Valorisation of Corncob Residue towards the Sustainable Production of Glucuronic Acid

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Materials.

Maleic acid (98%) was obtained from Adamas-beta (Shanghai, China). Corncob residue powder (60–100 meshes; 17.2 wt% of lignin, 62.4 wt% of cellulose, 0.1 wt% of hemicellulose, 4.5 wt% of ash and 15.8 wt% of others unknown) was provided by Shandong Futaste Investment Co., Ltd. (Shandong Province. China); Corncob residue powder was dried in an oven at 373 K before use. Glucose (99%), Glucuronic acid (98%) and CeO_2 (99%), was purchased from J&K Chemicals (Beijing, China). $HAuCl_4 \cdot 4H_2O$ was obtained from Chengdu Chemical Reagent Factory (Chengdu, China). The ultrapure water of 18.25 MΩ·cm^{-1} (298K) was used after degasification. Other general reagents used in this work were purchased from J&K Chemicals (Beijing, China).

Product analysis.

The liquid products were quantified by high performance liquid chromatography (HPLC) using a Shimadzu HPLC system equipped with a UV-vis detector and a refractive index detector and an HPX-87H Aminex Column (300 mm × 7.8 mm, Bio-Rad), which is tested to be a suitable column to successfully analyze gluconic acid, glucuronic acid and other organic aicds (Figure S4). The eluent was dilute H_2SO_4 aqueous solution (5 mM) with a flow rate of 0.60 mL·min^{-1}. The column temperature was maintained at 323 K. The concentrations of all components were determined by comparison to the standard calibration curves.

The conversion (Con.%) of corncob residue was calculated by the following equation:
$$\text{Con.} \% = (w_i - w_r)/(w_i) \times 100$$
The yield of GA and other products were calculated as the following equation:
$$\text{Yield (\%)} = (\text{mass of product})/(\text{mass of initial cellulose}) \times 100$$
Wherein, w_i and w_r represent the initial mass and reminded mass of corncob residue.

Quantum chemical computational details.

All calculations in this work were performed using Gaussian 09 program package [32] .Geometries were fully optimized in water solvent at the B3LYP/6-311 + G** level [33] and characterized by frequency analysis at 433 K. The self-consistent reaction field (SCRF) method based on the universal solvation model SMD [34] was adopted to evaluate the effect of solvent. Dispersion corrections were computed with Grimme's D3(BJ) method in optimization [35].The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism [36].

As for the behaviour of reactant on the Au(111) face, Vienna Ab Initio Package (VASP) [37] is employed to reveal the reaction mechanism at molecular level. Vienna Ab Initio Package (VASP) within the generalized gradient approximation (GGA) using the PBE [38] formulation was adopted. We have chosen the projected augmented wave

(PAW) potentials [39] to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn−Sham orbitals were allowed using the Gaussian smearing method with a width of 0.05 eV. The on-site corrections (DFT+U) [40] have been applied to the 4f electron of Au atoms. The electronic energy is considered self-consistent when the energy change was smaller than 10^{-5} eV. A geometry optimization is considered convergent when the force change was smaller than 0.02 eV/Å. Grimme's DFT-D3 methodology [41] is used to describe the dispersion interaction. The free energy is calculated using the equation:

$$G = E + ZPE - TS$$

where *G*, *E*, *ZPE* and *TS* represent the free energy, total energy from DFT calculations, zero point energy and entropic contributions, respectively. The transition state search has been obtained by the nudged elastic band methods. All the key intermediates and transition states are determined by energy span model.
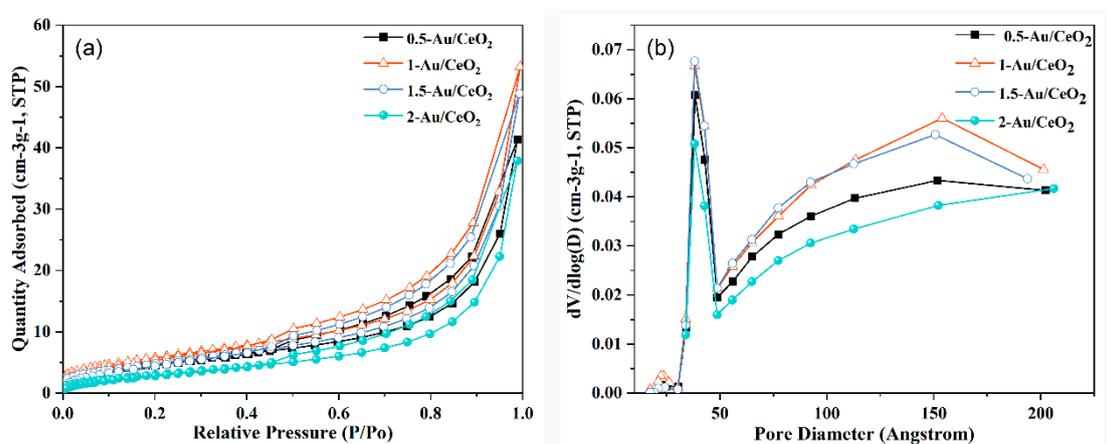

**Figure S1.** N_2 adsorption-desorption isotherm for the catalysts.
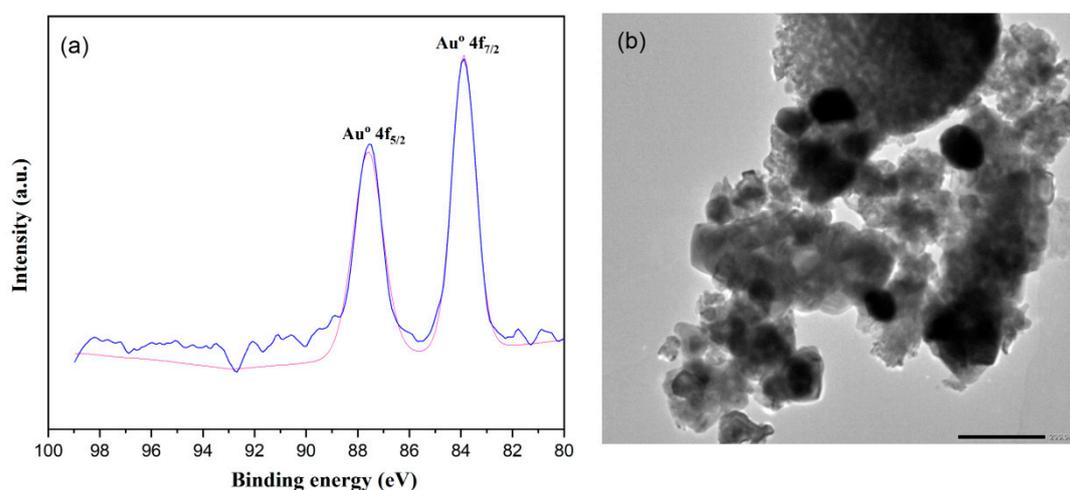
Figure S2. The characterizations of the spent Au/CeO_2 catalysts. (**a**) The XPS analysis of the prepared Au/CeO_2 catalyst. (**b**) The TEM image of Au/CeO_2 catalyst.
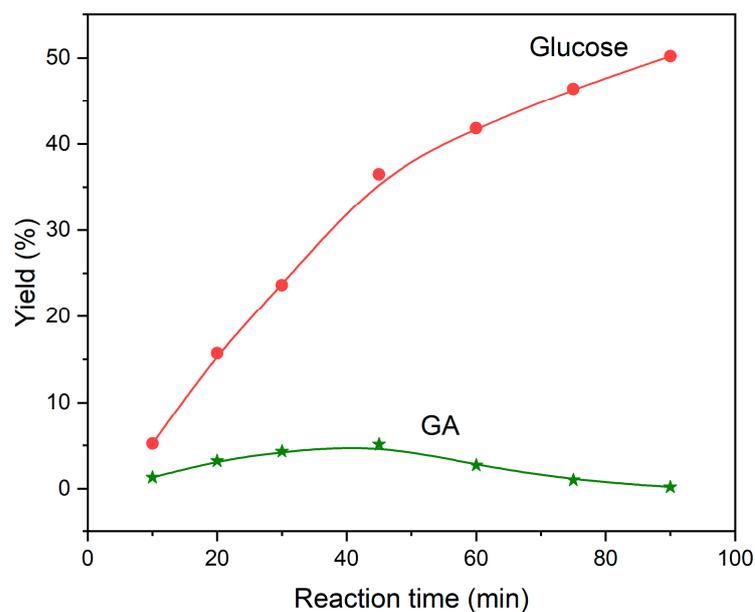
Figure S3. The time course of the glucose and GA formation during the conversion of corncob residue at 423 K.
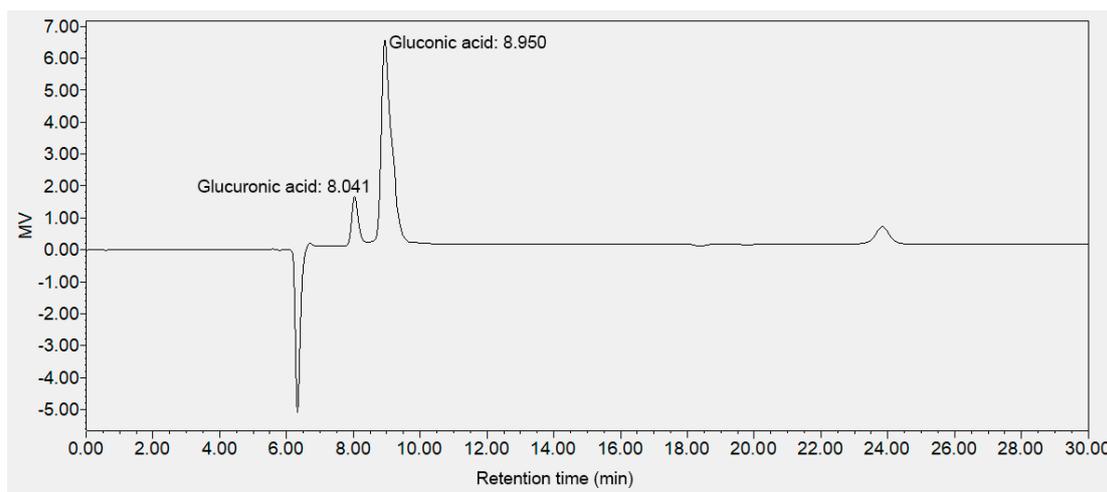
Figure S4. The HPLC analysis of the mixture of gluconic acid and glucuronic acid.

Table S1. Textural properties of the catalysts.

Entry	Catalyst	S^a (m²/g)	Pore Size^b (nm)	Au Elemental Composition^c (wt %)
1	0.5 wt% Au/CeO₂	205.3	26.6	0.50
2	1 wt% Au/CeO₂	201.1	26.0	0.99
3	1.5 wt% Au/CeO₂	197.9	25.7	1.47
4	2 wt% Au/CeO₂	197.0	25.4	1.96

^{a}Cu particle size of the catalysts was calculated using the Debye−Scherrer equation based on XRD analysis; ^{b}BET surface area (S), pore volume, and pore size were measured by N₂ adsorption−desorption; ^{c} Au elemental composition was calculated by ICP-AES analysis.

Table S2. The control experiments on the conversion of corncob residue to GA.[a]

	Cellulose Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
Maleic acid	100	3.5	0.1	5.0	0.3	0.2
Au/CeO_2	8	1.1	-	0.7	-	-

[a]Reaction conditions: 1.0 g Corncob residue; 0.1 g Au/CeO_2 or 5 mM maleic acid; 50 mL H_2O; O_2, 1 MPa; temperature, 443 K; time, 2.0 h.

Table S3. The catalytic activity of different Au-based catalysts on the conversion of corncob residue to GA.[a]

	Cellulose Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
Au/Al_2O_3	88.1	22.5	0.1	5.1	1.9	0.9
Au/ZrO_2	~100	56.7	0.6	3.2	2.0	1.5
Au/TiO_2	~100	59.1	1.1	4.4	3.5	4.0

[a]Reaction conditions: 1.0 g Corncob residue; 0.2 g catalysts; 5 mM Maleic acid; 50 mL H_2O; O_2, 1 MPa; temperature, 443 K; time, 2.0 h.

Table S4. The effect of the amount of maleic acid on the conversion of corncob residue to GA.[a]

The Amount of Maleic Acid	Cellulose Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
4 mM	~100	50.2	0.2	2.9	0.5	1.1
5 mM	~100	56.0	0.3	3.4	0.6	1.3
6 mM	~100	58.8	0.3	3.7	0.9	2.1
7 mM	~100	58.0	0.3	4.2	1.7	3.0

[a]Reaction conditions: 1.0 g Corncob residue; 0.1 g Au/CeO_2; 50 mL H_2O; O_2, 1 MPa; temperature, 443 K; time, 2.0 h.

Table S5. The effect of the amount of Au/CeO_2 on the conversion of corncob residue to GA.[a]

The Amount of Au/CeO_2	Cellulose Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
0.05 g	95	35.7	-	5.1	2.5	0.7
0.1 g	~100	58.8	0.3	3.7	0.9	2.1
0.2 g	~100	60.1	0.3	3.8	0.7	2.2
0.3 g	~100	58.0	0.5	4.2	1.2	2.8

[a]Reaction conditions: 1.0 g Corncob residue; 6 mM maleic acid; 50 mL H_2O; O_2, 1 MPa; temperature, 443 K; time, 2.0 h.

Table S6. The effect of the amount of O_2 pressure on the conversion of corncob residue to GA.[a]

O_2 Pressure	Cellulose Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
0.1 MPa	67	14.6	-	1.5	8.5	4.1
0.5 MPa	89	44.2	-	2.6	3.6	3.3
1.0 MPa	~100	60.3	0.3	3.7	0.7	2.1
1.5 MPa	~100	57.7	1.5	5.5	1.0	2.5

[a]Reaction conditions: 1.0 g Corncob residue; 0.2 g Au/CeO₂; 6 mM maleic acid; 50 mL H₂O; temperature, 443 K; time, 1.5 h.

Table S7. The effect of reaction temperature on the conversion of corncob residue to GA.[a]

Reaction Temperature (K)	Cellulose Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
423	67	50.2	0.2	2.9	0.5	1.1
433	89	56.0	0.3	3.4	0.6	1.3
443	~100	60.1	0.3	3.8	0.7	2.2
453	~100	57.2	0.3	4.5	1.5	2.0

[a]Reaction conditions: 1.0 g Corncob residue; 0.2 g Au/CeO₂; 6 mM maleic acid; 50 mL H₂O; O₂, 1 MPa; time, 2.0 h.

Table S8. The effect of reaction time on the conversion of corncob residue to GA.[a]

Reaction Time (h)	Cellulose Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
0.5	73	32.1	0.1	1.5	0.1	0.6
1	92	44.7	0.2	2.4	0.3	0.9
1.5	~100	60.3	0.3	3.7	0.7	2.1
2	~100	60.1	0.3	3.8	0.7	2.2

[a]Reaction conditions: 1.0 g Corncob residue; 0.2 g Au/CeO₂; 6 mM maleic acid; 50 mL H₂O; O₂, 1 MPa; temperature, 443 K;.

Table S9. The control experiments on the conversion of cellulose to GA.[a]

	Cellulose Conversion (%)[b]
Maleic acid	~100
Au/CeO₂	14

[a]Reaction conditions: 1.0 g Corncob residue; 0.2 g Au/CeO₂ or 6 mM maleic acid if used; 50 mL H₂O; O₂, 1 MPa; temperature, 443 K; time, 1.5 h. [b]The conversion is based on the solid residue.

Table S10. The control experiments on the conversion of glucose to GA.[a]

	Conversion (%)	Yield of Products (%)				
		GA	Glucaric Acid	Formic Acid	Glycolic Acid	Glyceric Acid
Maleic acid	~100	0.5	6.7	10.2	2.7	3.5
Au/CeO₂	~100	70.5	0.7	2.1	3.9	1.5

[a]Reaction conditions: 1.0 g Corncob residue; 0.2 g Au/CeO₂; 6 mM maleic acid; 50 mL H₂O; O₂, 1 MPa; temperature, 443 K; time, 1.5 h.

Table S11. The control experiments on the conversion of glucose to GA at different atmosphere.[a]

	Conversion (%)	Yield of Products (%)				
		GA	5-hydroxymethylfurfural	Formic Acid	Glycolic Acid	Glyceric Acid
N2	~100	16.7	18.0	4.5	0.9	2.1

[a]Reaction conditions: 1.0 g Corncob residue; 0.2 g Au/CeO₂; 6 mM maleic acid; 50 mL H₂O; N₂, 1 MPa; temperature, 443 K; time, 1.5 h.