Supplementary Information

Room Temperature, Near-Quantitative Conversion of Glucose into Formic Acid

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Experimental sections

Chemicals and materials

Sodium hydroxide (NaOH, 96%, AR), lactic acid (85%, AR) and acetic acid (99.5%, AR) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. D-glucose anhydrous (99.9%, AR), D-fructose (99.9%, BR), D-xylose (99.9%, BR), lithium hydroxide ($LiOH \cdot H_2O$, 95%, AR), KOH (85%, GR), potassium peroxydisulfate ($K_2S_2O_8$, 99.5%), formic acid (FA, 98%, AR), methanol (99.5%, AR), sucrose (99.9%, AR), xylan from corncob (95%), copper (Ⅱ) oxide powder (CuO, 99.0%), cerium (Ⅳ) oxide (CeO_2), barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$, AR) and glycolic acid (GA, 98%, CP) were obtained from Sinopharm Chemical Reagent Co., Ltd. Cellulose (microcrystalline) was purchased from Alfa Aesar. Hydrogen peroxide (H_2O_2, 30 wt% in water, AR), glycolaldehyde dimer, lithium perchlorate ($LiClO_4$, 99.9%), *tert*-butyl hydroperoxide solution (TBHP, 70 wt% in water), D-cellobiose (98%), and lactose anhydrous (98%, AR) were purchased from Aladdin Reagent Company. Oxone (4.5% active oxygen, a triple salt with the formula of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), D-erythrose (75% solution), starch soluble, and iron oxide magnetic nanoparticles solution (Fe_3O_4, 10~30 nm, 25% in water) were purchased from Shanghai Macklin Biochemical Co., Ltd. Gluconic acid (49~53 wt% in H_2O) and vanadium oxide (V_2O_5 , 99%) were supplied by Sun Chemical Technology (Shanghai) Co., Ltd. Hydrochloric acid (HCl, 36-38 wt%) and oxalic acid (100%) were provided by Yonghua Chemical Technology (Jiangsu) Co., Ltd. Pyruvaldehyde (40% w/w aq. solution), formaldehyde (37%~40%, AR) and inulin (97%) were offered by Shanghai Titan Scientific Co., Ltd. 1,3-

dihydroxyacetone (98%) and D-maltose monohydrate (98%) were provided by J&K Scientific Ltd. Sorbitol (98%) was bought from Innochem (Beijing) Technology Co., Ltd. D-glyceraldehyde (85%) was supplied by Bide pharmatech Ltd. Oxygen (O_2, 99.999%) was provided by Shanghai Weichuang Standard Reference Gas Analytical Technology Co., Ltd. Deionized (DI) water was used for solution preparations in all the experiments. The three types of reactors employed in the work include a common brown glass bottle, think-wall glass bottle and autoclave (see Figure S1).

Figure S1 The three types of reactors employed in the work. The brown bottle (left), the thick-wall bottle (middle) and the autoclave (right).

General reaction procedures

In a typical reaction, a brown glass bottle (~25 mL volume) with a plastic cap and PTFE seal was used as the reactor. In order to avoid the influence of temperature fluctuation due to weather change, the reactor was immersed into a water bath that heated with controlled temperature at 308 K (near the room temperature in summer in Shanghai when the project started). A certain amount of glucose was first loaded into

the bottle, and then desired concentrations of base solution as well as H_2O_2 solution (or the solution of other oxidants) was prepared and added into the bottle. For oxidant dosage, the stoichiometric demand for complete oxidation of glucose into formic acid and water was defined as 100% H_2O_2 supply. The chemical equation is as follow: $C_6H_{12}O_6 + 6H_2O_2 \rightarrow 6HCOOH + 6H_2O$. This method was also used to define the dosage of other oxidants. Then, the total volume of the reaction solution was adjusted to 10 mL with deionized (DI). During reactions, the mixed solution was thoroughly stirred by a magnetic stirrer bar. Please be cautious that the oxidant partially decomposed during the reaction and avoid closing the cap too tight. After a desired reaction time, the reactor was taken out from the water bath, and the pH of the reaction solution was immediately adjusted to neutral or weak acidic to quench the reaction by using 1 M HCl solution (Control experiments as shown in Figure S2 have proved that the substrate and products remained unchanged in neutral or weak acidic conditions). Next, the solutions were filtered by a 0.22 μm PES syringe filter and subjected to analyses. If not immediately analyzed, the solution samples should be stored in a refrigerator and evaluated within two days.

The model compound tests were conducted in the brown glass bottles in a similar way. 0.1 M concentration of model compounds were prepared in 0.6 M LiOH solution with 100% H_2O_2 added (the amount of H_2O_2 was calculated based on the carbon in the model compounds). The reactors were immersed in a water bath at 308 K and stirred for 8 h. Afterwards, the solutions were filtered and analyzed.

Contrast experiment using O_2 gas as the oxidant

The contrast experiment was conducted in an autoclave with gas valve at the side position (GAOYAO Instruments, 20 mL inner volume, SUS 316 material). In the experiment, 180 mg glucose, 10 mL 0.6 M LiOH solution and a magnetic stirrer bar were loaded into the autoclave which was firmly closed then. 5 bar O_2 gas was pumped into the autoclave through the side valve and tube (the gas exchange was repeated three times to expel the air in the reactor). Next, the autoclave was put into a water bath at 308 K and stirred thoroughly for a desired reaction time of 8 h. After the reaction, the liquid solution was filtered by a 0.22 μm PES syringe filter and analyzed.

Cellulose pretreatment and transformation

Ball milling method was adopted to pretreat cellulose prior to the transformation. The ball mill machine is the Pulverisette P7 Premium Line (Fritsch) with a chamber (made of zirconium oxide (ZrO_2)) volume of 45 mL and the balls (ZrO_2) have a diameter of 5 mm. In the ball mill pretreatment, 0.5 g cellulose and an equivalent amount of LiOH powder were loaded together without pre-mixing into the chamber of the ball mill reactor with 100 balls and the reactor was capped tightly. With the setting of ball milling time at 8 cycles and the speed at 650 rpm, the ball mill machine was operated (the milling time was counted by cycles and one cycle includes 10 min of milling time and 5 min of rest). After ball milling, the solid products went through an alumina grid and collected. A thick-wall glass bottle with PTFE cap was used as the

reactor for cellulose transformation (inner volume 38 mL). The glass bottle was wrapped with alumina foil to prevent any possible decomposition of the oxidant induced by the light. A desired amount of the pretreated mixture was dissolved in DI water (extra LiOH was added to meet the required 0.6 M concentration) in the reactor. Then, a desired dosage of H_2O_2 was introduced and the final solution volume was 10 mL. During the reaction, the reactor was heated at 323 K by a water bath and magnetically stirred. After a reaction time of 8 h, the reaction mixture was filtered and the solution was analyzed.

Product identification and quantification

Gas chromatography mass spectroscopy was were performed with a HP 5890 Series II GC equipped with a HP-INNOWAX capillary column (30 m × 0.25 mm ID, 0.25 μm film thickness) and 5898 B mass spectrometer. The acetylation procedures were as follow: the reaction solution (1 mL) was transferred into a vial, after which 1-methylimidazole (0.3 mL) and acetic anhydride (2 mL) were added. The vial was sealed with a cap and the acetylation was finished in 30 min under ambient conditions. High performance liquid chromatography (HPLC) analysis of reaction samples was performed on an Agilent 1200 system equipped with two consecutive KC-811 columns (SHODEX) to separate products and two detectors including a refractive index detector (RID) and a variable wavelength detector (VWD). The mobile phase was 0.002 M $HClO_4$ aqueous solution, with a flow rate of 1 mL/min. Product identification was

achieved by matching the retention time of authentic samples on HPLC and spiked tests of the reaction solutions were conducted to confirm the identification. Product quantification was undertaken by plotting external standard curves using authentic samples. Taking the calculation of FA yield as an example, a series of standard FA solutions were prepared and analysed, after which an external standard curve was obtained. Using the standard curve, the FA concentration in the liquid phase after reaction could be calculated. Note that one molecule of FA has only one carbon atom, while one molecule of glucose has six carbons. Herein, the product yield was based on the carbon yield by using the following equation:

$$\text{FA yield\%} = C_{FA}*V_T/M_{FA}*N^c_{FA} \,/\, m_{glucose}/M_{glucose}*N^c_{glucose}$$

where the C_{FA} is the concentration of FA in the reaction solution; V_T is the total volume of the reaction solution; $m_{glucose}$ is the mass of the glucose substrate; M_{FA} and $M_{glucose}$ are the molecular weight of FA and glucose respectively; N^c_{FA} and $N^c_{glucose}$ denote the number of carbon atoms in one molecule of FA or glucose (herein the N^c_{FA} is 1 and the $N^c_{glucose}$ is 6). The yields of other products were calculated in the same way. Besides, the conversion rate of the substrates after the reaction were calculated by using the following equations:

$$\text{Conversion\%} = (\text{mass of substrate} - \text{mass of unconverted})/\text{mass of substrate} \times 100\%$$

Table S1 The yields of by-products for glucose conversion with different oxidants [a]

Oxidants	TBHP	Oxone	$K_2S_2O_8$	$LiClO_4$
Fructose%	11.7	16.1	7.0	16.6
GA%	3.3	1.7	2.5	0
LA%	3.9	3.3	2.0	15.4

[a] The by-products when using H_2O_2 were listed in Fig.2 in the manuscript.

Table S2 The standard potentials of the employed oxidants [a]

Oxidants	H_2O_2	Oxone	$K_2S_2O_8$	$LiClO_4$
E^o (V)	1.78	1.81	2.01	1.20

[a] The values of the standard electrode potentials are relative to the standard hydrogen electrode at 298 K and ~1 bar (1 atm). For the Oxone, its active component is $KHSO_5$ whose E^o is used here.

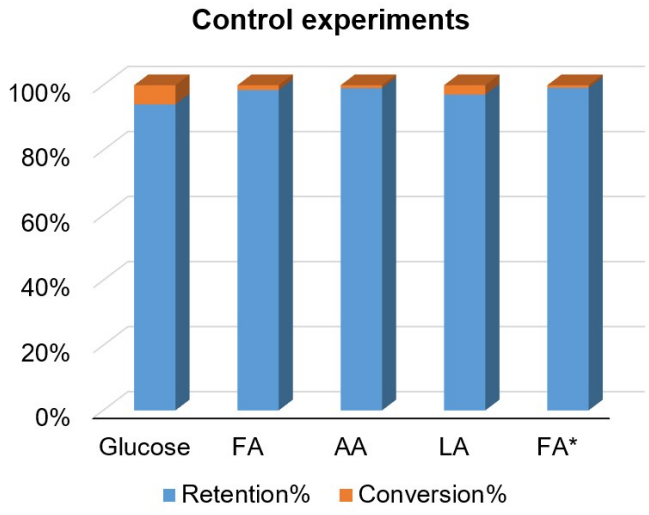

Figure S2 The control experiments of various substrates in the absence of a base. Reaction conditions: 0.1 M substrate, 100% H_2O_2, 10 mL, 308 K, 8 h. The * mark at the last entry means that the experiment was conducted under similar conditions but with the addition of the base LiOH (0.6 M).

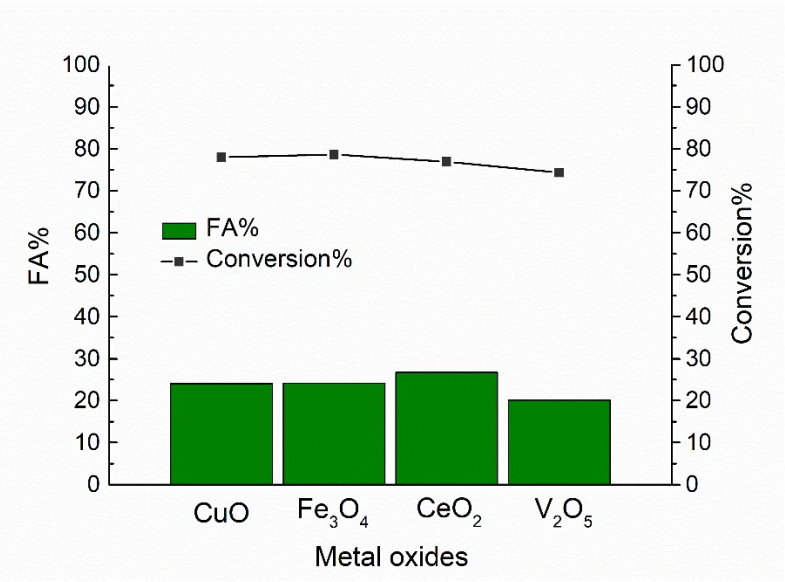

Figure S3 The glucose conversion and FA yield using H_2O_2 together with other metal oxides. Reaction conditions: 0.1 M glucose, 0.6 M LiOH, 30% oxidant, 0.01 M metal oxide, 10 mL water, 308 K, 8 h.

Table S3 FA production with different glucose concentrations at room temperature [a]

Entry	Glucose (M)	LiOH (M)	H_2O_2%	Conversion%	FA%
1	0.05	0.4	250%	98.6%	89.5%
2	0.05	0.4	300%	99.4%	91.3%
3	0.2	1.2	200%	98.2%	80.6%

[a] Reaction conditions: 10 mL, 308 K, 8 h.

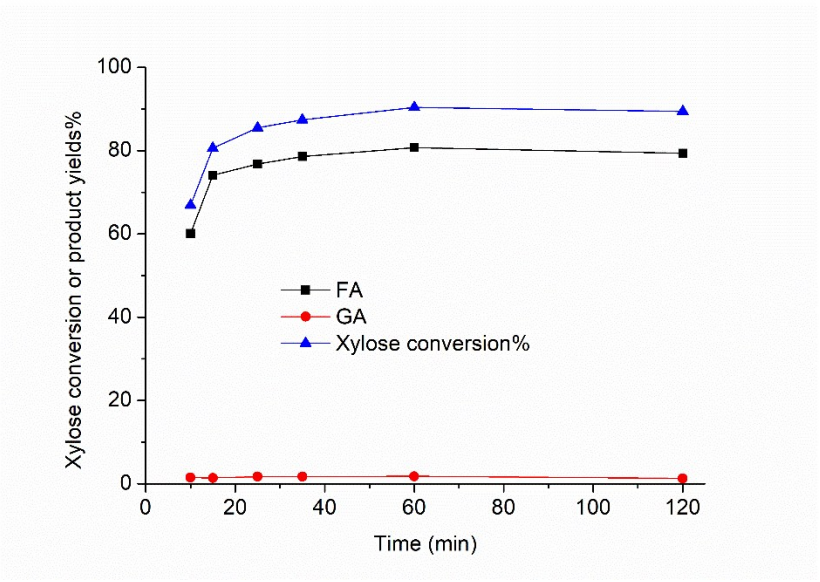

Figure S4 The product profiles of xylose conversion with different reaction times (of 10 min, 15 min, 25 min, 35 min, 1 h and 2 h). Reaction conditions: 0.1 M xylose, 0.6 M LiOH, 100% H_2O_2, 10 mL water, 308 K.

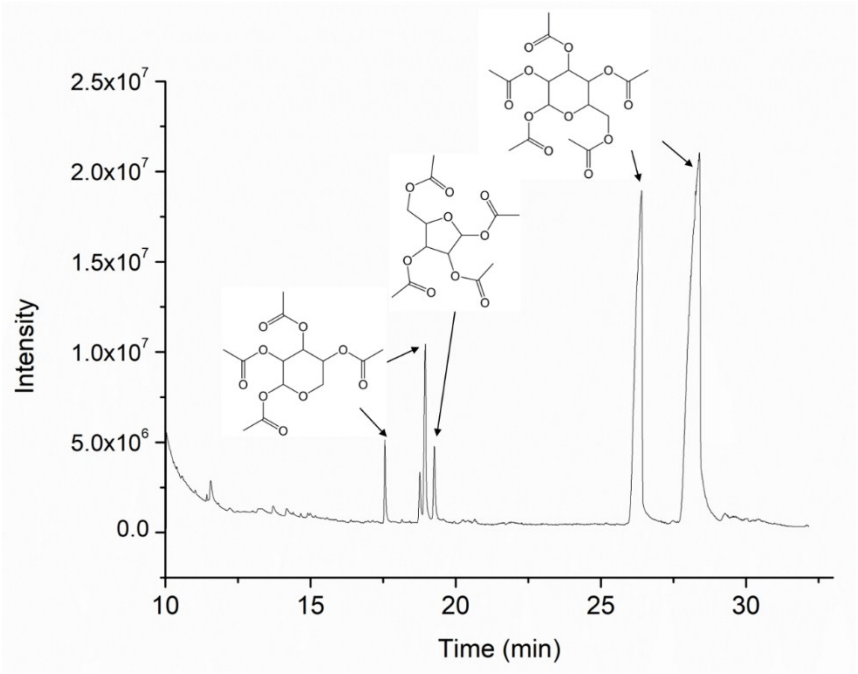

Figure S5 The GC-MS spectrum of acetylated reaction solution of glucose. Reaction conditions: 0.1 M glucose, 0.6 M LiOH, 100% oxidant, 10 mL water, 308 K, 0.5 h. Multiple peaks of pentoses were identified at around 17~19 min.