Supporting Information

One-pot Synthesis of Gluconic Acid from Biomass-derived Levoglucosan Using a Au/$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ Catalyst

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Analytical method.

The qualification and quantification of the products were analyzed using HPLC, strictly follows the method reported by the previous literatures where the products were identified by comparing the chromatograms with those of the standards.[1-3] The standard solutions of single compound for both reactant and various possible products have been prepared, and the HPLC chromatograms (RD signal and UV signal) of these standard compounds are shown in Figure S1, with the individual retention times listed in Table S1.

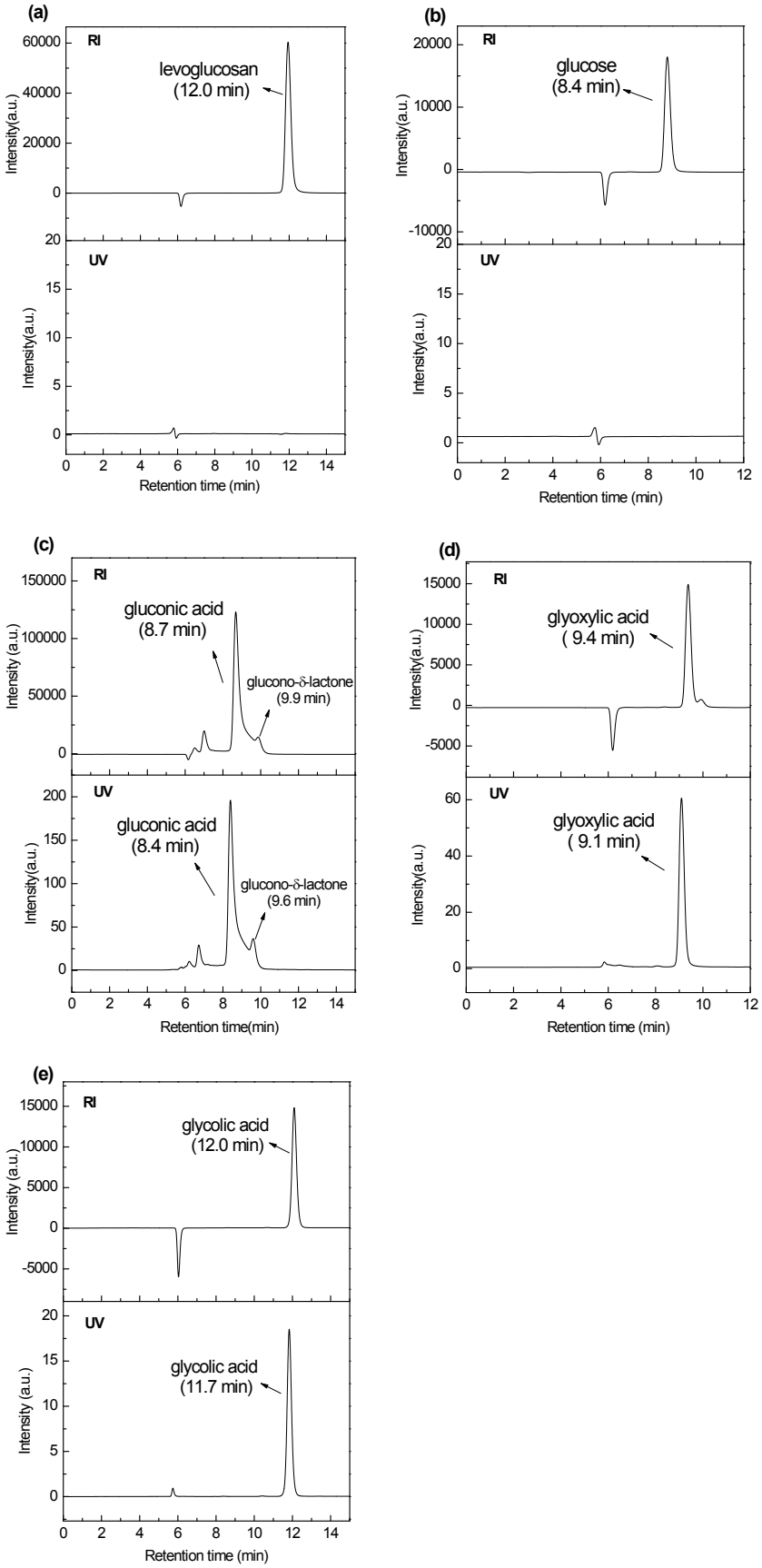

Figure S1. HPLC chromatograms of standards: (a) levoglucosan, (b) glucose, (c) gluconic acid, (d) glyoxylic acid, and (e) glycolic acid.

Table S1. The retention times of the standards.

Standard	Retention time (min)	
	RI	UV
levoglucosan	12.0	-
glucose	8.7	-
gluconic acid	8.7	8.4
glyoxylic acid	9.4	9.1
glycolic acid	12.0	11.7

It needs to be noted that there are two peaks emerged in the standard chromatograms of gluconic acid, as shown in Figure 1. The latter peak (RI and UV present at 9.9 min and 9.6 min respectively) is attributed to glucono-δ-lactone, because gluconic acid, possessing both carboxylic acid group and hydroxyl group, can undergo 1, 5 intramolecular esterification. In aqueous acid solution, the spontaneous dehydration happens, generating the anhydride glucono-δ-lactone that is in equilibrium with gluconic acid.[4] Moreover, there is an overlap of retention times in RI chromatograms between some compounds, like levoglucosan and glycolic acid, glucose and gluconic acid, as shown in Table S2. Hence, it will be difficult to find each concentration by just using the RI results. This problem can be readily solved by the combination of UV results, since no UV absorptions occur to levoglucosan and glucose standards at 230 nm wavelength.

The representative HPLC chromatograms of test samples after reaction is shown in Figure S2. Due to the inevitable co-existence of gluconic acid and glucono-δ-lactone, the former can be measured by its UV peak area, and the latter determined by either UV or RI results, which are used to obtain the quantification of total gluconic acid generated. As discussed earlier, RI peaks of gluconic acid and glucose overlapped, but glucose didn't have UV signal at the wavelength of 230 nm. After determination of gluconic acid concentration mentioned above, the amount of glucose can be readily calculated by subtracting the gluconic acid contribution from the total signal quantified in RI detector. This approach enables the measurement of glucose concentration in the

presence of gluconic acid. The same method was also adopted to quantify levoglucosan, which is intertwined with glycolic acid in RI, but not in UV chromatograms. The concentration of glycolic acid can be simply determined by its UV peak, since levoglucosan has no UV absorption at the wavelength of 230 nm. The amount of levoglucosan was then determined by subtracting the glycolic acid contribution from the total signal in RI detector. Care was taken to not overestimate the amount of gluconic acid, as a small but notable peak appears between the gluconic acid and glucono-δ-lactone (Figure S2). This small overlapping peak should be attributed to the glyoxylic acid, which was then deconvoluted and quantified from the UV peak area (more apparent in UV chromatogram than that of IR counterpart).

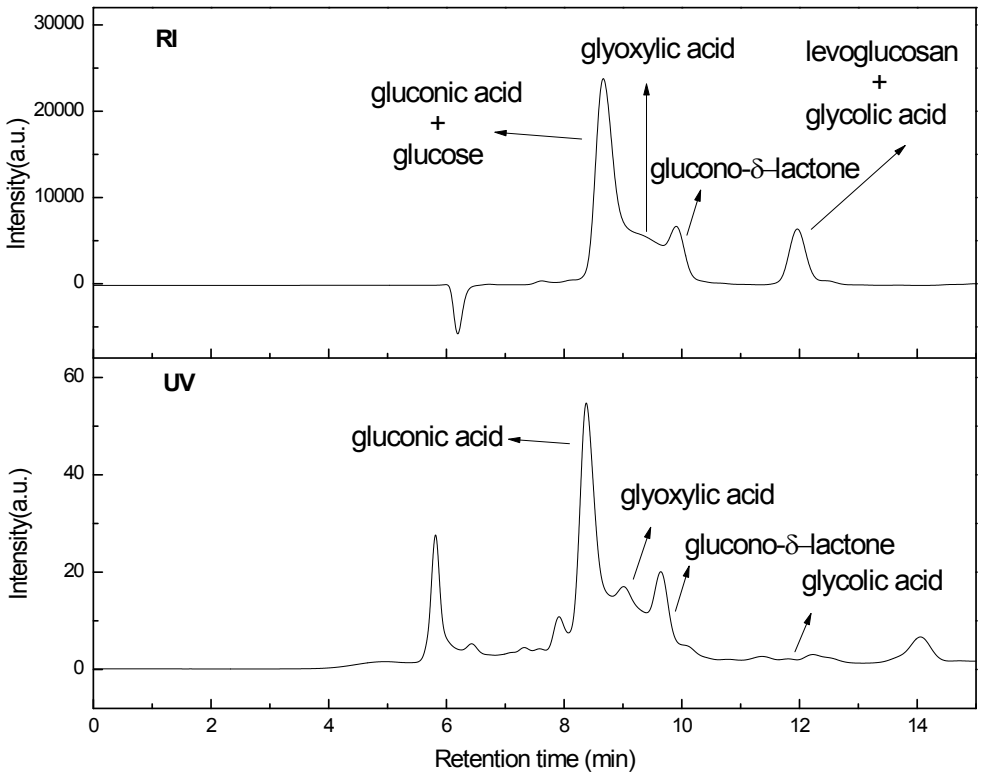

Figure S2. Representative HPLC chromatograms of reaction products.

Recycling experiments

For recycling experiments, a slight loss of catalyst would be inevitable during the catalyst recovery, filtration, drying and grinding steps. To offset the weight loss and ensure that the catalyst used in each run was 0.15 g, several batches were performed in

each recycling run, and the spent catalysts in each batch were collected, mixed, washed with deionized water, and then dried at 353 K overnight. 0.15 g of the obtained spent catalyst was then used in the next recycling run.

Separation and purification approach

The gluconic acid in the solution can be recovered and purified efficiently via reactive separation procedure. Typically, the obtained product mixture (mixed acids) can be first dehydrated, followed by esterification by addition of alcohol. Subsequently, the individual esters formed are separated by distillation and are hydrolyzed to obtain the corresponding organic acids. Usually, the purity of the separated acid can be higher than 98%.[5]

Table S2. Chemical composition and textural properties of prepared catalysts.

Catalyst	S_{BET} ($m^2 \cdot g^{-1}$)[a]	Au content (wt%)[b]	Other element content (wt%)[c]
$Cs_{2.5}H_{0.5}P_{12}O_{40}$	86	0.96	Cs (16.2), P (1.5)
ZrO_2-SO_4^{2-}	98	0.94	S(2.1)
TiO_2-PO_4^{3-}	51	0.95	P(7.4)
HZSM-5 (nSi/nAl=20)	473	1.0	-

[a] S_{BET} = Brunauer-Emmet-Teller surface area. [b] Determined by n-butylamine titration. [c] Determined by XRF.

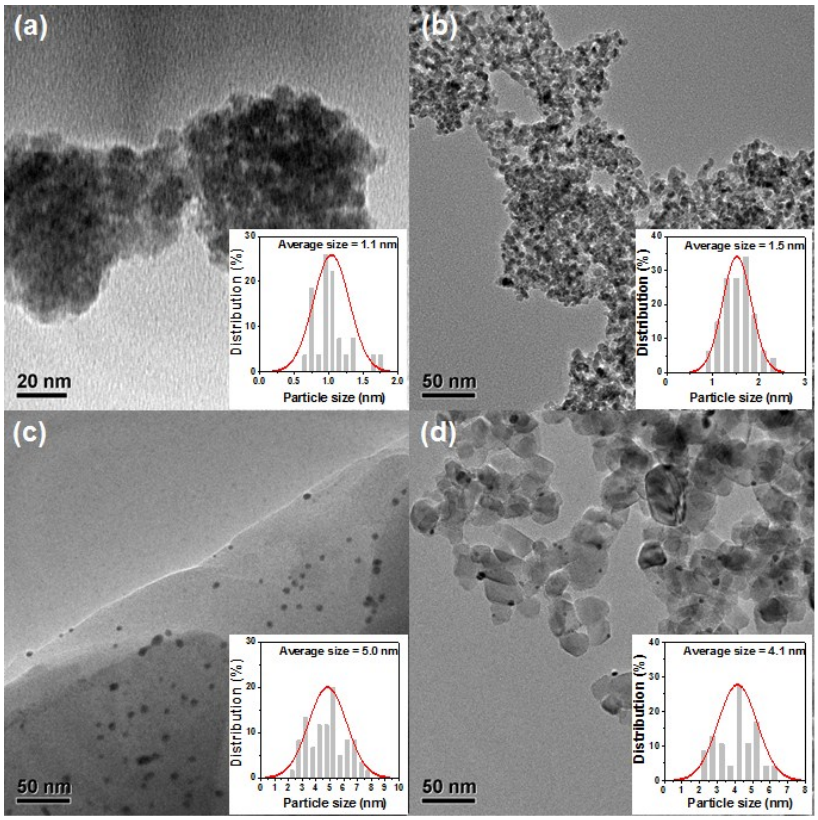

Fig. S3 TEM images of prepared catalysts and distribution of gold nanoparticles: (a) Au/ $Au/Cs_{2.5}H_{0.5}PW_{12}O_{40}$; (b) Au/ZrO_2-SO_4^{2-}; (c) Au/HZSM-5 (n_{Si}/n_{Al}=20) and (d) Au/TiO_2-PO_4^{3-}

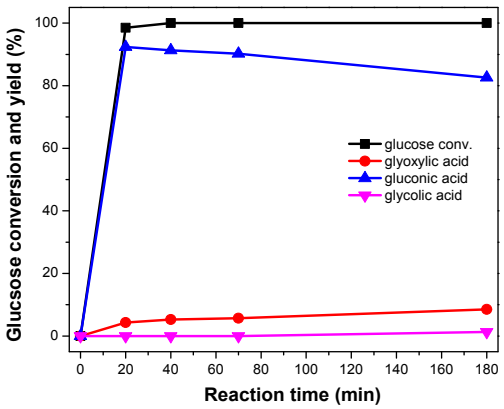

Fig. S4 Time course for conversion of glucose over $Au/Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst. Reaction conditions: glucose (77.1 mM), catalyst (0.15 g), H_2O (20 mL), 418 K, O_2 (0.5 MPa).

References

1. D. Santhanaraj, M. R. Rover, D. E. Resasco, R. C. Brown, S. Crossley, ChemSusChem, 2014, 7, 3132-3137.

2. P. Y. Qi, S. S. Chen, J. Chen, X. L. Zheng, Y. Z. Yuan, ACS Catalysis, 2015, 5, 2659-2670.

3. Y. L. Cao, X. Liu, S. Lgbal, P. J. Miedziak, J. K. Edwards, R. D. Armstrong, D. J. Morgan, J. W. Wang, G. J. Hutchings, Catalysis Science & Technology. 2016.6. 107-117.

4. A. M. Cañete-Rodríguez, I. M. Santos-Dueñas, J. E. Jiménez-Hornero, A. Ehrenreich, W. Liebl, I. García-García, Process Biochemistry 2016, 15, 1891-1903.

5. Maurya, R. Rahul, WO 2016/194003 A2