

*Supporting information for*

**Mechanistic Understanding of Salt-Assisted Autocatalytic Hydrolysis of  
Cellulose**

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**1. Experimental**

**2. Figures**

**Fig. S1** TGA analysis of cellulose and the solid residue in NaCl-H<sub>2</sub>O system at 220 °C for 30 min.

**Fig. S2** Comparison of cellulose conversion by one step and two steps.

**Fig. S3** Yield of the monomeric products in the liquid fraction under different reaction temperatures and systems.

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**Fig. S5** Application of NaCl-H<sub>2</sub>O in a biphasic system for the conversion of cellulose.

**Fig. S6** (A) pH values in sulfuric acid (SA)-H<sub>2</sub>O and NaCl-SA-H<sub>2</sub>O solutions after addition of cellulose at room temperature; (B) Ratio of the protons adsorption on the surface of cellulose in NaCl-SA-H<sub>2</sub>O and SA-H<sub>2</sub>O solutions;

**Fig. S7** Reaction solid residues and liquid products from FA-H<sub>2</sub>O and FA-NaCl-H<sub>2</sub>O systems.

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**Fig. S10** HPLC analysis of the liquid fraction in (A) HCl and (B) levulinic acid solutions.

**Fig. S11** FT-IR analysis of the original cellulose and the pretreated cellulose in H<sub>2</sub>O and D<sub>2</sub>O system at 210 °C for 30 min.

**Fig. S12** XRD analysis of cellulose before and after treatment using microwave at 220 °C.

**Fig. S13** FT-IR analysis of cellulose before and after treatment in NaCl-H<sub>2</sub>O system using microwave at 220 °C.

**Fig. S14** <sup>13</sup>C solid-state NMR analysis of cellulose before and after treatment in H<sub>2</sub>O and NaCl-H<sub>2</sub>O systems using microwave at 220 °C.

**3. Tables**

**Table S1** The pH values of the liquid fractions after the reaction at 210 °C.

**Table S2** Conversion of cellulose (%) in the four reaction systems at different temperatures for 15 min treatment.

## 1. Experimental

### Typical microwave treatment

Microcrystalline cellulose (Sigma Aldrich) and salts were mixed directly with deionised water in a 1:20 mass ratio in a microwave glass tube. This reaction tube was subsequently heated using a Mono Anton Parr microwave with continuous stirring at 1000 rpm. Temperature was monitored inside the reaction tube using a Ruby probe. Each reaction was heated from room temperature to the target temperature within 5 min, and held for differing periods. After treatment, the reaction system was cooled down below 70 °C using compressed air. The post-treatment slurry was filtered to separate the solid residue from the liquid fraction. The collected solid residue was dried in an oven at 105 °C overnight. The conversion of cellulose was determined by subtraction of “the amount of remaining solid” from “the amount of original cellulose added”, and the generation of humins in remaining solid was ignored.

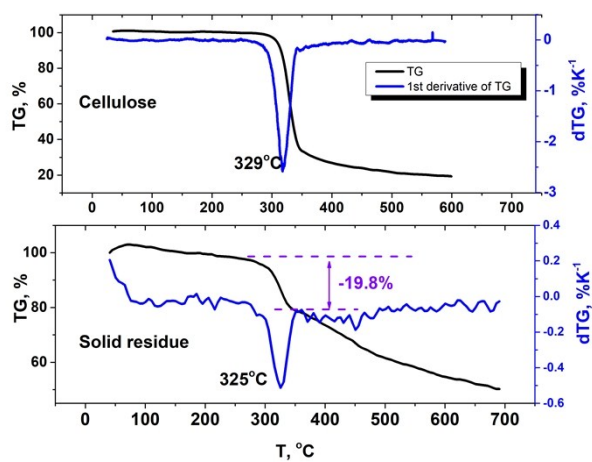
### Characterisation of the liquid fraction

HPLC analysis was run on an Agilent 1260 fitted with an Infinity II RI Detector. For sugars and acids analysis, the column used was an Agilent Hi-Plex H (7.7 × 300 mm, 8 µm (p/n PL1170-6830)). 0.005 M H<sub>2</sub>SO<sub>4</sub> solution was adopted as the mobile phase. An ACE C18 (250 x 4.6mm, 5µm particle size) column was used to analyse HMF and furfural with acetonitrile/water (25/75, vol. : vol.) used as the mobile phase with 0.8 ml/min flowing rate. The NMR samples were run on Bruker 400 MHz NMR spectrometer. The liquid products were fully dissolved into 0.5 mL D<sub>2</sub>O after all water was removed.

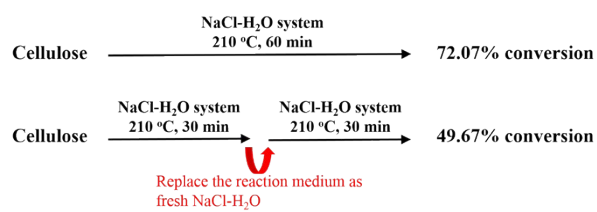
### Characterisation of the solid samples

The crystalline structures of microcrystalline cellulose and its reaction residues were examined by XRD measurement on a Bruker AXS D8 Advance. The diffracted intensity of Cu K $\alpha$  radiation (40 kV and 40 mA) was measured over the 2 $\theta$  range of 5° to 40°, and the crystallinity index (CI) of cellulose samples was calculated. FT-IR spectra of solid samples was performed on a Perkin Elmer Spectrum 400. The spectra of samples were recorded in attenuated total reflectance (ATR) mode, in the range of 4000-600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 32 scans. The <sup>13</sup>C CPMAS solid-state NMR experiments were carried out with a BRUKER AVIII 400 HD and a total of 800 scans were accumulated for each sample. The spin rate was 10000 Hz, and the relaxation delay was 5 s. Adamantane was used as reference for calibration of chemical shift.

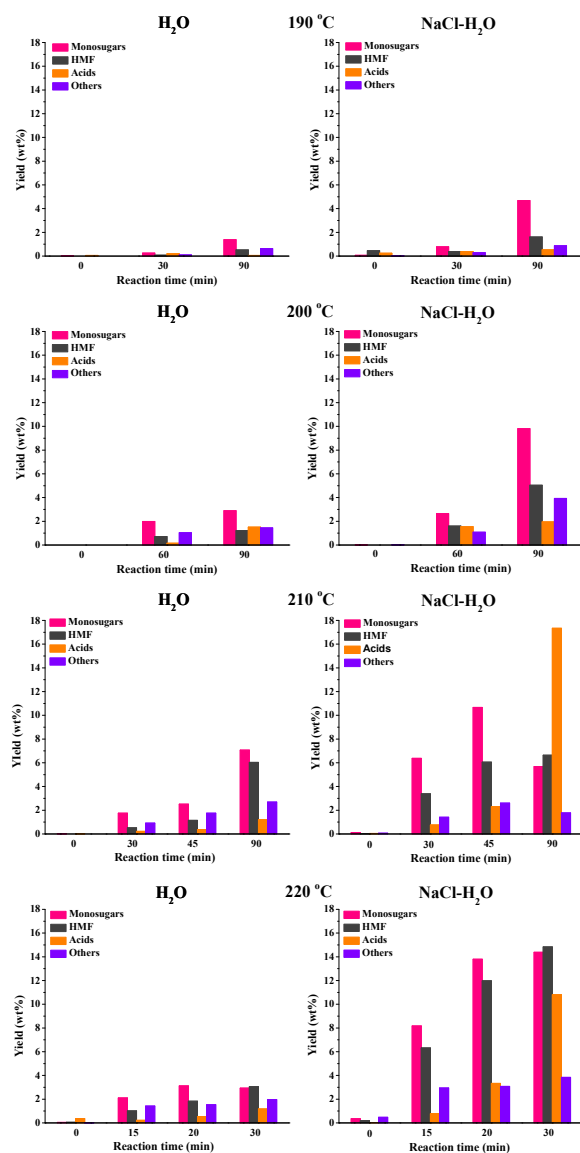
## 2. Figures



**Fig. S1** TGA analysis of cellulose and the solid residue in NaCl-H<sub>2</sub>O system at 220 °C for 30 min.



**Fig. S2** Comparison of cellulose conversion by one step and two steps.



**Fig. S3** Yield of the monomeric products in the liquid fraction under different reaction temperatures and systems. (Monosugars: glucose, fructose and rhamnose. Acids: formic acid, levulinic acid, lactic acid and acetic acid. Others: cellobiose, levoglucosan, levoglucosone and furfural).

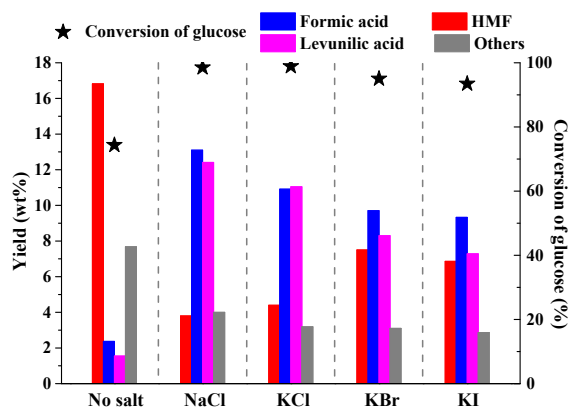


Fig. S4 HPLC analysis of salt-assisted conversion of glucose.

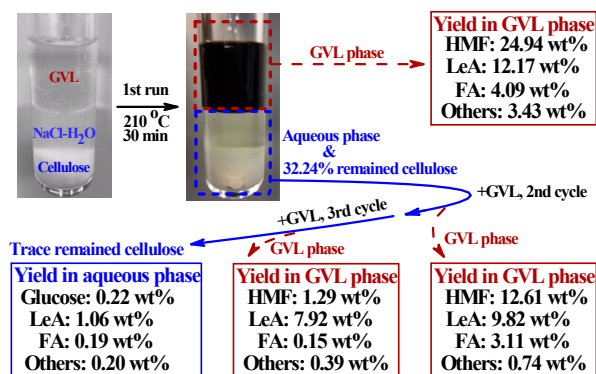


Fig. S5 Application of NaCl-H<sub>2</sub>O in a biphasic system for the conversion of cellulose.

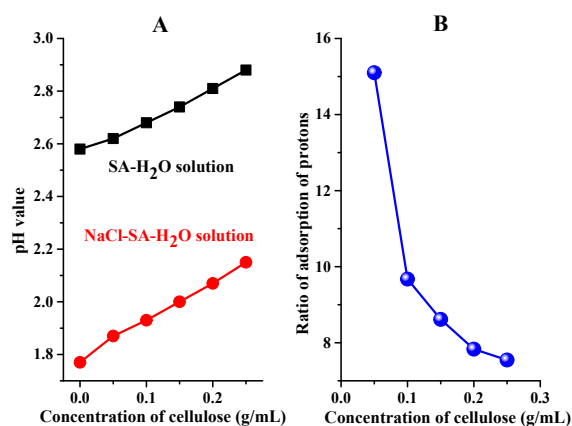
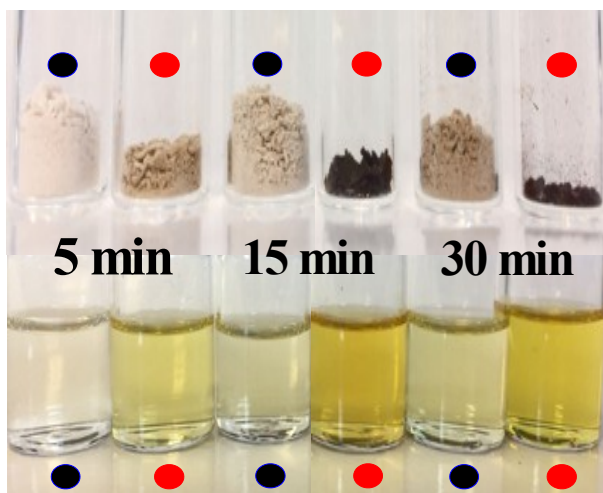
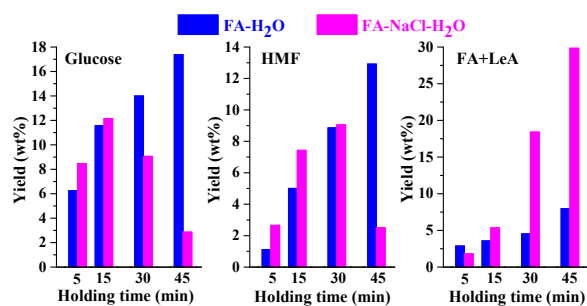


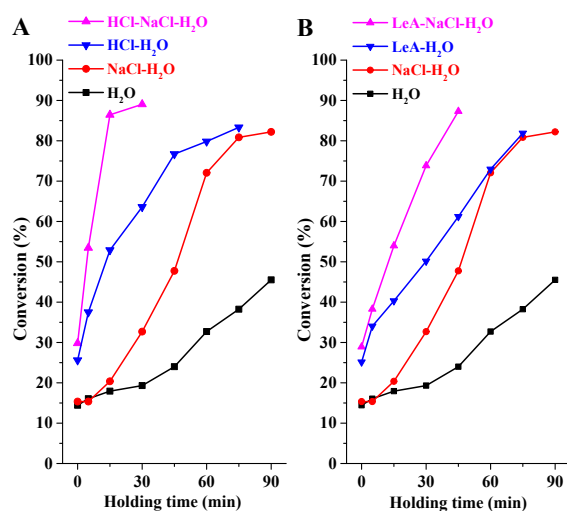
Fig. S6 (A) pH values in sulfuric acid (SA)-H<sub>2</sub>O and NaCl-SA-H<sub>2</sub>O solutions after addition of cellulose at room temperature; (B) Ratio of the protons adsorption on the surface of cellulose in NaCl-SA-H<sub>2</sub>O and SA-H<sub>2</sub>O solutions;



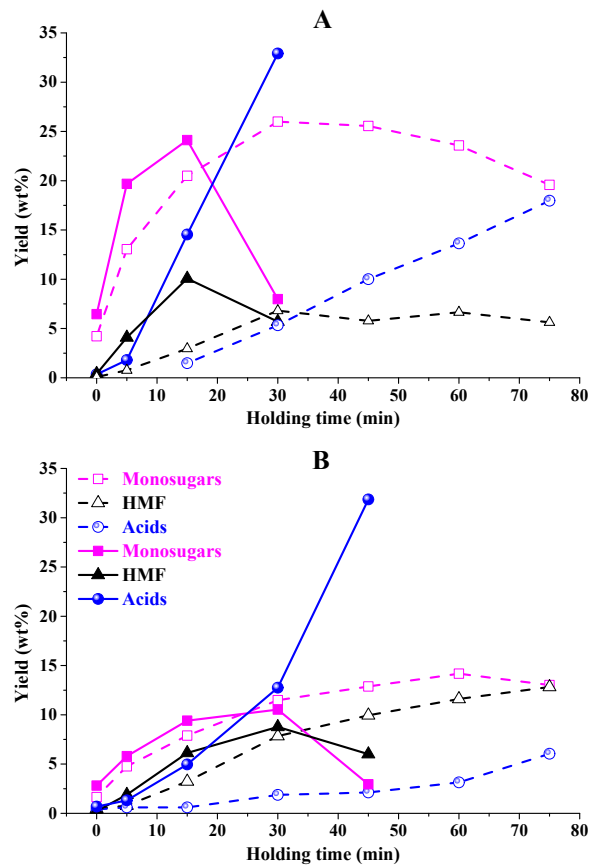
**Fig. S7** Reaction solid residues and liquid products from FA-H<sub>2</sub>O (black-dot labeled) and FA-NaCl-H<sub>2</sub>O (red-dot labeled) systems.



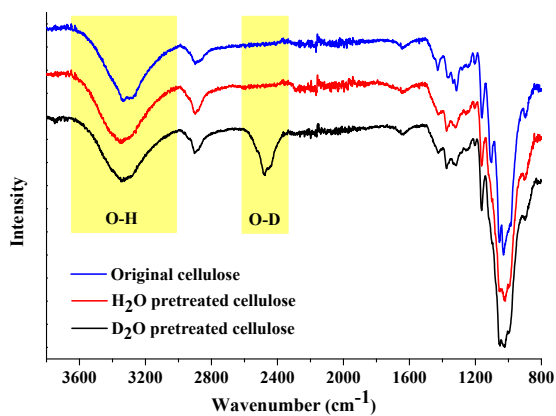
**Fig. S8** HPLC analysis of glucose, HMF and FA+LeA in FA-H<sub>2</sub>O and NaCl-FA-H<sub>2</sub>O systems.



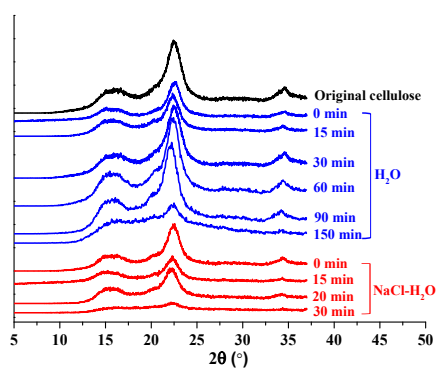
**Fig. S9** The effect of NaCl addition (20 wt%) in different acidic reaction medium on cellulose conversion at 210 °C. (A) HCl; (B) levulinic acid.



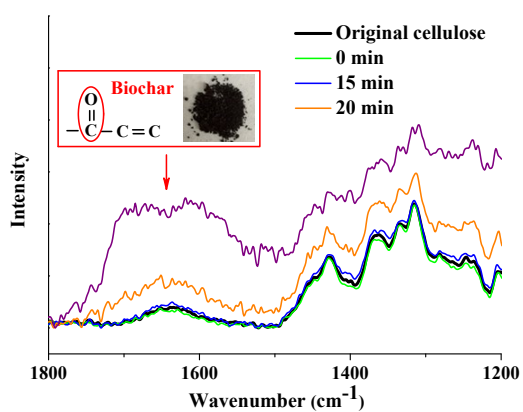
**Fig. S10** HPLC analysis of the liquid fraction in (A) HCl and (B) levulinic acid solutions. (Solid lines for NaCl-acid-H<sub>2</sub>O system; dash lines for acid-H<sub>2</sub>O system)



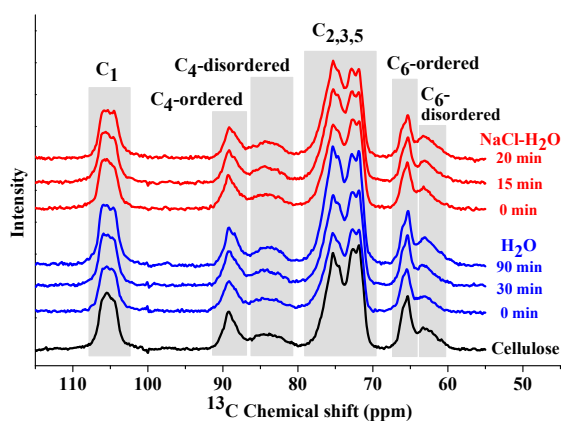
**Fig. S11** FT-IR analysis of the original cellulose and the pretreated cellulose in H<sub>2</sub>O and D<sub>2</sub>O system at 210 °C for 30 min.



**Fig. S12** XRD analysis of cellulose before and after treatment in H<sub>2</sub>O and NaCl-H<sub>2</sub>O systems using microwave at 220 °C.



**Fig. S13** FT-IR analysis of cellulose before and after treatment in NaCl-H<sub>2</sub>O system using microwave at 220 °C.



**Fig. S14** <sup>13</sup>C solid-state NMR analysis of cellulose before and after treatment in H<sub>2</sub>O and NaCl-H<sub>2</sub>O systems using microwave at 220 °C.



### 3. Tables

**Table S1** The pH values of the liquid fractions after the reaction at 210 °C.

	Holding time						
	0	5	15	30	45	60	90
H <sub>2</sub> O system	6.56	6.01	5.25	4.75	4.32	4.19	3.63
H <sub>2</sub> O-NaCl system	5.33	3.87	3.39	3.12	2.66	2.34	1.99

**Table S2** Conversion of cellulose (%) in the four reaction systems at different temperatures for 15 min treatment.

	170 °C	180 °C	190 °C
H <sub>2</sub> O	17.89	18.08	17.43
NaCl-H <sub>2</sub> O	18.85	18.68	18.02
FA-H <sub>2</sub> O	19.58	22.47	24.63
FA-NaCl-H <sub>2</sub> O	20.02	26.61	33.03