

## **Electronic Supplementary Information:**

### **Highly Selective Oxidation Monosaccharides to Sugar Acids at Room Temperature over Palladium Supported on Surface Functionalized Carbon Nanotubes**

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**Materials.** Nitric acid ( $\text{HNO}_3$ , 65%-68%) was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Gluconic acid sodium salt and multi-walled carbon nanotube (CNT) with outer diameters of 30-50 nm, inner diameters of 5-12 nm and length of 10-20  $\mu\text{m}$  were obtained from Macklin Reagent Corporation (Shanghai, China). Sodium hydroxide (NaOH), polyvinyl alcohol (PVA), sodium tetrachloropalladate ( $\text{NaPdCl}_4$ ), sodium borohydride ( $\text{NaBH}_4$ ) and palladium on activated charcoal (Pd/C) were bought from Aladdin Industrial Corporation (Shanghai, China). Glucose, xylose, xylonic acid calcium salt hydrate was obtained from Sigma-Aldrich (Shanghai, China). All purchased chemicals and reagents were analytical grade and used as received without further purification. Ultrapure water was used for the preparation of all solutions.

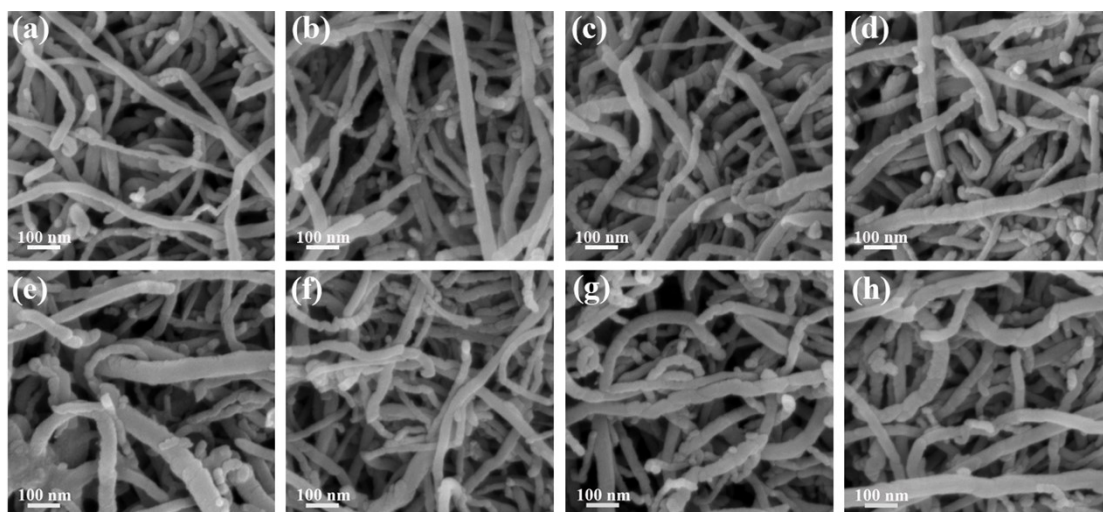
**Supports and catalysts characterization.** Powder X-ray diffraction (XRD) was carried out using a Bruker D8 Advance diffractometer using  $\text{Cu K}\alpha$  radiation. The operating voltage and current were 40 kV and 40 mA, respectively. The step length was  $0.02^\circ$  with scanning rate of  $2^\circ/\text{min}$ . Raman spectra of the CNTs supports were recorded on a LabRAM 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  $500\text{-}2500\text{ cm}^{-1}$ . The X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Ultra system and an  $\text{Al K}\alpha$  radiation source in order to study the elemental composition and the bonding configuration of the Pd/CNTs catalysts surface. The organic element composition of the catalysts was detected by Vario EL cube element analysis instrument. Inductive coupled plasma mass spectroscopy (ICP-MS) was performed on PerkinElmer NexION 300X to detect the Pd loadings of catalysts. Nitrogen adsorption-desorption isotherms were measured using Micromeritics ASAP 2460. The specific surface area of the samples was calculated by Brunauere-Emmette-Teller (BET) method. The average pore diameter and pore size distributions of the CNTs supports were evaluated by analyzing the desorption branch of isotherm in line with the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscope (SEM, Merlin) was employed to determine the surface morphology and structure of the samples. Transmission electron microscopy (TEM) images were gained on a JEOL

JEM-2100F electron microscopy operated at a 200 kV of acceleration voltage. The samples for TEM were ultrasonically dispersed in ethanol and then deposited on carbon-coated copper grids using capillary and dried in air for 30 min.

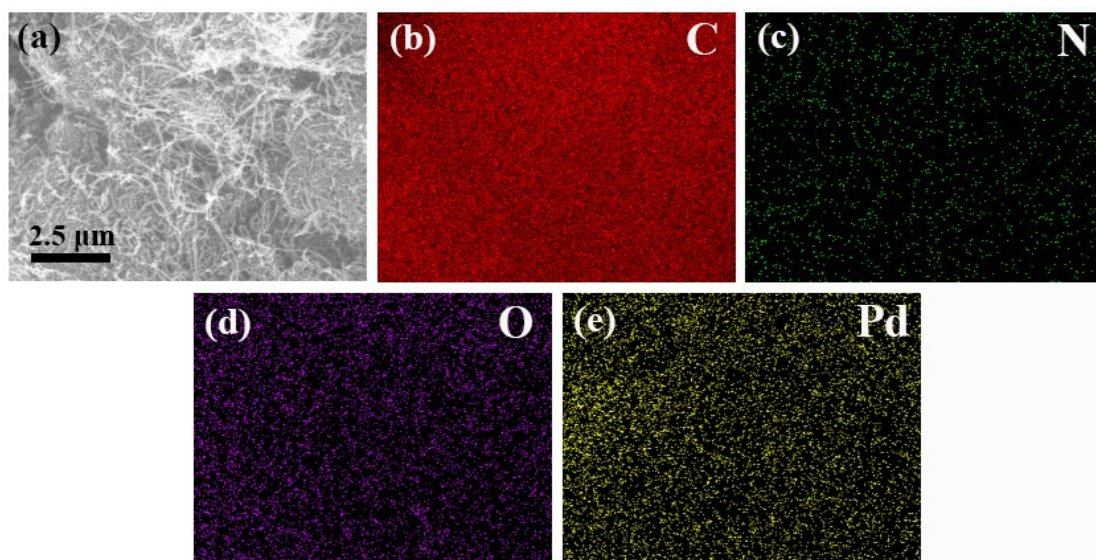
**Product analysis.** Gluconic acid, and xylonic acid were determined by HPLC (Agilent 1260 series) equipped with a UV detector at 210 nm and a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm × 9 μm). A 5 mM of H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as eluent with a flow rate of 0.6 mL/min. The column was thermostated at 35 °C by a column heater. The sampling loop has a volume of 20 μL. Glucose and xylose were measured using HPIC (Dionex ICS-3000) with an integrated amperometric detector and a CarboPac PA1 column at 30 °C. The ultrapure water was used as eluent. The concentrations of the products were calculated by comparing the calibration curve established with the external standard. The feedstock conversion and products yield were computed by the following equations:

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

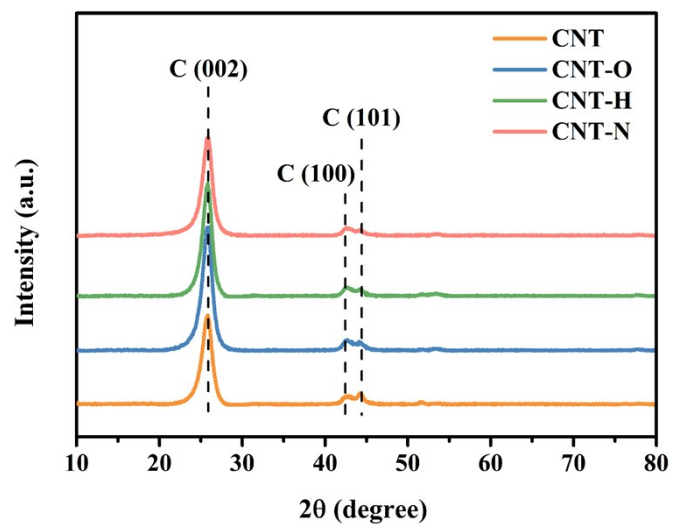
$$\text{Products yield (\%)} = \frac{\text{Moles of carbon in products}}{\text{Moles of carbon in feedstock input}} \times 100\% \#$$



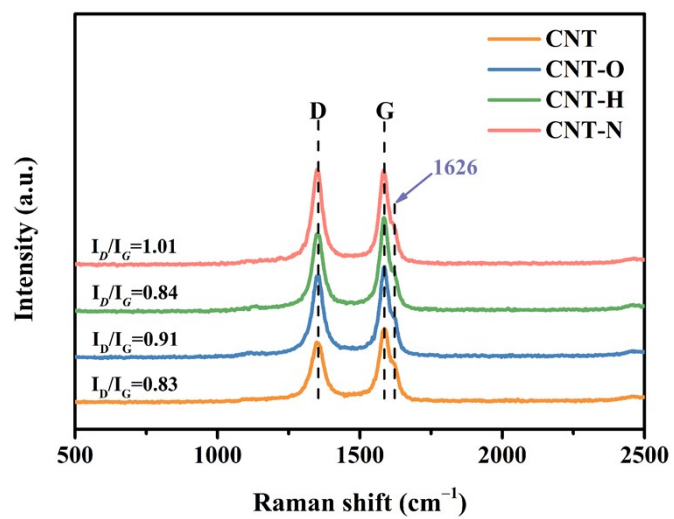
**Fig. S1.** SEM images of (a) CNT, (b) CNT-O, (c) CNT-H, (d) CNT-N, (e) Pd/CNT, (f) Pd/CNT-O, (g) Pd/CNT-H, and (h) Pd/CNT-N.



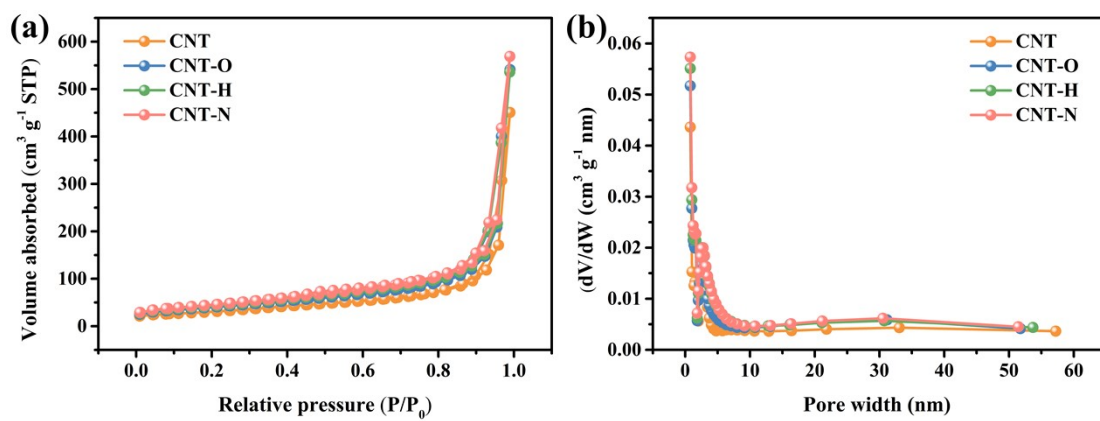
**Fig S2.** SEM image of (a) Pd/CNT-N and the corresponding elemental mapping images of (b) C, (c) N, (d) O, and (e) Pd elements.



**Fig. S3.** XRD patterns of CNT, CNT-O, CNT-H and CNT-N.

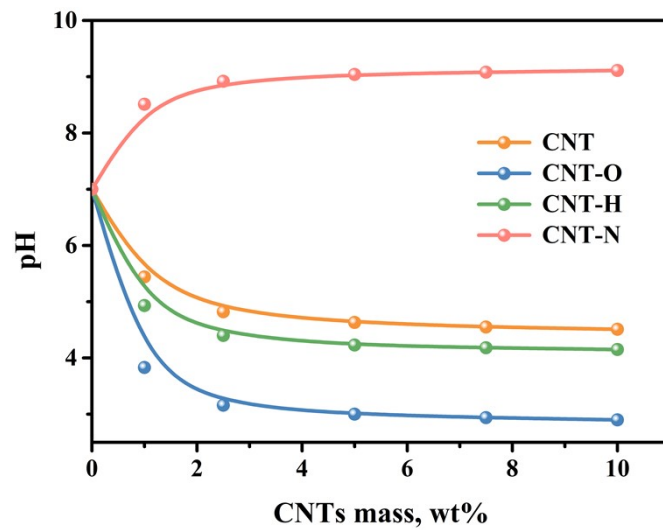


**Fig. S4.** Raman patterns of CNT, CNT-O, CNT-H and CNT-N.

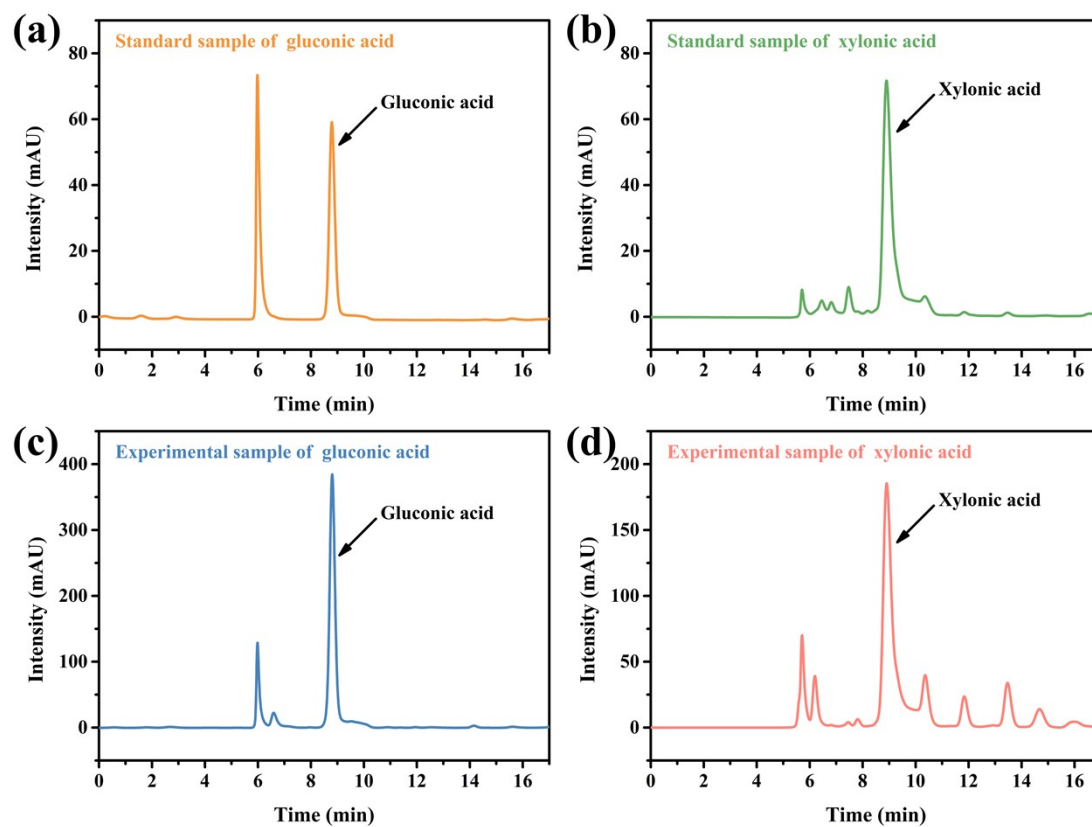


**Fig. S5.** (a) N<sub>2</sub> adsorption-desorption isotherm and (b) pore size distribution of CNT, CNT-O, CNT-H and CNT-N.

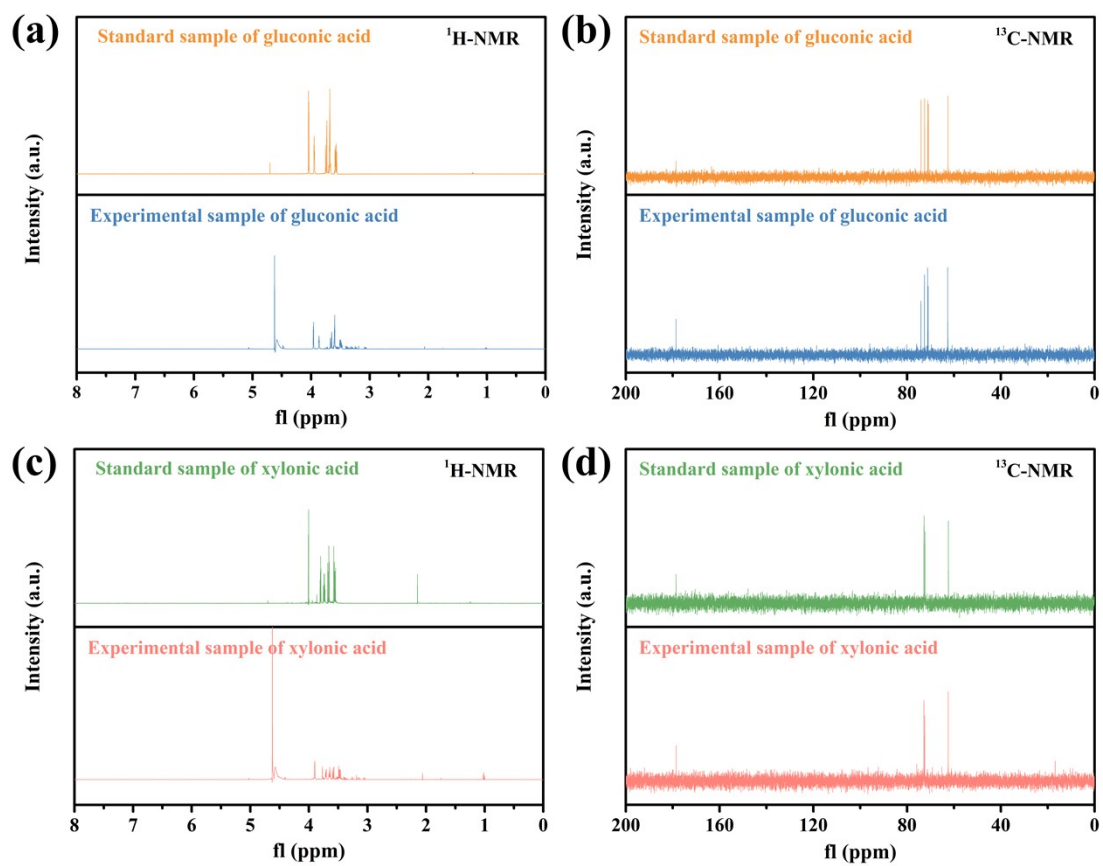




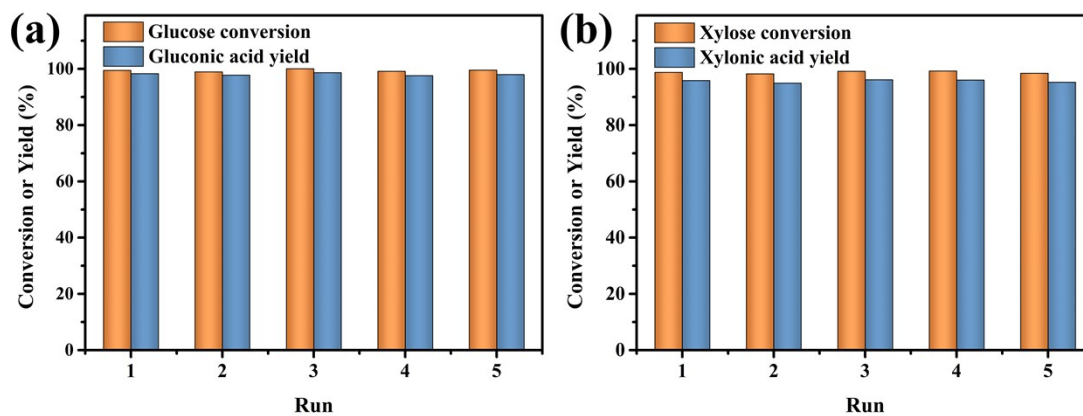
**Fig. S6.** Mass titration of CNT, CNT-O, CNT-H and CNT-N.



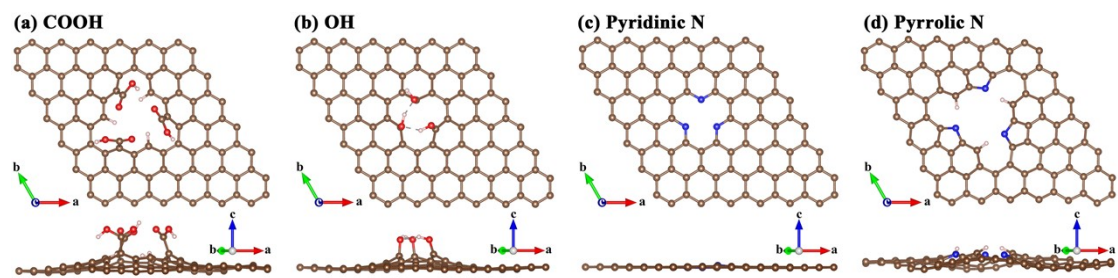
**Fig. S7.** HPLC spectra of standard samples of (a) gluconic acid and (b) xyloonic acid, and experiment samples of (c) gluconic acid and (d) xyloonic acid.



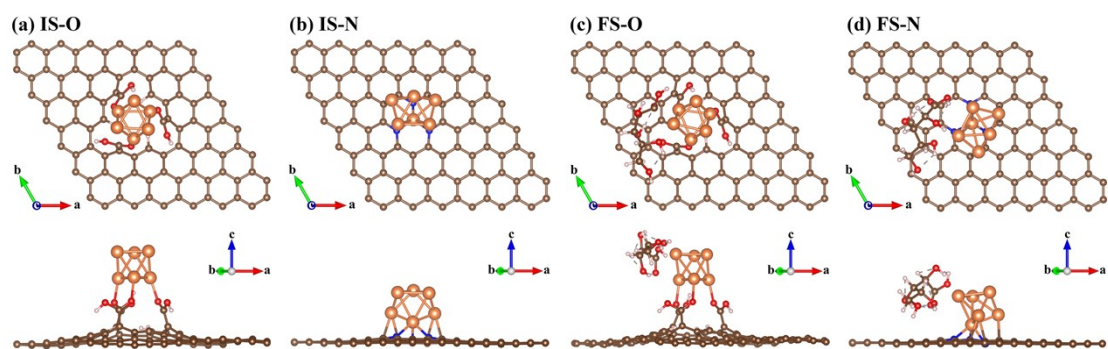
**Fig. S8.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of standard samples and experiment samples of (a, b) gluconic acid and (c, d) xylonic acid.



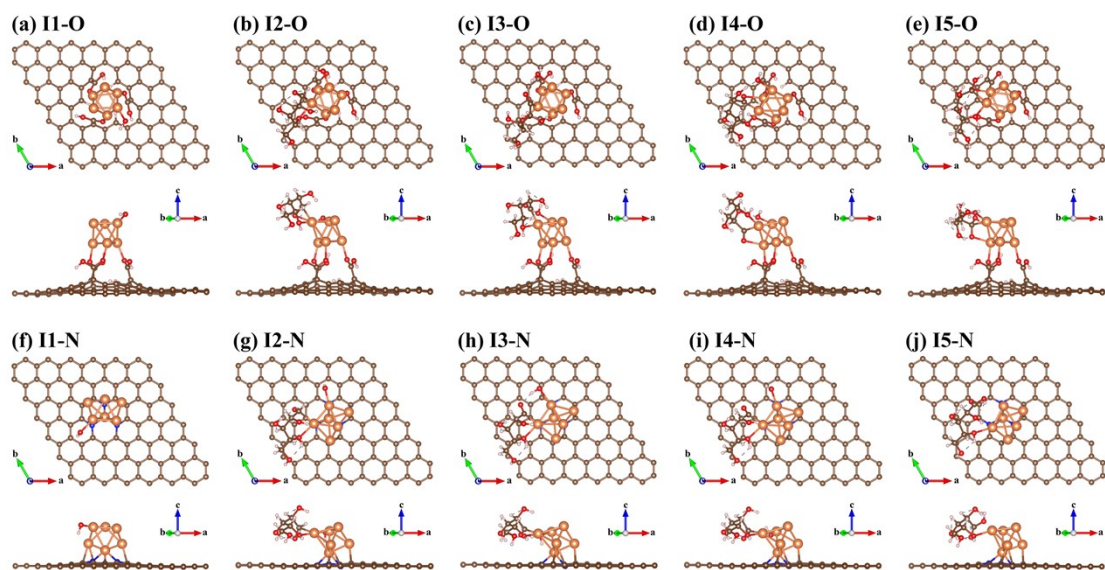
**Fig. S9.** Recycling test of Pd/CNT-N for selective oxidation of glucose (a) and xylose (b) at room temperature. Reaction conditions: 1 mmol glucose or xylose, 36 mg catalyst, 2 mmol NaOH, 25 ml water, 1 MPa O<sub>2</sub>, 30 °C, 180 min, 600 rpm.



**Fig. S10.** The geometric models of CNT-O support: the structures of a graphene layer modified by (a) three carboxyl groups, and (b) three hydroxy groups; The geometric models of CNT-N support: the structures of a graphene layer modified by (c) three pyridinic N atoms, and (d) three pyrrolic N atoms.



**Fig. S11.** The structures of initial state and final state of xylose oxidation over (a, c) Pd/CNT-O or (b, d) Pd/CNT-N.



**Fig. S12.** The structures of intermediate state of xylose oxidation over (a-e) Pd/CNT-O or (f-j) Pd/CNT-N.

**Table S1** Elemental composition and N<sub>2</sub> adsorption-desorption results of CNT-X.

Entry	Sample	Content (%)				S <sub>BET</sub> , m <sup>2</sup> /g	V <sub>pore</sub> , m <sup>3</sup> /g	D <sub>pore</sub> , nm
		C	O <sup>a</sup>	N	H			
1	CNT	94.67	4.91	–	0.42	110.91	0.69	6.62
2	CNT-O	92.85	6.61	–	0.51	151.96	0.83	7.33
3	CNT-H	96.42	3.22	–	0.35	153.76	0.82	7.13
4	CNT-N	96.42	2.71	0.55	0.32	158.13	0.87	6.82

<sup>a</sup>O=100–C–H–N.



**Table S2** The Pd content was measured by ICP-MS <sup>a</sup>.

Entry	Sample	Pd content (wt%)
1	Pd/CNT	2.10
2	Pd/CNT-O	2.04
3	Pd/CNT-H	2.07
4	Pd/CNT-N	1.99

<sup>a</sup> Inductively Coupled Plasma Mass Spectrometer.

**Table S3** Selective oxidation of glucose or xylose over various catalysts <sup>a</sup>.

Entry	Catalyst	Conversion (%)		Yield (%)	
		Glucose	Xylose	Gluconic acid	Xyonic acid
1	No catalyst	87.7	89.2	Trace	Trace
2	CNT	89.5	92.3	Trace	Trace
3	CNT-O	88.9	91.4	Trace	Trace
4	CNT-H	90.4	93.5	Trace	Trace
5	CNT-N	91.3	94.6	Trace	Trace
6	Pd/CNT-N	99.4	98.7	98.3	95.8
7	Pd/CNT-N <sup>b</sup>	5.4	6.7	0.9	1.8
8	Pd/CNT-N <sup>c</sup>	60.1	56.2	2.2	4.3
9	Pd/C <sup>d</sup>	90.4	94.2	77.8	75.2

<sup>a</sup> Reaction conditions: 1 mmol glucose or xylose, 36 mg catalysts, 2 mmol NaOH, 25 ml water, 1 MPa O<sub>2</sub>, 30 °C, 180 min, 600 rpm.

<sup>b</sup> Reaction without NaOH.

<sup>c</sup> Reactor purged with nitrogen.

<sup>d</sup> Pd/C catalyst was purchased from Aladdin Industrial Corporation Co. Ltd. (Shanghai, China).

**Table S4** Activation energy barrier of xylose oxidation over Pd/CNT-O or Pd/CNT-N <sup>a</sup>.

Entry	Catalysts	Activation energy barrier (eV)		
		Dissociation of C-H	Formation of adsorbed xylonic acid	Oxidation of xylose
1	Pd/CNT-O	0.66	0.43	0.66
2	Pd/CNT-N	0.56	0.22	0.56

<sup>a</sup> Calculations by DFT.