Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Direct Conversion of Cellulose into Glycolic Acid by A Zinc-Stabilized UV-Fenton Reaction

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Experiment

Materials

ZnO, $FeCl_2 \cdot 4H_2O$ and other reagents are purchased from Sigma-Aldrich. Paper cellulose and H_2O_2 (30%) are purchased from Aladdin company. All the reagents are used as received. The salt of GA-Zn is prepared by mixing 1 mol $Zn(OH)_2$ with 2 mol GA in solution and then dried in vacuum oven at 40 ^{o}C for several hours. Deionized water with specific resistivity higher than 18.2 MΩ•cm from a three-stage Milli-Q Plus 185 purification system is used in the experiment. The UV radiation device (NMT500) is produced by Shenzhen Naimeite industrial equipment company.

Decomposition of cellulose by Zinc-stabilized UV-Fenton method

Zinc-stabilized UV-Fenton method is used to decompose paper cellulose. 1.0g dry paper is split into small pieces and put in a glass disk. 50mL of 6% H_2O_2, 0.1g of ZnO and 0.03g of $FeCl_2 \cdot 4H_2O$ are added into the glass disk under stirring. After agitation, the glass disk together with a water bath is put into a temperature controllable UV apparatus (500w, 365nm) and treated with UV radiation for 1h. The distance between the UV lamp and the cellulose is 15cm and the temperature maintains at 25^{o}C by cooling system. The UV-free reaction happens in dark place for 24 hours. The cellulose residue together with the solution is dried in vacuum oven at 40 ^{o}C. The yield of over oxidative products CO_2 and H_2O is calculated as the weight of total solid before and after reaction. The soluble products are washed out by deionized water. After filtration, products are collected by drying the solution in vacuum oven at 40 ^{o}C and then analyzed by HPLC. The insoluble cellulose residue is immersed in 1 M HCl until un-reacted ZnO and precipitated yellow Fe_2O_3 are thoroughly removed. The cellulose residue is separated by filtration and then washed twice with deionized water. After drying in the oven at 80^{o}C overnight, It is weighed to calculate the CR.

Stability of various GA products in UV-Fenton reaction

As to the stability test chemical products, 1.0g GA and GA-Zn are respectively mixed with 50mL of 6% H_2O_2, and 0.03g of $FeCl_2 \cdot 4H_2O$ in a glass disk under stirring. For GA-Zn, both acidic (tuned to pH 1 by HCl addition) and original neutral conditions are respectively chosen to do the tests. The glass disk together with a water bath is then put into a temperature controllable UV apparatus (500w, 365nm) and treated with UV radiation for 1h. The distance between the UV lamp and the cellulose was 15cm and the cooling system could maintain the temperature at 25^{o}C. The metal hydroxide precipitation appeared during pH adjustment is removed by filtration (0.2 μm membrane). After filtration, products are dried in vacuum oven at 40 ^{o}C and then analyzed.

Proton nuclear magnetic resonance (1H NMR) spectroscopy

^{1}H NMR spectra of the chemicals and products (all in D2O) were recorded on a 400 MHz AVANCE III Bruker NMR spectrometer (Bruker, Switzerland). The ^{1}H NMR measurements were carried out with an acquisition time of 3.2 s, a pulse repetition time of 2.0 s, a 30 pulse width, 5208 Hz spectral width, and 32 K data points.

High performance liquid chromatography (HPLC)

HPLC was carried out on an Aglient 1260 instrument equipped with MWD refractive index detector (Aglient 1260, MWDVL, USA) and a Aminex HPX-87H carbohydrate column (BioRad). The mobile phase was 5 mM of H_2SO_4, and the flow rate was 0.4 mL/min.

Fourier transform infra-red (FTIR) spectroscopy

The FTIR spectra of GA, GA-Na and GA-Zn were recorded with NICOLET 6700 (NICOLET, America) using KBr pellets.

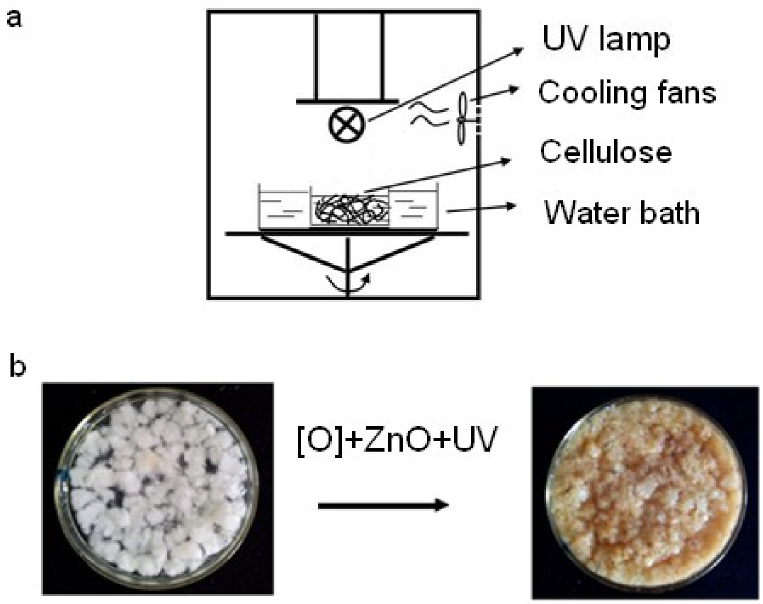

Figure S1. Schematic illustration of UV irradiation system (a) and paper morphology change before and soon after UV irradiation (b)

The products in the supernatant were a mixture of acids, polyols and sugars including glucose (Glu), fructose (Fru), glycolic acid (GA), glycerol (Gly), formic acid (FA) and acetic acid (AA) from ^{1}H NMR results (Figure S2).

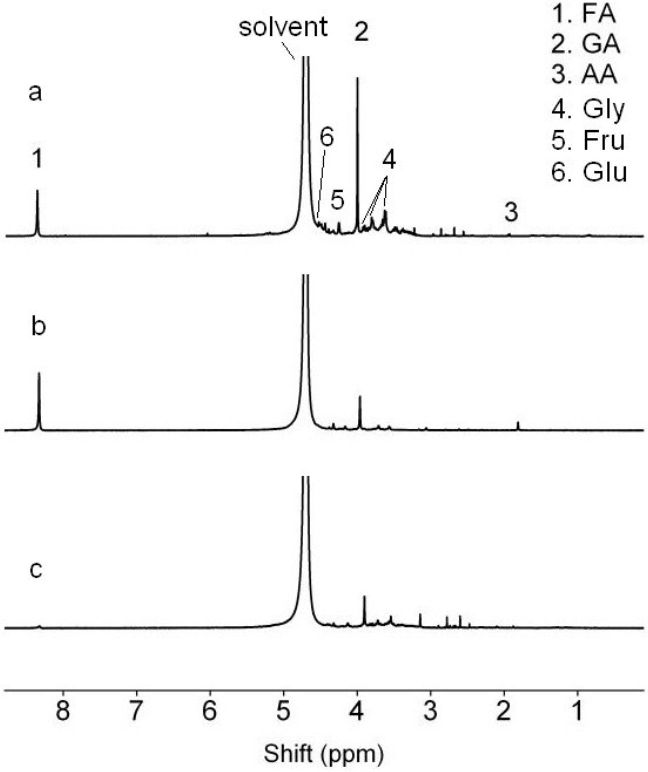

Figure S2. ^{1}H NMR spectra of products in the supernatant of G1 (a), G2 (b) and G3 (c)

Standard ^{1}H NMR and HPLC spectra of commercial available chemicals were showed in Figure S3 (from top to bottom): Glu, Fru, GA, Gly, FA and AA.

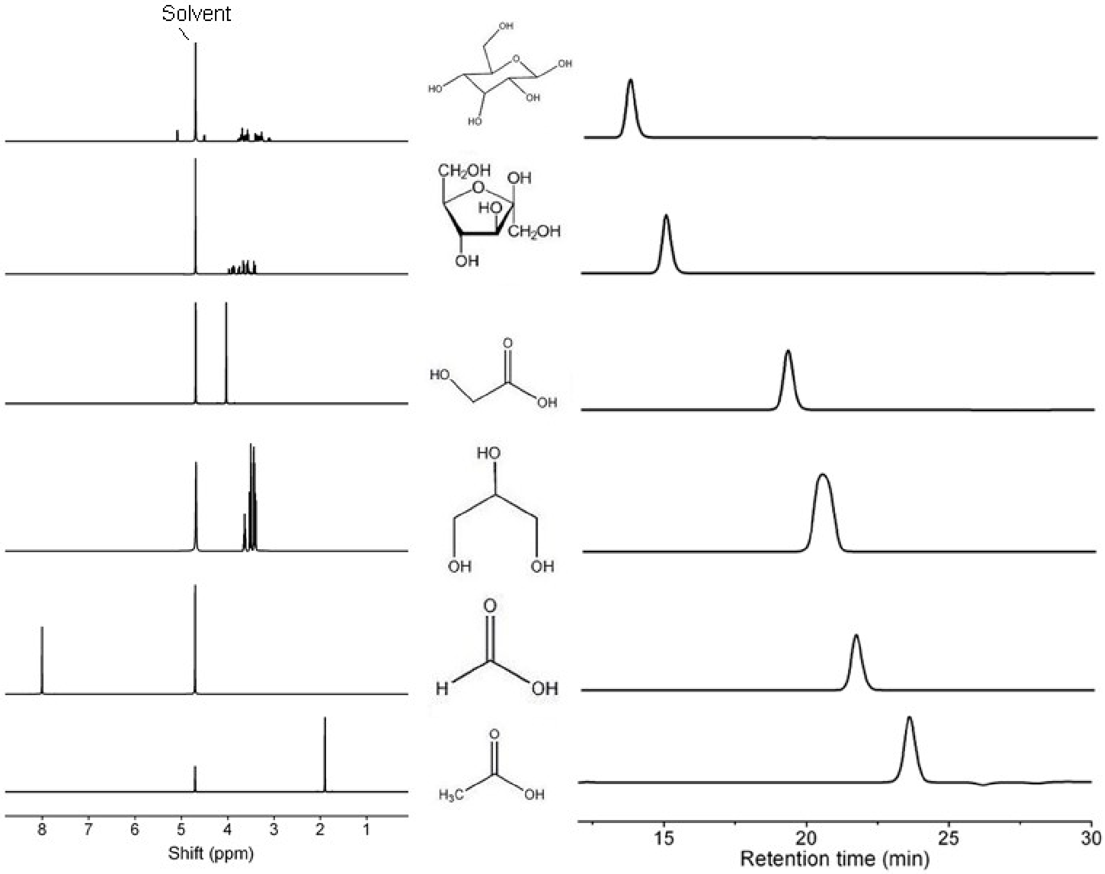

Figure S3 Standard ^{1}H NMR (left) and correlated HPLC (right) spectra of commercial chemicals

The degradation of cellulose was repeated twice consecutively by using the cellulose residue of G1 as starting material at the same zinc-stabilized UV-Fenton condition. The yield data calculated from HPLC was listed in Table S1.

Table S1. Yields of 2 consecutive degradation products

Repetition	CR [mg/h][a]	Yields [wt%][b]							
		GA	FA	AA	Gly	Glu	Fru	CO_2[c]	others
1	60	32	19	1	5	19	5	23	6
2	50	29	14	<0.1	7	22	8	26	4

The stability of 4 intermediates was tested at traditional UV-Fenton condition. The NMR result (Figure S4) showed that most Glu, Fru, Gly and GA changed to very low molecular products such as FA. The degradation products of Glu and Fru were mixtures of GA, FA, AA and Gly which is similar to cellulose degradation products. Gly was degraded to GA, FA and AA. GA was further degraded to FA and AA.

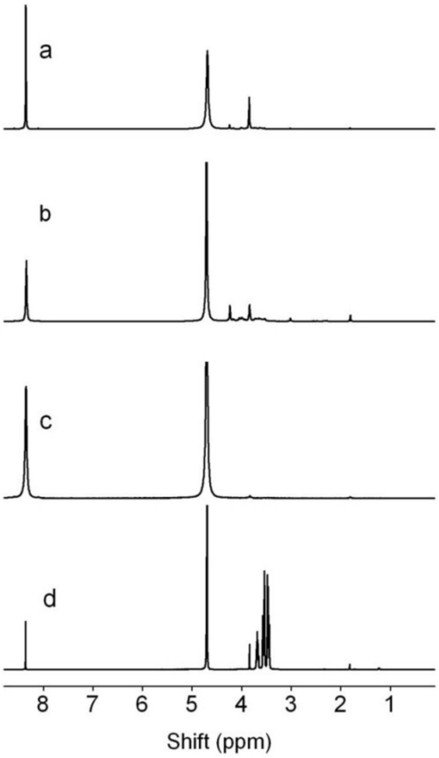

Figure S4. ^{1}H NMR spectra of degradation (traditional UV-Fenton condition) products in the supernatant of Fru (a), Glu (b), GA (c) and Gly (d)

We further checked the stability of various GA forms (Figure S5, as the supporting information for Table 2).

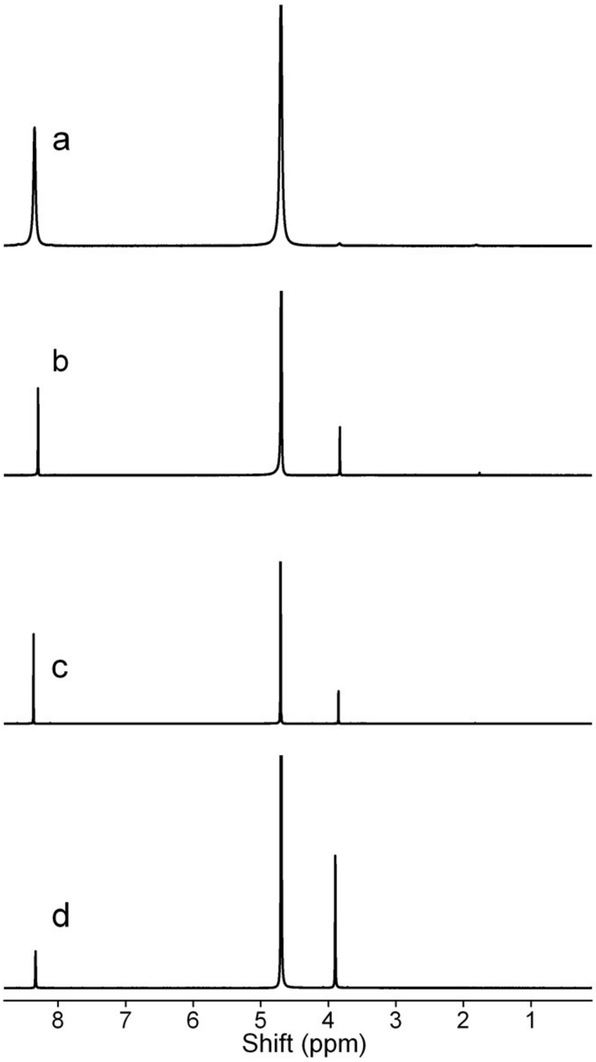

Figure S5 ^{1}H NMR spectra of degradation products in the supernatant of GA (pH=1, a), GA (pH=7, b), GA-Zn (pH=1, c) and GA-Zn (pH=7, d)

Complex of Zn and GA was confirmed by Fourier transform infrared spectroscopy (FTIR). The C=O stretching vibration peak at 1735 cm^{-1} which existed in GA and GA-Na, but disappeared completely after forming GA-Zn complex (Figure S6).

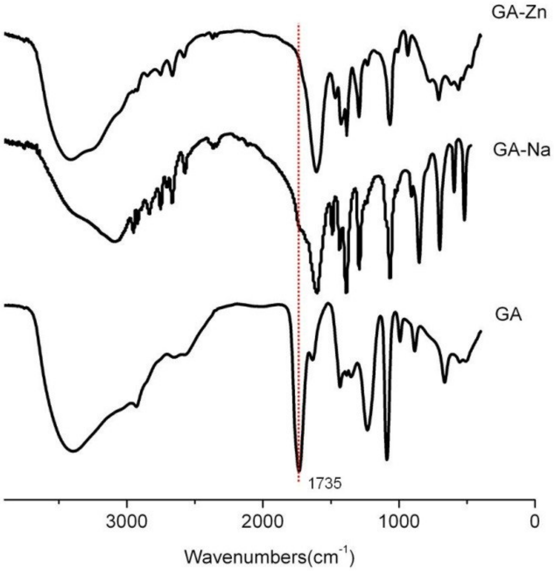

Figure S6. FTIR spectra of GA-Zn, GA-Na and GA