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CRITICAL REVIEW
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Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends?

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ARTICLE

Highly selective photocatalytic oxidation of biomass-derived chemicals to carboxyl compounds over Au/TiO_2

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Baowen Zhou,[a,b] Jinliang Song,[a,]* Zhanrong Zhang,[a] Zhiwei Jiang,[a] Pei Zhang[a] and Buxing Han[a,b,]*

Highly selective transformation of biomass-derived chemicals into value-added chemicals is of great importance. In this work, selective photoxidation of various biomass-derived chemicals, including ethanol, glucose, xylose, 2-furaldehyde, 5-hydroxymethyl-2-furfural, and furfuralcohol to the corresponding carboxyl compounds were studied using atmospheric air as the oxidant at ambient temperature. It was found that the reactions could be carried out efficiently over Au nanoparticles (AuNPs) supported on TiO_2 (AuNPs/TiO_2) under both ultraviolet (UV) and visible light in Na_2CO_3 aqueous solution. At the optimized conditions, the selectivities for desired products were higher than 95% for all the reactions. Detailed studies indicated that the surface plasmon resonance of AuNPs and the band-gap photoexcitation of TiO_2 were responsible for visible-light-responding and UV-light-responding activity, respectively. Na_2CO_3 acted as the promoter for the visible-light-induced oxidation and the inhibitor of reactive oxygen species with strong oxidation power under UV light.

Introduction

Efficient transformation of abundant and renewable biomass to fuels, value-added chemicals and materials has attracted much attention.[1-4] Oxidation of biomass and its derivatives can provide a wide variety of value-added chemicals such as formic acid,[5] acetaldehyde,[6] gluconic acid,[7] lactic acid,[8] oxalic acid,[9] and arabinose,[10] *etc*. However, highly selective oxidation of biomass and its derivatives to specific valuable compounds, especially to carboxyl compounds, which are important intermediates to produce food additives, pharmaceuticals and fine chemicals, is still challenging during thermal catalysis due to the harsh conditions and the multifunctional structure of biomass. Although photocatalysis provides a mild route for biomass conversion, controlling selectivity in photocatalytic oxidation of biomass is also quite difficult because semiconductor-based photocatalysis generally is "non-selective",[11] especially using water as the solvent.[12] Currently, TiO_2-based materials are the most widely used catalysts in photocatalytic oxidation of biomass, ascribing to their chemical and thermal stability, low toxicity and cost, and resistance to photocorrosion.[13] But the low photocatalytic selectivity significantly limited the application of TiO_2-based photocatalysts due to the formation of reactive oxygen species with strong oxidation power (*e.g.* hydroxyl radical). Furthermore, UV light for photoactivating TiO_2 only accounts for *ca.* 4.5% of solar energy whereas visible light contributes to *ca.* 50%. Therefore, it is highly desirable to explore novel routes for highly selective oxidation of biomass to specific products by effective utilization of solar energy, especially for the production of carboxyl compounds from biomass in water.

It is known that gold nanoparticle (AuNP) is an excellent visible-light-responding photocatalyst due to the surface plasmon resonance (SPR) effect.[14-16] Under the irradiation of visible light, AuNPs can also generate energetic or hot electrons and cause rapid heating themselves. These characteristics make AuNPs to be fascinating photocatalysts for selective photoxidation, including conversion of benzyl alcohols to aldehydes,[17] isopropanol to acetone,[18] and formaldehyde to carbon dioxide,[19] etc. In particular, these photoxidation processes over AuNPs did not involve the formation of reactive oxygen species with strong oxidation power (e.g. hydroxyl radicals), which are generally considered as "non-selective" species in photoxidation by causing the deep oxidation of the substrates. Therefore, AuNPs have great potential for selective photoxidation of biomass and its derivatives to carboxyl compounds by the SPR effect, which has rarely been reported.

Herein, we demonstrate that the hybrid of AuNPs and TiO_2 was very selective and active for oxidation of various

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[a] *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190 (China)*
E-mail: songjl@iccas.ac.cn; hanbx@iccas.ac.cn.
[b] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

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biomass-derived feedstocks to corresponding carboxyl compounds under both UV and visible light in water using atmospheric air as the oxidant. In this approach, the band-gap photoexcitation of TiO_2 and the SPR effect of AuNPs were simultaneously used to enhance the photoxidation, showing an efficient protocol for utilizing solar energy with wide-range wavelength. Additionally, the addition of bases, such as Na_2CO_3, could enhance the reaction by acting as the promoter of visible-light-induced oxidation and the inhibitor of reactive oxygen species with strong oxidation power under UV light.

Results and discussion

Catalytic activities of different catalysts

Selective oxidation of ethanol to acetic acid can be considered as an important reaction in biomass transformation because ethanol can be produced from the fermentation of inedible biomass. However, current routes for the production of acetic acid from ethanol suffer from low selectivity and/or harsh reaction conditions.[20,21] Herein, we selected photoxidation of ethanol to acetic acid as a model reaction (Scheme S1). Initially, catalytic activity of various catalysts was examined by employing atmospheric air as the oxidant at ambient temperature in water (Fig. 1). As shown in Fig. 1a, the amount of acetic acid yielded from visible-light-driven ethanol oxidation over AuNPs/TiO_2 and AuNPs/ZrO_2 were about 5 times and 3.5 times larger than that obtained when the reaction was thermally performed in dark. Obviously, the reaction did not occur in dark or upon visible light irradiation over TiO_2 and ZrO_2 without AuNPs. Diffuse reflectance UV-Vis spectra of the catalysts (Fig. 1b) showed that both AuNPs/TiO_2 and AuNPs/ZrO_2 exhibited obvious absorption peak at *ca.* 550 nm while the bare supports showed no absorption at the same wavelength. The absorption peak in visible light range is attributed to the SPR effect of the AuNPs,[22] which can photocatalyze the aerobic oxidation of ethanol to acetic acid. Meanwhile, action spectrum in Fig. 1c demonstrated that there was an optimal value of catalytic activity for AuNPs/TiO_2 at the strongest absorption of 550 nm, which was consistent with the SPR intensity. These results suggested that visible-light-responding activity resulted from the SPR effect of AuNPs. Furthermore, TEM and XPS analysis showed that the supports affected the diameter distributions (Fig. S1) and the surface chemical states (Fig. S2) of the AuNPs. As shown in Figs. S1b and 1d, compared with AuNPs/ZrO_2, AuNPs/TiO_2 had much less AuNPs with larger size (>5 nm), which was inactive for plasmonic photocatalysis.[18a] Meanwhile, the binding energy of Au 3d on TiO_2 shifted to lower energy region compared with that on ZrO_2 (Fig. S2), which was caused by that the stronger binding of AuNPs with the oxygen vacancies on TiO_2 than that on ZrO_2.[18] These might be the main reasons for the difference in catalytic activity between AuNPs/TiO_2 and AuNPs/ZrO_2 under visible light. Additionally, the loading amount of AuNPs significantly affected the activity of plasmonic photocatalysis (Fig. S3). It was found that the catalytic activity increased with the AuNPs loadings (<3 wt%). However, the activity decreased at higher AuNPs loadings (>3 wt%) resulted from the increased amount of AuNPs with larger size (>5 nm, Fig. S4), which had been proved to be inactive for plasmonic photocatalysis.[18a]

In addition, bare TiO_2 exhibited catalytic activity under UV light, while the reaction did not occur over ZrO_2 under the same conditions because the energy of the incident light (350-400 nm) was higher than the band gap of TiO_2 (3.2 eV) but lower than that of ZrO_2 (5.0 eV). Meanwhile, although AuNPs supported on ZrO_2 adsorbed UV light *via* interband electron transitions (from 5d to 6 sp, an absorption peak at about 300 nm, Fig. 1b),[23] there was no obvious difference in catalytic activity of AuNPs/ZrO_2 under UV light and in dark (Fig. 1a). This ruled out the possibility that UV-light-responding activity was resulted from the interband electron transition of AuNPs. Therefore, UV-light-responding catalytic activity was due to the band-gap excitation of TiO_2, which was enhanced by loading AuNPs as electron sinks and catalytic sites.[24]

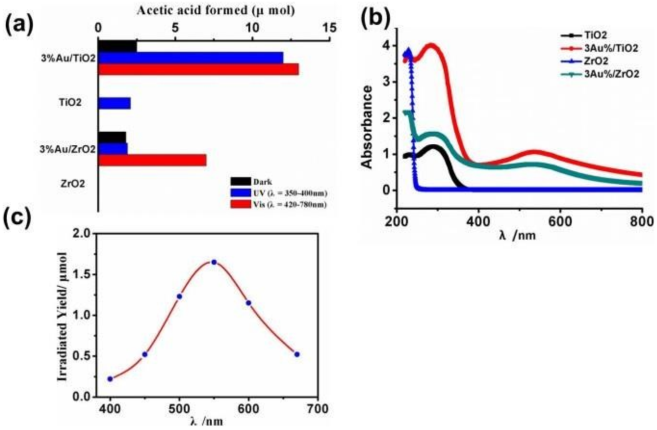

Fig. 1. (a) Amounts of acetic acid yielded from aerobic oxidation of ethanol over different catalysts. (b) Diffuse reflectance UV-Vis spectra of the catalysts. (c) Action spectrum of AuNPs/TiO_2 with 3 wt% Au for aerobic oxidation of ethanol to acetic acid, irradiated yield = total yield - thermal yield. Reaction conditions: ethanol, 100 μmol; water, 1 mL; illuminated area, 2 cm^2; Na_2CO_3, 100 μmol; temperature, 30 °C; time, 4 h; photocatalysts, 0.025 g. The scale of the errors in Fig. 1a for these experiments was ±0.2-1.0 μmol.

Influence of Na_2CO_3 on the reaction

It is well known that reactive oxygen species (*e.g.* hydroxyl radicals and singlet oxygen) with strong oxidation power can cause the deep oxidation of the substrates over TiO_2-based photocatalysts in water, and thus decrease the selectivity of the desired products. From Fig. 2a and 2b, it can be found that 6% of ethanol was converted to acetic acid with a selectivity of 40% without Na_2CO_3 under UV light, whereas the selectivity of acetic acid dramatically increased up to nearly 100% after adding Na_2CO_3. In our reaction system, hydroxyl radicals and singlet oxygen were obviously detected by electron spin resonance (ESR) analysis without Na_2CO_3 under UV light (Fig. 2c and 2d). After adding Na_2CO_3, hydroxyl radicals and singlet oxygen were evidently prohibited. Na_2CO_3 might serve as a sacrificial agent for the hydroxyl radicals and singlet oxygen. This may be the reason why the selectivity of acetic acid increased evidently after the addition of Na_2CO_3. It was different for the situation upon visible light. Ethanol was converted to acetic acid with high selectivity (nearly 100%) even without Na_2CO_3 because there were no hydroxyl radical (Fig. S5) and singlet oxygen observed in the system with/without Na_2CO_3 under visible light. However, the conversion of ethanol increased from 3% to 13% when the concentration of Na_2CO_3 increased from 0 to 0.1 mol/L. It indicated that Na_2CO_3 accelerated the transformation of ethanol upon visible light because basic environment was beneficial for the oxidation,[25] which will be discussed in the subsequent sections. However, further increasing of Na_2CO_3 concentration was not stimulative for the reaction.

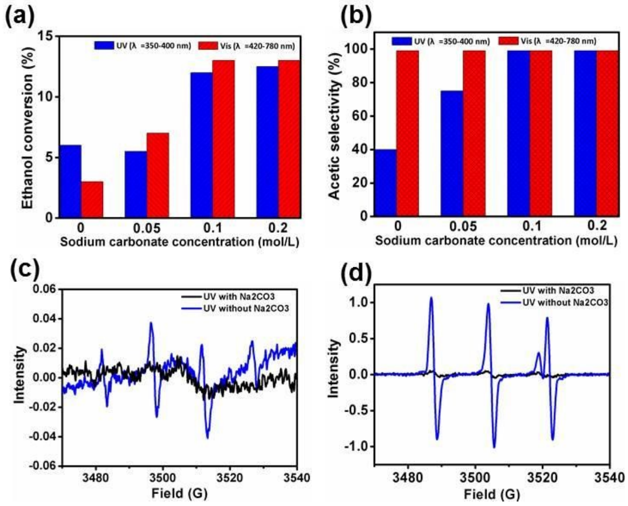

Fig. 2. Dependence of (a) the conversion of ethanol and (b) the selectivity of acetic acid on the concentration of Na_2CO_3. (c) ESR spectra of hydroxyl radicals in the aqueous suspension of AuNPs/TiO_2 under UV light with and without Na_2CO_3. (d) ESR spectra of singlet oxygen in the aqueous suspension of AuNPs/TiO_2 under UV light with and without Na_2CO_3. Reaction conditions: ethanol, 100 μmol; water, 1 mL; UV light (λ = 350-400 nm, 0.3 W/cm^2) or visible-light (λ = 420-780 nm, 0.3 W/cm^2); illuminated area, 2 cm^2; AuNPs/TiO_2 with 3 wt% Au, 0.025 g; temperature, 30 °C; time, 4 h. The scale of the errors for these experiments was ±1.2-2.9%.

Effect of different additives on the reaction

The influence of different additives was further examined (Table 1), and the results suggested that the conversion of ethanol and the selectivity of acetic acid strongly depended on the additives. Under visible light irradiation, ethanol was selectively converted into acetic acid (Entries 2, 5, 7 and 9) because hydroxyl radical was not generated with or without additives. In contrast, hydroxyl radicals were easily formed in acidic or neutral aqueous solution under UV light irradiation (Fig. S6). As a result, the selectivity of the reaction conducted with $NaNO_3$, without additive, and with HCl were only 57%, 40%, and 36%, respectively (Entries 1, 4 and 10). Additionally, a control experiment using $NaNO_3$ as the additive without AuNPs/TiO_2 under visible light (λ=420-780 nm) showed that there was no ethanol oxidation happened (Entry 3), which could exclude the possibility that $NaNO_3$ might act as the oxidant for the oxidation reaction. Furthermore, the addition of Na_2CO_3 and K_2CO_3 strongly inhibited the generation of hydroxyl radicals caused by UV light illumination, and thus the selectivity of acetic acid was improved significantly (Entries 6 and 8). In addition, the conversion of ethanol could be enhanced by Na_2CO_3 and K_2CO_3 under both UV and visible light. These results further proved that basic environment was favourable for achieving high activity and selectivity under both UV and visible light.

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Table 1. Influence of different additives on the reaction.[a]

Entry	Additive	Radiation	Ethanol Conv./%[b]	Acetic. Sel./%[b]
1	$NaNO_3$	UV	6 (±1.1)	57
2	$NaNO_3$	Vis	7 (±0.8)	99
3[c]	$NaNO_3$	Vis	0	--
4	NO	UV	6 (±1.2)	40
5	NO	Vis	3 (±0.4)	99
6	Na_2CO_3	UV	12 (±2.1)	>99
7	Na_2CO_3	Vis	13 (±1.9)	>99
8	K_2CO_3	UV	11 (±1.3)	99
9	K_2CO_3	Vis	12.5 (±0.7)	99
10	HCl	UV	12.5 (±2.2)	36
11	HCl	Vis	12.8 (±1.9)	85

[a]Reaction conditions: ethanol, 100 μmol; additive, 100 μmol; water, 1 mL; AuNPs/TiO_2 with 3 wt% Au, 0.025 g; UV light (λ=350-400 nm, 0.3 W/cm^2) or visible-light (λ=420-780 nm, 0.3 W/cm^2); time, 4 h; illuminated area, 2 cm^2; temperature, 30 °C. [b]Conv. = Conversion. Acetic. Sel. = Acetic acid Selectivity. The data in parentheses are the errors (%). [c]Without Au/TiO_2.

Effect of light intensity and reaction temperature

As expected, the light intensity affected the reaction significantly. As shown in Fig. 3a and 3b, the thermally catalytic activity was very low without light irradiation at ambient temperature. Both UV and visible light dramatically enhanced the reaction, and the yield of acetic acid increased with the enhancement of the light intensity. The contribution of visible light increased from 58% at 0.1 W/cm^2 to 81% at 0.3 W/cm^2 (Fig. 3a). Similar results were observed under UV light (Fig. 3b). These results confirmed that both UV and visible light improved the aerobic oxidation efficiency although the reactions were proceeded *via* different mechanisms.[26] Furthermore, although the contribution of thermal effect increased with increasing reaction temperature from 30 to 60 °C under both visible (Fig. 3c) and UV (Fig. 3d) light, the light irradiation still made the predominant contribution to the oxidation at ambient temperature. Additionally, control

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experiments showed that oxidation of ethanol did not obviously proceed in inert atmospheres (nitrogen and argon) within 4 hours upon visible light irradiation. By comparison, ethanol could be converted to acetic acid with considerable conversion (13%) and high selectivity of aceitic acid (>99%) in air under the same reaction conditions. These results evidenced that oxygen was the primary oxidant in the reaction.

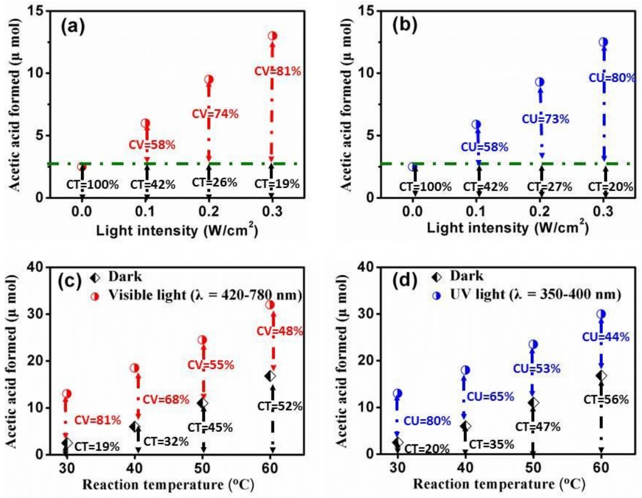
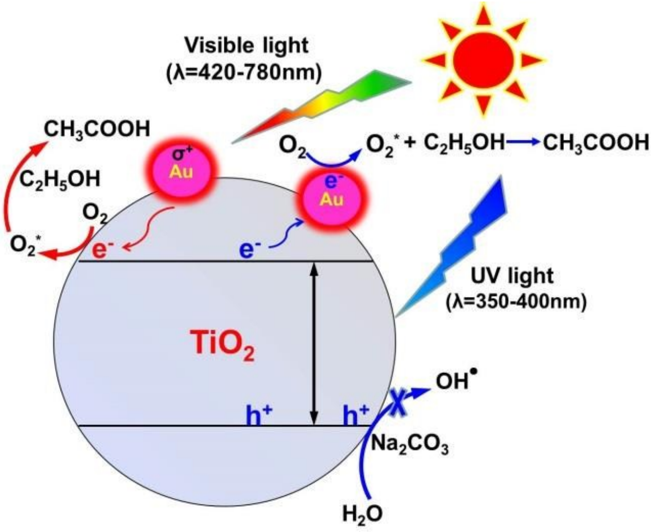


Fig. 3. The effect of visible (a) and ultraviolet light (b) intensity and reaction temperature (c and d) on the catalytic activity of AuNPs/TiO_2 for selective oxidation of ethanol to acetic acid. Reaction conditions: ethanol, 100 μmol; water, 1 mL; UV light (λ = 350-400 nm) or visible-light (λ = 420-780 nm) irradiation time, 4 h; illuminated area, 2 cm^2; AuNPs/TiO_2 with 3wt% Au, 0.025 g; Na_2CO_3, 100 μmol. CV = contribution of visible light, CU = contribution of UV light, CT = contribution of thermal effect. The scale of the errors for these experiments was ±0.5-1.4 μmol.

Mechanism

Based on the above experimental results and the related studies in literatures,[27-30] a possible mechanism for light-driven selective oxidation of ehthanol over AuNPs/TiO_2 by air is proposed and is shown schematically in Scheme 1. On one hand, upon visible-light irradiation, the oscillation of electrons on AuNPs was induced by the SPR effect. The photoactivated electrons were then released from AuNPs and injected into the conduction band of TiO_2,[31] which was further consumed to activate O_2. The activated oxygen participated in the oxidation process, and acetic acid was subsequently generated. On the other hand, when catalysts were irradiated by UV light, the electrons were photoexcited to the conduction band from the valence band of TiO_2 and trapped by the supported AuNPs. Oxygen was then activated by the photogenerated electrons over AuNPs and further involved in the oxidation of ethanol to acetic acid. Na_2CO_3 removed the active oxygen species with high oxidation potential under UV light, and thus resulting in the high selectivity.



Scheme 1. Proposed mechanism for light-induced highly selective oxidation of ethanol to acetic acid by air in water at ambient temperature.

Selective oxidation of other biomass-derived chemicals

We further explored the selective oxidation of a variety of biomass derivatives to the corresponding carboxylic acids and the results are summarized in Table 2. As discussed above, ethanol could be smoothly oxidized under visible-light or UV light to afford acetic acid in high yields (Entry 1). Meanwhile, glucose and xylose could be converted to gluconic acid and xylose acid with high selectivity, respectively (Entries 2 and 3). Under the same conditions, the required time for complete conversion of ethanol was longer than that for the equivalent glucose and xylose. The main reason is that the aldehyde group showed higher catalytic activity than the hydroxyl group. Furthermore, 2-furaldehyde and 5-hydroxymethyl-2-furfural, two important platform chemicals derived from biomass, could also be selectively oxidized in our catalytic system. 2-Furaldehyde could be directly transformed into 2-furoic acid with high selectivity without the cleavage of the furan ring (Entry 4). For 5-hydroxymethyl-2-furfural, the aldehyde group was preferentially oxidized rather than the hydroxyl group (Entry 5). A kinetics experiment indicated that the hydroxyl group could be further oxidized to yield 2,5-furandicarboxylic acid after the aldehyde group was completely converted (Fig. S7), however, the rate of hydroxyl oxidation was much slower than that of aldehyde oxidation. These results illustrated the higher activity of the aldehyde group. Furfuralcohol, another important bio-derivative, could be efficiently oxidized to foric acid through the process of the formation of furfuraldehyde as the intermediate (Entry 6).

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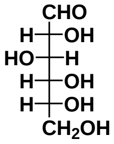
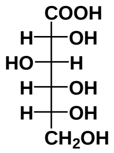
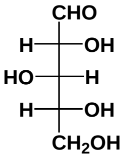
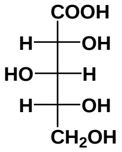
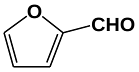
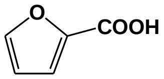
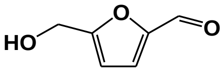
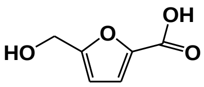
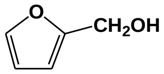
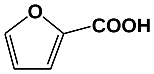
Table 2. UV and visible light for aerobic oxidation of various biomass-derivatives in water over AuNPs/TiO_2.[a]

Entry	Substrates	Time (h)	Conv./%[b]		Products	Yield/%[b]	
			UV	Vis		UV	Vis
1	CH_3CH_2OH	40	98	99	CH_3COOH	92 (±2.3)	99
2		4	>99	>99		94 (±1.2)	99
3		6	>99	>99		96 (±1.6)	98
4		8	>99	>99		92 (±0.9)	96 (±1.8)
5[c]		8	>99	>99		90 (±3.1)	95 (±2.4)
6		48	>99	>99		90 (±3.0)	93 (±2.1)

[a] Reaction conditions: substrates, 100 µmol; water, 1 mL; AuNPs/TiO_2 with 3 wt% Au, 0.025 g; UV light (λ = 350-400 nm, 0.3 W/cm^2) or visible light irradiation (λ = 420-780 nm, 0.3 W/cm^2); illuminated area, 2 cm^2; Na_2CO_3, 100 µmol; temperature, 30 °C. [b] Conv. = Conversion. The data in parentheses were the errors (%). [c] Na_2CO_3, 200 µmol.

Reusability of AuNPs/TiO_2

The reusability experiments indicated that AuNPs/TiO_2 could be used at least four cycles without obvious decrease in activity and selectivity for photoxidation of glucose to gluconic acid (Fig. 4). The TEM image of the recovered AuNPs/TiO_2 was similar with the fresh one (Fig. S8), further indicating AuNPs/TiO_2 was stable in our reaction system.

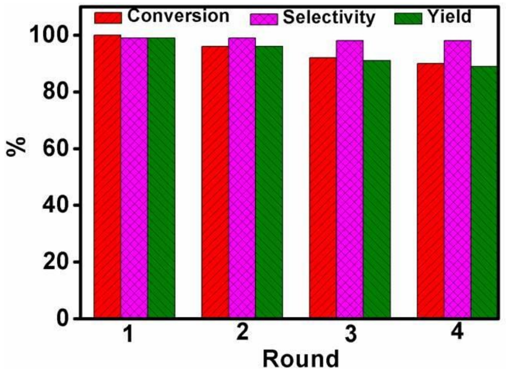


Fig. 4. Reusability of Au/TiO_2 for visible-light-induced selective oxidation of glucose by air in water at ambient temperature. Reaction conditions: glucose, 100 µmol; water, 1 mL; AuNPs/TiO_2 with 3 wt% Au, 0.025 g; visible light (λ = 420-780 nm, 0.3 W/cm^2) irradiation time, 4 h; Na_2CO_3, 100 µmol; temperature, 30 °C.

Conclusions

In summary, ethanol, glucose, xylose, 2-furaldehyde, 5-hydroxymethyl-2-furfural, and furfuralcohol can be oxidized effectively and very selectively to the corresponding carboxyl compounds using atmospheric air as the oxidant over AuNPs/TiO_2 under both UV and visible light in Na_2CO_3 aqueous solution. In the reaction, visible-light-responding activity mainly results from the surface plasmon resonance of AuNPs, and the band-gap photoexcitation of TiO_2 is the reason for the UV-light-responding activity, which can be enhanced with AuNPs by serving as electron sinks and providing catalytic active sites. Na_2CO_3 acts as an inhibitor of reactive oxygen species with strong oxidation power under UV light, *e. g.*, hydroxyl radicals and singlet oxygen. For the visible-light-induced oxidation, Na_2CO_3 behaves as an effective promoter for the reaction. This work provides an effective and mild approach for highly selective oxidation of biomass-derived feedstocks into valuable carboxyl compounds at ambient and greener conditions, and photocatalysis has great potential in the field of biomass transformation.

Experimental

Materials

2-furaldehyde (99%), 5-hydroxymethyl-2-furfural (98%), 2-furoic acid (98%), 2,5-furandicarboxyl acid (97%), and acetic acid (99%) were obtained from J&K Scientific Co., Ltd. Glucose (99%), gluconic acid (50 wt% aqueous solution), and furfuralcohol (98%) were offered by Alfa Aesar. TiO_2 (P-25), xylose (99%), and ethanol (99.5%) were purchased from Acros. All chemicals were used without further purification. Double distilled water was used throughout the experiments.

Preparation of Au/TiO_2 and Au/ZrO_2

We described the preparation of Au/TiO_2 because the procedure for fabricating Au/ZrO_2 were nearly the same, and the major difference was that different supports were employed. In a typical experiment, 0.5 g of TiO_2 powder was dispersed in an aqueous solution of $HAuCl_4$ with a desired concentration. 4.25 mL of lysine (0.5 mol/L) was subsequently added to the mixture under vigorous stirring in 10 min. After stirred for 1 h, 10 mL aqueous solution of $NaBH_4$ (0.0265 g) was then added into the dispersion in 10 min by dropwise. Then, the mixture was stirred for 24 h. Finally, the solid was collected, washed with distilled water and ethanol, and then dried at 60 ^oC for 12 h under vacuum.

Characterization of the catalysts

The transmission electron microscopy (TEM) images of the catalysts were recorded on a TEM JEOL-1011 with an accelerating voltage of 120 kV. The sample was dispersed in ethanol by sonication and dropped on an amorphous carbon film supported on a copper grid for the TEM analysis. The contents of gold in the catalysts were determined by ICP-AES method (VISTA-MPX). The X-ray photoelectron spectra (XPS) analysis of the catalysts was recorded on an ESCALab220i-XL. The electron spin resonance analysis was conducted on a Bruker E500.

Photocatalytic reactions

The photocatalyatic reactions were performed in a cylindrical stainless-steel reactor of 10 mL. There was a quartz window at the top of the reactor for the light illumination. In a typical experiment, 1 mL of water, desired amount of photocatalyst, additives, and substrates were added into the reactor. The reactor was connected to the atmospheric air and then irradiated by a xenon lamp for a desired reaction time, and the irradiated area was 2 cm^2. The reaction mixtures were analyzed by HPLC with a Shimadzu LC-20AT pump, a Shimadzu UV-Vis SPD-20A detector and a Shimadzu RID-10A detector, and a Benson BP-800 H+ column at 55 ^oC. 5 mmol/L aqueous solution of H_2SO_4 was used as the mobile phase at a flow rate of 0.6 mL/min. The chemicals in the reaction mixture were identified by LC-MS (LCMS-2010, Shimadzu) as well as by comparing retention time to the respective standards in the HPLC traces.

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References

1 C. Z. Li, X. C. Zhao, A. Q. Wang, G. W. Huber and T. Zhang, *Chem. Rev*., 2015, **115**, 11559-11624.

2 J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger and J. A. Dumesic, *Science*, 2014, **343**, 277-280.

3 S. H. Zhu, Y. F. Xue, J. Guo, Y. L. Chen, J. G. Wang and W. B. Fan, *ACS Catal*., 2016, **6**, 2035-2042.

4 B. W. Zhou, J. L. Song, H. C. Zhou, T. B. Wu and B. X. Han, *Chem. Sci.*, 2016, **7**, 463-468.

5 J. Albert and P. Wasserscheid, *Green Chem*., 2015, **17**, 5164-5171.

6 J. L. Gong and C. B. Mullins, *J. Am. Chem. Soc.*, 2008, **130**, 16458-16459.

7 H. D. Zhang, N. Li, X. J. Pan, S. B. Wu and J. Xie, *Green Chem*., 2016, **18**, 2308-2312.

8 M. G. Manas, J. Campos, L. S. Sharninghausen, E. Lin and R. H. Grabtree, *Green Chem.*, 2015, **17**, 594-600.

9 Z. W. Jiang, Z. R. Zhang, J. L. Song, Q. L. Meng, H. C. Zhou, Z. H. He and B. X. Han, *ACS Sustainable Chem. Eng*., 2016, **4**, 305-311.

10 M. Bellardita, E. I. Gracia-Lopez, G. Marci, B. Megna, F. R. Pomilla and L. Palmisano, *RSC Adv*., 2015, **5**, 59037-59047.

11 S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro and L. Palmisano, *J. Am. Chem. Soc.*, 2008, **130**, 1568-1569.

12 V. Augugliaro, T. Caronna, V. Loddo, G. Marci, G. Palmisano, L. Palmisano and S. Yurdakal, *Chem. Eur. J.*, 2008, **14**, 4640-4646.

13 G. Zhang, C. S. Ni, X. B. Huang, A. Welgamage, L. A. Lawton, P. K. J. Robertson and J. T. S. Irvine, *Chem. Commun.*, 2016, **52**, 1673-1676.

14 C. L. Wang and D. Astruc, *Chem. Soc. Rev.*, 2014, **43**, 7188-7216.

15 J. L. Long, H. J. Chang, Q. Gu, J. Xu, L. Z. Fan, S. C. Wang, Y. G. Zhou, W. Wei, L. Huang, X. X. Wang, P. Liu and W. Huang, *Energy Environ. Sci.,* 2014, **7**, 973-977.

16 (a) J. Thomas and M. Yoon, *Appl. Catal. B.*, **2012**, 111-112, 502-508; (b) D. He, X. Jiao, P. Jiang, J. Wang and B.-Q. Xu, *Green Chem.*, **2012**, 14, 111-116; (c) S. Zhu, S. Liang, Q. Gu, L. Xie, J. Wang, Z. Ding and P. Liu, *Appl. Catal. B.*, **2012**, 119-120, 146-155.

17 A. Tanaka, K. Hashimoto and H. Kominami, *J. Am. Chem. Soc.*, 2012, **134**, 14526-14533.

18 (a) D. Tsukamoto, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *J. Am. Chem. Soc.*, 2012, **134**, 6309-6315; (b) M. Chen and W. Goodman, *Acc. Chem. Res.*, 2006, **39**, 739-746.

19 X. Chen, H. Y. Zhu, J. C. Zhao, Z. T. Zheng and X. P. Gao, *Angew. Chem. Int. Ed.*, 2008, **47**, 5353-5356.

20 Y. Y. Gorbanev, S. Kegnaes, C. W. Hanning, T. W. Hansen and A. Riisager, *ACS Catal*., 2012, **2**, 604-612.

21 C. H. Christensen, B. Jorgensen, J. Rass-Hansen, K. Egeblad, R. Madsen, S. K. Klitgaard, S. M. Hansen, M. R. Hansen, H. C. Andersen and A. Riisager, *Angew. Chem. Int. Ed.*, 2006, **45**, 4648-4651.

22 L. Q. Liu, S. X. Ouyang and J. H. Ye, *Angew. Chem. Int. Ed.*, 2013, **52**, 6689-6693.

23 K. Yamada, K. Miyajima and F. Mafune, *J. Phys. Chem. C*, 2007, **111**, 11246-11251.

24 J. Q. Yan, G. J. Wu, N. J. Guan and L. D. Li, *Chem. Commun.*, 2013, **49**, 11767-11769.

25 G. J. ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636-1639.

26 J. L. Wang, R. A. Ando and P. H. C. Camargo, *Angew. Chem. Int. Ed.*, 2015, **54**, 6909-6912.

27 J. C. Serrano-Ruiz, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, **40**, 5266-5281.

28 A. V. Puga, A. Forneli, H. Garcia and A. Corma, *Adv. Funct. Mater.*, 2014, **24**, 241-248.

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DOI: 10.1039/C6GC03022J

29 Y. J. Zhang, G. H. Zhao, Y. N. Zhang and X. F. Huang, *Green Chem.*, 2014, **16**, 3860-3869.
30 N. Dimitratos, J. A. Lopez-Sanchez and G. J. Hutchings, *Chem. Sci.*, 2012, **3**, 20-44.
31 Y. Tian and T. Tatsuma, *J. Am. Chem. Soc.*, 2005, **127**, 7632-7637.