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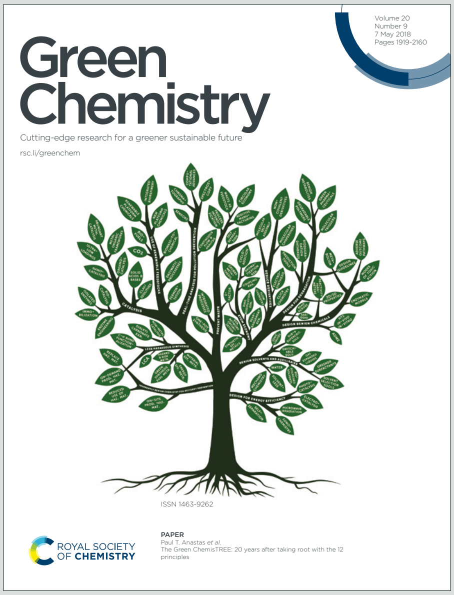

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ARTICLE

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

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Herein, a facile and efficient method was developed to selectively transform glucose into formic acid at room temperature. After parameter optimization, formic acid was obtained at an unprecedented 91.3% yield with a reaction time of 8 h in lithium hydroxide aqueous solution with hydrogen peroxide as the oxidant. The synergistic effects of the base and the oxidant promoted the glucose conversion at room temperature and enhanced the selectivity towards FA. Besides, the employed mild conditions have suppressed FA decomposition that often occurred under harsh conditions, which further improved the FA selectivity. A series of model compound tests were conducted to probe possible intermediates based on which a plausible reaction pathway was proposed. In addition, the process is applicable to various carbohydrates such as cellobiose, starch, xylan, etc. This work opens up a simple, mild but effective way to produce FA from renewable biomass resources, which would remarkably alleviate the energy consumption, capital costs, handling risks, etc.

Introduction

The inevitable depletion of fossil oils with drastically elevated carbon dioxide (CO_2) level in the atmosphere have become a vital, global problem and gained constantly growing attentions. In the past decades, enormous efforts were made to seek for alternative renewable resources to supply the society with energy and chemicals.[1-8] Biomass represents the largest carbon resource on Earth, and is also an inherently suitable feedstock for chemical production due to the rich functional groups in its structure. Among various biomass resources, cellulosic biomass is abundant, widely available and low cost whose valorization is the most prevalently studied and reported. Hitherto, a diversity of chemicals has been obtained from glucose and cellulose *via* various transformation strategies.[9-18] Formic acid (FA), with a systematic name methanoic acid is a broadly-used versatile chemical. It has a variety of applications in agricultural, pharmaceutical, rubbery, leather, textile, food industries, etc., because it is relatively noncorrosive, nontoxic and readily biodegradable. Besides, it is also utilized as a building block in organic synthesis, a reducing agent and/or solvent in diverse chemical reactions. Moreover, FA is an efficient and eco-friendly energy carrier for hydrogen storage (with a high volumetric capacity of 53.4 g/L) and thus a value-added medium in hydrogen energy utilization.[19] The global market of FA in 2019 is estimated to be around US$ 619 million and predicted to keep a steady increase in the forthcoming years.

At present, the commercial production of FA is primarily based on non-renewable fossil feedstock *via* a two-step route: the carbonylation of methanol with carbon monoxide (CO) under ~40 bar pressure and the subsequent hydrolysis of the methyl formate into FA. In the past decades, persistent efforts have been made to explore alternative renewable resources such as biomass for FA production.[20] So far, there were three general chemical strategies to obtain FA from cellulosic biomass including hydrolysis, wet oxidation and catalytic oxidation. The hydrolysis method normally employs an acid catalyst to transform glucose or cellulose with simultaneous production of levulinic acid and FA at around 413-473 K, in which FA is usually a by-product with relatively low yield.[21-25] In wet oxidation, an oxidant is often utilized in basic solution to promote the decomposition of glucose into FA at elevated temperature.[26-28] For example, glucose was transformed in the presence of hydrogen peroxide (H_2O_2) in sodium hydroxide (NaOH) aqueous solution at 523 K under about 75 bar pressure, producing FA with about 75% yield.[27] For catalytic oxidation, both a catalyst (such as heteropoly acids, metal oxides, etc.) and an oxidant are employed.[29-31] In a previous work, with $NaVO_3$ and H_2SO_4 as the catalysts, about 68.2% yield of FA was obtained from glucose at 433 K under 30 bar oxygen (O_2) gas.[32] Besides, about 85% FA

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yield (the current benchmark) was achieved from glucose under 363 K and 20 bar O_2 gas using the homogeneous Keggin-type polyoxometalate catalyst ($H_8PV_5Mo_7O_{40}$).[33] However, a biphasic solvent system was required and the reaction time was relatively long of around two days.

Overall, the previous reports of FA production from glucose were carried out under high pressure and high temperature (363-573 K, 20-75 bar), in which considerable energy inputs and expensive equipment were needed. Besides, high-pressure handling has increased the safety risks especially for large-scale manufacture. Very recently, room-temperature conversion of glucose into lactic acid (LA) with high yields was disclosed,[34] which exemplifies the distinctive merits of biomass utilization *via* a mild process to overcome the aforementioned problems. Inspired by the work, we tested for the first time the potential to obtain FA from glucose at room temperature and ambient condition, by a simple and low-cost method using a common oxidant and base. In the paper, the reaction system was established by oxidant screening, base selection and parameter optimization. Under optimized conditions, near-quantitative glucose conversion was realized within a relatively short period of 8 h, and the highest FA yield was obtained at 91.3% (with the selectivity > 90%) which to the best of our knowledge is a new record for FA formation from biomass resources. The lithium hydroxide (LiOH) has played a major role in promoting glucose conversion at room temperature, while the H_2O_2 as well as the mild conditions were crucial for the high FA selectivity. Control experiments and model compound tests were conducted to investigate the oxidation mechanism and the reaction pathway. Lastly, the developed process was applied to diverse biomass feedstock including different monosaccharaides, disaccharides and polysaccharides.

Results and discussion

Oxidant screening

Initially, various common oxidants were examined to transform glucose at room temperature in basic aqueous solutions (see Fig. 1a). Encouragingly, most of the oxidants led to the formation of FA under such mild conditions. Note that the product existed in the form of formate instead of formic acid, herein FA was used as an abbreviation for the product (similar cases for other organic acid products). The glucose conversions were high for all the oxidants (65%~85%), whereas the FA yields were quite different depending on the oxidative species. Among them, H_2O_2 was the most effective one to promote FA generation with 29.5% yield, followed by the organic peroxide *tert*-butyl hydroperoxide (TBHP) producing FA with slightly lower 23.6% yield which is reasonable since TBHP is more sterically hindered compared to H_2O_2. The commercial oxidant Oxone also led to a satisfactory FA yield of 19.1%, whereas the potassium peroxydisulfate ($K_2S_2O_8$) and lithium perchlorate ($LiClO_4$) resulted in low FA yields of 7.2% and 0.8% (The yields of by-products were provided in Table S1). According to the data, the abilities of various oxidizing agents to generate FA were in the order: H_2O_2 > TBHP > Oxone > $K_2S_2O_8$ > $LiClO_4$. The H_2O_2 was frequently used in biomass pretreatments and transformations and its excellent oxidation ability has been previously described.[35-37] Among the oxidants, the ClO_4^- species has the lowest standard electrode potential, but herein the ability to produce FA from glucose was not correspondingly related to the standard potentials of these oxidants (see Table S2 for the respective standard potentials) otherwise the $S_2O_8^-$ would outperform the rest. Hence, the effectiveness of H_2O_2 was not merely associated with its oxidative capacity. In addition, the combined uses of H_2O_2 with other metal oxides were attempted (e.g. H_2O_2 + V_2O_5, etc.) in an effort to enhance the oxidation efficiency, but no improvement was observed and using H_2O_2 alone resulted in the best performance (see Fig. S3).

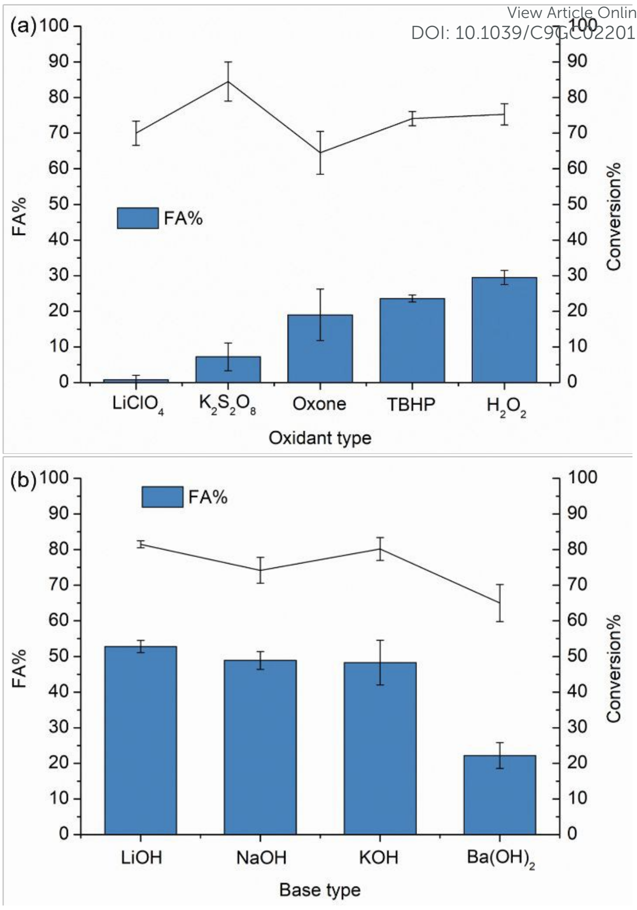

Fig. 1 (a) The conversion rates and FA yields using different oxidants. Reaction conditions: 0.1 M glucose, 0.6 M LiOH, 30% oxidant, 10 mL water, 308 K, 8 h; (b) the conversion rates and FA yields using different bases. Reaction conditions: 0.1 M glucose, 0.6 M OH^- concentration, 100% H_2O_2, 10 mL water, 308 K, 8h.

Base screening

The type of the base could also be an influential factor for FA production from glucose. Several typical bases including LiOH, NaOH, potassium hydroxide (KOH) and barium hydroxide ($Ba(OH)_2$) were studied at room temperature to convert glucose in the presence of 100% H_2O_2 (see Fig. 1b). Note that $Ba(OH)_2$ was not stable in the reaction system because it reacted with the oxidant H_2O_2 to form white precipitates barium peroxide

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(BaO_2), leading to relatively low FA yield of about 22.2%. The other bases did not cause any precipitations, and the FA yields were 61.0%, 58.2% and 57.0% respectively by using LiOH, NaOH and KOH. Thus, the three alkaline bases produced FA in almost comparable yields (slightly higher FA yield when using LiOH), which infers that the different types of cations in these bases have negligible influences on FA generation. Namely, unlike the oxidants, the effects of base type were insignificant in the reaction. The results did not quite coincide with previous works where NaOH was regarded as the best type of base for glucose conversion into FA.[27] The inconsistency might signify the different behaviors of bases interacting with glucose at room temperature compared to those under harsh conditions. It was likely that the anion OH^- of the base mainly involved in glucose transformation at room temperature while the cations (Na^+, K^+, etc.) came into play when temperature and pressure elevated.

Parameter optimizations

After screening, H_2O_2 was selected as the oxidant and LiOH as the base in the following experiments. The impact of H_2O_2 concentration on FA formation was scrutinized by varying the H_2O_2 concentration in a wide range from 30% to 250%. As shown in Fig. 2a, the H_2O_2 concentration exerted prominent influence on the reaction. First, a gradual and almost linear growth in glucose conversion rates was noticed (from 75.3% to 99.7%) with increased H_2O_2 concentration. Meanwhile, the FA yield was considerably enhanced from 29.5% to a nearly three-fold value of 88.8%, along with the decrease of yields for side products such as fructose, glycolic acid (GA), etc. The drastically improved FA yield was not just because of the increased conversion efficiency, but more importantly due to the raised selectivity towards FA. In Fig. 2a, the FA selectivity at each point was plotted as a gray line, which shows an obvious upward climb with increased H_2O_2 concentration. With 30% H_2O_2, the FA selectivity was around 39.2%, which rose to as high as 83.0% and ~90% when H_2O_2 concentration was 200% and 250% respectively. Hence, the increase in H_2O_2 concentration has significantly boosted the FA selectivity for the reaction and was predominantly responsible for markedly improved FA yield. This specific function of H_2O_2 on changing product selectivity in glucose transformation has not been unravelled previously. Besides, another interesting finding is that the increased H_2O_2 concentration altered the species of the products. At low H_2O_2 concentration of 30%, fructose, GA and LA were detected as by-products with yields of 21.5%, 7.4% and 4.6%. Nevertheless, further increase in H_2O_2 concentration led to the disappearance of LA product.

Next, the base concentration was varied from 0.2 M to 1.0 M. As shown in Fig. 2b, a sharp rise in glucose conversion was noted from 47.8% to 81.5% when LiOH concentration increased from 0.2 M to 0.4 M, and then a slower improving rate with further increase in LiOH concentration reaching ~92% at 1.0 M. Similar trends were observed for the FA yield which grew accordingly with the glucose conversion rate. Distinct from the influence of H_2O_2 concentration, the base concentration showed negligible impact on FA selectivity which remained nearly unchanged in the experiments. Thus, more concentrated base solution principally stimulated the glucose conversion leading to concurrent, non-selective increases of the products (including FA, fructose and GA). A contrast experiment was undertaken (see Fig. S2) in which only the oxidant was supplied without the use of any base, the glucose was barely converted and no FA was formed. The result supports that the essential function of the base is to activate glucose and advance its transformation. The optimal LiOH concentration was selected at 0.6 M because satisfactory conversion was readily achieved and the base usage was relatively small.

In addition, different glucose concentrations were examined in the reaction system (see Table S3). Starting from a dilute glucose solution of 0.05 M, a slightly higher FA yield was realized at 91.3% in the presence of sufficient H_2O_2. Besides, using 0.2 M glucose solution, a remarkable FA yield of 80.6% was still obtained which demonstrates the potential of the reaction system to process more concentrated feedstock solutions. Despite the mild conditions, the FA yield is superior to those reported in previous literatures. Apart from the notably enhanced FA selectivity by concentrated H_2O_2, the mild conditions are also beneficial for high FA yielding. FA conversion

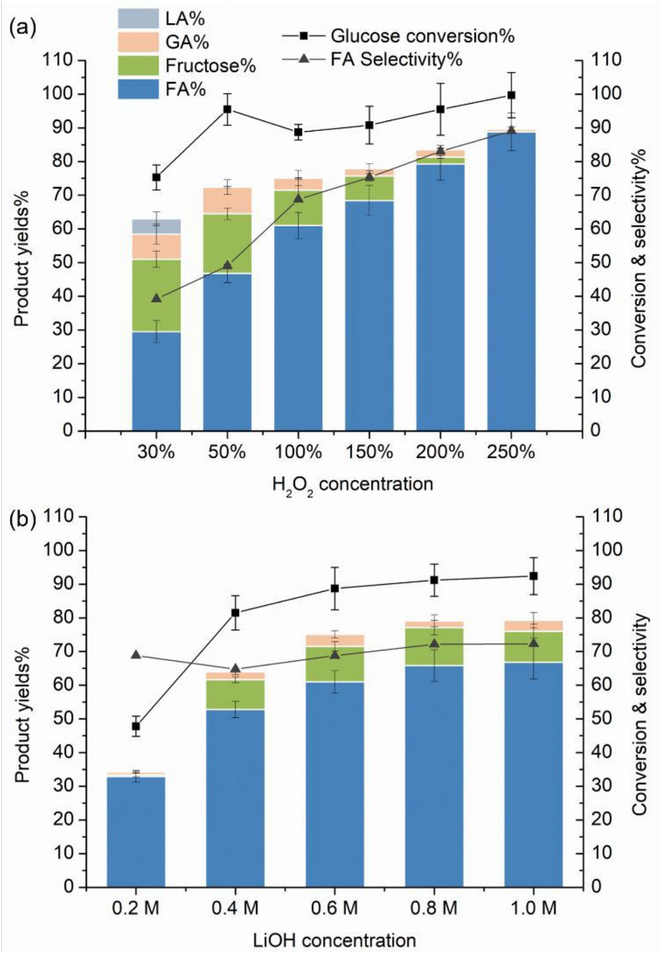

Fig. 2 (a) The influence of H_2O_2 concentration and (b) LiOH concentration on glucose transformation and product selectivity. The corresponding variations are made based on the original conditions: 0.1 M glucose, 0.6 M LiOH, 100% H_2O_2, 10 mL water, 308 K, 8 h.

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into CO_2 was often observed in previous literatures,[29, 33, 38] and the side reaction normally caused decreased FA selectivity. In our reaction system, this problem was obviated since FA was quite stable under such mild conditions as indicated by the control experiment (see Fig. S2). Less than 1% of FA was decomposed under employed conditions in a reaction period of 8 h, showing that the side reaction was significantly hindered. Therefore, both the mild conditions and the use of sufficient H_2O_2 were assigned as the main reasons for the high FA selectivity. Moreover, engaging mild conditions is beneficial which allows the reaction to be undertaken in a common, low-cost container with minimal energy inputs and considerably reduced handling risks.

Product evolution with reaction time

The glucose conversion and product profile were monitored with reaction time ranging from 0.5 h to 10 h both in the absence or presence of the oxidant (see Fig. 3). Without H_2O_2, glucose was gradually consumed in LiOH solution (see Fig. 3a). ~10% of the glucose was converted at 0.5 h, which steadily rose to 57.8% at 4 h and then 80.3% at 10 h. At the initial stage (within 4 h), fructose was accumulated as the dominant product whereas it decreased slowly after 4 h. At the same time, a continuous increase of LA yield occurred during the whole reaction time and LA became the major product in the latter stage. After the reaction time of 10 h, LA was obtained in a relatively high yield of 46.7%. Notably, no GA was detected in the entire period, meanwhile, trace amounts of FA and acetic acid (AA) were determined (~1% yield). The results corroborate with our previous assumption that the base was crucial for glucose conversion (glucose was readily transformed without the oxidant), while provide further information that the base was not able to promote FA generation. In fact, the product distribution was similar with those of previous papers when glucose was transformed in basic solutions.[34, 39-41] Under the influence of the base, glucose was dominantly isomerized into fructose and then cleaved into LA *via* retro-aldol condensation. When H_2O_2 (100% amount) was introduced into the system, distinct product profile was displayed (see Fig. 3b): FA was identified as the paramount product during the whole period with fructose and GA generated as the side products, whereas no LA was detected. Besides, the glucose conversion was averagely increased, which was 25.6%, 81.9% and 90.9% respectively at the reaction time of 0.5 h, 4 h and 10 h, showing that the oxidant has further promoted glucose conversion. Herein, the distinct product profiles further confirmed that the presence of H_2O_2 has preferentially favored the FA formation and inhibited parallel reactions such as glucose isomerization. Furthermore, the drastic change in product species suggests that the H_2O_2 may fundamentally affect the cleavage patterns of glucose and shift the reaction pathway.

Reaction pathways and proposed mechanism

To understand the reaction pathway, a series of model compound tests were conducted using possible intermediates as the substrates under employed conditions (100% H_2O_2, 0.6 M LiOH). As shown in Table 1, first, the organic acids were insignificantly converted and produced low FA yields. Gluconic acid was seldom converted generating FA with ~3% yield, and this suggests that glucose oxidation into its corresponding acid is not involved in the reaction pathway to produce FA. When LA was engaged as the substrate, 28.4% LA was converted and AA was formed in 11.4% yield with no FA product detected. This explains the presence of AA as a minor product in Fig. 3a, furthermore, the result has ruled out the possibility of LA as an intermediate for FA formation. Meanwhile, the substrates AA and oxalic acid were not transformed with no products detected. GA was converted with a rate of 24.6% and FA production with 10.0% yield, which infers that the -OH group was more reactive than the -COOH group that is almost inactive. Other alcohol species such as sorbitol and methanol were examined, and FA was obtained in 15.9% and 7.5% yield which substantiates the assumption. Nonetheless, the organic acids and alcohol species resulted in rather low FA yields, and thus they were unlikely the key intermediates for FA production.

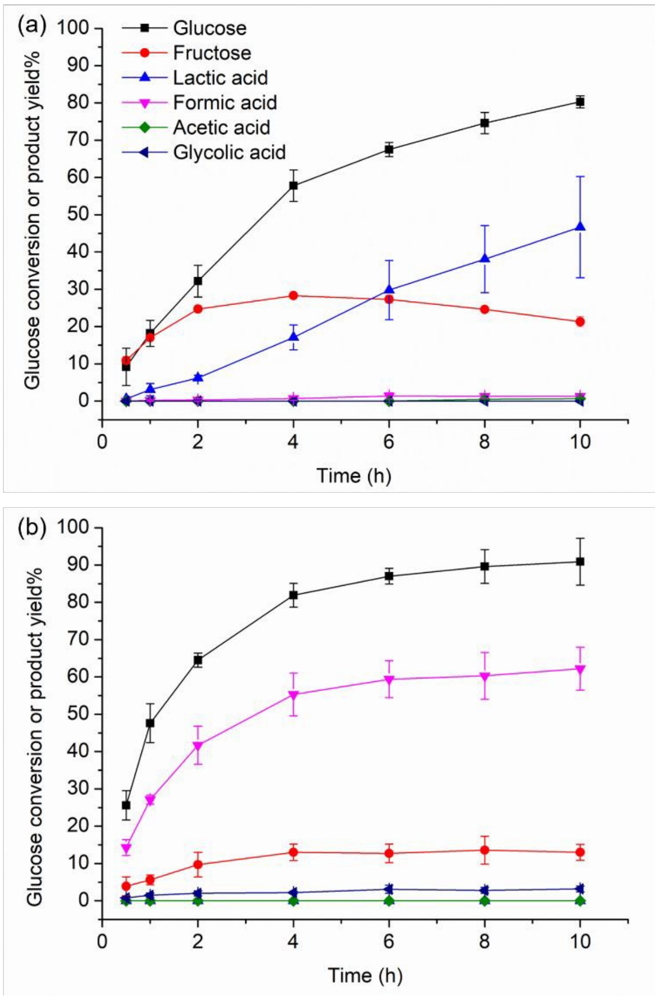

Fig. 3 The product distributions evolved with reaction time (a) in the absence of H_2O_2 and (b) in the presence of 100% H_2O_2. Reaction conditions: 0.1 M glucose, 0.6 M LiOH, 10 mL water, 308 K.

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Table 1 The reaction of model compounds to produce FA under room temperature [a]

Entry	Substrate	Conversion%	Product yields%			
			FA%	LA%	AA%	GA%
1	Gluconic acid	3.5	3.3	0	0	0
2	Lactic acid	28.4	0	71.6	11.4	0
3	Glycolic acid	24.6	10.0	0	0	75.4
4	Oxalic acid	0	0	0	0	0
5	Acetic acid	0	0	0	100	0
6	Sorbitol	16.0	15.9	0	0	0.2
7	Methanol	26.2	7.5	0	0	0
8	Formaldehyde	100	95.4	0	0	0
9	Glycolaldehyde (dimer)	100	95.0	0	0	1.2
10	Glyceraldehyde	100	57.7	12.9	0	17.5
11	Pyruvaldehyde	100	11.5	54.8	26.6	0
12	1,3-dihydroxyacetone	100	30.6	14.9	2.9	37.7
13	Erythrose	55.9	33.5	0	0.8	0
14	Fructose	91.6	58.3	0	0	21.0
15	Xylose	99.1	89.1	0	0	2.2

[a] Reaction conditions: 0.1 M substrate, 0.6 M LiOH, 100% H_2O_2, 10 mL water, 308 K, 8 h.

Compared to organic acids and alcohols, aldehyde/ketone species generally displayed superior activity. For example, the formaldehyde and glycolaldehyde dimer (the C_1 and C_2 aldehydes) were quantitatively converted affording FA with appreciable yields of 95.4% and 95.0%. Hence, these two aldehydes were very active species to form FA. Although the formaldehyde would be structurally easier to produce FA than the glycolaldehyde, comparable performances were obtained under employed reaction conditions. Meanwhile, some C_3 species (including glyceraldehyde, 1,3-dihydroxyacetone and pyruvaldehyde) were completely converted. However, the FA yields were obviously lower than the C_1 and C_2 aldehydes, which were 57.7%, 30.6% and 11.5% respectively. The reason might be that these species were more prone to be transformed into other products. Increased yields of GA and LA were determined when using glyceraldehyde and 1,3-dihydroxyacetone as the substrates, especially, the pyruvaldehyde afforded LA and AA as the major products with high yields of 54.8% and 26.6%. Indeed, the pyruvaldehyde was a well-recognized intermediate to generate LA instead of FA.[34] As a result, these C_3 species were probably not the key intermediates for FA formation. Besides, the C_4 aldehyde erythrose was converted with 55.9% rate and a FA yield of 33.5%. The relatively poor performance of erythrose as the substrate for FA production was previously reported in a catalytic oxidation work,[31] whereas the reason for it remained unclarified. Herein, the low conversion efficiency has caused the inferior FA yield.

Furthermore, xylose and fructose were tested (the C_5 and C_6 sugars). The performance of fructose was similar to that of glucose producing FA in 58.3% yield, which implies that glucose isomerization is not a necessary step for FA generation. Besides, no LA product was detected from fructose indicating that the degradation of fructose did not follow the retro-aldol condensation pathway in the presence of H_2O_2. Particularly, the long-carbon-chain substrate xylose has led to an extraordinary FA yield of 89.1%, which was considerably higher than those from the shorter-chain aldehydes (the C_2, C_3 and C_4 aldehydes) and comparable with those from the C_1 and C_2 aldehydes. Although the reason behind the phenomenon is still unclear, it is tentatively assumed that the xylose was highly active to be cleaved at multiple sites into one formaldehyde molecule and two glycolaldehyde molecules thus leading to the high FA yield.

Xylose displayed unexpectedly high activity to produce FA which indicates that the pentose is probably a crucial intermediate for FA generation. The conversion and product profiles of xylose conversion with different reaction times were examined (see Fig. S4). Much faster reaction kinetics than glucose can be observed that ca. 67% of xylose was readily transformed within a short period of 10 min. At 15 min, the conversion rate exceeded 80%. FA was the dominant product with trace amounts of GA detected. The data suggested that xylose may exist in very low concentration as the intermediate during the reaction because of its remarkably high reactivity and thus not detected on HPLC. In an effort to probe it, *in-situ* water-phase acetylation was undertaken for the solution after glucose was converted under employed conditions with a reaction time of 0.5 h. The acetylated sample was analysed on GC-MS. In the GC-MS spectrum (see Fig. S5), there were mainly

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solvent and derivation reagent peaks before the retention time of 10 min (not shown). At the retention time of about 17~19 min, the peaks were assigned to the acetylated pentoses, while the two large peaks at about 26 min and 28 min were assigned to the acetylated hexoses. The presence of multiple peaks was originated from the acetylation process. Based on the combined model compound tests, reaction profiles and GC-MS analysis, it is deduced that the pentose such as xylose is a key intermediate for glucose conversion into FA.

Based on the information provided by the model compound tests, the reaction pathways for glucose conversion into FA in basic aqueous solution at room temperature were tentatively proposed (see Fig. 4). First, the aldehyde species in the reaction are more probable to be the intermediates than the organic acids and alcohols. Besides, the initial cleavage of glucose at different positions would strongly affect the FA yield. For instance, the α-scission at the C1-C2 position is supposed to be the most advantageous pathway to produce FA, by which the active C_1 and C_5 aldehydes would be generated as the intermediates (Route 1). The α-scission is more likely to occur at the aldehyde end of glucose instead of at the C5-C6 position, because the -CHO group boasts superior activity than the -OH group in our reaction system. The deduction coincides with previous reports that α-scission was regarded as the main pathway for FA production from glucose.[27] On the other hand, although the erythrose was not a very active intermediate to afford FA, the cleavage at the C2-C3 position (β-scission) of glucose could still lead to satisfactory FA yield due to the formation of the highly active glycolaldehyde intermediate (Route 2).

Conversely, the rupture at the middle (C3-C4 position) is not a favorable pathway which would result in low FA yield and more side products such as LA, GA, etc. (Route 3). As aforementioned, LA was not observed any more in the presence of 50% H_2O_2 (see Fig. 2a), inferring that the concentrated H_2O_2 has possibly impeded the reaction pathway of C3-C4 cleavage. Probably, the increase in H_2O_2 concentration has constantly shifted the reaction pathway. For example, at 100% and 200% H_2O_2 concentration, the FA yield was ~61% and ~80% respectively. The increase is likely to be realized by altering the cleavage pattern from a main β-scission pathway towards the α-scission pathway. Hence, in the presence of concentrated H_2O_2, the main reaction pathway is proposed as follows: the glucose is first transformed into its open-chain form, and then the α-scission takes place to generate formaldehyde and xylose. The formaldehyde intermediate is immediately oxidized into FA upon its formation due to the high activity, and the xylose is likely to undertake rapid decomposition into formaldehyde and glycolaldehyde which are selectively oxidized into FA product. In addition, glucose isomerization into fructose was a side reaction observed in the basic solution, and fructose may be further converted into FA which is one of the possible reaction pathways as well (as shown in Route 4). In Route 4, the formed fructose is likely to undertake similar cleavage patterns as glucose (at C1-C2, C2-C3 and C3-C4 positions) to produce smaller aldehydes such as formaldehyde which was further oxidized into formic acid.

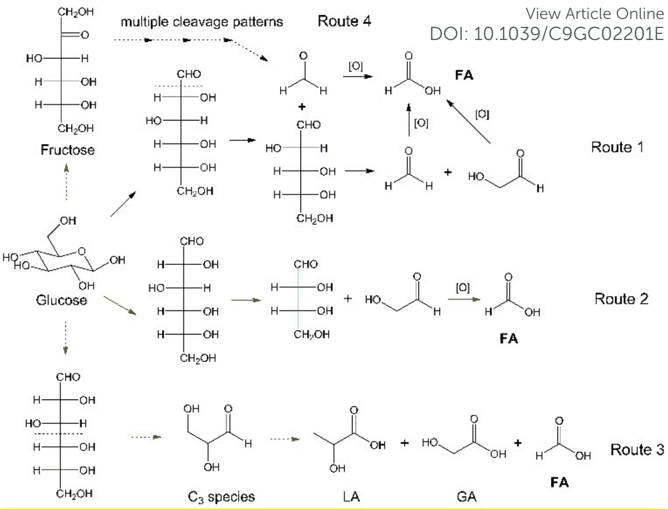

Fig. 4 The proposed reaction pathways. The primary cleavage of glucose at C1-C2, C2-C3 and C3-C4 position was depicted by black solid arrows (Route 1), gray solid arrows (Route 2) and gray dashed arrows (Route 3). The conversion *via* fructose was also proposed as a side pathway (Route 4).

For the oxidative cleavage of glucose at room temperature, one key question remained is about the oxidation mechanism. During the reaction, partial decomposition of the H_2O_2 occurred in which O_2 gas was released. Meanwhile, it also generated free radicals that are strong oxidizing species such as the hydroxyl radical (•OH) and the superoxide ion (O_2^{-}•). Hence, it is important to figure out which of them is the main active component. A control experiment was undertaken replacing H_2O_2 with pressurized O_2 gas. Under 5 bar O_2 gas, 80.1% of glucose was transformed but the FA yield was merely 12.9% (much lower than the ~60% yield when 100% H_2O_2 was added). This shows that the oxidation mainly follows a free radical mechanism while O_2 gas-assisted oxidation was minor. Previously, it was reported that the presence of base could accelerate the generation of O_2^{-}• and •OH radicals from H_2O_2,[42] which are strong oxidative species and probably the crucial active components promoting FA formation in our system. In this way, the oxidative capacity of H_2O_2 were reinforced in basic solutions at room temperature. As a result, the base and the oxidant are both indispensable for room temperature transformation of glucose into FA, and the synergy between them resulted in the high efficiency and selectivity of the reaction system.

The scope of the biomass feedstock

Apart from the monosaccharides (xylose and fructose), various disaccharides and polysaccharides were used as the feedstock for FA production to test the scope of the reaction process (see Table 2). Except sucrose which generated FA with a very low yield of 4.8% (Entry 1), the other disaccharides cellobiose, maltose, and lactose (Entry 2-4) produced FA with considerably high yields of 73.7%, 68.1% and 75.6% (small amounts of GA, glucose/fructose as minor products). These data suggest that the reaction system is applicable to most of the disaccharides and able to break down the glycosidic linkage to produce FA.

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Cellobiose and maltose are linked by two glucose molecules *via* different patterns of β(1→4) or α(1→4) but they produced comparable amounts of FA, which shows that the two linkage patterns did not exert distinct influences on FA formation. In lactose, one glucose molecule is substituted by one galactose molecule, but no apparent change was found in FA production. This indicates that the epimer of glucose as the constitute did not affect the formation pathway of FA neither. For sucrose, it consists of one glucose unit and one fructose unit connected *via* (1→2) bond between C1 on the glucosyl unit and C2 on the fructosyl unit. Probably, this type of linkage hampered the reaction pathway to produce FA and therefore led to the very low FA yield. In sucrose transformation, glucose and fructose were detected in 36.3% and 10.9% yields, which suggests that the hydrolysis of the sucrose occurred very partially. However, the further degradation of them into FA was somehow inhibited.

In addition, polysaccharides including starch, xylan, inulin and pretreated cellulose (Entry 5-8) were attempted under similar conditions. The starch and inulin generated FA with yields of 14.5% and 5.4%, and the insignificant yields were possibly due to the lack of hydrolysis ability to cleave the glycosidic bonds when the feedstock possesses high molecular weights. Nonetheless, 73.1% FA yield was achieved when using the polysaccharide xylan (the major constituting unit is xylose). The result is in agreement with the previous experiment (Table 1, Entry 10) and verified the special effectiveness of the reaction system for C_5 sugar-based biomass. When transforming cellulose, a previous pretreatment method was used by grinding cellulose and LiOH in a ball mill to destruct its robustness and enhance its solubility to some extent (no separation was necessary after the pretreatment).[43] Less concentrated cellulose solution and elevated temperature (323 K) were employed for better dissolution. The conversion of cellulose under such mild conditions were still challenging with ~3% yield of FA obtained. Nevertheless, it manifests the potential of cellulose conversion into FA under mild conditions. Future improvements could be made, for example, by integrating a hydrolysis catalyst and/or implementing a more suitable pretreatment protocol.

Table 2 The scope of the biomass feedstock for FA production [a]

Entry	Feedstock	Glucose%	Fructose%	FA%	GA%
1	Sucrose	36.3	10.9	4.8	0.7
2	Cellobiose	2.2	0	73.7	0.9
3	Lactose	0	1.1	75.6	0.8
4	Maltose	4.7	0	68.1	1.2
5	Starch	0.6	0	14.5	0.9
6	Inulin	0.5	5	5.4	0.9
7	Xylan	0	0	73.1	1.2
8	Cellulose[b]	0	0	2.5%	0

[a] Reaction conditions: 0.1 M feedstock (monomer-based), 0.6 M LiOH, 200% H_2O_2, 10 mL water, 308 K, 8 h.

[b] The concentration of pretreated cellulose was 0.03 M, the reaction temperature was 323 K and LiOH was increased to 1.0 M.

Conclusions

In this work, a simple and efficient method was explored to convert glucose into FA in dilute basic solutions with H_2O_2 as the oxidant under extremely mild conditions. The synergy between the base and oxidant has led to reinforced oxidative capacity of the reaction system, whereas the base mainly prompts glucose conversion and the oxidant enhances FA selectivity. Moreover, the mild conditions obviate the problem of FA decomposition and further contributes to the improved FA selectivity. These multiple factors have resulted in highly efficient and selective FA production, with the highest yield obtained at 91.3%. The control experiments and model compound tests have shed light on the reaction pathway and mechanism. The C1-C2 cleavage was identified as the most advantageous to produce FA followed by the C2-C3 cleavage, nonetheless the cleavage at C3-C4 position was the least effective pathway. Besides, the cleavage mainly follows a free radical mechanism rather than the O_2 gas-promoted mechanism.

The developed process furnishes a desirable solution to reduce the capital costs, the energy consumption and associated environmental impacts if conducted under harsh conditions, making it attractive for scaling up and potential practical applications. Note that LiOH is used in the paper as a demonstration, whereas inexpensive NaOH will be preferable for economic concerns. Besides, since the products were in the form of organic acid salts, future efforts can be made to develop highly-dispersed solid base nanocatalysts to ease the product separation. To be economically viable and compete with the mature in-market technologies, future directions are to reduce the oxidant dosage possibly by adding an oxidizing promoter and to directly convert biopolymers such as cellulose. Although the reaction process was applicable to transform several other biomass resources particularly xylan into FA with satisfactory yields, but currently it is still difficult to transform cellulose under such mild conditions. Future improvements can be made, for example, by exploiting an additive/promoter to facilitate the cleavage of the glycosidic bonds or adopting more effective pretreatment methods. The work unraveled the unique chemistry of glucose in basic, oxidative environments for near-quantitative FA production for the first time, and we anticipate the work will induce increased academic interests to exploit the huge potentials in mild biomass utilization processes and eventually push the processes towards industrialization.

Conflicts of interest

There are no conflicts to declare.

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