Photocatalytic conversion of biomass-based monosaccharides to lactic acid by ultrathin porous oxygen doped carbon nitride

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Highlights:

- The Ut-OCN had controllable tunable bandgaps and lower PL intensity.
- High yields of lactic acid achieved from different biomass-based monosaccharides photocatalyzed by Ut-OCN.
- Catalyst was reusable for over 10 cycles without deterioration in this activity.
- Good yield of lactic acid was observed from one-thousand-fold scale-up experiment.

ABSTRACT

Application of photocatalysis to biorefinery conforms to the requirement of sustainable development of the society. It is of great significance, yet limited success has been achieved. Here, we report oxygen atom doped on the ultrathin porous carbon nitride
(Ut-OCN) as an efficient photocatalyst for lactic acid production. The Ut-OCN photocatalyst represents an increase in the absorption range of visible-light via tunable band structure. Remarkably, the photocatalyst exhibited effective activity with lactic acid yield above 89.7%, and this system is universal for the synthesis of lactic acid from biomass-based monosaccharides. Catalytic poisoning and recycling experiments revealed that the selectivity of ·O₂⁻ is superior to ·OH, h⁺, ¹O₂, in proper order. The photocatalyst is highly stable and recyclable. Moreover, the yield of lactic acid of one-thousand-fold scale-up experiment irradiated by sunlight retained 98.4% of one-time experiment. It is believed that this work paves a way for the lactic acid production via photocatalysis.

**KEYWORDS:** Biorefinery; Lactic acid; Photocatalysis; Ut-OCN; Magnify experiment

1. **Introduction**

Recently, the exhaustion of petroleum-based resources and increasing environmental pollution have caused concerns widely. In response to these problems,
exploring and utilizing the renewable resource has received much attention. Nowadays, many research efforts have been focused on the development and use of biomass [1, 2] and solar energy. [3, 4] Biomass is not only renewable energy, but also the only renewable carbon source. It can be used to produce various fuels, [5, 6] synthesize a series of high-valued chemicals, [7] and even prepare different types of functional materials. [8, 9] Photocatalysis is a key technology to realize the efficient utilization of solar energy, an abundant resource of renewable energy. Up to now, photocatalysis has shown the advantages of high-efficiency, low energy consumption, low cost, easy operation, mild reaction conditions and wide applicability, leading to an active new frontier in catalysis. [10-13] Despite of advantages in photocatalysis, developing biorefinery via photocatalytic technology remains in its early stage. [14, 15]

Lactic acid (2-hydroxy propionic acid), as an important renewable chemical building block of biorefinery, arouses the interests of researchers in various fields. It is one of the top 12 high-value bio-based platform molecules identified by the United States Department of Energy, [16, 17] which can be widely used in the food, cosmetic and pharmaceutical industry. [18] Lactic acid can be used as precursors to prepare biodegradable polymers (polylactic acid) [19] and other commodity chemicals [20-22] (e.g., propanoic acid, ethyl lactate, acrylic acid, 2,3-pentanedione, propylene oxide). It can be a starting material for the synthesis of biodegradable solvents (lactic acid esters) [18, 19] and alternative liquid fuels. [23] Current methods of producing lactic acid include biological and chemical syntheses. The biological synthesis of lactic acid is through the fermentation of glucose or corn starch, [24] and yet no single fermentation system is generic for all different types of biomass feedstocks. Moreover, the biological processes suffered from some drawbacks, such as high separation cost, slow kinetics and poor scalability. [25] Thus, many research efforts for producing lactic acid have been shifted to chemical synthesis, including homogeneous and heterogeneous catalysis. For homogeneous catalysis, different bases and transition metal ions were used as catalysts for the production of lactic acid. Yan et al. [26] reported that a yield of ~27.0% in lactic acid could be obtained from glucose and cellulose catalyzed by homogeneous base catalysts (e.g., NaOH and Ca(OH)₂). Furthermore, ~57.0 mol% of lactic acid was observed in the xylose-Ca(OH)₂ solution at 200 °C. [27] Zn²⁺ ions were used to catalyze the synthesis of lactic acid from glucose or sucrose in subcritical water at 300 °C. [28] Interestingly, a later report demonstrated that the yield of lactic acid was decreased with
the increasing concentration of Zn\textsuperscript{2+} ions. [29] Despite of the successful syntheses for lactic acid by homogeneous catalysis, achieving high yields in low temperature remains a challenge.

Thus, many researches turned to heterogeneous catalysis owing to their irreplaceable superiority in catalysis, such as easy to be recovered, feasible to be used repeatedly, and less pollution to the environment. [30] For example, Chambon et al. [31] showed that the heterogeneous Lewis acids (e.g., tungstated alumina and tungstated zirconia) are selective catalysts for the conversion of cellulose to lactic acid with yields of 27.0\% and 18.5\%, respectively. The Lewis acidic zeotype materials (e.g., Sn-Beta) were used for the formation of lactic acid ( < 30.0\%) from mono- and disaccharides in the water. [32] Much lower yields of lactic acid or methyl lactate from glucose with, have been catalyzed by solid base catalysts, such as hydrotalcites, [33] magnesium [34] and noble metal-based catalysts. [35] Yang et al. [30] recently demonstrated that lactic acid was produced directly from xylose or xylan over ZrO\textsubscript{2} in the pH neutral aqueous solutions, with yields of 42.0\% and 30.0\%, respectively. However, the yields of lactic acid from biomass-based feedstocks were still low using heterogeneous catalysts, and the reaction temperatures were still high. To overcome these drawbacks, herein, we will demonstrate the photocatalytic technology based on a new type of carbon nitride to produce lactic acid in high yield, low temperature and with the applicability to all different types of biomass feedstocks.

Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}), a metal-free and green photocatalyst, has recently attracted widespread interest due to its excellent photocatalytic activities. [36-38] Conventional synthesis of g-C\textsubscript{3}N\textsubscript{4} involves the thermal polymerization of urea, thiourea, melamine or dicyanamide. [36, 37] However, pure g-C\textsubscript{3}N\textsubscript{4} suffers from not only a limited absorption range to visible light but also a high carrier recombination rate, leading to poor photocatalytic activity. [38] To overcome these problems, various strategies, such as heteroatom doping, [39-41] morphological control, [42] sensitization with dyes, [43] hybridization with \(\pi\)-conjugated graphitic carbon materials, [44] and coupling with other semiconductors [45-47] or conductors, [48] have been developed to improve the photocatalytic activity of g-C\textsubscript{3}N\textsubscript{4}. The obtained functional carbon nitride materials can activate thermodynamically unfavorable chemical reactions, such as water splitting, [49, 50] CO\textsubscript{2} reduction, [51, 52] N\textsubscript{2} fixation, [53] biorefinery, [54, 55]
and NO removal. [56, 57] The carbon nitrile photocatalysts do not suffer from the multifarious process, harsh reaction conditions, high production costs, and low controllability. Despite their advantages, these photocatalysts have not been exploited for the production of lactic acid from biomass-based sugars.

Herein, we developed a facile and universal approach for selectively synthesis of lactic acid from biomass-based monosaccharides photocatalyzed by oxygen atom doped on the ultrathin porous carbon nitride (Ut-OCN). The Ut-OCN with controlled band structures was prepared by a mild, economical and environmentally-benign method. The catalyst not only has excellent selectivity toward lactic acid from various C5 and C6 sugars, but also possesses good recycling performance. The effects of ·O$_2^-$, \textsuperscript{1}O$_2$, ·OH and h$^+$ in the system were investigated. As combined with the obtained byproducts and other experimental data in this work, a possible reaction mechanism of fructose conversion to lactic acid was proposed. Furthermore, a thousand-fold scale-up experiment of the constructed lactic acid production system was also investigated to verify the large-scale application of the process.

2. Experimental section

2.1. Preparation of CN and Ut-OCN

In this work, the pristine g-C$_3$N$_4$ was designated as CN. The CN was obtained by direct calcining the melamine with a 10 °C/min ramp rate and keeping at 550 °C for 4 h under flowing nitrogen (99.99%, 50 mL/min). Ut-OCN photocatalysts were prepared by thermal polymerization assisted with manganese acetate solution. In a typical procedure, a certain amount of manganese acetate was dissolved in deionized water, and then a certain amount of melamine was added into the solution with constant stirring, until a paste was obtained. The paste was then calcined at 550 °C in a tube furnace for 4 h. The obtained solid samples were fully grinded and named as Ut-OCN.

2.2. Photooxidation of fructose and other C6 or C5 sugars to lactic acid catalyzed by CN and Ut-OCN

The activity of CN and Ut-OCN was investigated with fructose as raw material under visible-light irradiation. In a typical method, 100 mg of fructose and a certain amount of CN or Ut-OCN photocatalysts were added into the solution with different pH values. The obtained reaction system was stirred for 30 min under dark conditions.
and then carried out at different temperatures for a period of time with constant stirring under the visible-light irradiation. Once the optimum reaction conditions have been laid down, the effects of this system for the conversion of others C6 and C5 sugars such as mannose, rhamnose, glucose, xylose and arabinose, were investigated.

2.3. Poisoning experiments of active oxygen species

The effects of different active oxygen species on the synthesis of lactic acid from fructose catalyzed by Ut-OCN was investigated via poisoning experiments. 100 mg of fructose, 60 mg of Ut-OCN and a certain amount of sacrificial agent were added into the 10 mL of KOH solution (3.0 mol/L). The obtained reaction system was stirred for 30 min under dark conditions and then carried out at 50 °C for 90 min under the visible-light irradiation.

2.4. Catalytic recycling and one-thousand-fold scale-up experiments

The recycling experiment: 100 mg of fructose and 60 mg of Ut-OCN were added into the 10 mL of KOH solution (3.0 mol/L), and the obtained system was stirred for 30 min under dark condition and then carried out at 50 °C for 90 min under the visible-light irradiation. In all cases, the catalysts were recovered after reaction by centrifuging for 5 min (8,000 rpm). The solid was washed with distilled water for several times until the supernatant became neutral. The washed catalysts were dried at 80 °C for at least 10 h prior to reuse.

The one-thousand-fold scale-up experiment was performed using the similar procedure which has been discussed above with slightly modification. In a typical procedure, 100.0 g of fructose and 60.0 g of Ut-OCN were added into the 10,000 mL of KOH solution (3.0 mol/L), and then the system was performed at room temperature for 30 min with constant stirring under the dark condition. Afterwards, the system was carried out at room temperature for 90 min under sunlight irradiation.

2.5. Products analysis

All the samples were immediately syringed out, filtered and analyzed by high-performance liquid chromatography (HPLC, Agilent 1260 series) with a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm × 9 μm). 5 mM H₂SO₄ was used as the
mobile phase with a flow rate of 0.5 mL/min, as well as the column temperature and the detector were set at 40 °C. [58] The concentrations of the products were determined by comparing the calibration curve established with the external standards. The conversion of fructose and the yields of the products were calculated by the following equations: [59]

\[
\text{Conversion (\%)} = \frac{\text{Moles of carbon in feedstock consumed}}{\text{Moles of carbon in feedstock input}} \times 100\%
\]

\[
\text{Product yield (\%)} = \frac{\text{Moles of carbon in organic acid}}{\text{Moles of carbon in feedstock input}} \times 100\%
\]

3. Results and discussion

3.1. Photocatalyst synthesis, characterization and density functional theory calculations

The Ut-OCN photocatalyst was prepared by direct thermal polymerization of a mixture of melamine, manganese acetate and water (Fig. 1A), while the CN photocatalyst was obtained via calcination of melamine. The morphology of Ut-OCN was observed by scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscopy (AFM). The results of SEM showed that the Ut-OCN possessed sheet-like structures (Fig. 1B, C). To illustrate the composition of Ut-OCN, the elemental mapping of Ut-OCN photocatalysts were presented in Fig. 1D, E, F, and the results evidenced the successful introduction of O atoms in Ut-OCN. Meanwhile, the EDS results showed that the content of O element in the catalyst was 2.7 wt% (Fig. 1G), which gave further proof of the existence of O atoms in the catalyst.

To further investigated the structures of CN and Ut-OCN, the TEM and AFM were performed. As shown in Fig. 1H-K, obvious holes were observed on the surface of Ut-OCN, as compared with CN. The AFM images further showed that the CN and Ut-OCN nanosheets were all hundreds of nanometers in width (Fig. 1L-O). However, the thickness of them is different, for CN is \(~4.0\) nm (Fig. 1M) and for Ut-OCN is \(~1.5\) nm.
The reduced thickness of photocatalysts play two roles. On the one hand, the specific surface area of the sample was increased as the thickness reduced, facilitating the adsorption and mass transfer of the biomass reforming processes. On the other hand, the thinner samples can greatly improve the mobility of photogenerated carriers during the biomass reforming process, thereby enhancing the photocatalytic activity. [60] The $N_2$ sorption isotherms of CN and $Ut$-OCN (Fig. 2A) exhibited type IV isotherm patterns, which were indicative of abundant mesoporous in these photocatalysts. It was found that the result was in line with the TEM results. The pore width of CN and $Ut$-OCN were shown in Fig. 2B, and the surface area increased from 47.9 to 142.7 m$^2$/g for CN and $Ut$-OCN, respectively. The aforementioned characterization of $Ut$-OCN would be helpful to increase the accessibility of reactants-photocatalysts interface and mass transfer.

The chemical structures of CN and $Ut$-OCN were characterized by X-ray diffraction (XRD) patterns and Fourier transform infrared (FT-IR) spectroscopy. As shown in Fig. 2C, no striking difference between CN and $Ut$-OCN were observed, and they all showed a typical IR pattern of CN, with three major bands. The first peak presented at 805 cm$^{-1}$ is caused by the out-of-plane bending of the heptazine rings, indicating that basic melon units exist with the NH/NH$_2$ groups. [38] The series of peaks between 1150 and 1700 cm$^{-1}$ belong to N-C=N heterorings in the “melon” framework, which are related to the skeletal stretching vibrations of the aromatic rings. [38] The broad peaks between 3100 and 3400 cm$^{-1}$ are assigned to the N-H stretching vibration. [38] As shown by the XRD patterns in Fig. 2D, the $Ut$-OCN and CN have similar crystalline structures, implying that $Ut$-OCN preserves the structure framework of CN. The diffraction peaks at 12.8° and 27.4° belong to (100) and (002) planes of CN (JCPDS 87-1526), representing the in-plane packing and interfacial stacking of CN, respectively. [61] After doping O atoms, the peaks gradually weakened, suggesting that CN or its molecular precursors were attacked by manganese acetate, resulting in the loss and change of ordered structures within the framework.

To investigate the chemical composition and status of elements in the $Ut$-OCN, the XPS was performed. As shown in Fig. 2E, the spectrum confirms that the presence of C, N, O in $Ut$-OCN. The narrow scan C 1s XPS spectrum of $Ut$-OCN was shown in Fig. 2F, and the peaks were observed in 287.3, 286.9 and 284.3 eV, corresponding to the covalent bonds of C-N-C, C-O and C-C, respectively. [62]
the N 1s spectra gave three peaks at 400.2, 399.1 and 397.5 eV, which are attributed to the N-H, N-(C), and sp²-hybridized nitrogen (C=N-C). [62] The O 1s XPS spectra of Ut-OCN (Fig. 2H) contain two peaks at 531.6 and 530.8 eV, attributed to the C-O and OH groups, respectively. [63] These results indicated that O atoms are successfully introduced into the framework of Ut-OCN.

The doping of O atoms into Ut-CN clearly changed the optical properties and light harvesting abilities of the obtained samples. Fig. 3A shows the UV-vis DRS of CN and Ut-OCN. As compared with CN powder, the color of Ut-OCN changed from yellow to light yellow (inset in Fig. 3A), and a significant red-shift absorption of visible-light was observed, indicating that Ut-OCN exhibits enhanced optical absorption than CN. The Kubelka-Munk function was used to estimate the bandgaps of the as-prepared samples. The bandgaps of CN and Ut-OCN narrowed progressively from 2.60 to 2.30 eV (inset in Fig. 3A). The reasons for the change are most likely that the doping of O atoms may change the electronic arrangement of Ut-OCN samples. To further investigate the electronic energy of CN and Ut-OCN, the Mott-Schottky (M-S) plots and ultraviolet photoelectron spectra (UPS) were performed. As shown in Fig. 3B, the positive slopes of M-S plots for CN and Ut-OCN were observed, indicating that they are all n-type semiconductor. [64] The slopes of CN and Ut-OCN are \(7.6190 \times 10^9\) and \(4.3956 \times 10^9\), as well as their electron concentration are \(1.4038 \times 10^{20}\) cm\(^{-3}\) and \(2.4332 \times 10^{22}\) cm\(^{-3}\), respectively (Fig. 3B). [51, 65] Apparently, the increase in electron concentration of Ut-OCN is favorable to the biomass reforming process. Furthermore, the flat potential of CN and Ut-OCN were -1.60 V and -1.42 V vs. NHE, respectively. Fig. 3C displays the UPS results of CN and Ut-OCN, and the work functions were obtained by the UPS results, for Ut-OCN is 4.64 eV (21.1-16.56 eV) and for CN is 4.12 eV (21.2-17.08 eV). Obviously, the Ut-OCN can effectively capture the excited electrons and restrain the recombination of charge carrier than CN for the enhanced electron concentration and higher work function [51, 66]. In addition, the valence bands position (VB) of CN and Ut-OCN are -5.44 eV (vs vacuum) and -5.32 eV (vs vacuum), respectively. Correspondingly, the VB position of CN and Ut-OCN is 1.0 and 0.88 eV, respectively [51, 67]. Therefore, the electronic energy band positions of CN and Ut-OCN are clearly. The Ut-OCN suffers from lower conduction and valence band positions (Fig. 3D), which may be caused by O-doping in the samples. [68]
To understand the effect of O doping on electronic properties of CN nanosheets, first-principles calculations of the CN and Ut-OCN with different functional groups were carried out (Fig. 4). The lattice geometry and fundamental properties of the defect-free CN were in good agreement with previous reported values. [38] After introducing a hydroxy group into the unit cell of CN, the bandgap energy of Ut-OCN decreased from 2.59 eV (CN) to 2.30 eV, producing a doping state in the upper bandgap, which was consistent with the results of UV-vis DRS. However, there was a slightly distortion leading to restructure the orthogonal architecture of Ut-OCN since the symmetric hydrogen bonds were destroyed. The results revealed that the introduction of hydroxy groups was a very important factor to stably adjust the electronic structure of Ut-OCN.

To reveal the effect of hydroxy group on melon backbone, we calculated the adsorption energy of fructose molecules located on the CN and Ut-OCN. According to the calculated results (Table S1), the adsorption energy of fructose on the Ut-OCN surface was a little stronger (about 0.08 eV) than that of CN. Obviously, the carboxyl moiety of fructose tended to adsorb on the -NH2 group or -OH group, in which fructose lied with a curved structure on the substrate and could be easily adsorbed on the functional groups of the CN. The differences of preferential molecular locations between CN and Ut-OCN were attributed to the strong local electrostatic potential differences on different units for the introduction of hydroxy groups. Hydrogen bonds between them facilitated the adsorption progression and formed a more stable geometry (Fig. 5). The consequence was the spatial separation of the electron-hole pair, thereby reducing their recombination and increasing the interfacial charge transfer for the required reaction. More importantly, the result shows that the introduction of hydroxy groups in the framework of Ut-OCN might be an effective strategy to enhance adsorption of fructose.

To further elucidate the charge separation and recombination behavior of as-prepared samples, the photoluminescence (PL) spectra of CN and Ut-OCN were performed (Fig. 6A). By comparison with CN, Ut-OCN showed lower PL intensity, indicating that the charge recombination was inhibited in Ut-OCN. These results suggested that the 2D structure as well as the increased pore volume and specific surface area promote the charge transfer in Ut-OCN, resulting in less charge recombination. [69] Furthermore, a red-shift of exciton energy from PL spectroscopy with doping of O atoms was observed. The reduced binding energy of exciton was
always related to the narrow of bandgaps of Ut-OCN, which is consistent with the observation obtained from UV-vis DRS. The photoelectrochemical performances of CN and Ut-OCN were investigated by the linear sweep voltammetry (LSV), transient response photocurrent and electrochemical impedance responses (EIS). A large value of photocurrent for Ut-OCN was observed as compared with CN (Fig. 6B, C), indicating that the Ut-OCN has higher photogenerated charge ability, thereby enhancing its photocatalytic activity. Furthermore, the Ut-OCN shows good and reproducible response photocurrent under the repeatedly switched ON/OFF illumination cycles when compared with CN. [70] In the irradiation of visible light, the diameter of semicircular Nyquist plots of Ut-OCN is smaller than CN, indicating that Ut-OCN owns good photocatalytic response as well as retains the decreased electron transfer resistance from the electrode to electrolyte molecule. [71] All the results suggested that Ut-OCN has strong electron transfer ability and photo generated carrier separation ability when compared with CN, leading to an enhanced photocatalytic activity.

3.2. Optimization of reaction conditions for synthesizing lactic acid

The photocatalytic performance of CN and Ut-OCN samples were evaluated via the production of lactic acid from fructose under visible-light irradiation. Initially, the selective oxidation of fructose to lactic acid photocatalyzed by CN or Ut-OCN (50 mg) was performed at 20 °C in the KOH solution (3 mol/L) for 60 min, respectively. Only a trace amount of lactic acid was observed in CN, while 43.0% yield of lactic acid was found as catalyzed by Ut-OCN, indicating that Ut-OCN is an efficient photocatalyst in the synthesis of lactic acid from fructose. The effects of different conditions on the synthesis of lactic acid photocatalyzed by Ut-OCN were then investigated. As we known, reaction temperature plays a crucial role in biorefinery. Higher reaction temperature speeds up the conversion rate while often promoting undesired side reactions. As shown in Fig. 7A, the yield of lactic acid was increased at first and then slightly decreased with increasing reaction temperature, which gives the highest production of lactic acid at 50 °C. Among the processes, lower temperatures benefit for the synthesis of glucose and formic acid, while higher temperatures accelerate the production of acetic acid, evidencing decreased yield of lactic acid at a high reaction temperature. Furthermore, tetrulose was also observed in these processes. Although the conversion of fructose increased with the raise of reaction temperature (Fig. 7A, S1A),
the increase in yields was not so significant, resulting in a same trend in the selectivity toward lactic acid (Fig. S1B). Following this, the effects of different amounts of catalyst dosages were investigated. As the Ut-OCN dosages increased from 5 to 60 mg, the yield of lactic acid increased to 68.3%. However, a slight decrease in lactic acid yield (66.7%) was observed when the Ut-OCN dosage was increased to 70 mg (Fig. 7B). It is possible that fructose molecules adsorbed on the surface of Ut-OCN became unstable species with the increased activity, leading to the reduced activation energy of the entire reaction. The selectivity (Fig. S1B) and the yield of lactic acid had shown a similar change, and the conversion (Fig. 7B, S1A) of lactic acid increased with the raising amount of Ut-OCN. Furthermore, the glucose, formic acid, acetic acid and tetrulose were observed during these processes.

pH also plays an important role in the synthesis of lactic acid photocatalyzed by Ut-OCN. As shown in Fig. 7C, only 7.9% of lactic acid was obtained in the KOH solution (0.1 mol/L). When the concentration of KOH solution raised to 0.5 mol/L, the yield of lactic acid obviously increased to 49.9%, and then the yield increased as the KOH concentration up to 3.0 mol/L. However, when the concentration of KOH was more than 3.0 mol/L, the yield of lactic acid began to decrease. That is, perhaps, because more oxidative species were produced with the increase of alkalinity in the reaction system, resulting in the excessive oxidation of the obtained lactic acid to other byproducts. A similar trend was observed in the selectivity of lactic acid (Fig. S2B). The conversion of fructose was increased with raising the concentration of KOH solution (Fig. 7C, S2A). Meanwhile, glucose, formic acid, acetic acid and tetrulose were all observed in these processes. Finally, the effects of different reaction times on the synthesis of lactic acid from fructose were investigated. With the increase of irradiation time, both the yield (Fig. 7D) and selectivity (Fig. S2B) of lactic acid increased at first, and then decreased after 90 min. This may be because the extended reaction time made the obtained lactic acid to form other compounds. As in other cases, the conversion of fructose was also increased with raising reaction time (Fig. 7D and S2B). Similarly, the byproducts of glucose, formic acid, acetic acid and tetrulose were observed in these processes.

3.3. The recycling stability of Ut-OCN on the synthesis of lactic acid from fructose
The recycling stability of photocatalyst is an important parameter to limit the application of photocatalytic oxidation technology. In this work, the selective photocatalytic oxidation of fructose to lactic acid was carried out at 50 °C in the presence of KOH solution (3.0 mol/L) and Ut-OCN (60.0 mg) for 90 min. In all cases, the Ut-OCN photocatalysts were recovered after reaction by centrifuging for 5 min at 8,000 rpm. The recovered solid catalysts were washed with distilled water for several times until the supernatant became neutral. The washed catalysts were dried at 80 °C for at least 10 h prior to reuse. The conversion of fructose and the yield or selectivity of lactic acid decreased from 98.1% to 97.9%, 69.5% to 66.8% and 70.8% to 68.2%, and retained nearly 99.8%, 96.1% and 96.3% of their original values in the tenth recycling run (Fig. 7E), respectively, suggesting that the Ut-OCN photocatalysts have excellent stability and recycling ability.

3.4. The photocatalytic universality of Ut-OCN on the photocatalytic synthesis of lactic acid from different biomass-based monosaccharides

In recent years, the wider universality of substrate for catalysts has been the research focus. Here, the selective oxidation of different biomass-based monosaccharides to lactic acid photocatalyzed by Ut-OCN was investigated. The selective photocatalytic oxidation of different pentose sugars or hexose sugars to lactic acid catalyzed by Ut-OCN was performed at 50 °C in the presence of KOH solution (3.0 mol/L) for 90 min. As shown in Fig. 7F, the yields of lactic acid obtained from xylose and arabinose are 89.7% and 68.3%, respectively, and the yields of lactic acid from hexose sugars were 69.6% (fructose), 63.9% (glucose), 45.9% (mannose) and 28.6% (rhamnose), respectively. The conversion of xylose, arabinose, fructose, glucose, mannose and rhamnose was 99.2%, 99.5%, 98.1%, 96.9%, 84.7% and 65.1%, respectively (Fig. 7F). Correspondingly, the selectivity of them was 90.4%, 68.6%, 70.9%, 65.9%, 54.2% and 43.9%, respectively (Fig. 7F). Obviously, the yields of lactic acid from pentose sugars are slightly higher than those from hexose sugars. In brief, the Ut-OCN is a highly effective photocatalyst for the synthesis of lactic acid from different biomass-based monosaccharides.

3.5. The comparison of the effects of Ut-OCN and different reported catalysts on the synthesis of lactic acid from biomass-based monosaccharides
To have a better understanding of the catalyst system, the effectiveness of Ut-OCN was compared to those of catalysts reported previously. [28, 30, 32, 72-79] As shown in Table 1, Ut-OCN is an efficient photocatalyst for the synthesis of lactic acid from fructose (Table 1, entry 1), glucose (Table 1, entry 5), xylose (Table 1, entry 12), and mannose (Table 1, entry 15). For synthesis of lactic acid from fructose, although most of them have good yields of lactic acid, they suffered from high reaction temperatures and complex catalyst preparation processes (Table 1, entries 2-4). With regard to the synthesis of lactic acid from glucose, the Rut 160 and TiO₂ reaction systems were performed at mild condition, but the lactic acid was not the main product, and the yields of lactic acid were only < 1.0% and ≥ 6.0%, respectively (Table 1, entries 6, 7). The Sn-Beta-NH₂ and Nb₂O₅ Nanorod reaction systems have excellent conversion of glucose, the yields of lactic acid were lower than that of Ut-OCN, and they all suffered from high reaction temperatures (Table 1, entries 8, 9). Although the Al(III)-Sn(II) and Sn-Beta zeolite reaction systems have excellent conversion of glucose and yields of lactic acid via thermo-catalysis, they all suffered from high reaction temperatures and pressures (Table 1, entries 10, 11). For production of lactic acid from xylose, the reactions were carried out at shorter reaction times when compared with Ut-OCN system, but they suffered from high reaction temperatures and high pressures as well as low yields (Table 1, entries 13, 14). In addition, for the synthesis of lactic acid from mannose, the ZnSO₄ catalytic system suffered from harsh reaction conditions (300 °C, 25 MPa) when compared with Ut-OCN system, and the yield of lactic acid is lower than that of Ut-OCN. Obviously, the Ut-OCN photocatalyst system was much better than other reported catalyst systems reported.

3.6. One-thousand-fold scale-up experiment

To address the potentiality of industrial application of the Ut-OCN photocatalyst for the synthesis of lactic acid, a thousand-fold scale-up experiment was performed in this work (Fig. 8). The reaction conditions were slightly different from the optimum conditions. In a typical procedure, 100.0 g of fructose and 60.0 g of Ut-OCN were added into the 10,000 mL of KOH solution (3.0 mol/L), and then the system was carried out at room temperature for 30 min with constant stirring under the dark conditions. Afterwards, the system was carried out at room temperature (~20.0 °C) for 90 min under sunlight irradiation. The yield of lactic acid reached to 49.1% in the one-
thousand-fold scale-up experiment. With an overall consideration of comprehensive economic and environmental factors, the photocatalytic system for the synthesis of lactic acid from fructose catalyzed by Ut-OCN provides a great potential for industrial production of lactic acid.

3.7. The effects of different oxidation active species on the photocatalytic synthesis of lactic acid

ESR spin trapping is a reliable and direct method to identify and quantify short-lived radicals and paramagnetic species. Fig. 9A shows the ESR spectra obtained from the solutions containing TEMPO and CN or Ut-OCN under dark or visible-light irradiation conditions. Obviously, under the dark conditions with photocatalysts (CN or Ut-OCN), or the visible-light irradiation conditions without photocatalysts, the systems exhibit a stable triplet ESR spectrum with an intensity of 1:1:1, which is attributed to the characteristic peaks of TEMPO. Once the e' was transferred to TEMPO, the hydroxyl amine of TEMPOH was formed, reducing the signal of TEMPO. The signal gradually flattened with increasing of irradiation time in the CN or Ut-OCN systems, suggesting that more e' were produced during these processes (Fig. S3A, B). Compared with CN, lower signal was observed in the system of Ut-OCN (Fig. S4), indicating that the e' was produced from photo-excited CN or Ut-OCN, and Ut-OCN greatly enhanced the reactivity of the photo-induced e'. This may be due to that the Ut-OCN has low Fermi level, resulting in the increased availability of e' for photoreductions. Meanwhile, the changes in the signals of h+ in the systems of CN and Ut-OCN were similar to those of e', respectively, and the results are shown in Fig. 9A, S5A-B and S6.

DMPO can react with ·O₂⁻ and ·OH to form the adducts of DMPO/·O₂⁻ and DMPO/·OH, respectively, thereby presenting the corresponding signals of ESR spectra. In unirradiated systems or the systems with DMPO but no photocatalysts, no ESR signals were observed (Fig. S7A, B and Fig. 9B). As the irradiation time increased, stronger signals were produced (Fig. S8). Interestingly, the signal presented by the system of Ut-OCN was better than that by CN within the same irradiation time (Fig. 9B). These results suggested that increased amounts of ·O₂⁻ species were generated in the systems, thereby taking part in the selective photocatalytic oxidation. Furthermore, the trend of ·OH signal strength change was presented in the Fig. S9A-B, S10 and 9C, which is the same as the ·O₂⁻ species discussed above. The only difference is that the
signal of DMPO/·OH exhibited four-line spectrum with relative intensity of 1:2:2:1, whereas the DMPO/\( \cdot \text{O}_2^- \) system presented the four-line spectra with identical intensities.

Singlet oxygen (\( ^1\text{O}_2 \)) is a special form in existence, as a highly selective oxidant. The characteristics of \( ^1\text{O}_2 \) structure reveal that they do not have ESR signals, and thus it needs to be identified by TEMPONE. As shown in Fig. 9D, no signal was observed in the presence of dark conditions or the systems with catalysts but no TEMPONE (Fig. S11A, B and Fig. 9D). Once TEMPONE and CN or \( \text{Ut-OCN} \) were added into the systems with irradiation, three signals with an intensity of 1:1:1 were presented, showing that \( ^1\text{O}_2 \) was produced. With increasing irradiation time, the ESR signals enhanced gradually (Fig. S12), and the intensity of \( \text{Ut-OCN} \) system was more than that of CN in the presence of the same irradiation (Fig. 9D).

To identify the roles of different oxidative species in the selective photocatalytic oxidation of fructose to lactic acid, a series of experiments were carried out with different sacrificial agents, such as tryptophan (Trp) for \( ^1\text{O}_2 \), \( p \)-phthalic acid (PTA) for \( \cdot \text{OH} \), KI for \( h^+ \) and \( p \)-benzoquinone (BQ) for \( \cdot \text{O}_2^- \), and the results are given in Fig. 10. As compared to the experiment without sacrificial agent, the yield of lactic acid decreased in the order of the systems with KI, Trp, PTA and BQ. The results show that, on the one hand, all the \( ^1\text{O}_2 \), \( h^+ \), \( \cdot \text{OH} \) and \( \cdot \text{O}_2^- \) species benefit for the production of lactic acid from fructose, even though the \( \cdot \text{O}_2^- \) plays a major role for the synthesis of lactic acid from fructose.

3.8. Possible mechanism for the conversion of fructose photocatalyzed by \( \text{Ut-OCN} \)

Various oxidative active species were detected by ESR, and all of them could play a vital role in the synthesis of lactic acid from fructose (Fig. 9). Meanwhile, in addition to lactic acid, glucose, formic acid and acetic acid were all observed in these processes. Thus, based on the experimental results and previous reports, [59, 80, 81] we proposed a plausible reaction mechanism for the conversion of fructose photocatalyzed by \( \text{Ut-OCN} \) (Fig. 11). Firstly, the hydrolysis reaction of fructose was performed to give glyceraldehyde and dihydroxyacetone, respectively, under the effects of \( ^1\text{O}_2 \), \( \cdot \text{O}_2^- \), \( \cdot \text{OH} \), \( h^+ \). The pyruvaldehyde was then obtained by dehydration, and after a series of steps, it was converted to lactic acid. Furthermore, glucose was produced by isomerization from
fructose. Subsequently, the glucose was α-oxidized or β-oxidized, respectively, to give six molecules of formic acid. In addition, the intermediate III was also produced from fructose. It could be transformed to intermediate I and acetic acid via oxidative α-dicarbonyl cleavage. It could be also converted to intermediate IV via isomerization, and then converted to tetrulose and acetic acid by hydrolytic β-dicarbonyl cleavage. Meanwhile, the obtained lactic acid could be further oxidized to formic acid and acetic acid.

4. Conclusions

In summary, we developed a generic approach for the synthesis of lactic acid from biomass-based monosaccharides photocatalyzed by Ut-OCN. The obtained Ut-OCN samples prepared by direct thermal polymerization of melamine assisted by manganese acetate, not only exhibit an increase in the absorption range of visible-light, but also present lower charge recombination. The Ut-OCN showed a universality of substrates, which can selectively photocatalytic oxidation of different biomass-based pentose sugars and hexose sugars to lactic acid, and the yields of lactic acid from pentose sugars are slightly higher than those from hexose sugars. The \( ^1 \text{O}_2 \), \( \bullet \text{O}^+ \), \( \cdot \text{OH} \) and \( \cdot \text{O}_2^- \) are all beneficial for the production of lactic acid from fructose, and the \( \cdot \text{O}_2^- \) plays an important role in the synthesis of lactic acid. Furthermore, the Ut-OCN was stable after 10 rounds of catalytic recycling. The one-thousand-fold scale-up experiment for the lactic acid production indicated that the industrial production of lactic acid via this reaction system is feasible, considering the feasibility of the reaction conditions, or the economic and environmental considerations of the reaction process. The study provides a new facile route to selectively oxidize biomass-based monosaccharides into lactic acid via photocatalysis.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CRediT authorship contribution statement

Jiliang Ma: Conceptualization, Methodology, Investigation, Writing-original draft, Visualization, Funding acquisition. Dongnv Jin: Investigation, Testing, Data analysis, Writing, Visualization. Yancong Li, Gaojie Jiao and Xinze Li: HPLC Analysis, Characterization, Validation. Qiong Liu: Photoelectrochemical measurements and analysis, Funding acquisition. Dequan Xiao: Validation, Writing-review & editing, Funding acquisition. Yanzhu Guo, Lingping Xiao, Xiaohong Chen and Jinghui Zhou: Supervision, Writing-review & editing. Runcang Sun: Funding acquisition, Resources, Investigation, Project administration, Supervision, Writing-review & editing.

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Fig. 1. Illustration of preparation of Ut-OCN (A), SEM of Ut-OCN (B, C), and element mapping images of Ut-OCN: C element (D), N element (E), and O element (F), (G): the EDS spectrometer of Ut-OCN. TEM of CN (H, I) and Ut-OCN (J, K). AFM of CN (L, M) and Ut-OCN (N, O).
Fig. 2. N₂ adsorption isotherm (A) and the BJH pore size distribution (B) of CN and Ut-OCN. FT-IR spectra (C) and XRD patterns (D) of CN and Ut-OCN. XPS spectra of Ut-OCN photocatalyst: Survey (E), C 1s (F), N 1s (G), and O 1s (H).
Fig. 3. UV-vis DRS for CN and Ut-OCN (A). Inset in (A) shows a digital photograph and the plot of transformed Kubelka-Munk function versus photo energy for CN and Ut-OCN samples. Mott-Schottky plots of CN and Ut-OCN at frequencies of 500, 800, 1000 Hz in 0.5 M Na$_2$SO$_4$ and 0.2 M phosphate buffer electrolyte (B). Ultraviolet photoelectron spectra (UPS) as well as linear intersection for CN and Ut-OCN (C). Relative band alignment of CN and Ut-OCN (D).

Fig. 4. The band structures and corresponding density of states (DOS) of CN (A) and Ut-OCN (C), the valence band maximum (VBM) was set to be 0 eV. The top views of crystal structures of CN (B) and Ut-OCN (D), respectively. Color code: C, gray; N, blue; O, red; H, white.
Fig. 5. (A, B) Top and (C, D) side views of the optimal structures of a fructose molecule adsorbed on the CN and Ut-OCN, respectively. Color code: C, gray; N, blue; O, red; H, white.

Fig. 6. Photoluminescence (PL) emission spectra of CN and Ut-OCN (A). Average chopped linear sweep voltammetry (LSV) scans plots of CN and Ut-OCN (B). Periodic ON/OFF photocurrent response of CN and Ut-OCN in 0.5 M Na$_2$SO$_4$ electrolyte under visible light irradiation ($\lambda > 420$ nm) at 0.5 V vs. Ag/AgCl electrode (C). Electrochemical impedance spectroscopy Nyquist plots in the visible light illumination of CN and Ut-OCN (D).
Fig. 7. The effects of different conditions on the synthesis of lactic acid, (A): reaction temperature, (B): catalyst dosage, (C): the concentration of KOH solution, (D): reaction time. Recycling of *Ut*-OCN photocatalyst (E). The selectively oxidation of different biomass-based monosaccharides to lactic acid photocatalyzed by *Ut*-OCN (F).

Fig. 8. One-thousand-fold scale-up experiment for the synthesis of lactic acid catalyzed by *Ut*-OCN under sunlight irradiation at room temperature.
**Fig. 9.** TEMPO ESR spin-labeling for h^+ (A) and DMPO ESR spin-trapping for ·O_2^- (B) and ·OH (C) as well as TEMPONE ESR spin-labeling for ^1O_2 (D), (a: in the dark conditions or irradiation without spin-labeling, b and c represent CN and Ut-OCN under the same irradiation time, respectively).

**Fig. 10.** The effects of different oxidation active species on the synthesis of lactic acid from fructose.
Fig. 11. Possible reaction pathway for the conversion of fructose photocatalyzed by \( Ut-OCN \) under visible-light irradiation.
Table 1. The effects of different catalysts on the synthesis of lactic acid from different biomass-based monosaccharides with various conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Samples</th>
<th>Thermo-catalysis</th>
<th>Photocatalysis</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fructose</td>
<td>Ut-OCN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>≥98.0</td>
<td>69.6</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>Fructose</td>
<td>Al(□)-Sn(□)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;99.0</td>
<td>90.0</td>
<td>[72]</td>
</tr>
<tr>
<td>3</td>
<td>Glucose</td>
<td>(C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;SnO&lt;sub&gt;c&lt;/sub&gt;</td>
<td>-</td>
<td>&gt;91.8</td>
<td>63.0</td>
<td>[73]</td>
</tr>
<tr>
<td>4</td>
<td>Sn-Beta</td>
<td>-</td>
<td>-</td>
<td>&gt;99.0</td>
<td>27.0</td>
<td>[32]</td>
</tr>
<tr>
<td>5</td>
<td>Ut-OCN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>&gt;96.9</td>
<td>63.9</td>
<td>This work</td>
</tr>
<tr>
<td>6</td>
<td>Glucose</td>
<td>Rut 160&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;60.0</td>
<td>&lt;1.0</td>
<td>[74]</td>
</tr>
<tr>
<td>7</td>
<td>Glucose</td>
<td>TiO&lt;sub&gt;f&lt;/sub&gt;</td>
<td>-</td>
<td>≥6.0</td>
<td></td>
<td>[75]</td>
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<tr>
<td>8</td>
<td>Glucose</td>
<td>Sn-Beta-NH&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;99.0</td>
<td>56.0</td>
<td>[76]</td>
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<tr>
<td>9</td>
<td>Glucose</td>
<td>Nb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; Nanorod&lt;sup&gt;h&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;99.0</td>
<td>39.0</td>
<td>[77]</td>
</tr>
<tr>
<td>10</td>
<td>Glucose</td>
<td>Al(□)-Sn(□)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;99.0</td>
<td>81.0</td>
<td>[72]</td>
</tr>
<tr>
<td>11</td>
<td>Glucose</td>
<td>Sn-Beta zeolite&lt;sup&gt;i&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;98.0</td>
<td>67.1</td>
<td>[78]</td>
</tr>
<tr>
<td>12</td>
<td>Xylose</td>
<td>Ut-OCN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;99.2</td>
<td>89.7</td>
<td>This work</td>
</tr>
<tr>
<td>13</td>
<td>Xylose</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;j&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
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<tr>
<td>14</td>
<td>Xylose</td>
<td>LaCoO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;k&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>37.9</td>
<td>[79]</td>
</tr>
<tr>
<td>15</td>
<td>Mannose</td>
<td>Ut-OCN&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>&gt;84.6</td>
<td>45.9</td>
<td>This work</td>
</tr>
<tr>
<td>16</td>
<td>Mannose</td>
<td>ZnSO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;l&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>40.0</td>
<td>[28]</td>
</tr>
</tbody>
</table>

Reaction conditions: <sup>a</sup> 50.0 °C, 1.5 h.  <sup>b</sup> 463 K, N<sub>2</sub>: 3.0 MPa, 2.0 h.  <sup>c</sup> 210.0 °C, 0.5 h.  <sup>d</sup> 160.0 °C, 20.0 h.  <sup>e</sup> Stainless Steel Autoclave: 24.0-29.0 °C, Air: 5 bars.  <sup>f</sup> 75.0 °C, NaOH: 0.06 M.  <sup>g</sup> 190.0 °C, 2.0 h.  <sup>h</sup> 250.0 °C, 4.0 h.  <sup>i</sup> 200.0 °C, He: 4.0 MPa, 0.5 h.  <sup>j</sup> 200.0 °C, N<sub>2</sub>: 2.4 MPa, 40.0 min.  <sup>k</sup> 200.0 °C, N<sub>2</sub>: 200.0 Psi, 1.0 h.  <sup>l</sup> High pressure tube reactor: 300.0 °C, 25.0 MPa.