Electronic Supplementary Material

Efficient oxidation of monosaccharides to sugar acids under neutral condition in flow reactors with gold-supported activated carbon catalysts

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1 Materials

D-glucose (99.5%), D-xylose (98%) and activated carbon (100 mesh, AR, 99%) were purchased from Sigma-Aldrich Co., Ltd. Gold chloride trihydrate ($HAuCl_4·3H_2O$, ≥99.9% trace metals basis), polyvinyl alcohol (PVA), and sodium borohydride ($NaBH_4$) were supplied by Aladdin Chemistry Co., Ltd (Shanghai, China). Sodium ethanoate, potassium formate, disodium oxalate and gluconic acid sodium salt (AR, 99%) was obtained from Macklin Reagent Corporation (Shanghai, China). Xylonic acid calcium salt hydrate was supplied by TLC Pharmaceutical Standards Ltd. Sulfuric acid (AR, 98%) was bought from Guangzhou Chemical Reagent Factory (Guangzhou, China). All purchased chemicals and reagents were used as received without further purification. Ultrapure water was used for the preparation of all solutions.

2 Catalyst characterization

Powder X-ray diffraction (XRD) was carried out using a PANalytical X'pert Powder diffractometer using Cu Kα radiation. The operating voltage and current were 40 kV and 40 mA, respectively. The step length was 0.02° with a scanning rate of $2°·min^{-1}$. Raman spectra of AC and Au/AC were recorded on a Lab RAM Aramis confocal Raman microscopic system. A green laser at 532 nm was used as the excitation source, and the spectra were recorded in the range of 500–2500 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Ultra system and an Al Kα radiation source in order to analyze the elemental composition and the bonding configuration of the Au/AC catalyst surface. An Agilent 5800 Inductively Coupled Plasma Emission Spectrometer (ICP-OES) was performed to detect the Au loadings of the catalysts. The test samples were pretreated by aqua regia. Nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature using a Micromeritics ASAP 2460. The specific surface area of the samples was calculated by the Brunauer-Emmett-Teller (BET) method. The average pore diameter and pore size distributions of the carbon supports were evaluated by analyzing the desorption branch of the isotherm in line with the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM) images were derived on a ZEISS Merlin (Jena, Germany) operated at 10 kV acceleration voltage. Transmission electron microscopy (TEM) images were gained on a Thermo Fisher TalosF200X electron microscopy operated at 200 kV acceleration voltage. The samples for TEM were ultrasonically dispersed in ethanol and then deposited on carbon-coated copper grids using a capillary and dried in air for 30 min.

3 Product analysis

Xylonic acid and gluconic acid were analyzed using HPLC (Agilent 1260 series) equipped with a UV detector at 210 nm and a Bio-Rad Aminex HPX-87H column (300 mm×7.8 mm×9 μm). Xylose and glucose were measured using HPIC (Dionex ICS-6000) with a CarboPac PA1 column. Ultrapure water was used as the eluent. The concentrations of the reactant’s glucose and xylose, and the products gluconic acid and xylonic acid were obtained using the external standard method. The conversion of reactants and products were calculated according to the following equations, respectively:

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

$$\text{Yield (\%)} = \frac{\text{Moles of carbon in sugar acid}}{\text{Moles of carbon in feedstock input}} \times 100\%$$

4 Oxidation of monosaccharides in continuous flow reactors

The WHSV was calculated using the following equation; where c_{feed} is the monosaccharides concentration of the feedstock solution, v_{feed} is the flow rate of the feedstock solution, m_{cata} is the mass of catalyst used in the reaction.

$$\text{WHSV}=\frac{c_{feed}\times v_{feed}}{m_{cata}}$$

The turnover number (TON) and turnover frequency (TOF) for oxidating monosaccharides into sugar acid are calculated using the following equation. $n_{\text{sugar converted}}$ is the number of moles of sugar converted, and $n_{\text{sugar acid}}$ is the number of moles of sugar acid produced. $n_{\text{active site}}$ is the number of moles of surface metal sites on the catalyst determined by using the truncated cubic octahedron model to sum the surface and bulk metal atoms of all individual particles counted from TEM images. (see Fig 1d).

$$\text{TON}=\frac{n_{\text{sugar acid}}}{n_{\text{active sites}}} \qquad \text{TOF}=\frac{n_{\text{sugar converted}}}{n_{\text{active sites}}\, t}$$

The reaction kinetics of monosaccharides oxidation is calculated according to the following equation:

$$-\frac{dC_M}{dt}=kC_M$$

$$\int_{C_{M,0}}^{C_M}-\frac{dC_M}{C_M}=\int_0^t k\,dt$$

$$\ln\frac{C_{M,0}}{C_M}=kt$$

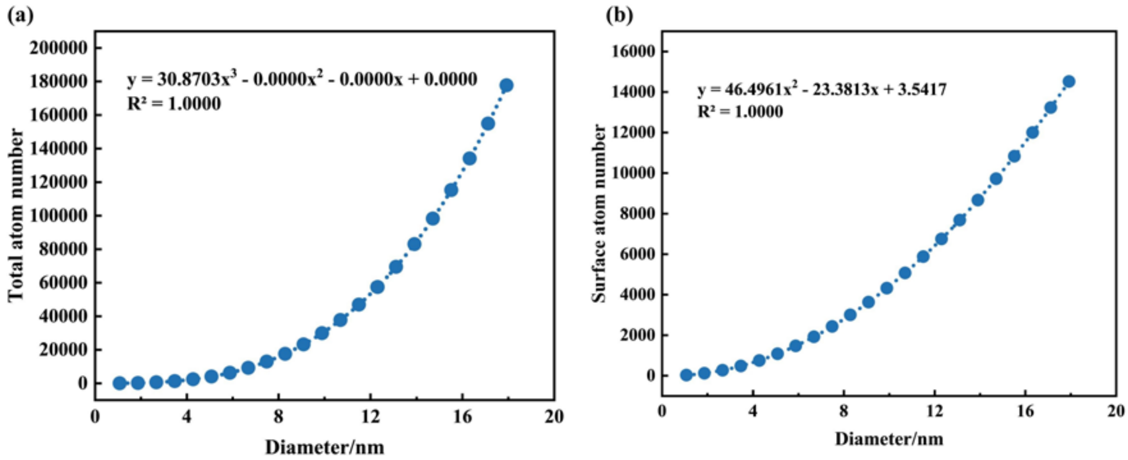
where k is the reaction rate constant (min^{-1}), C_M is concentration of monosaccharides in aqueous solution ($mol\cdot L^{-1}$), $C_{M,0}$ is the initial monosaccharide concentration in the aqueous feedstock solution, t is the reaction/retention time (min), which equal to the void volume of the reaction column divided by the monosaccharide flow rate. The activation energy was also calculated using the temperature dependence of the rate constant (k) expressed by the Arrhenius equation as below:

$$\ln k=\ln A-\frac{E_a}{RT}$$

where Ea is the apparent activation energy of the reaction ($J\cdot mol^{-1}$), T is the absolute temperature (K), A is the pre-exponential or frequency factor (min^{-1}) and R is the universal gas constant (=8.314 $J\cdot K^{-1}\cdot mol^{-1}$). The activation energy and pre-exponential factor were determined by plotting ln(k) versus 1/T.

5 Calculation of the dispersion of Au particles

The particle size distribution was estimated by statistical analysis of at least 300 measurements. Metal dispersion (defined as ratio between surface and total metal atoms) was calculated back from particle size distribution using the truncated cubic octahedron model to sum the surface and bulk metal atoms of all individual particles counted from TEM images (Fig. 1d). The curves and formulas used to calculate total and surface atom number are shown in the following figures, then the active sites were calculated based on the metal loading as well as the molar mass of the metal atoms.



Fitting curves of diameter of Au size and corresponding (a) total atom number, (b) surface atom number.

$$M_{total.Au}=30.8703d^{3}+0.0000d^{2}-0.0000d+0.0000$$

$$M_{surface.Au}=46.4961d^{3}-0.0000d^{2}+23.3813d+3.5417$$

Figures

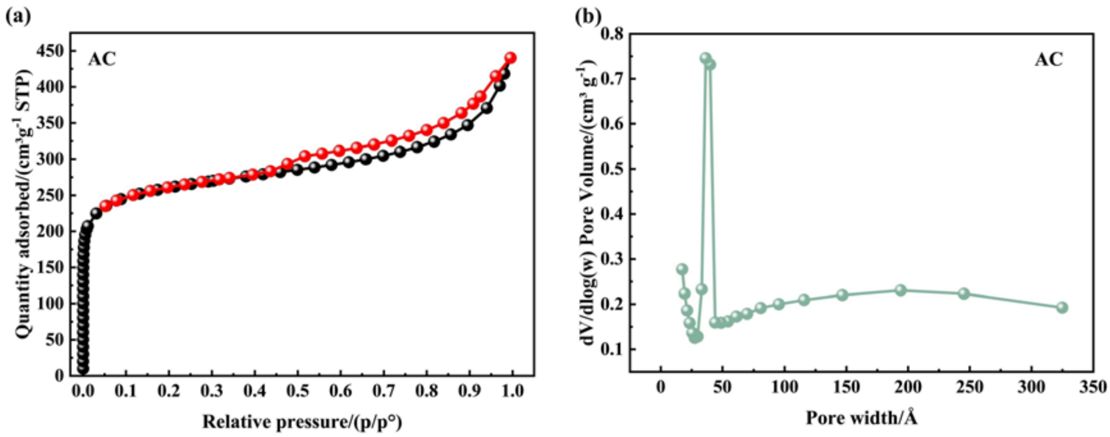


Fig. S1 (a) N_2 adsorption-desorption isotherm and (b) pore size distribution of AC

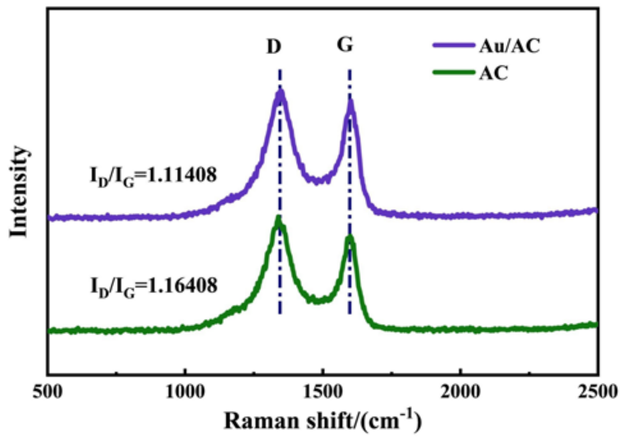


Fig. S2 The Raman spectra of AC and Au/AC

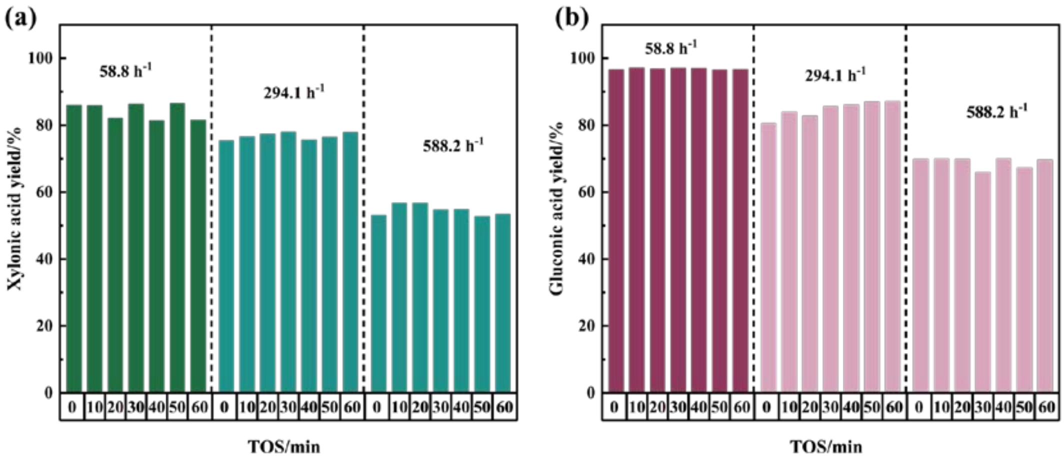


Fig. S3 Changes in the yield of (a) xylonic acid yield and (b) gluconic acid with the addition of weight hourly space velocity (WHSV), all of the experiments were operated under 80 °C, feeding flow rate of 0.5 mL·min^{-1}, 5 bars of O_2 at 30 mL·min^{-1} of flow rate over 150 mg of Au/AC catalyst in the reactor.

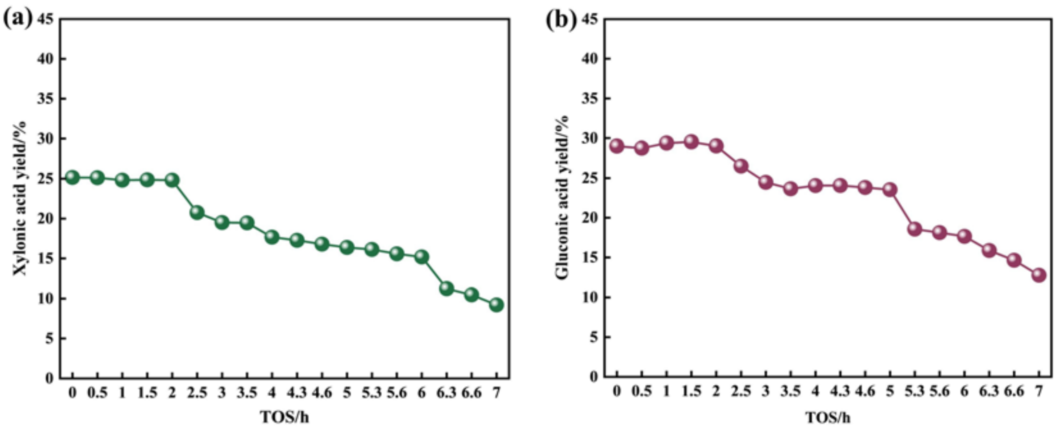


Fig. S4 Sugar acid yields from continuous oxidation of monosaccharides in a continuous flow reactor for 7 hours, (a) xylonic acid yield and (b) gluconic acid. Reaction conditions:80 ℃, amount of Au/AC=100 mg, the feed solution consisted of 20 mg·mL^{-1}, the flow rate=0.5 mL·min^{-1}, the O_2 flow rate=30 mL·min^{-1}, the O_2 pressure=5 bars.

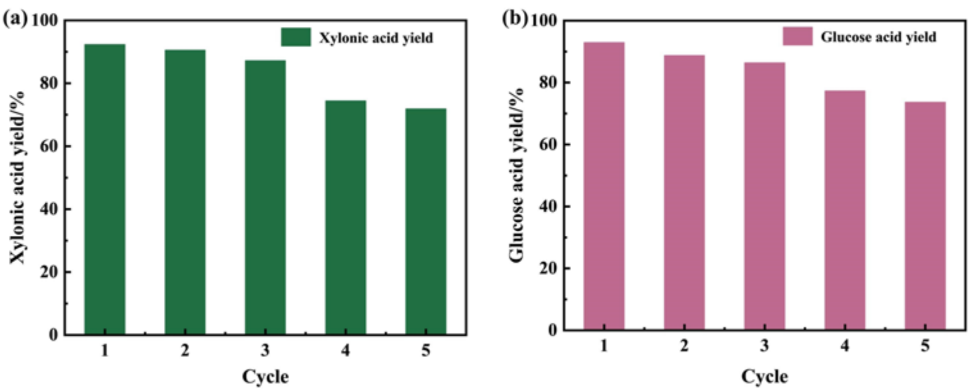


Fig. S5 Recycle of Au/AC for base-free oxidation of base-free oxidation of (a) xylose to xylonic acid and (b)glucose to gluconic acid. Calcination process under 573 K in H_2 as regeneration steps, the temperature of 90 °C, a reaction time of 180 min, 50 mg of Au/AC, and O_2 pressure of 5 bars for xylose of 150 mg or glucose of 180 mg.

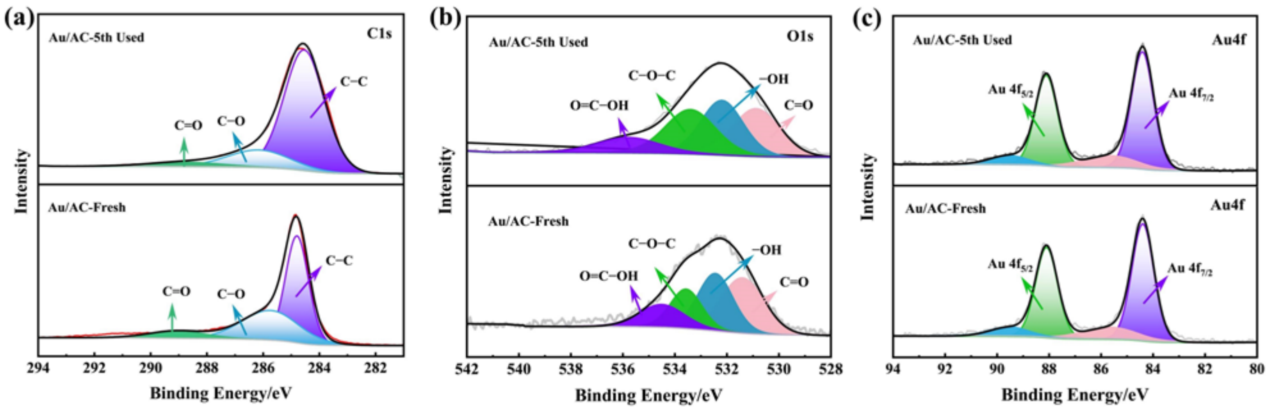


Fig. S6 XPS spectra of (a) C 1s, (b) O 1s and (c) Au 4f of catalysts of the fresh and 5th used on oxidation of glucose to gluconic acid.

Tables

Table S1 The BET specific surface area and BJH pore size and pore volume of AC and Au/AC

Sample	$S_{BET}/m^2\cdot g^{-1}$	$V_{pore}/cm^3\cdot g^{-1}$	D_{pore}/nm
AC	972.33	0.51	5.51
Au/AC	855.96	0.48	6.09

Table S2 ICP-OES analysis of Au/AC

Sample	Metal loading/wt% [a]	Metal loading/wt% [b]
Au/AC	0.68	0.70

Test methods: a for ICP-OES, b for quantitative XPS analysis.

Table S3 ICP-OES analysis of Au/AC-fresh prepared and 5th used on glucose oxidation

Sample	Au/AC-fresh	5th-used-Au/AC
Metal loading/wt%	0.68	0.62