Carbon nanotube-supported gold nanoparticles as efficient catalysts for selective oxidation of cellobiose into gluconic acid in water medium

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Electronic Supplementary Information

1. Experimental details

(1) Catalyst preparation

Multi-walled carbon nanotubes (CNTs) with outer diameter of 20-80 nm and inner diameter of 3-5 nm were prepared by an established method.[1] The CNTs were typically pretreated in concentrated HNO_3 (68 wt%) at 110 °C under refluxing conditions to remove the remaining Ni catalyst and the amorphous carbon. For comparison, HNO_3 with different concentrations and concentrated HCl (37 wt%) were also applied for CNT pretreatment. Our ICP analysis showed that no Ni remained in the CNT after treatment with HNO_3 or HCl.

Au catalysts on various supports were typically prepared by impregnating the supports with an aqueous solution of $AuCl_3$, followed by drying at 100 °C. Then, the catalysts were subjected to H_2 reduction at 350 or 250 ^oC for 2 h.

(2) Catalyst characterization

N_2 sorption, TEM, XPS and NH_3-TPD were used to characterize the structures and the physicochemical properties of catalysts. N_2 sorption at 77 K was carried out with a Micromeritics Tristar 3000 surface and porosimetry analyzer, and the surface area was evaluated using the BET method. TEM measurements were performed on a Tecnai F30 electron microscope (Phillips Analytical) operated at an acceleration voltage of 300 kV. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. Drops of the suspensions were applied on a copper grid coated with carbon. XPS measurements were carried out with a Quantum 2000 Scanning ESCA Microprob instrument (Physical Electronics) using Al-K_α radiation. NH_3-TPD measurements were performed using a Micromeritics AutoChem II 2920 instrument connected to a ThermoStar GSD 301 T2 mass spectrometer.

(3) Catalytic reaction

The conversion of cellobiose was performed in a 75 mL Teflon-lined stainless-steel autoclave. Cellobiose purchased from Alfa Aesar (0.30 mmol) and the catalyst (typically, 0.05

g) were added into the autoclave pre-charged with H_2O (20 mL). After the introduction of O_2 with a certain pressure (typically, 0.5 MPa), the reaction was started by heating the mixture up to a reaction temperature (typically, 145 °C). After the reaction, the liquid products were analyzed by HPLC (Shimazu LC-20A) equipped with a RI detector and a TransgenomicTM CARBONSep CHO-620 column (10μm, 6.5×300 mm) using H_2O as a mobile phase.

2. Conversion of gluconic acid over different supports

Table S1 Oxidation of gluconic acid over different supports[a]

Catalyst	Gluconic acid conversion /%
SiO_2	5.7
Al_2O_3	67
MCM-41	20
H-ZSM-5	16
MgO	97
AC	10
Graphite	24
XC-72	28
CNT	14

[a]Reaction conditions: Gluconic acid, 0.060 mmol; H_2O, 10 mL; O_2 pressure, 0.5 MPa; catalyst, 0.05 g; T = 145 °C; time, 1 h.

3. Oxidation of cellobiose catalysed by CNT-supported some transition metal catalysts

Table S2 Oxidation of cellobiose by O_2 over CNT-supported some transition metal catalysts (metal loading, 0.5 wt%)[a]

Catalyst	Cellobiose conversion /%	Selectivity[b] /%		Gluconic acid yield /%
		Glucose	Gluconic acid	
Pd/CNT	41	73	7.0	2.9
Pt/CNT	53	53	23	12
Rh/CNT	20	50	20	4.0
Cu/CNT	73	56	0	0
Ag/CNT	17	59	6.0	1.0
Au/CNT[c]	91	0	60	55
Au/CNT[d]	81	4.0	84	68

[a]Reaction conditions: cellobiose, 0.30 mmol; H_2O, 20 mL; O_2 pressure, 0.5 MPa; catalyst, 0.05 g; T = 145 °C; time, 3 h. [b]Other products include acetic acid, glycolic acid, oxalic acid and succinic acid. [c]Reduced at 350 °C. [d]Reduced at 250 °C.

4. Au 4f XPS spectra of the 0.5 wt% Au/CNT catalysts reduced at different temperatures

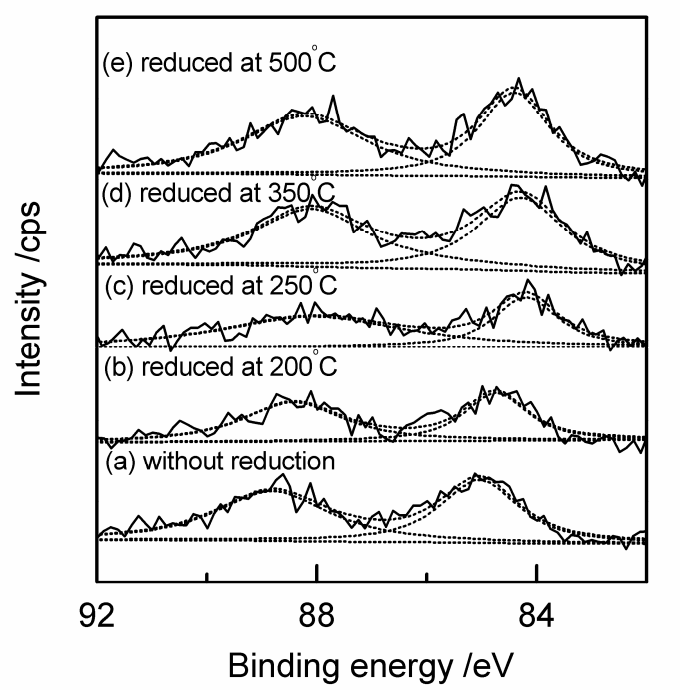

Fig. S1 Au 4f XPS spectra of the 0.5 wt% Au/CNT catalysts reduced at different temperatures. The dotted lines are the curve-fitting results.

5. Conversion of gluconic acid over the 0.5 wt% Au/CNT catalysts reduced at different temperatures

Table S3 Oxidation of gluconic acid over the 0.5 wt% Au/CNT catalysts reduced at different temperatures[a]

Reduction temperature /°C	Gluconic acid conversion /%
200	3.7
250	2.6
350	9.7
500	11

[a]Reaction conditions: Gluconic acid, 0.12 mmol; H_2O, 20 mL; O_2 pressure, 0.5 MPa; catalyst, 0.05 g; T = 145 °C; time, 1 h.

6. Conversion of gluconic acid over the 0.5 wt% Au/CNT catalysts with CNT pretreated by different concentration HNO_3 or by HCl

Table S4 Oxidation of gluconic acid over the 0.5 wt% Au/CNT catalysts with CNT pretreated by different concentration HNO_3 or by HCl[a]

CNT pretreatment	Gluconic acid conversion /%
37 wt% HCl	24
5 wt% HNO_3	10
22 wt% HNO_3	5.5
37 wt% HNO_3	4.8
68 wt% HNO_3	2.6

[a]Reaction conditions: Gluconic acid, 0.12 mmol; H_2O, 20 mL; O_2 pressure, 0.5 MPa; catalyst, 0.05 g; T = 145 °C; time, 1 h.

7. TEM micrographs and Au particle size distributions for the 0.5 wt% Au/CNT catalysts with CNT pretreated by different concentration HNO_3 or by HCl

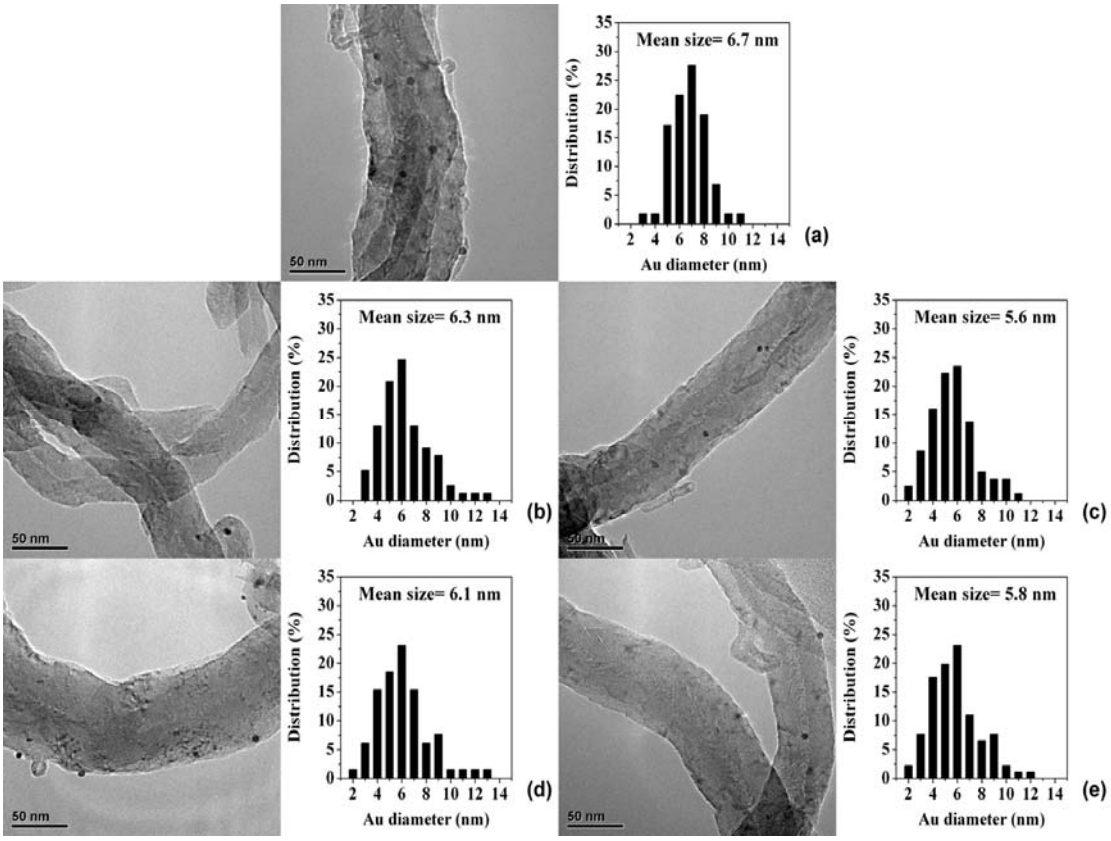

Fig. S2 TEM micrographs and Au particle size distributions for the 0.5 wt% Au/CNT catalysts with CNT pretreated by different concentration HNO_3 or by HCl. (a) by 37 wt% HCl; (b)-(e) by HNO_3 with concentrations of 5 wt%, 22 wt%, 37 wt% and 68 wt%, respectively.

8. Effect of reaction temperature on catalytic performances of the 0.5 wt% Au/CNT catalyst (reduced at 250 °C) for selective oxidation of cellobiose

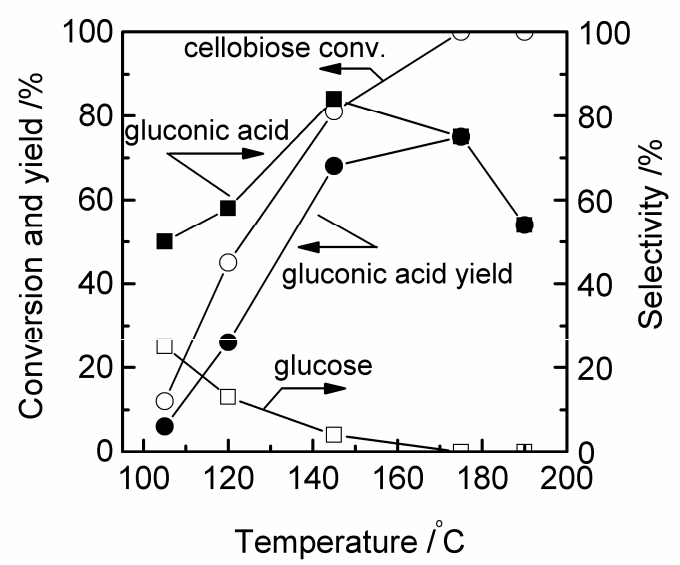

Fig. S3 Effect of reaction temperature on catalytic performances of the 0.5 wt% Au/CNT catalyst (reduced at 250 °C) for selective oxidation of cellobiose. Reaction conditions: cellobiose, 0.30 mmol; H_2O, 20 mL; O_2 pressure, 0.5 MPa; catalyst, 0.05 g; time, 3 h.

9. Time course for cellobiose conversion over the 0.5 wt% Au/CNT catalyst (reduced at 250 °C)

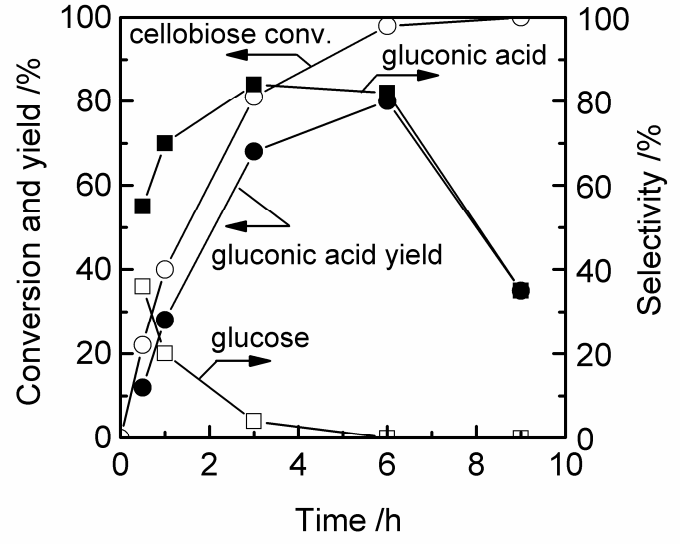

Fig. S4 Time course for cellobiose conversion over the 0.5 wt% Au/CNT catalyst (reduced at 250 °C). Reaction conditions: catalyst, 0.050 g; T = 145 °C; cellobiose, 0.30 mmol; H_2O, 20 mL; O_2 pressure, 0.5 MPa.

References

1 P. Chen, H. B. Zhang, G. D. Lin, Q. Hong and K. R. Tsai, *Carbon*, 1997, **35**, 1495.