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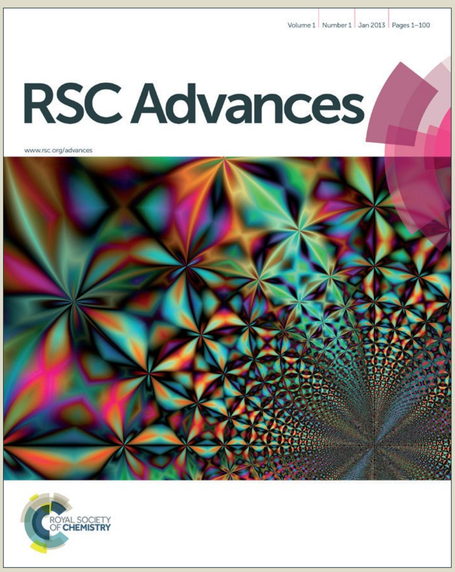

Graphical abstract

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

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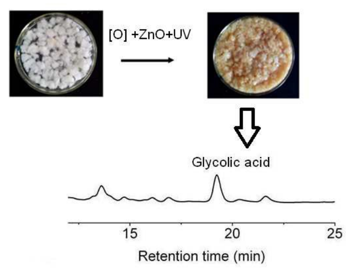

Direct conversion of cellulose into glycolic acid at mild conditions was realized by a zinc-stabilized UV-Fenton reaction.

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

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A novel zinc-stabilized UV-Fenton reaction is created to decompose cellulose at a mild, organic solvent-free condition. Cellulose is successfully decomposed to form valuable C2 chemical, namely glycolic acid. The Zinc ion enhances the yield glycolic acid via complexation. The whole process is simple, rapid and controllable. This method shows a great commercial potential due to its simplicity and mild reaction conditions.

In nature, photosynthesis is a most well-known process used by plants or other organisms to convert carbon dioxide (CO_2) and water (H_2O) into biomass in the sunlight.[1] With the help of chlorophyll, light is effectively absorbed to initiate the conversion. Subsequently, a great deal of non-food competing biomass such as cellulose and lignin are produced. In recent years, thoroughly aware of the inevitable depletion of fossil resources in near future, further exploitation of non-food competing biomass to fabricate chemicals and bio-based polymers attracts great attention of scientific researchers. It becomes one of the most important research directions.[2] Cellulose is the most abundant source of renewable biomass in the world which accounts for approximately 40% of the total photosynthesis products. Conversion of cellulose into chemicals is a vital way of replacing petro-chemicals. Nevertheless, until today, it is still difficult to find an effective way to convert cellulose into valuable chemicals.

Besides photosynthesis, light can also initiate photo-decomposition of natural materials.[3] UV-Fenton reaction is such a typical photo-decomposition process, which is happened in degradation of cellulose by brown-rot fungi in nature.[4] Brown-rot fungi could separate useful sugars from degradation products before the happening of over-oxidation, whereas the traditional Fenton reaction is too strong to control and nearly all of the biomass and organic chemicals are directly decomposed to CO_2 and H_2O. Hence a controlled Fenton reaction is desired if we want to obtain valuable chemicals from degradation based method. Glycolic acid (GA) is a valuable C2 chemical which has been used as metal detergents, dyeing and tanning agents, skin exfoliator and moisturizer, and so on. Although GA existed in some plant leaves and microbes,[5] its mass production still relies on a synthesis route using fossil resources and toxic chemicals. In this communication, a zinc stabilized UV-Fenton reaction is created to obtain GA from cellulose at the first time. Through the stabilization of the small molecular products by zinc ion, the strength of Fenton reaction is controlled. Due to the organic-solvent-free and energy-input-free nature, the controlled UV-Fenton reaction exhibits a great potential in green conversion and green process of non-food competing biomass.

In the experiment, paper cellulose is chosen as the original biomass. It is split into uniform small pieces before reaction. The catalytic system includes H_2O_2, $FeCl_2$, and ZnO. The reaction is carried out under UV radiation (500W, 365nm). The paper cellulose was apparently swollen and then floated on the top of the reaction mixture soon after the UV treatment (Figure S1). The degradation products were quantitative analysed by HPLC method (correlated ^1H NMR spectra were shown in Figure S2). The results exhibited in Table 1 and Fig. 1 (Standard ^1H NMR and HPLC spectra of commercial chemicals are listed in Figure S3,) show that the conversion rate of cellulose degraded by the zinc-stabilized UV-Fenton reaction reaches at 60mg/h with only 27% yield of CO_2. In comparison, the conversion rate of cellulose decomposition remains at 70mg/h in traditional Fenton reaction under UV radiation. But, the yield of CO_2 increases to 54%. Experimental data obviously reflects the confined effect on cellulose photodecomposition by zinc stabilization. As to the small molecular products, the yield of glycolic acid (GA) obtained in zinc-stabilized UV-Fenton reaction is 33% (see Table 1). This value is 8.25 times of the value of GA yield from the traditional Fenton reaction. It shows that the use of Zn^{2+} induces the product GA of Fenton reaction to avoid over oxidation. The too strong characteristic of Fenton reaction (Glu, Fru, Gly and GA are not stable in traditional UV-Fenton reaction, Figure S4) in decomposition of biomass resources is simultaneously changed. The products from zinc-added condition are stabilized at small molecular chemicals rather than completely decomposed into CO_2 and H_2O.

And then, the decomposition reaction happened without UV radiation is also tested. The conversion rate of cellulose decomposition extremely reduces to only 2mg/h with 15% GA yield (see Group 3 in Table 1). Although the confined effect still appears, the reaction speed reduces to very low value. That is to say, the zinc-stabilized Fenton reaction in practical operation no doubt needs to be accelerated by UV radiation. Moreover, the unreacted cellulose residue can be used for further degradation and the result shows very good reproducibility at the same zinc-stabilized UV-Fenton conditions (Table S2).

Table 1 Product yield and conversion rate produced from Fenton reaction before and after Zinc stabilizatione.

Group [a]	Yield (wt%) [b]								CR (mg/h) [d]
	GA	FA	AA	Gly	Glu	Fru	CO_2 [c]	Others	
1	33	14	- [e]	2	14	3	27	7	60
2	4	31	2	4	0.3	0.4	54	4.3	70
3	15	6	- [e]	8	6	4	49	9	2

[a] Group 1 is operated to covert cellulose by zinc-stabilized UV-Fenton reaction, Group 2 utilizes the traditional Fenton reaction for cellulose decomposition, Group 3 also uses zinc-stabilized catalytic system but the reaction runs without UV or light radiation; [b] The yield of products are obtained from HPLC, GA, FA, AA, Gly, Glu Fru respectively represent glycolic acid, formic acid, acetic acid, glycerol, glucose and fructose; [c] The conversion of CO_2 is calculated by the weight difference of total system before and after reaction, [d] the conversion rate (CR) is calculated as follows: $CR=(W_f - W_r)/t$, where W_f is the original weight of the cellulose, W_r is the residual weight of cellulose, and t is the reaction time, [e] less than 0.1%.

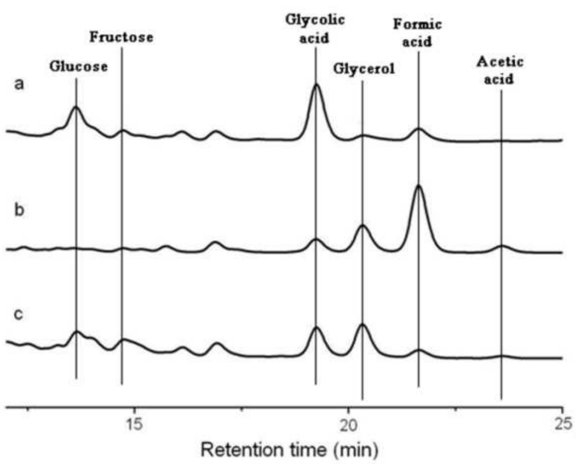


Fig. 1 HPLC spectra of the products from the decomposition of cellulose obtained by zinc-stabilized UV-Fenton reaction (a), traditional Fenton reaction (b) and zinc-stabilized Fenton reaction without UV and light radiation (c).

The product GA is a valuable C2 chemical. In fact, the most important application of GA is the C2 platform for producing bio-based polymers.[6] With the high active bifunctional groups in its molecular structure, GA is not only directly synthesized to polymer with high performance, but it is also very easy to convert to various C2 monomers for the polymerization of polyester, polyurethane, and polyamide (see Fig. 2). In recent years, many literatures begin to emphasize the fabrication of GA by means of fermentation and traditional chemical catalysis.[7,8] However, until today, the complicated routes and serious conditions required in these processes are still not satisfied. From our research work, the novel zinc-stabilized UV-Fenton reaction represents a rapid and simple one-step process to produce GA from cellulose under mild conditions. And the speed of the degradation process is also controllable. The UV light radiation is like a switch to control the beginning and the ending of the conversion. And the yield of valuable small molecular chemicals is obviously improved. Considering all these advantages, this simple and effective process to produce valuable small molecular chemicals from biomass will undoubtedly receive extensive attention and then wildly apply in the future.

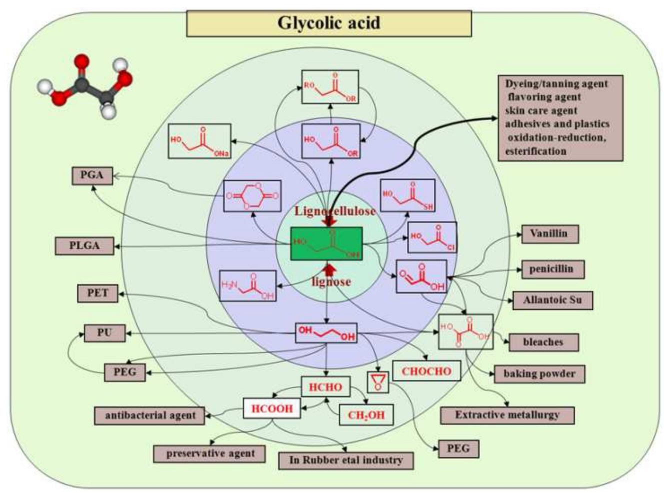


Fig. 2 Various routes to utilize GA in chemical agents and the monomers for the synthesis of bio-based polymers.

To investigate the impact of Zn^{2+} on the stabilization of GA in Fenton reaction, GA and the salt of GA-Zn are respectively reacted in the aqueous solution of H_2O_2 and $FeCl_2$ under UV radiation. As shown in Table 2, it exhibits the products of 94% FA and 2% AA at pH=1. Almost all the GA is consumed. After pH increases to 7, 54% FA produces. 46% GA remains after reaction. When GA-Zn is reacted at pH=1, the yield of FA is reduced to 70%. After increasing the pH value to 7, only 17% FA can be detected in the product. 83% Ga can be detected. This result reflects the obvious difference related to the stabilization of GA by Zn^{2+}. Majority GA keeps unchanged during the strong oxidative environment of UV-Fenton reaction by forming complex with Zn^{2+}. The stability of GA is an essential consideration and that is why whole degradation experiments are designed to be carried out at neutral pH condition.

Table 2 Evaluating the stabilization of GA and GA-Zn in UV-Fenton reaction.

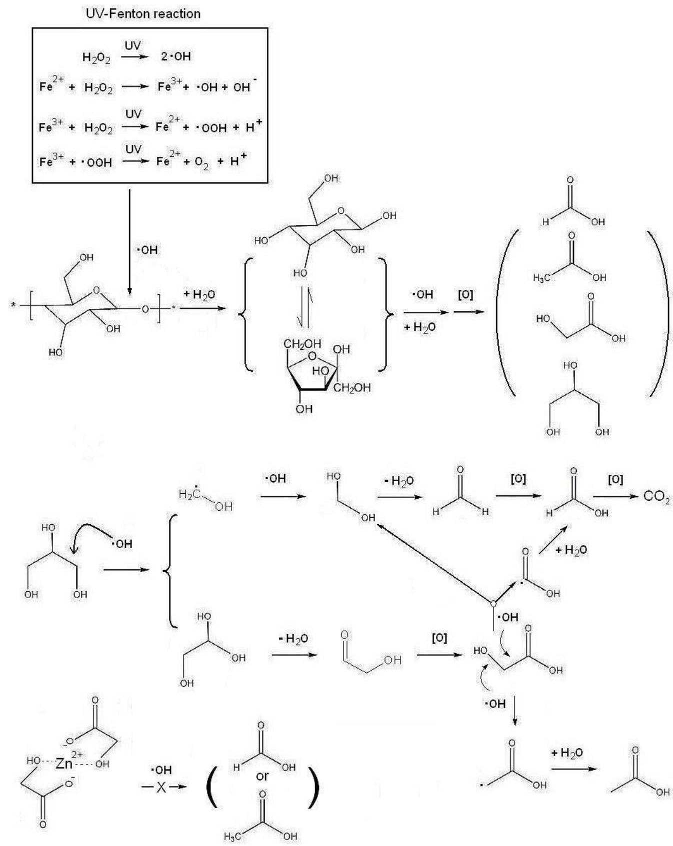
	pH	The ratio of GA, FA and AA after reaction (mol) [a]
GA	1	4:94:2
GA	7	46:54:0
GA-Zn	1	30:70:0
GA-Zn	7	83:17:0

[a] The molar ratio of GA, FA and AA in products is calculated by NMR. (Figure S5)

This particular stabilization can be attributed to the complexation between GA and Zn^{2+}. As we know, GA, as one of organic acids, usually uses as the complex agent of transition-metal ion (particular nickel ion) in the solution of electrolysis plating.[9] The disappearance of C=O stretching vibration peak by Fourier transform infrared spectroscopy (FTIR) method also indicates formation of GA-Zn complex (Figure S6). By complexation, the stabilization of plating solution is extremely improved. And this effect can be also enhanced by increasing the pH up to 6-7. Understanding the effect of complexation on stabilization, the methodology is utilized to control the strength of UV-Fenton reaction of cellulose for the first time. As a result, the controlled UV-Fenton reaction is finally established.

Based on the products obtained from cellulose degradation, we propose a pathway for cellulose degradation depicted in scheme 1: a series of consecutive reactions happen in the cellulose degradation process including the hydrolysis of cellulose to soluble monosaccharide, fragmentation and oxidation of saccharides to organic acids. During fragmentation, hydroxyl radicals could attack both glycosidic bond and C-C single bond.[10,11] The formation of GA-Zn complex prevents the over-oxidation of GA. Since Gly has been produced from cellulose and existed as a stable intermediate, literatures for Gly oxidation can be used to explain part of the mechanism. Prasanna et al. found that Gly can be converted to GA and FA by an alkaline hydrogen peroxide degradation based method.[12] They increased the yield of FA by using a Pd-complex catalyst. By using a ^{13}C labeling based method, they further proved that the FA can be produced from both the secondary and primary carbons of Gly while the carbonyl carbon of GA originates only from the secondary carbon of Gly. They proposed 2-carbon hydroxyl aldehyde and formaldehyde as intermediates as well, though aldehyde compounds are not stable enough to be detected in their reaction mixture. In another report, cellobiose was degraded by electrodes generated hydroxyl radicals to produce FA.[11b] Although it was proposed as the intermediate of FA, formaldehyde still cannot be detected even in such a mild oxidative environment. Thus, precise experimental apparatuses to detect those short life-time intermediates are demanded for further mechanism investigation.

Although the hypothesis needs further research effort to reach perfect, two steps supported by two outstanding phenomena make the proposed pathway very unique. Firstly, the production of reductive product Gly from cellulose in an oxidative reaction environment has not been reported by other methods, though other polyols such as ethylene glycol has been obtained from cellulose in a reductive reaction environment.[13] Secondly, the production of AA from GA (Table 2 & Figure S5) challenges traditional hydroxyl radicals reaction mechanism which believes hydrogen atom abstraction is the way that hydroxyl radicals react on organic compounds.[14,15]



Scheme 1. Hypothetical pathway for cellulose degradation by controlled UV-Fenton reaction.

In summary, we have developed a novel process of zinc-stabilized UV-Fenton reaction to simulate a controlled degradation of cellulose. Cellulose is decomposed to form valuable C2 chemical, namely GA. With the forming of GA-zinc complex, the strength of the UV-Fenton reaction of cellulose is successfully reduced. The yield of the GA is improved with 8.25 times. The process of the controlled UV-Fenton reaction is simple, rapid and happened in very mild conditions. It is expected to be extensively applied and upgrade the importance of UV irradiation based method in biomass conversion.

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Notes and references

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