

One-pot Reduction of Metal Oxides/Salts with Carbohydrate Biomass under Mild Hydrothermal Conditions

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ABSTRACT Development of novel strategies to make full use of highly functionalized biomass molecules to expand its application fields is crucial to biomass utilization. Due to possessing diverse reducing functional groups such as hydroxyl and aldehyde, carbohydrate biomass can be employed as reductant for metallic material preparation. Particularly, the reducing ability of carbohydrate biomass is enhanced under hydrothermal conditions. The reported studies focused

on reduction of metal ions in acidic solution with the aid of biomass. However, we found alkali hydrothermal conditions are favorable to metal compounds reduction, even direct conversion metal oxides to metals. Meanwhile, low molecular weight organic acids were obtained from biomass oxidation. Based on our previous research on direct reduction of CuO and NiO into the corresponding metals, herein, we investigated metal salts reduction with carbohydrates and compared the reduction performance on glucose and cellulose which are the two most abundant carbohydrates with and without alkali addition. Moreover, conversion of other metal oxides (Fe_2O_3 , MnO_2 , Co_3O_4 , PbO_2) with glucose were studied to illustrate the feasibility to direct reduction of metal oxides with carbohydrates under alkali hydrothermal conditions. The reduction pathway study showed not only carbohydrates but also decomposed intermediates can reduce metal oxides. This study may provide an alternative approach to metal preparation in hydrometallurgy.

1. Introduction

Biomass utilization has attracted considerable attention as a vital strategy to alleviate the excessive dependence on fossil fuels and also to reduce carbon emissions.¹⁻³ An expected approach to biomass utilization should adapt to the molecular property of functionalized biomass molecules to improve the efficiency and reduce the cost in application.⁴⁻⁵ Leaching of metal ions from ores and reduction to elementary substance is a well-known hydrometallurgical process. The target metal can be extracted from ores either by reduction roasting followed by acid leaching or directly by reductive acid leaching using various reducing agents, which generally involves methanol, dimethyl sulfoxide, oxalic acid, pyrite, aqueous sulfur dioxide and so on.⁶⁻⁷ Many efforts have been devoted to developing green and cost-effective reducing agent.⁸

Glucose and cellulose which represent the basic compositions of carbohydrate biomass are the most abundant monosaccharide and polysaccharide on Earth. Actually, cellulose is a linear polymer of D-glucose with β -1,4-glycosidic bonds, and thus both possess similar reducing functional group such as hydroxyl and aldehyde. Glucose is soluble in water but cellulose is insoluble at room temperature due to the robust crystal structure. However, cellulose can be easily decomposed to oligosaccharides and monosaccharides in high temperature water (HTW) due to the combination of cleavage of hydrogen bonds within the cellulose crystal and decrease of hydrogen linkage among water molecules, as well as partially attributed to the hydrolysis reaction in HTW.⁹⁻¹⁰ Obviously, HTW enhances the reducing ability of cellulose. Hence, the nontoxic, cheap and abundant carbohydrate biomass may be employed as an alternative and environmentally friendly reducing agent in the hydrometallurgical process.

Almost all reported studies focused on reduction of Ag (I),¹¹⁻¹² Au (III),¹³⁻¹⁴ Cu (II),¹⁵⁻¹⁷ and Mn (IV)^{7, 18-24} in acidic solution with the aid of carbohydrate biomass. The corresponding elemental metals (e.g. Ag, Au, Cu) or low valent metal ions (e.g. Mn (II)) were obtained by reductive acid leaching process. In our research on hydrothermal conversion of carbohydrates into value-added chemicals, we found carbohydrates were favorable to selective oxidation to low molecular weight organic acids such as acetic acid and formic acid in alkali solution.^{3, 25-28} Further studies demonstrated not only metal ions but also metal oxides can be directly reduced under mild alkali hydrothermal conditions.²⁹⁻³¹ Although one-pot reduction of CuO and NiO into Cu and Ni were achieved respectively with glucose and cellulose, the different performance between glucose and cellulose with and without alkali are ambiguous, and the feasibility to other metal oxides reduction need to be examined. In this paper, we compared the reduction ability of glucose and cellulose under alkali hydrothermal and studied their performance on metal salts reduction. In addition,

reduction of other metal oxides (Fe_2O_3 , MnO_2 , Co_3O_4 , PbO_2) with glucose were investigated and the possible reduction mechanism was proposed.

2. Experimental Section

2.1 Materials

All metal oxides (200-mesh), salts and glucose were analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. α -Cellulose (powder) and standard substances were purchased from Sigma-Aldrich. All reagents were used as test materials without further purification.

2.2 Experimental procedure

The experiments were carried out in a Teflon-lined stainless-steel batch reactor with an inner volume of 30 mL. Typically, a desired amount of metal oxide and carbohydrate were added into the alkali solution and stirred with a magnetic blender for several minutes. Then, the mixture was put into the reactor and heated in the oven which had been preheated to the given temperature for several hours. After the reaction, the reactor was taken out of oven and cooled naturally to room temperature. The liquid products were filtered with a 0.22 μm filter membrane for chromatographic measurements. The precipitate was washed with distilled water and absolute ethanol several times to remove impurities for determination.

2.3 Product Analyses

The solid samples analyses were determined by X-ray diffraction (XRD) on the Bruker D8 Advance XRD equipped with $\text{Cu } K\alpha$ radiation. The scanning rate of $0.1^\circ\cdot\text{s}^{-1}$ and 2θ range from 20° to 90° were set with 40 kV accelerating voltage and 30 mA flux. The diffraction patterns were

compared with reference data of ICDD PDF-2. Notably, the reduction rate of metal oxides was calculated based on the XRD quantitative analyses using software TOPAS 4.2.³² The fundamental parameter approach (FPA) was adopted which involved the geometric and unit-specific parameters.³³ The solid particle size and morphology were measured on an EyeTech Particle Size Analyzer and scanning electron microscopy (SEM) of Philips XL30 D6716, respectively.

The liquid samples analysis was conducted by high-performance liquid chromatography (HPLC) measurement on Agilent 1260 serials equipped with UV-Vis detector. Two Shodex RSpak KC-811 columns were used in series and mobile phase was 2 mM HClO₄ with a flow rate of 1 mL·min⁻¹. Liquid samples determination was also analyzed by gas chromatography-mass spectrometry (GC-MS) on Agilent 7890A GC system with a 5795C inert MSD. A HP-INNOWax capillary column with dimensions of 30 m × 250 μm × 0.25 μm was used for separation of samples. Details on the test conditions of HPLC and GC-MS were provided elsewhere.^{25, 34}

3. Results and Discussion

3.1 Reduction of metal oxides

Complete reduction of CuO and NiO

XRD analyses (Figure S1-S4) showed not only glucose but also cellulose can directly reduce CuO and NiO to the corresponding elemental metal powders under alkali hydrothermal conditions. The optimized reaction parameters were listed in Table 1. Generally, glucose is favorable to reduction than cellulose because of reduction of dissolution and hydrolysis procedures. However, a higher concentration of alkali (~0.4 M NaOH) can enhance the CuO reduction and significantly shorten the reaction time. Moreover, reduction of NiO needs higher concentration of alkali and longer reaction time than that of CuO. It is probably due to lower leaching of Ni and higher value of ΔG_{red}

(Gibbs free energy for reduction of metal oxide).³⁵ As to the size of obtained Cu and Ni powder, both measurements from laser particle size analyzer and SEM indicated smaller and more uniform particles were formed and the diameters were around 500 nm.³⁰⁻³¹

Table 1. Reaction conditions for complete reduction of CuO and NiO.

Feedstock	CuO	NiO
Glucose^a	250 °C, 3 h, 0.1 M NaOH, 0.4 M glucose ,0.24 M CuO	250 °C, 4 h, 5 M NaOH, 0.4 M cellulose, 0.2 M NiO
Cellulose^a	250 °C, 1.5 h, 0.4 M NaOH, 0.4 M cellulose, 0.24 M CuO	250 °C, 4.5 h, 5 M NaOH, 0.4 M cellulose, 0.2 M NiO

^a Both the concentration of glucose and cellulose were 0.4 M in this study.

While metal oxides were reduced to metals, glucose and cellulose was oxidized to low molecular weight organics. The liquid samples were tested by GC-MS and HPLC as shown in Figure S5-S12. No matter reduction of CuO or NiO with glucose or cellulose, organic acids such as lactic acid, acetic acid, acrylic acid and formic acid and cyclopentanone derivatives formed after hydrothermal treatment. The obvious difference between glucose and cellulose as reductant is dihydric alcohols significant formation with cellulose, especially for NiO reduction. Notably, these dihydric alcohols play an important role in the metal oxides reduction and experimental results will be discussed in the mechanism study section.

Partial reduction of Fe (III), Mn (IV), Co (III), Pb (IV) compounds

To examine the feasibility to reduction of metal oxides with carbohydrates, we newly conducted a series of experiments with other general metal oxides and glucose under optimal conditions referred to reduction of CuO and NiO. First, several iron oxides and hydroxides, Fe₂O₃, Fe₃O₄, Fe(OH)₂ and FeO were reacted with glucose in the absence and presence of alkali. The results showed about 70% of Fe₂O₃ was reduced to Fe₃O₄ with 2.5 M NaOH at 250 °C for 6 h (Figure 1,

quantitative calculation based on TOPAS software). However, no matter increasing the reaction time or alkali concentration, Fe (II) compounds cannot further reduced to elemental Fe. In the previous work, Fe_2O_3 can be reduced completely to Fe with glycecol,³⁶ indicating the influence of reaction medium to metal oxides reduction. Although no Fe formed with glucose, Fe_3O_4 obtained facilitates magnetic separation and has potential application in separating associated metals in hydrometallurgy process. Subsequently, alkali hydrothermal reduction of MnO_2 was investigated. As illustrated in Figure 2, main product was Mn_3O_4 after the reaction with NaOH at 250 °C for 3 h. The following research on Co_3O_4 reduction showed almost all Co_3O_4 was reduced to CoO after 6 h with 1 M NaOH, indicating reduction of Co (III) is easier than that of Mn (IV) and Fe (III) in alkali solution. For PbO_2 reduction with glucose, as seen in Figure S13, several Pb (II) compounds were obtained with 1 M NaOH for 6 h. These results demonstrated a possibility of selective reduction of mixed metal oxides by facile adjusting the alkali concentration and magnetic separation. Experiments with true metal oxides ores containing various metals such as Fe, Ni, Cu, Co and Mn are in progress.

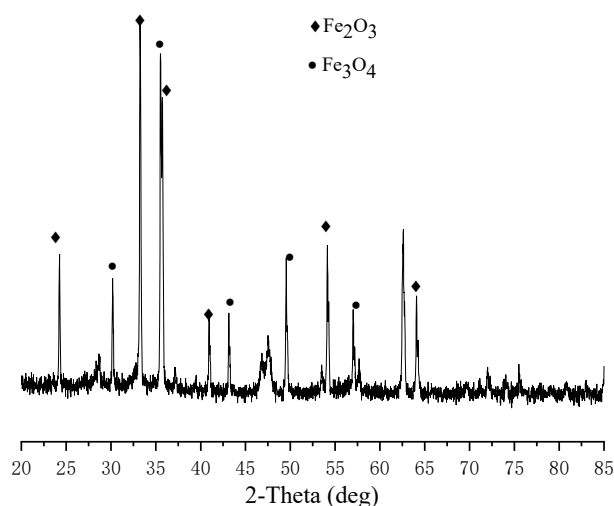


Figure 1. XRD patterns of solid product after Fe_2O_3 reduction with glucose (250 °C, 6 h, 2.5 M NaOH, 0.4 M glucose, 0.2 M Fe_2O_3)

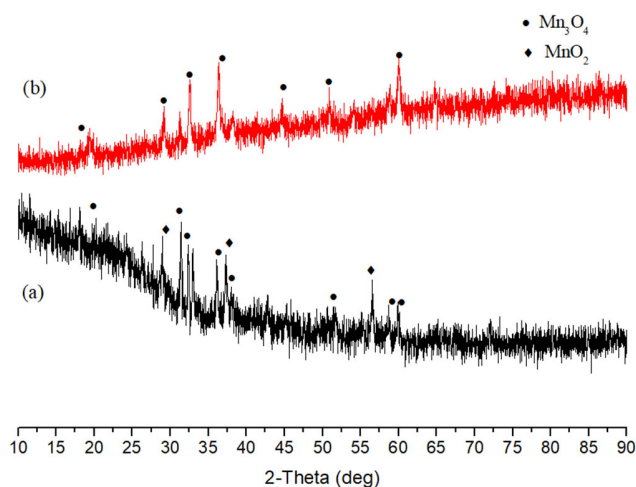


Figure 2. XRD patterns of solid products after reactions of 0.4 M glucose and 0.2 M MnO_2 without (a) and with (b) 2.5 M NaOH (250 °C, 3 h).

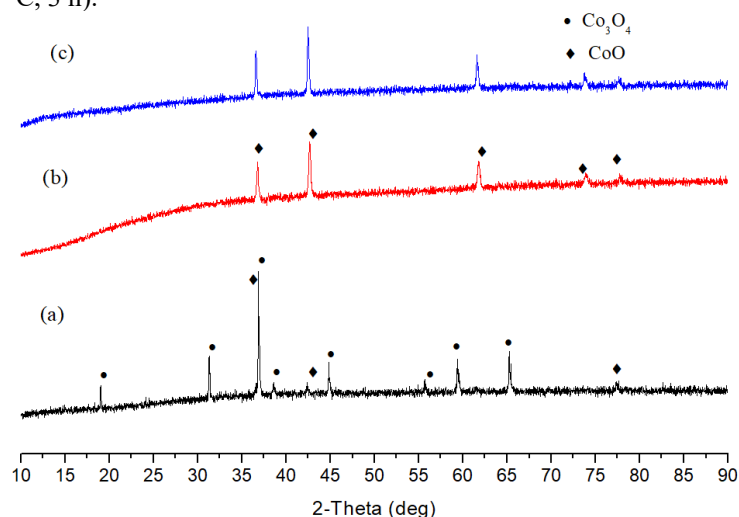


Figure 3 XRD patterns of solid products before (a) and after reactions of 0.4 M glucose and 0.2 M Co_3O_4 for 6 h (b) and 12 h (c) (250 °C, 1 M NaOH).

3.2 Reduction of metal salts

To examine the reduction performance of carbohydrate without alkali, salts of Cu, Ni and Fe were tested in the following experiments. Four Cu salts, CuSO_4 , CuCl_2 , $\text{Cu}(\text{NO}_3)_2$ and $\text{Cu}_2\text{P}_2\text{O}_7$ were first studied with glucose at 160 °C and 250 °C. As shown in Figure 4 & 5, $\text{Cu}_2\text{P}_2\text{O}_7$ can be reduced to Cu at both temperatures. As to CuSO_4 , the lower temperature is favorable to CuSO_4 reduction due to sulfate decomposition at higher temperatures. On the contrary, a higher temperature benefits

the reduction of $\text{Cu}(\text{NO}_3)_2$. Further liquid samples analyses (Figure S16 & 17) showed there was oxalic acid after the reaction of $\text{Cu}(\text{NO}_3)_2$ with glucose. It is likely the CuC_2O_4 formation at lower temperature prevents the complete reduction of $\text{Cu}(\text{NO}_3)_2$. An unexpected find is little reduction for CuCl_2 under these conditions, indicating the significant influence of anions on the Cu^{2+} reduction.

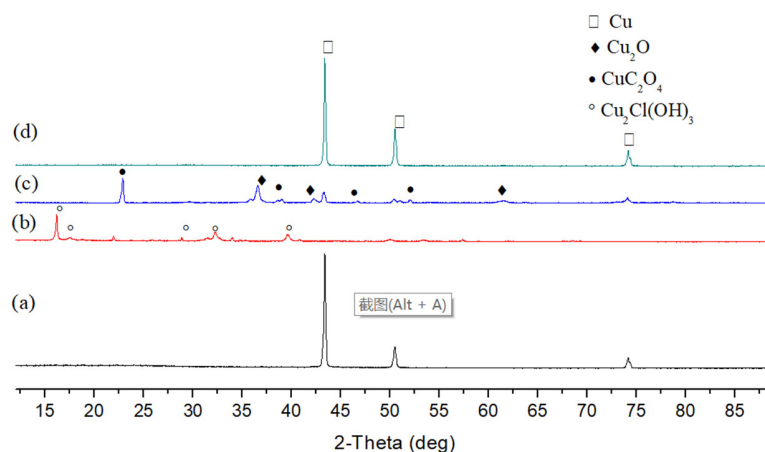


Figure 4. XRD patterns of solid products after the reduction of CuSO_4 (a), CuCl_2 (b), $\text{Cu}(\text{NO}_3)_2$ (c) and $\text{Cu}_2\text{P}_2\text{O}_7$ (d) by glucose without NaOH (160 °C, 6 h).

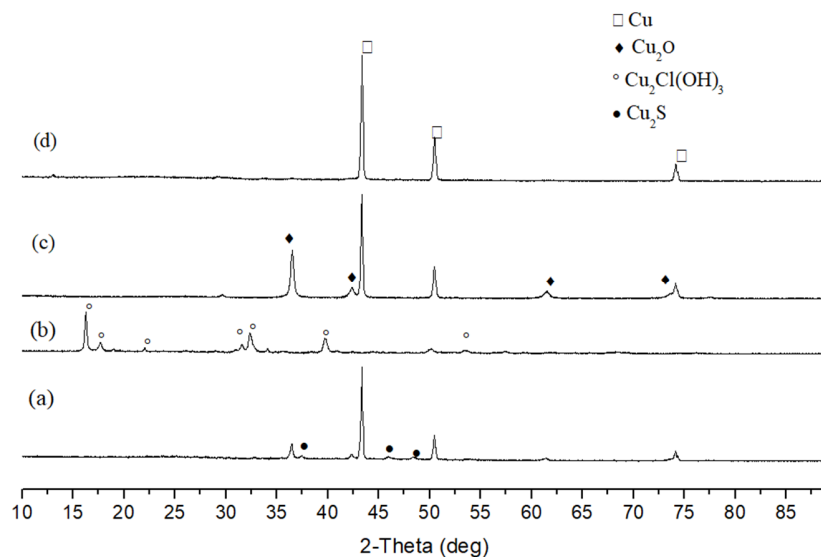


Figure 5 XRD patterns of solid products after the reduction of CuSO_4 (a), CuCl_2 (b), $\text{Cu}(\text{NO}_3)_2$ (c) and $\text{Cu}_2\text{P}_2\text{O}_7$ (d) by glucose without NaOH (250 °C, 3 h).

In the subsequent experiments with Ni salts, NiCl_2 , NiSO_4 and $\text{Ni}(\text{Ac})_2$ were selected. No obvious Ni or Ni compounds peaks occurred in XRD patterns, indicating glucose cannot direct reduce Ni salts. For Fe salts reduction, no matter $\text{Fe}(\text{NO}_3)_3$ or FeCl_3 , the major solid phase was Fe_3O_4 which was partially reduced product. Hence, the reduction performance of glucose to metal salts without alkali is universally weaker than that to metal oxide with alkali under hydrothermal conditions.

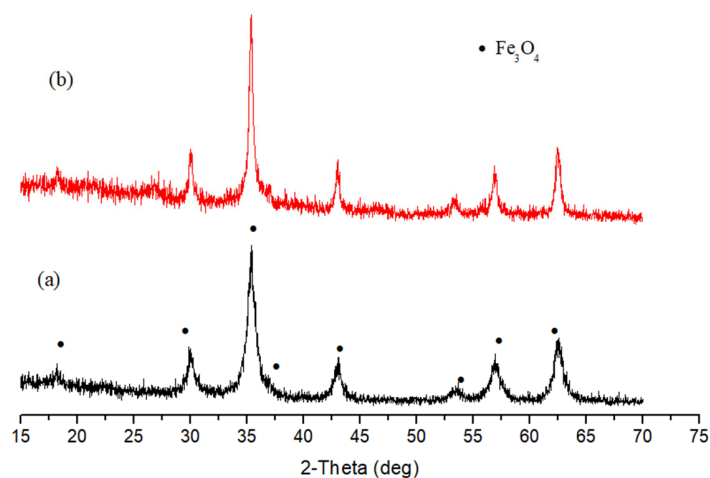


Figure 6 XRD patterns of solid products after reduction of $\text{Fe}(\text{NO}_3)_3$ (a) and FeCl_3 (b) by glucose, respectively (250 °C, 3 h).

3.3 Possible pathway of metal oxides/salts reduction

Metal stability under alkali hydrothermal conditions

In the study on CuO reduction with carbohydrates, we found excessively high concentration of alkali is unfavorable to Cu formation. The reason is probably that Cu is unstable in the hot alkali solution. To verify this conjecture, we examined the stability of Cu, Ni, Fe and Mn under alkali hydrothermal conditions. As shown in Figure 7a, Cu is stable with 0.4 M NaOH at 250 °C for 1.5 h. However, as the NaOH concentration increased to 1 M, Cu_2O (12.5 wt%) and CuO (3.7 wt%) were obtained (Figure 7b). Cu oxides formation may attribute to Cu react with alkali, followed by

dehydration. Unlike Cu, Ni phase was not changed with NaOH no matter 0.4 M or 5 M (Figure S18). Fe displayed unstable even without alkali at 250 °C and a 30.4 wt% yield of Fe_3O_4 was achieved. As addition of 1M NaOH, Fe oxidation rose sharply and Fe_3O_4 yield increased to 84.1 wt% (Figure 8). Mn is the most unstable metal in HTW among the tested materials. As illustrated in Figure 9, almost all Mn transformed to Mn_3O_4 without alkali and MnO_2 with 2.5 M NaOH, respectively. Therefore, the metal stability under alkali hydrothermal conditions should be paid special attention in the alkali choice.

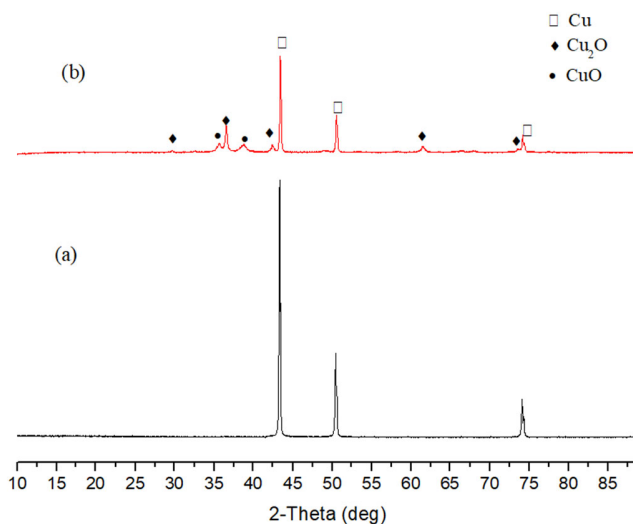


Figure 7 XRD patterns of solid products after reactions of Cu with 0.4 M (a) and 1 M (b) NaOH (250 °C, 1.5 h).

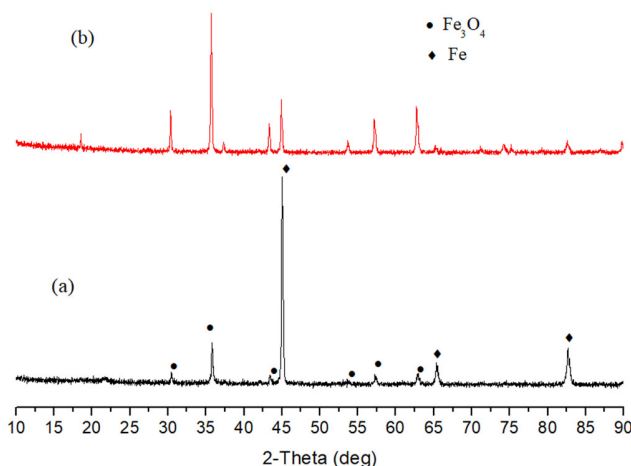


Figure 8 XRD patterns of solid products after reactions of Fe and water in the absence (a) and presence of (b) 1 M NaOH (250 °C, 6 h).

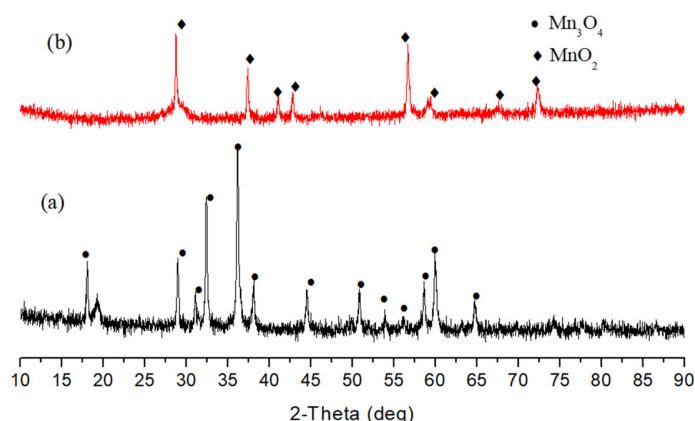


Figure 9 XRD patterns of solid products after reactions of Mn and water without (a) and with (b) 2.5 M NaOH (250 °C, 3 h).

Role of intermediates of carbohydrate decomposition

Lactic acid is one of the major liquid products under alkali treatment of carbohydrates. We have proved lactic acid can reduce CuO to Cu in the acid solution,³⁰ whereas the reduction effect was limited in the alkali environment. Further study on NiO reduction with glucose showed no reductive products formed. Through analyzing the chromatograms of the samples before and after reactions, dihydric alcohols, ethylene glycol (EG), propylene glycol (PG) and butylene glycol (BG) ordinarily existed in the liquid samples, especially with cellulose as reductant. Experiments of these three dihydric alcohols and NiO with NaOH were carried out and the XRD results (Figure S19) indicated almost all NiO was converted to Ni for 3 h at 250 °C. Analyses for liquid samples of EG experiment (Figure S20) showed glycolic acid formation except formic acid and lactic acid. Obviously, glycolic acid is the oxidized product of EG, also demonstrating EG engaged in the reduction.

Proposed pathway of metal oxides/salts reduction

As to metal oxides reduction, polysaccharides initially hydrolyzed to reductive monosaccharides. The monosaccharides such as glucose and fructose were coordinated with metal ions leaching from metal oxides and converted to low molecular weight organic acids. Meanwhile, metals ions were reduced via coordination-reduction reaction. Not only carbohydrates but also their decomposed intermediates such as dihydric alcohols and lactic acid participate in the reduction of metal oxides.

For metal salts reduction with carbohydrates, previous reports proposed carbohydrates were oxidized to carbon dioxide and not involved detail pathway for metal ions reduction.^{6, 21-22} In fact, carbohydrates were usually partially oxidized no matter in the hot acid or alkali solution. Analyses of liquid samples with Cu salts (Figure S16 & 17) showed some reductive organic intermediates such as lactic acid and oxalic acid from glucose partial oxidization were found. Although no direct evidence for coordination compounds during the transition state, we believe coordination-reduction reaction plays a crucial role in metal salts reduction with carbohydrate as reductant.

4. Conclusions

In this study, we compared the reduction ability of glucose and cellulose under alkali hydrothermal and studied their performance on metal salts and other metal oxides except CuO and NiO reduction. The results showed reductive ability of cellulose was enhanced under alkali hydrothermal conditions. One-pot direct reduction of metal oxides with carbohydrates under alkali hydrothermal conditions is a feasible and efficient strategy to metal compounds reduction. The reduction pathway study showed not only carbohydrates but also decomposed intermediates can reduce metal oxides. This study may provide an alternative approach to metal preparation in hydrometallurgy.

ASSOCIATED CONTENT

Supporting Information

The following files are available free of charge.

XRD patterns of solid products (Figure S1-4, S18-19, PDF)

HPLC and GC-MS chromatograms of liquid products (Figure S5-17, S20, PDF)

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

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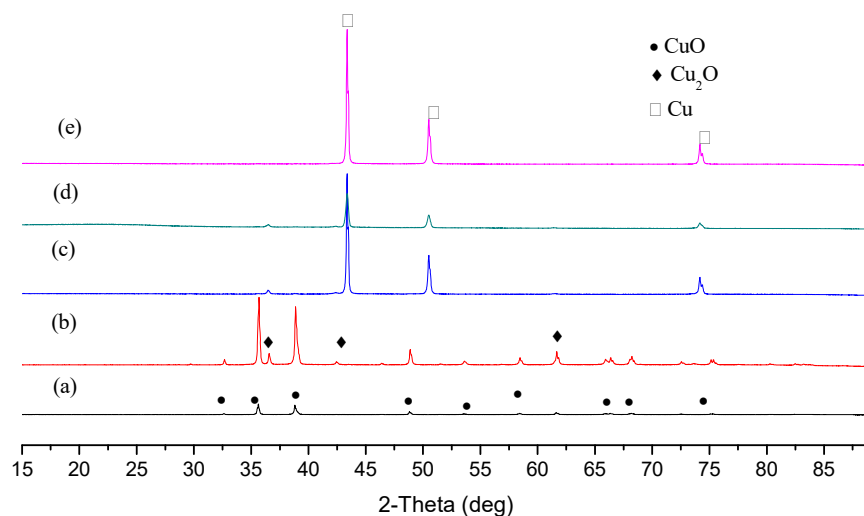


Figure S1 XRD patterns of solid products after reactions of glucose and CuO for 3 h at different temperatures: (a) CuO; (b) 150 °C, 0.4 M NaOH; (c) 220 °C, 0.4 M NaOH; (d) 250 °C, without NaOH; (e) 250 °C, 0.4 M NaOH

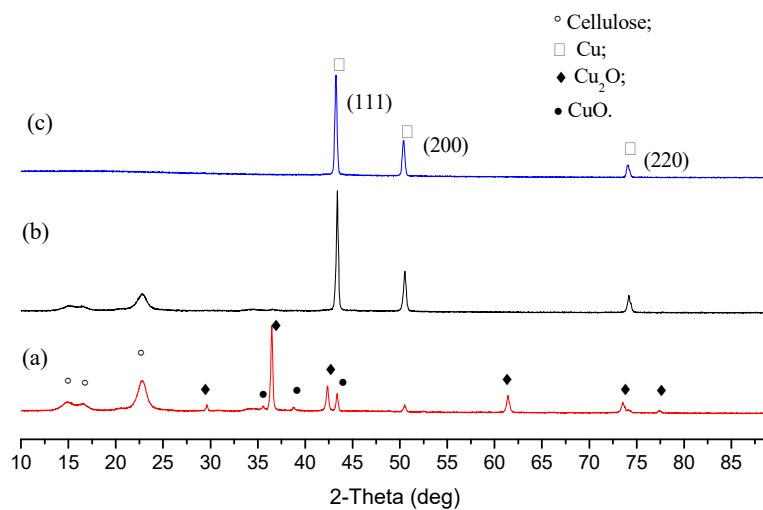


Figure S2 XRD patterns of solid products after reactions of cellulose and CuO with (a) 220 °C, 0.4 M NaOH, 1.5 h; (b) 250 °C, 0.4 M NaOH, 1.5 h; (c) 250 °C, without NaOH, 3 h.

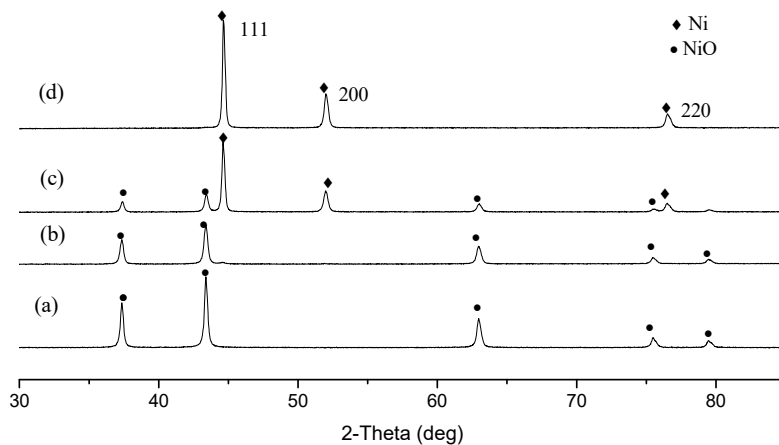


Figure S3 XRD patterns of solid products after reactions of glucose and NiO with different reaction conditions: (a) 250 °C, without NaOH, 6 h; (b) 220 °C, 2.5 M NaOH, 6 h; (c) 250 °C, 2.5 M NaOH, 4 h; (d) 250 °C, 5 M NaOH, 4 h.

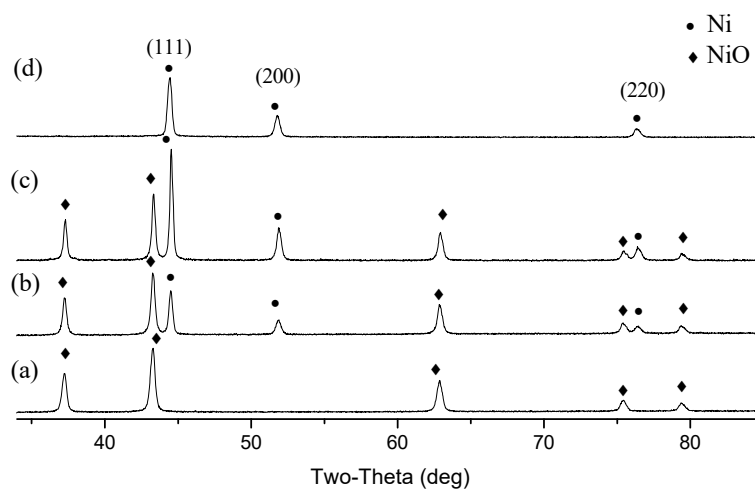


Figure S4 XRD patterns of solid products after reactions of cellulose and NiO at 250 °C ((a) without NaOH, 6 h; (b) NaOH 2.5 M, 3 h; (c) NaOH 5 M, 3 h; (d) NaOH 5 M, 4.5 h).¹

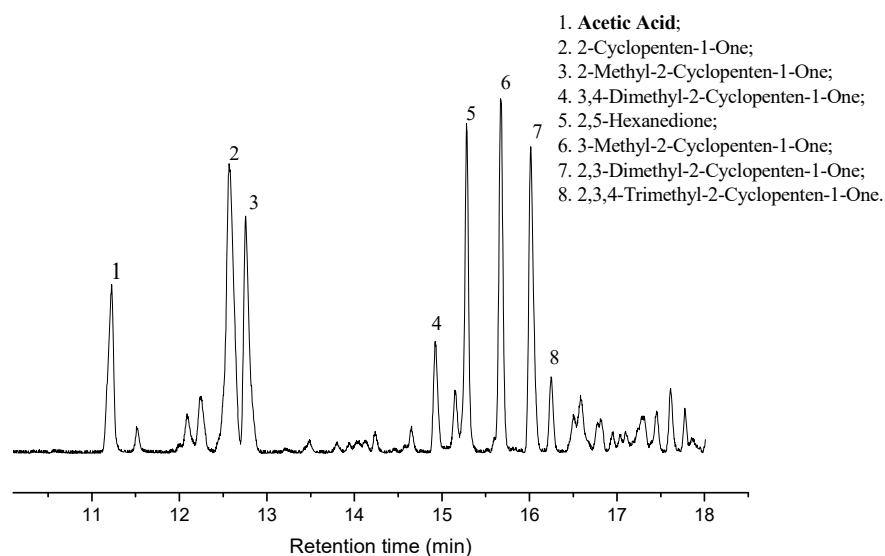


Figure S5 GC-MS chromatogram of the sample after the reaction of glucose and CuO (250 °C, 0.4 M NaOH, 3 h).

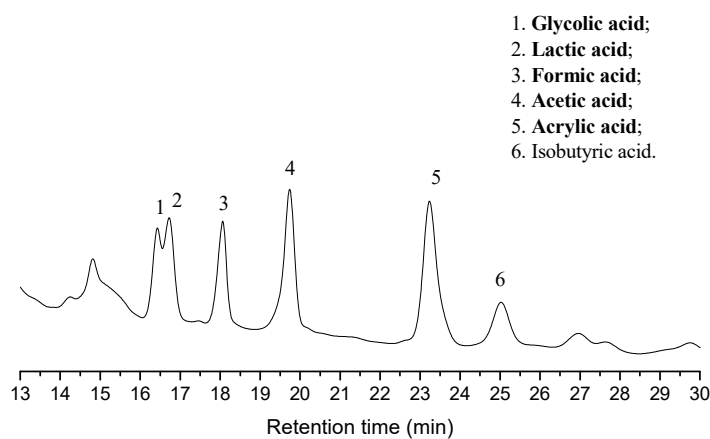


Figure S6 HPLC chromatogram of the liquid sample after the reaction of glucose and CuO (250 °C, 0.4 M NaOH, 3 h).

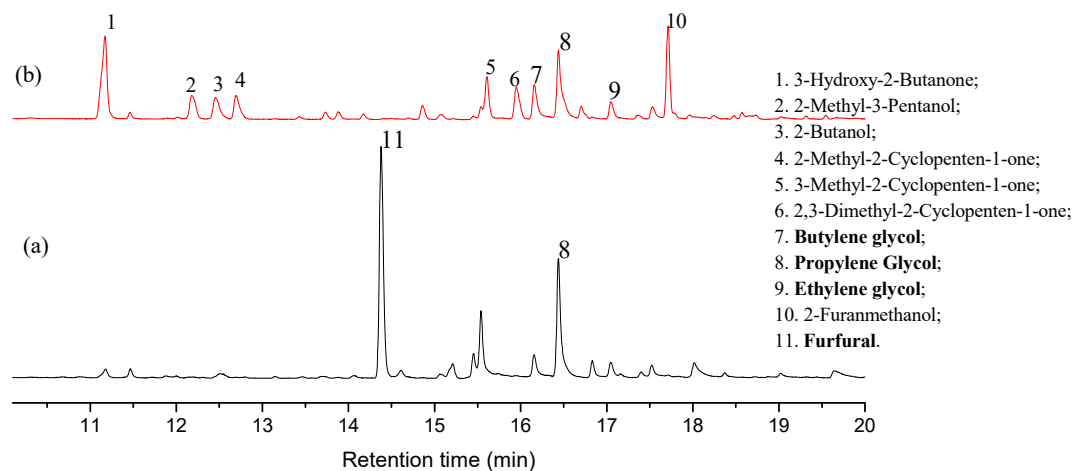


Figure S7 GC-MS chromatograms of samples after reactions of cellulose and CuO without (a) and with 0.4 M NaOH (b) (250 °C, 1.5 h).

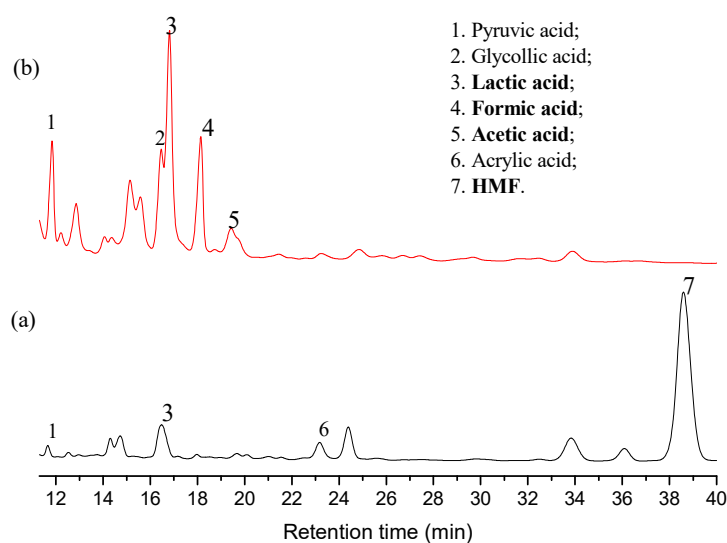
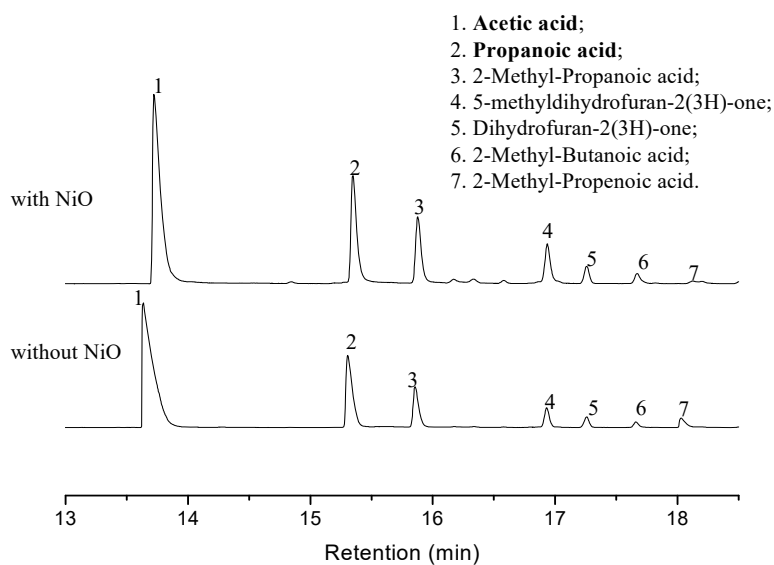
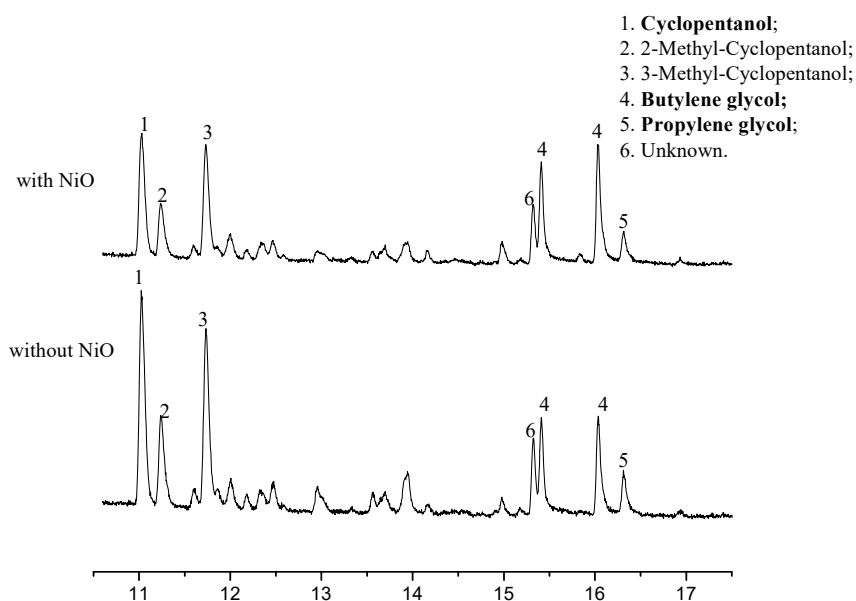


Figure S8 HPLC chromatograms of liquid samples after the reaction of cellulose and CuO in the absence (a) and presence (b) of 0.4 M NaOH (250 °C, 1.5 h).



(a)



(b)

Figure S9 GC-MS chromatograms of samples with (a) adjustment of pH by using HCl and (b) without adjustment of pH after the reaction of glucose with and without NiO (250 °C, 5 M NaOH, 4 h).

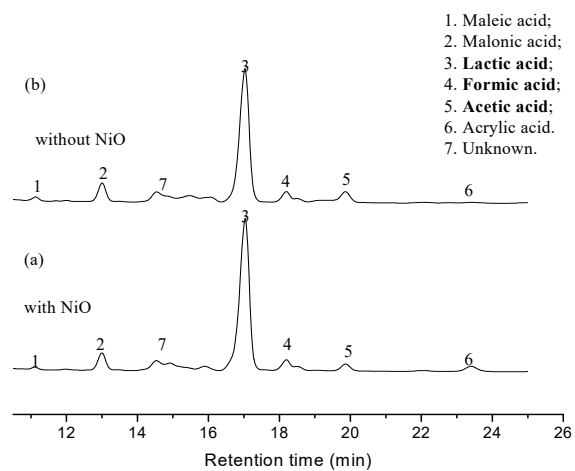
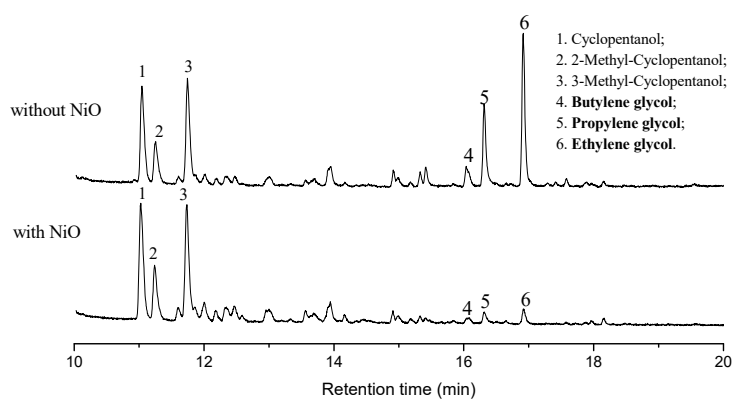
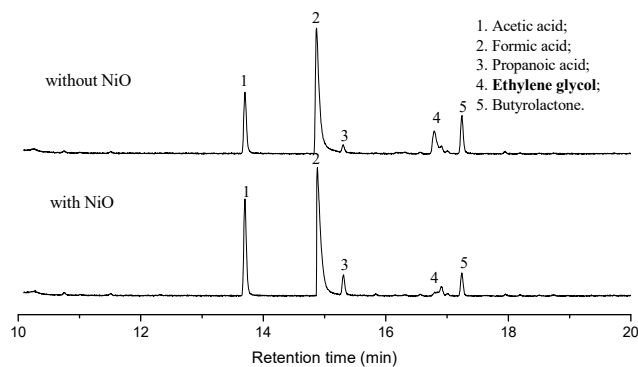


Figure S10 HPLC chromatograms of liquid samples after the reaction of glucose with (a) and without (b) NiO (250 °C, 5 M NaOH, 4 h).



(a)



(b)

Figure S11 GC-MS chromatograms of samples without (a) and with (b) adjustment of pH using HCl after the reaction of cellulose in the presence and absence of NiO (250 °C, 5 M NaOH, 4.5 h).¹

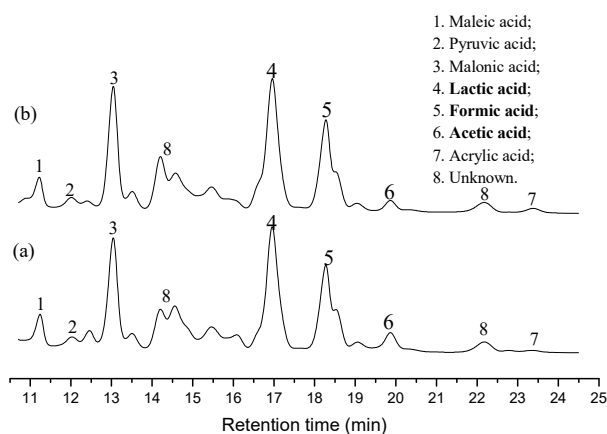


Figure S12 HPLC chromatograms of liquid samples after reactions of cellulose in the presence (a) and absence (b) of NiO (250 °C, 5 M NaOH, 4.5 h).¹

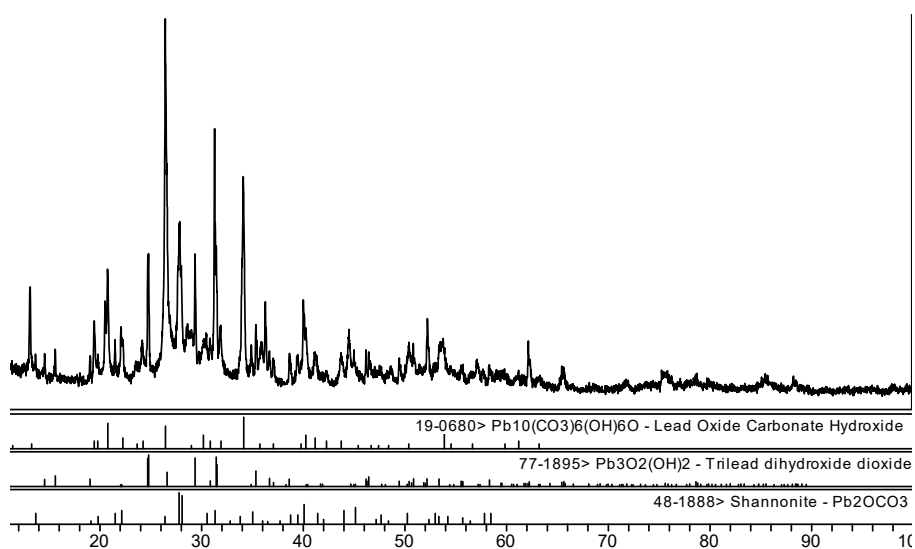


Figure S13 XRD patterns of solid products after the reaction of 0.4 M glucose and 0.2 M PbO₂ (250 °C, 1 M NaOH, 6 h).

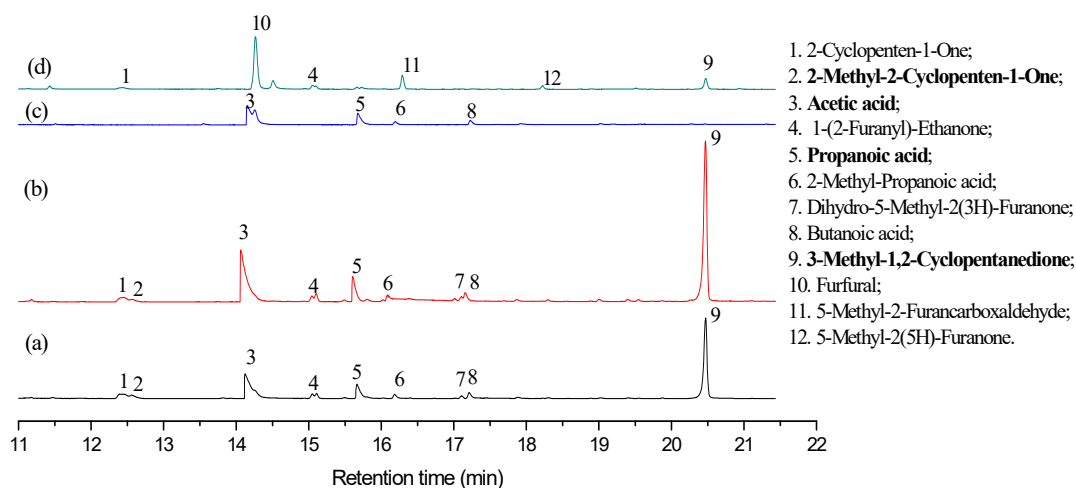


Figure S14 GC-MS chromatograms of liquid samples after the reduction of CuSO_4 (a), CuCl_2 (b), $\text{Cu}(\text{NO}_3)_2$ (c) and $\text{Cu}_2\text{P}_2\text{O}_7$ (d) by glucose (160 °C, 6 h).

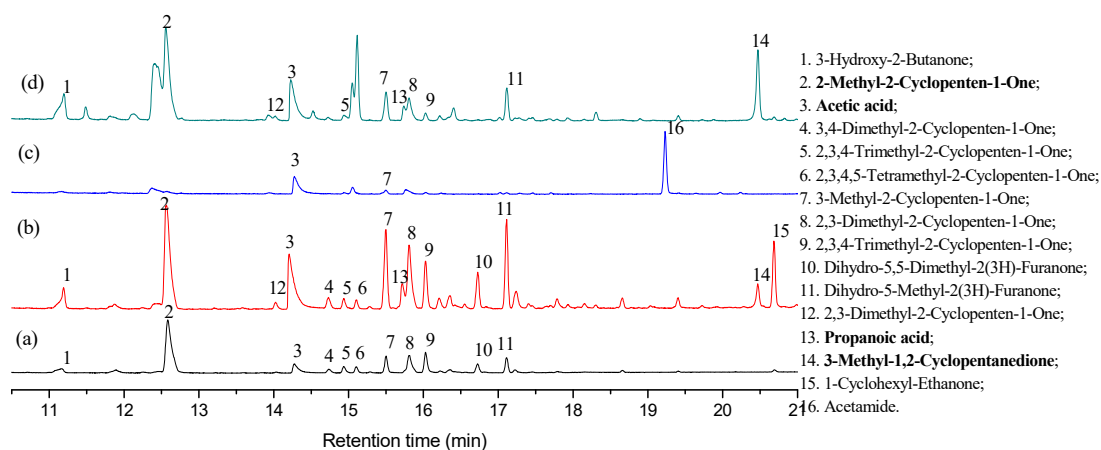


Figure S15 GC-MS chromatograms of liquid samples after the reduction of CuSO_4 (a), CuCl_2 (b), $\text{Cu}(\text{NO}_3)_2$ (c) and $\text{Cu}_2\text{P}_2\text{O}_7$ (d) by glucose (250 °C, 3 h).

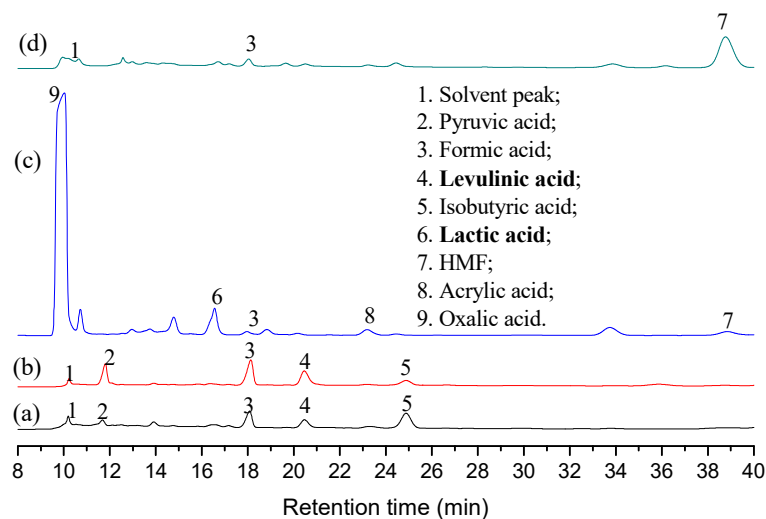


Figure S16 HPLC chromatograms of liquid samples after the reduction of CuSO_4 (a), CuCl_2 (b), $\text{Cu}(\text{NO}_3)_2$ (c) and $\text{Cu}_2\text{P}_2\text{O}_7$ (d) by glucose (160 °C, 6 h).

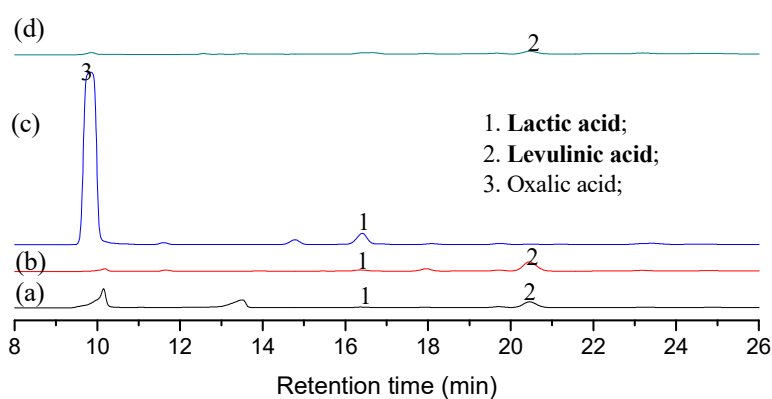


Figure S17 HPLC chromatograms of liquid samples after the reduction of CuSO_4 (a), CuCl_2 (b), $\text{Cu}(\text{NO}_3)_2$ (c) and $\text{Cu}_2\text{P}_2\text{O}_7$ (d) by glucose (250 °C, 3 h).

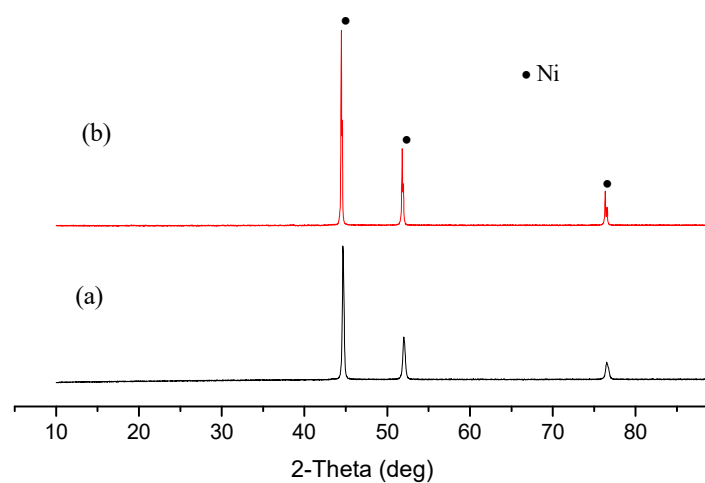


Figure S18 XRD patterns of solid products after the reaction of Ni with 0.4 M (a) and 5 M (b) NaOH (250 °C, 3 h).

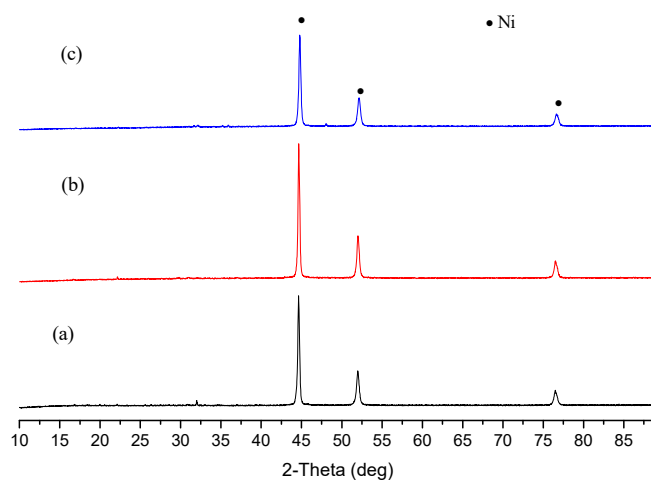


Figure S19 XRD patterns of solid products after reduction of NiO by ethylene glycol (EG) (a), propylene glycol (PG) (b), butylene glycol (BG) (c) (250 °C, 5 M NaOH, 3 h).

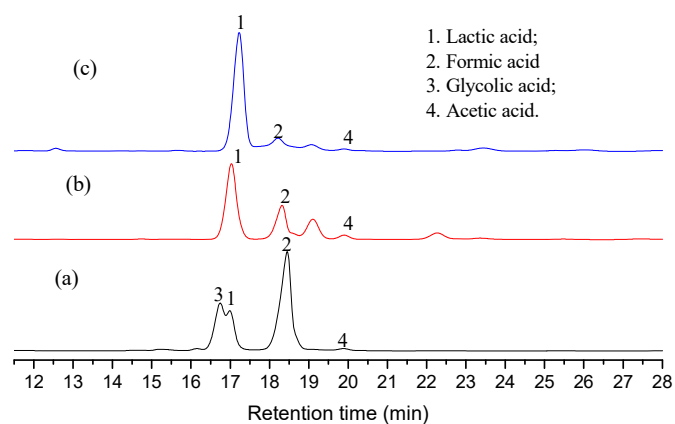


Figure S20 HPLC chromatograms of liquid samples after reduction of NiO by EG (a), PG (b), BG (c) (250 °C, 5 M NaOH, 3 h).

References:

1. Yao, G.; Zeng, X.; Li, Q.; Wang, Y.; Jing, Z.; Jin, F., Direct and highly efficient reduction of nio into ni with cellulose under hydrothermal conditions. *Ind. Eng. Chem. Res.* **2012**, *51* (23), 7853-7858.