalline structure of cellulose changes from cellulose I to cellulose II, and its crystallinity decreases accordingly. This change in structure and crystallinity makes the cellulose more conducive to solid acid-catalyzed hydrolysis.

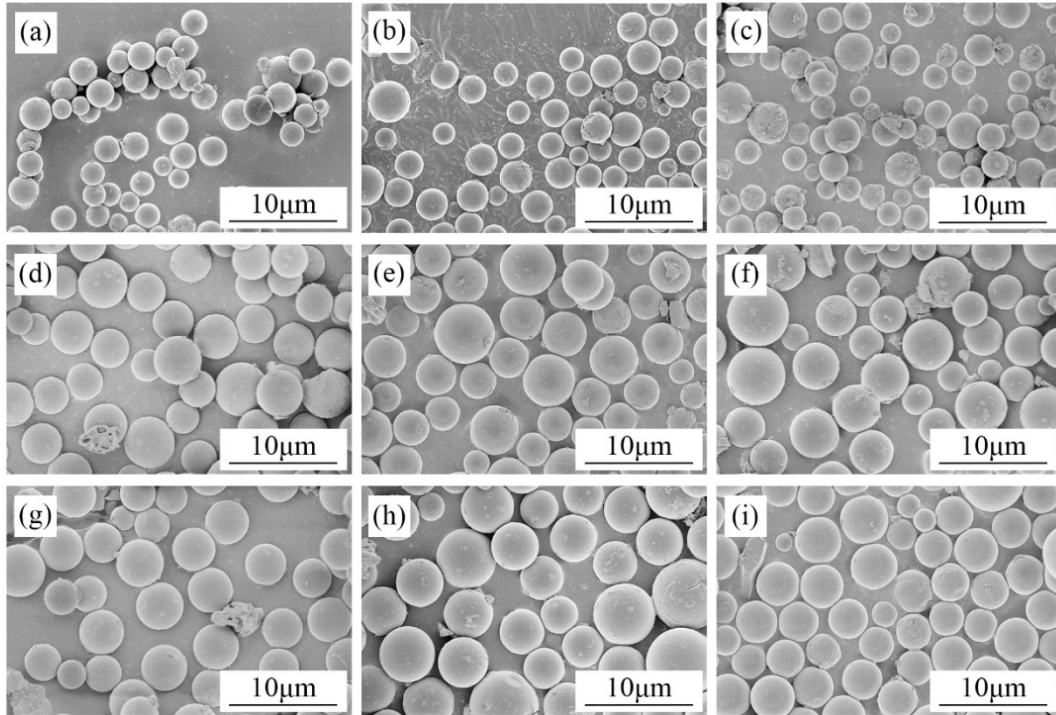


Figure S2. SEM images of P160-6 (a), P160-8 (b), P160-10 (c), BP160-6 (d), BP160-8 (e), BP160-10 (f), BP180-6 (g), BP180-8 (h), and BP180-10 (i).

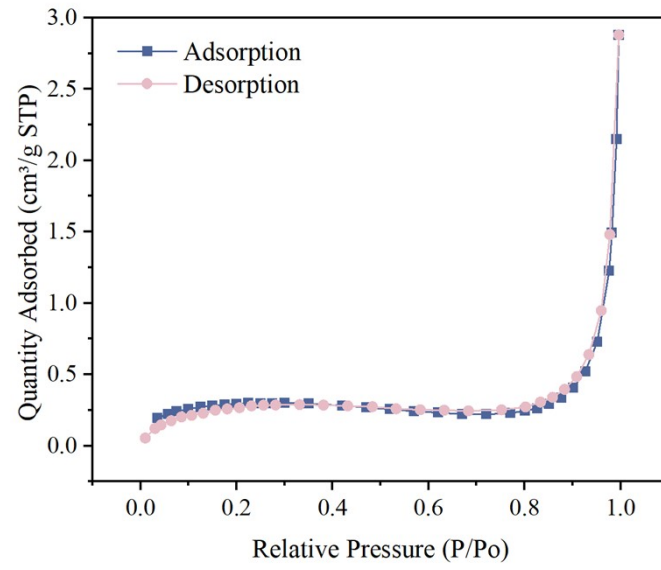


Figure S3. N₂ adsorption-desorption isotherms curve of BP160-10.

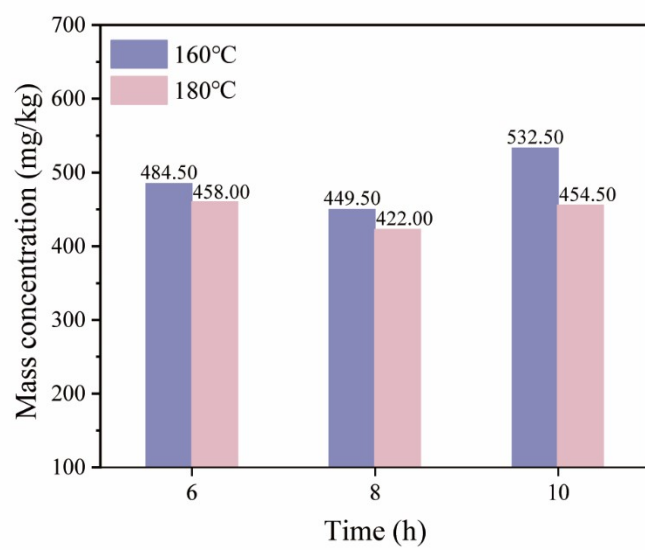


Figure S4. B element average mass concentration image of BP catalysts obtained at different hydrothermal conditions by ICP-OES.

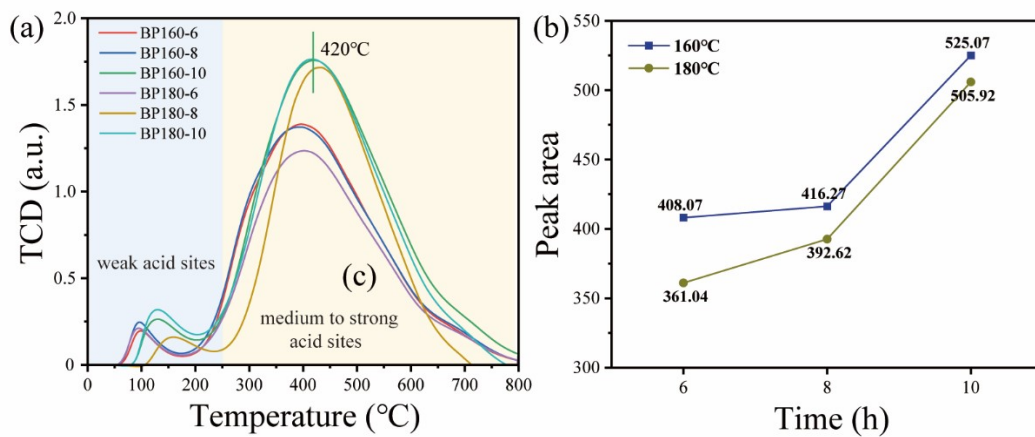


Figure S5. NH₃-TPD image of BP catalysts (a) and the area diagram of peak integration (b).

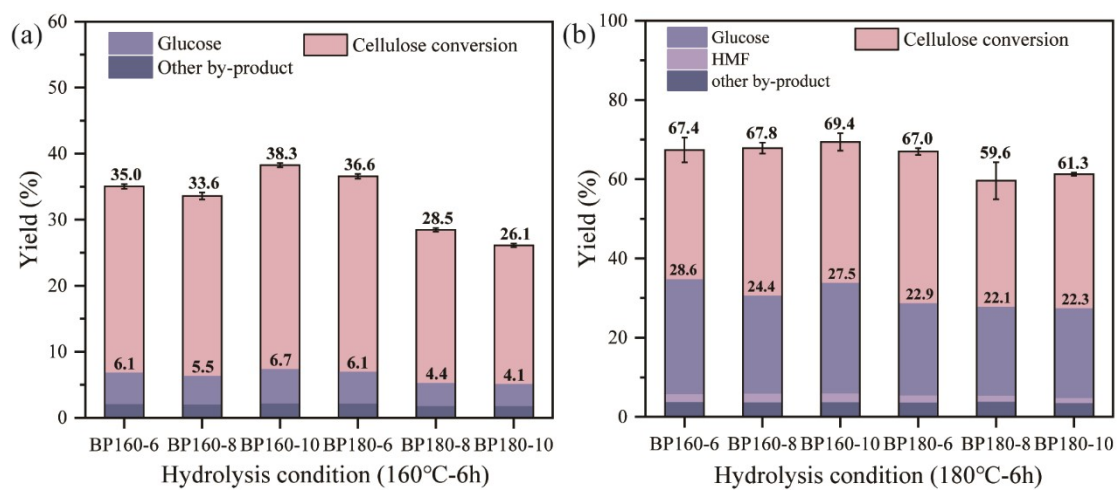


Figure S6. Images of detailed hydrolytic products at 160 °C/6 h (a) and 180 °C/6 h (b).

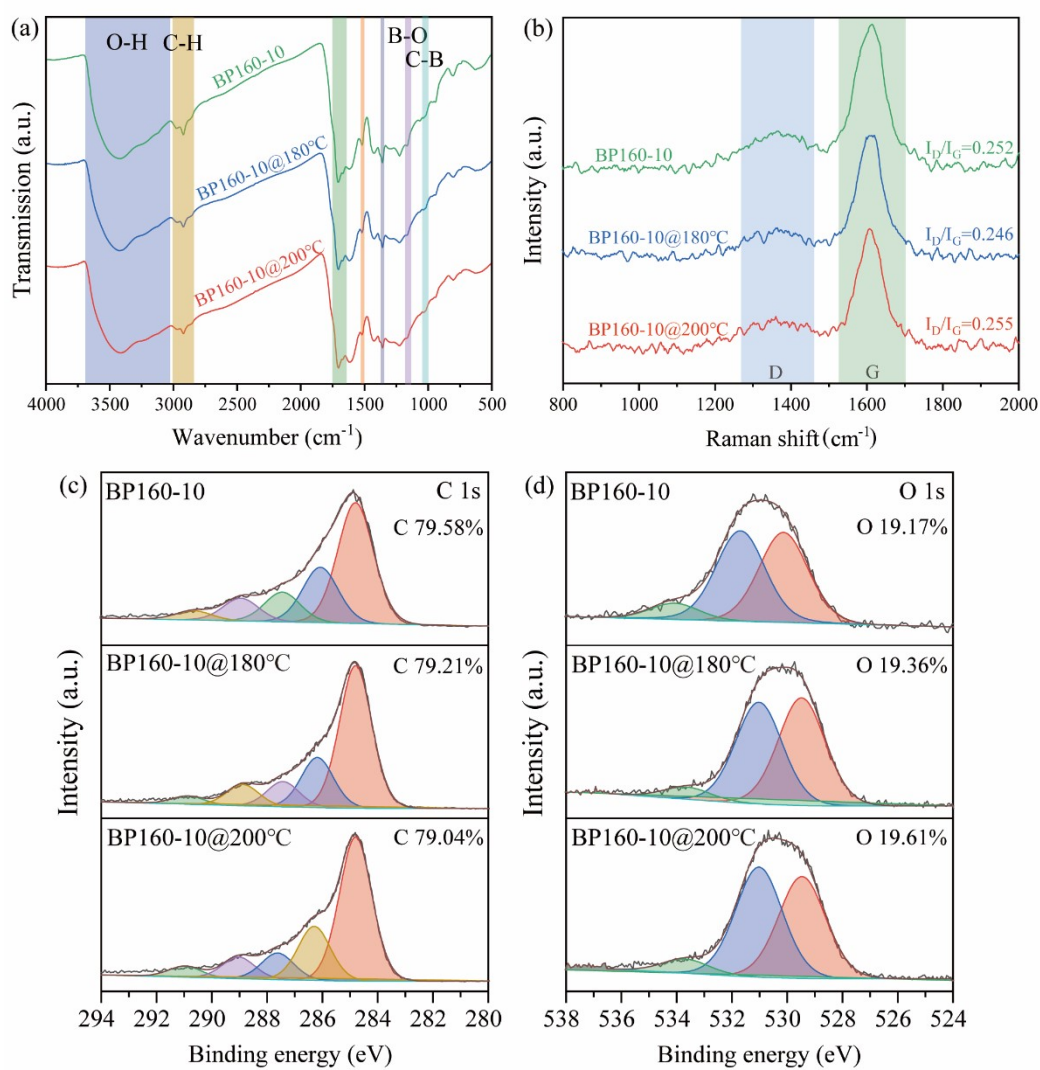


Figure S7. FT-IR (a), Raman (b) spectra and XPS survey spectra of C 1s (c) and O 1s (d) of BP160-10 before hydrolysis and after hydrolysis at 180 °C and 200 °C.

Table S1 Some solid acid-catalyzed hydrolysis reactions of cellulose to glucose.

	Catalyst	Solvent	Reaction condition	Conv. (%)	Glu. (%)	Ref.
1	Amberlyst-70	[EMIM][Cl]	140 °C, 5h	-	11	6
2	Si-propyl sulfonic acid	[EMIM][Cl]	140 °C, 5h	-	40	6
3	HY zeolite	[EMIM][Cl]	130 °C, 4.5h	-	28	7
4	MCM-48	H ₂ O	230 °C, 0.5h	-	14.1	8
5	CD-C	H ₂ O	200 °C, 1.5h	-	28.9	9
6	E-Carbon	H ₂ O	215 °C	-	31	10
7	BP160-10	H ₂ O	200 °C, 4h	97.33	38.23	This work
8	N-SB	H ₂ O	180 °C, 1h	63	42	11
9	SO ₄ ²⁻ /SnO ₂	H ₂ O	190 °C,	50.1	26.8	12
10	CNS	H ₂ O	100 °C, 6h	47	1.17	13
11	SACOH	H ₂ O	150 °C	38	10	14
12	ACOH	H ₂ O	150 °C	26	2	14

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