Electronic Supplementary Information (ESI)

# Efficient Base-Free Oxidation of Monosaccharide into Sugar Acid under Mild Conditions using Hierarchical Porous Carbon Supported Au Catalysts

Xintong Meng[a], Zengyong Li[a], Di Li[a], Yiming Huang[a], Jiaojiao Ma[a], Chuanfu Liu *[a] and Xinwen Peng *[a]

[a] *State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510000, China*

* Corresponding authors:

Email: chfliu@scut.edu.cn (Prof. C. Liu); fexwpeng@scut.edu.cn (Prof. X. Pen)

Number of Pages: 26.
Number of Figures: 19.
Number of Tables: 5.

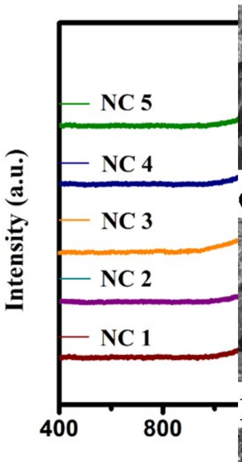



**Figure S2.** Raman spectrum of NC-x.

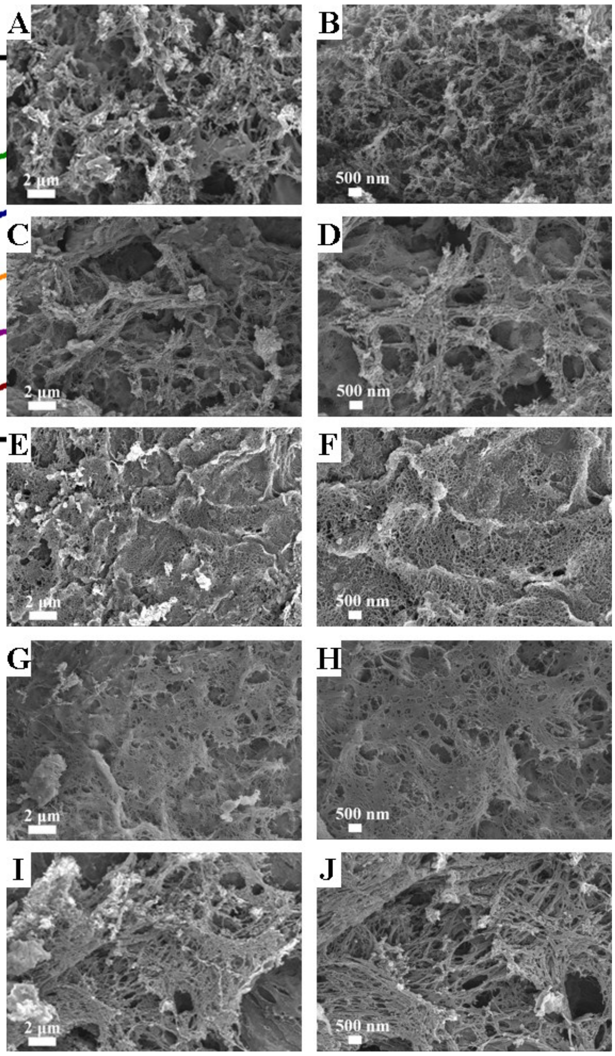



**Figure S1** SEM images of (A,B) NC-1; (C,D) NC-2; (E,F) NC-3; (G,H) NC-4; (I,J) NC-5.

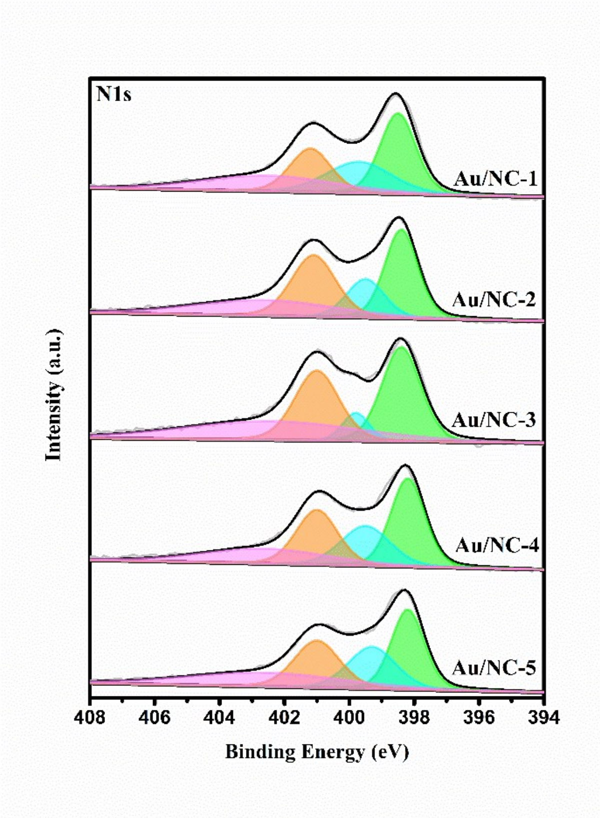



**Figure S3.** N1s spectrum of NC-x.

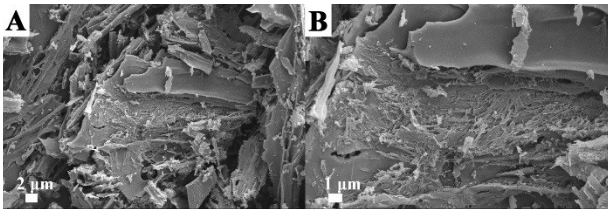



**Figure S4.** SEM images of FNC.

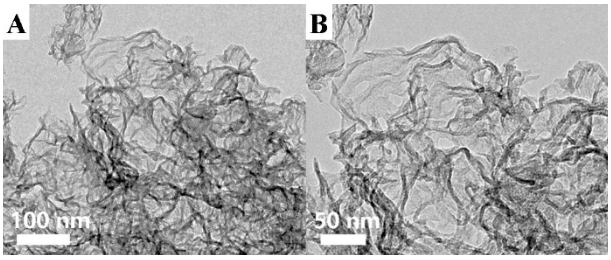



**Figure S5.** TEM images of NC-3.

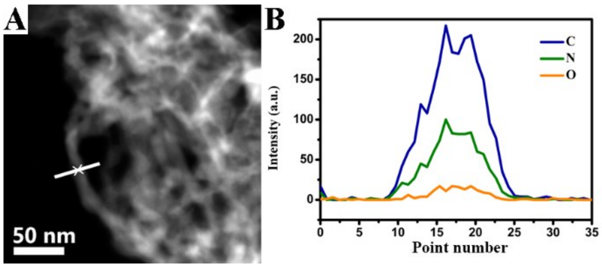



**Figure S6.** STEM image of NC-3 (A) and the line scan of NC-3.

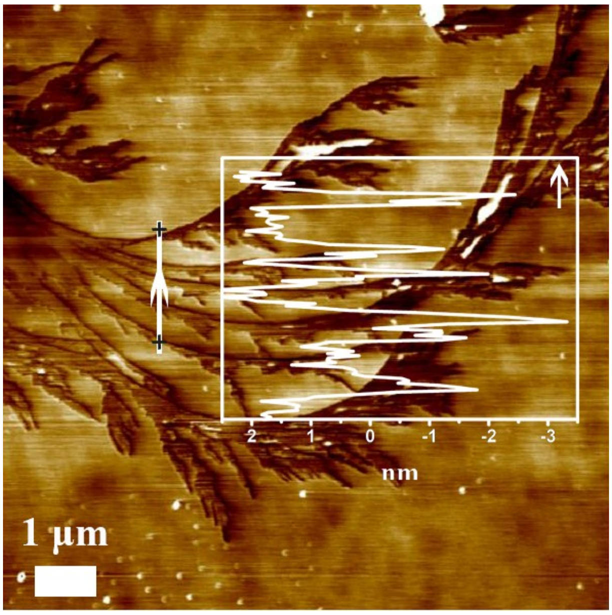



**Figure S7.** AFM image of Au/NC-3.

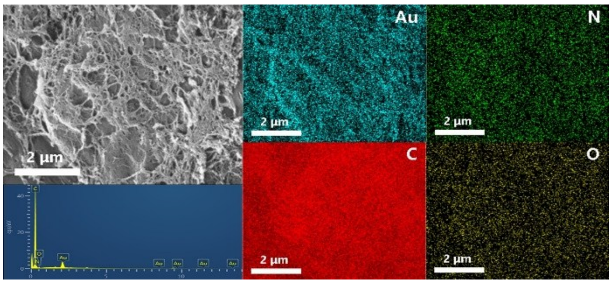



**Figure S8.** Elemental mapping of Au, N, C and O in Au/NC-3.

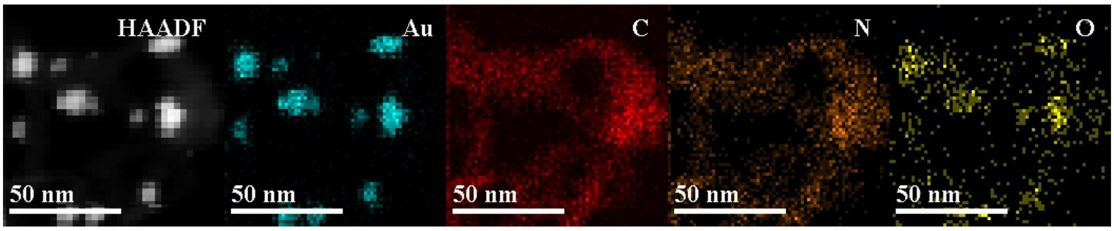



**Figure S9.** HAADF-STEM and element mapping of Au, C, N and O in Au/NC-3.

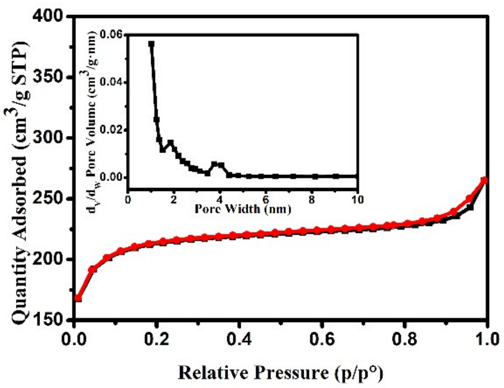



**Figure S10.** Nitrogen adsorption isotherm of the Au/NC-3. The insert image represents the BJH pore size distribution of NC-3.

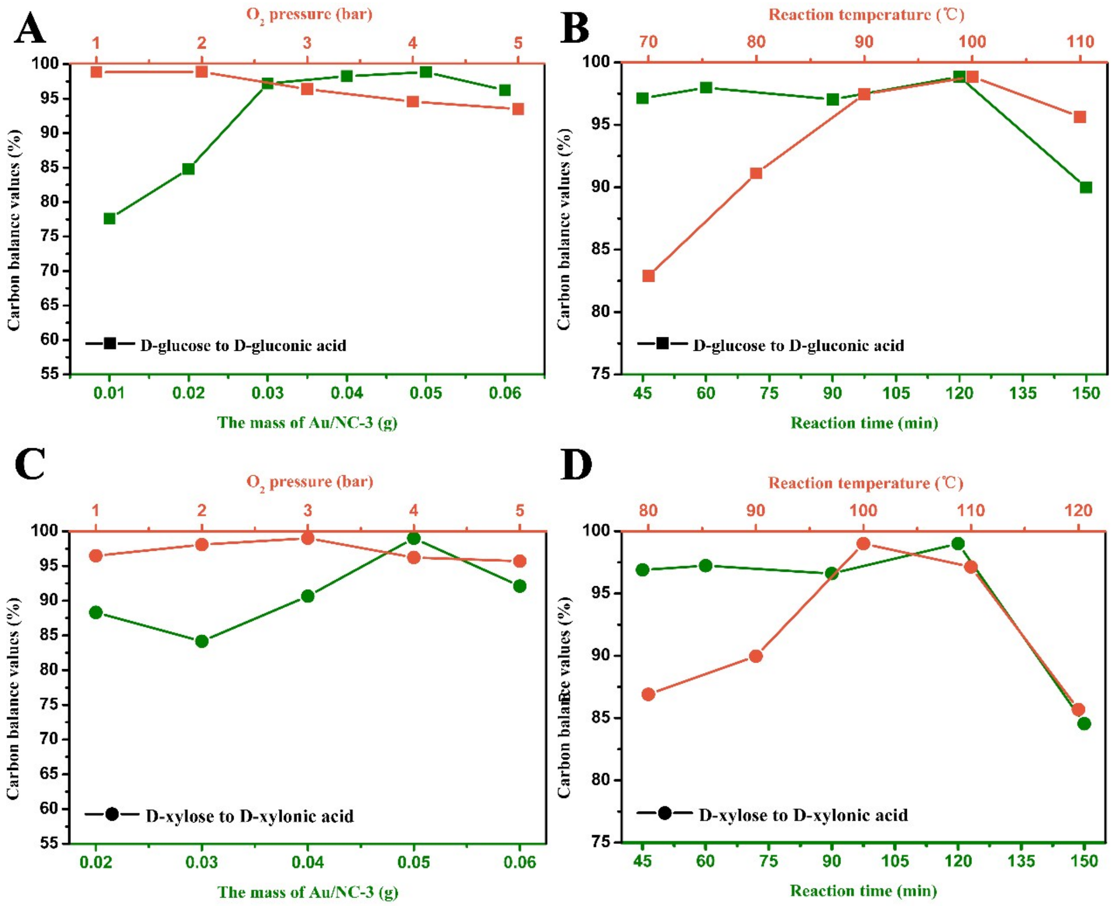



**Figure S11.** Carbon balance values of D-glucose convert into D-gluconic acid under different oxygen pressures and the mass of Au/NC-3 (A), as well as different temperatures and different reactions (B). Carbon balance values of D-xylose convert into D-xylonic acid under different oxygen pressures and the mass of Au/NC-3 (C), as well as different temperatures and different reactions (D). Reaction conditions: glucose=0.2g, H2O=30mL, stirring speed=1000 rpm(A, B); xylose=0.2g, H2O=30mL, stirring speed=1000 rpm (C, D). Carbon balance values calculated as the ratio of carbon in glucose quantified as products.[1]

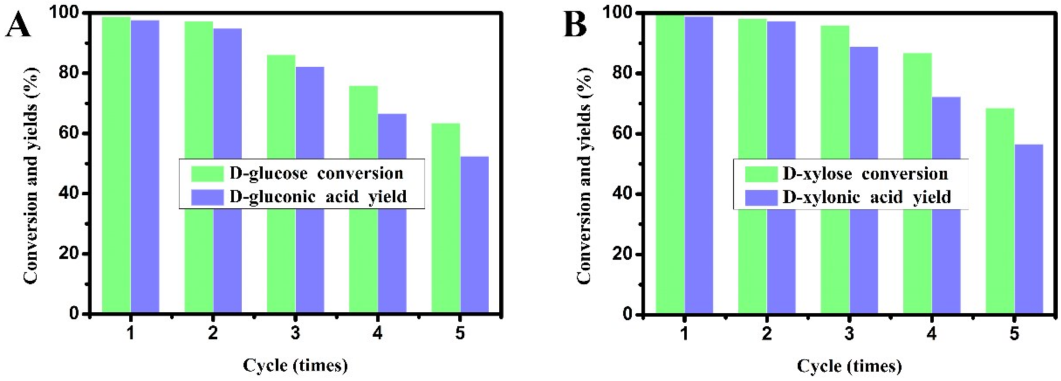



**Figure S12.** Recycle of Au/NC-3 for base-free oxidation of glucose to gluconic acid (A) and base-free oxidation of xylose to xylonic acid (B). Calcination process under 573 K in air as regeneration steps.

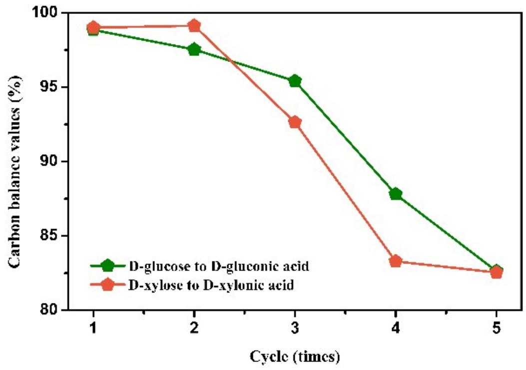



**Figure S13.** Carbon balance values of recycle of Au/NC-3 for base-free oxidation of D-glucose to D-gluconic acid and D-xylose to D-xylonic acid. Carbon balance values calculated as the ratio of carbon in glucose quantified as products.

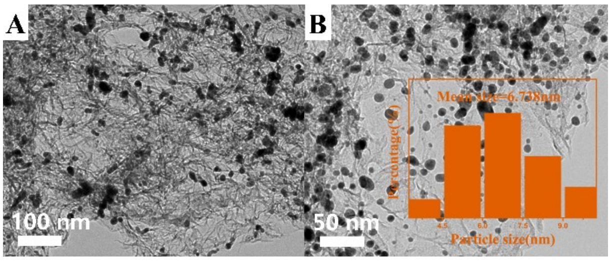



**Figure S14.** TEM images of 5$^{th}$ reused of Au/NC-3(A, B). The inset in B shows the size distribution of Au NPs from 100 particles.

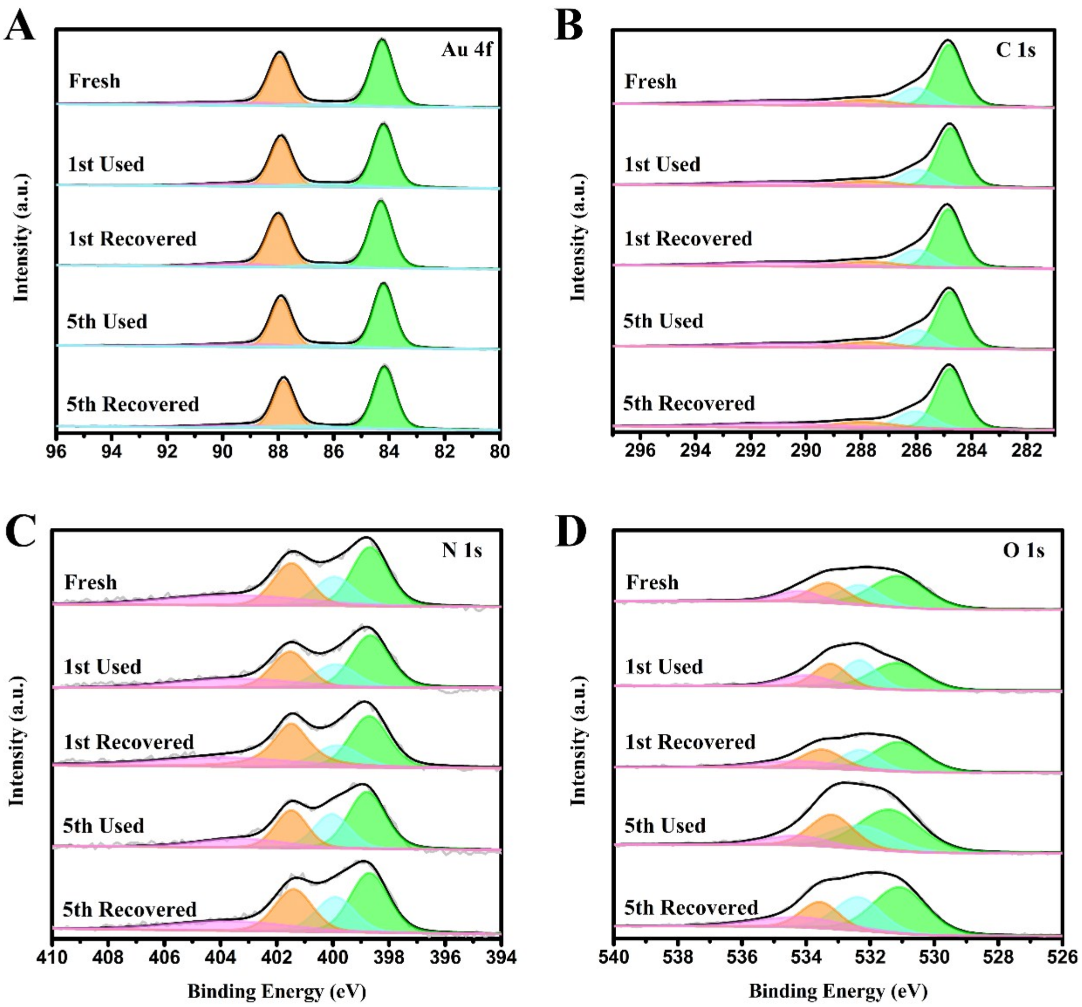



**Figure S15.** XPS spectra of (A) Au 4f, (B) C 1s, (C) N 1s and (D) O 1s of catalysts of the fresh, 1$^{st}$ used, 1$^{st}$ recovered, 5$^{th}$ used and 5$^{th}$ recovered on base-free oxidation of D-glucose to D- gluconic acid.

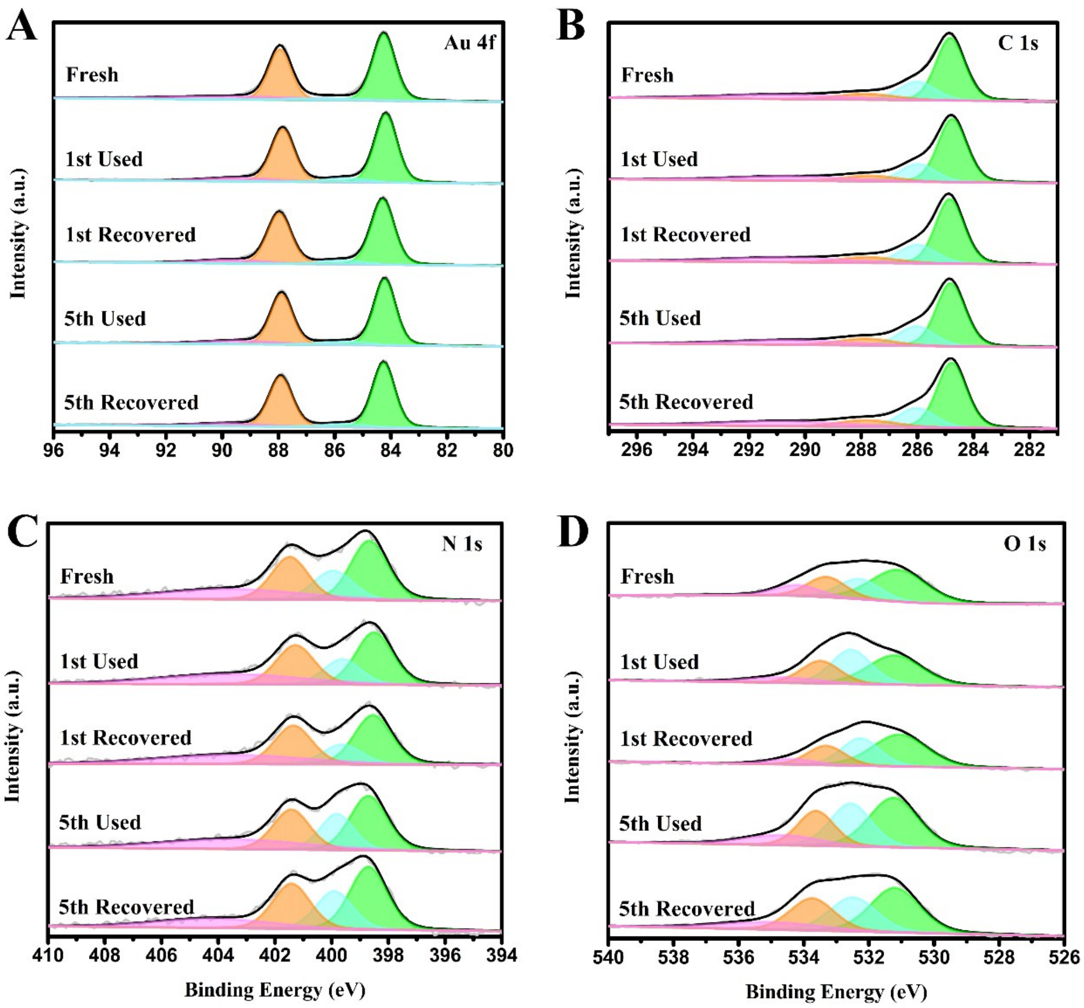



**Figure S16.** XPS spectra of (A) Au 4f, (B) C 1s, (C) N 1s and (D) O 1s of catalysts of the fresh, 1$^{st}$ used, 1$^{st}$ recovered, 5$^{th}$ used and 5$^{th}$ recovered on base-free oxidation of D-xylose to D- xylonic acid.

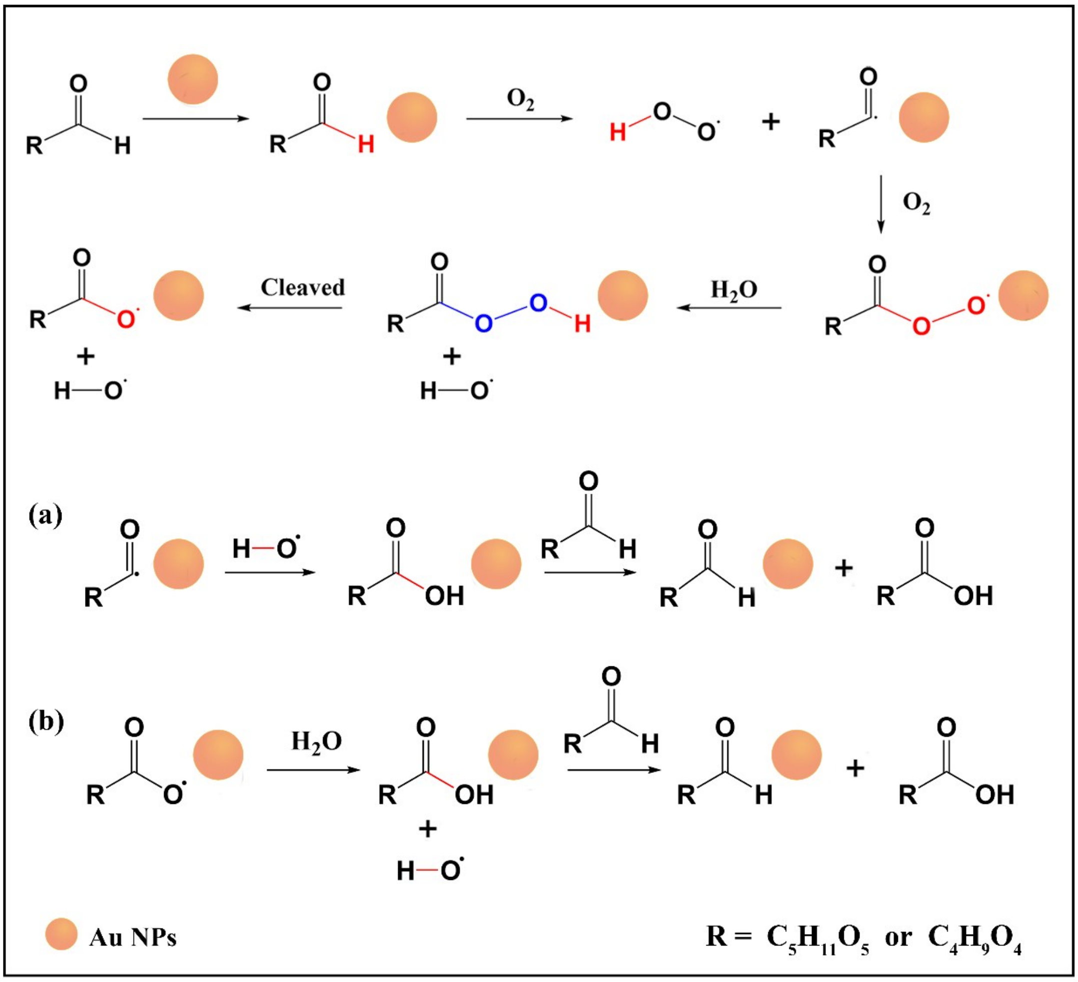
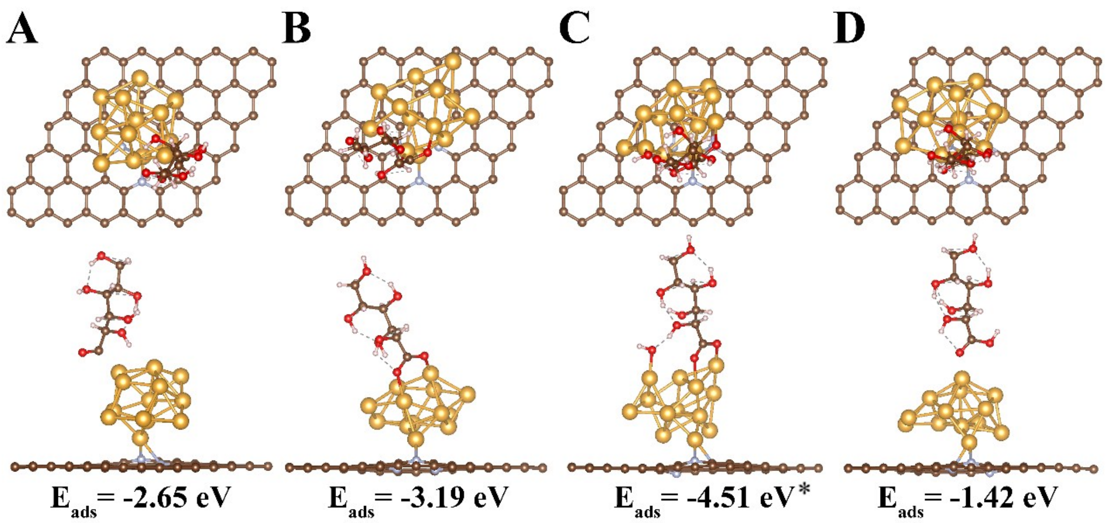
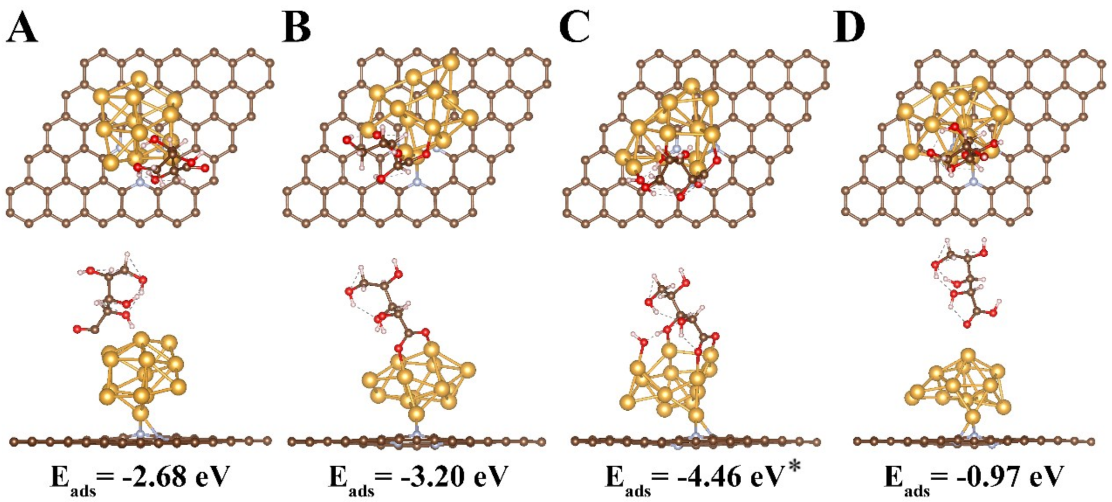



**Figure S17.** The plausible mechanism for base free oxidation of pentose or hexose catalyzed by Au/NC-3.




* RC(O)OOH tends to be cleaved to RC(O)O and OH on the surface of $Au_{13}$. The value of 4.51 is the energy of (RC(O)O + OH) relative to unabsorbed RC(O)OOH.

**Figure S18.** The optimized structure of intermedium of base-free oxidation reaction on D-glucose convert to D-gluconic acid, RCO・ (A), RC(O)O・ (B), RC(O)O・ + OH・ (C), D-gluconic acid (RC(O)OH) (D) adsorbed on the $Au_{13}$ cluster supported on graphene doped a vacant site with three pyridinic N, respectively. The catalyst models are same as those in Figure 2. The adsorption energies are marked correspondingly. R= $C_5H_{11}O_5$.




* RC(O)OOH tends to be cleaved to RC(O)O and OH on the surface of $Au_{13}$. The value of 4.46 is the energy of (RC(O)O + OH) relative to unadsorbed RC(O)OOH.

**Fig S19.** The optimized structure of intermedium of base-free oxidation reaction on D-xylose convert to D-xylonic acid, RCO・ (A), RC(O)O・ (B), RC(O)O・ + OH・ (C), D-xylonic acid (RC(O)OH) (D) adsorbed on the $Au_{13}$ cluster supported on graphene doped a vacant site with three pyridinic N, respectively. The catalyst models are same as those in Figure 2. The adsorption energies are marked correspondingly. R= $C_4H_9O_4$.

**Table S1.** Raman shift and $I_D/I_G$ of NC-x series.

| | **NC-1** | **NC-2** | **NC-3** | **NC-4** | **NC-5** |
|---|---|---|---|---|---|
| **D band($cm^{-1}$)** | 1364.12 | 1349.1 | 1348.02 | 1356.61 | 1354.11 |
| **G band($cm^{-1}$)** | 1594.42 | 1596.92 | 1586.87 | 1594.42 | 1606.93 |
| **$I_D/I_G$** | 1.0236 | 1.0297 | 1.1157 | 1.0643 | 1.0143 |

**Table S2.** Element composition based on CHNS element analysis of NC-x series.

| | NC-1 | NC-2 | NC-3 | NC-4 | NC-5 |
|---|---|---|---|---|---|
| **C** (wt%) | 69.58 | 72.76 | 70.48 | 68.56 | 67.40 |
| **N** (wt%) | 9.36 | 9.69 | 10.20 | 11.15 | 12.33 |
| **H** (wt%) | 2.03 | 1.97 | 2.17 | 2.86 | 2.24 |

**Table S3.** Peak area ratio for Pyridine N, Graphite N from XPS.

| | **NC-1** | **NC-2** | **NC-3** | **NC-4** | **NC-5** |
|---|---|---|---|---|---|
| **Pyridine N** | 29.66% | 32.81% | 34.00% | 32.94% | 29.43% |
| **Graphite N** | 20.57% | 26.67% | 30.56% | 24.87% | 23.83% |
| **Pyrrolic-N** | 23.70% | 15.63% | 20.39% | 21.44% | 22.27% |
| **N-oxides** | 26.07% | 25.52% | 15.06% | 20.76% | 24.48% |

**Table S4.** ICP-OES analysis of Au/NC-x series.

| | **Au/NC-1** | **Au/NC-2** | **Au/NC-3** | **Au/NC-4** | **Au/NC-5** | **Au/FNC** |
|---|---|---|---|---|---|---|
| **Metal loading (wt%)** | 0.75 | 0.89 | 0.97 | 0.87 | 0.80 | 0.35 |

**Table S5.** Base-free oxidation of D-glucose and D-xylose catalyzed by Au/NC-x.

| | Conversion (%) | | Yield (%) | | Selectivity (%) | |
|---|---|---|---|---|---|---|
| | D-glucose [a] | D-xylose [b] | D-gluconic acid [a] | D-xylonic acid [b] | D-gluconic acid [a] | D-xylonic acid [b] |
| Au/NC-1 | 69.39 | 79.87 | 61.80 | 66.23 | 89.06 | 82.92 |
| Au/NC-2 | 86.89 | 88.13 | 80.07 | 84.71 | 92.15 | 96.11 |
| Au/NC-3 | 98.76 | 99.86 | 97.62 | 98.76 | 98.85 | 98.90 |
| Au/NC-4 | 91.08 | 95.91 | 86.78 | 89.21 | 95.28 | 93.01 |
| Au/NC-5 | 89.57 | 84.15 | 78.02 | 76.23 | 87.11 | 90.59 |

[a] Reaction conditions: D-glucose (0.2 g), Au/NC-3 (0.05 g), water (30mL), $O_2$ (2 bar), stirring speed (1000 rpm), 120min and 100 ℃. [b] Reaction conditions: D-xylose (0.2 g), water (30mL), $O_2$ (3 bar), Au/NC-3 (0.05 g), stirring speed (1000 rpm), 120min and 100 ℃.

# References

1. J. Iglesias, J. Moreno, G. Morales, J. A. Melero, P. Juárez, M. López-Granados, R. Mariscal and I. Martínez-Salazar, *Green Chemistry*, 2019, **21**, 5876-5885.