

## [Supplementary Information]

### Improved Electrocatalytic Activity for Ethanol oxidation by Pd@N-doped Carbon from Biomass

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#### Experimental Chemicals

D-glucosamine hydrochloride, glucose, Ludox-HS 40, ammonium acid fluoride, and palladium chloride were purchased from Sigma-Aldrich. Potassium hydroxide, absolute ethanol and 5wt.% Nafion 117 solution are purchased from Aladdin. Commercial Pd@AC (active carbon) is gifted by ZHEJIANG NHU CO., LTD. All other reagents are of analytical grade and used without further purification.

#### Synthesis of catalysts

The catalysts were synthesized according our previous work.<sup>1a</sup> In a typical procedure, 4g D-glucosamine hydrochloride and 3.75 g Ludox-HS 40 were mixed in an aqueous solution. The mixture was heated at 80°C in an oil bath upon stirring overnight to remove the water. The as-prepared compound was grinded finely and then preliminary carbonized for 24h at 180°C by hydrothermal carbonization (HTC) process. The remaining black material was heated to 1000°C at 10°C/min and held for 1 h under N<sub>2</sub> atmosphere. Then, NH<sub>4</sub>HF<sub>2</sub> solution (4 mol/L) was selected to get rid of silica template by stirring for 2 days. The dispersion was then filtered and the solid was washed with water and ethanol. After filtering, the black products was dried at 80°C overnight in a vacuum oven. The synthesis of HC (non-nitrogen hydrothermal carbon from glucose) was the same as CN except that the carbon source was glucose. An ultrasonic-assisted method was applied to deposit Pd on CN and HC.<sup>1b</sup> Typically, 0.4 g support was dissolved in 10 mL water under ultrasound for 15 min. Then, 4 mL

PdCl<sub>2</sub> (0.01g/mL) aqueous solution was added into the support solution, holding for another 15 min. Then, 10mL NaBH<sub>4</sub> solution (0.2% w/w) was added to this suspension and the dispersed PdCl<sub>2</sub> was reduced to Pd nanoparticles and deposited on CN immediately. Finally, Pd@CN was separated by filtration, washed with water several times and dried at 70°C overnight. Pd@HC was also synthesized by US method.

### **Material Structural and Morphological Characterization**

The Pd content was measured by ICP-AES (IRIS Intrepid II XSP, Thermo Fisher Scientific, USA). The Pd content of Pd@AC, Pd@HC and Pd@CN were 5% wt., 3% wt., 3.3% wt. respectively. Elemental analysis was performed by Elementary Varo MACRO. The content of nitrogen in CN was about 7.0 %. TEM (Model JEM-1230, JEOL Co. Ltd., Japan) characterization was operated at an accelerating voltage of 80 kV. The diffraction data were collected at room temperature with 2θ scan range between 10° and 80° using a wide-angle X-ray diffraction (Model D/tex-Ultima TV, 1.6 kV, Rig-aku, Japan) equipped with Cu Kα radiation (1.54 Å). The X-ray photoelectron spectra were obtained with an ESCALAB MARK II spherical analyzer using a magnesium anode (Mg 1253.6 eV) X-ray source. All XPS spectra were corrected using the C 1s line at 284.5 eV, and curve fitting and background subtraction were accomplished.

As shown in figure 2, the Pd nanoparticles are uniformly dispersed on supports. According to the procedures described by Mahata and Vishwanathan<sup>2</sup> and Anderson, the dispersion (D), i.e., the fraction of exposed Pd in the catalyst, can be roughly calculated by the following equation:

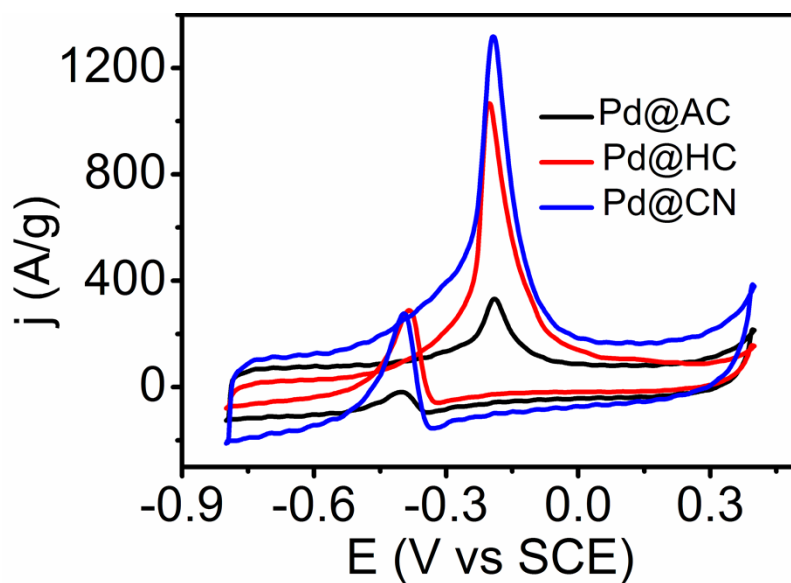
$$D (\text{Pd dispersion}) = 1.12/d \text{ (mean diameter of Pd nanoparticles, nm)}$$

Accordingly, the D value of Pd@AC, Pd@HC and Pd@CN were determined to be 0.26, 0.28, and 0.29 respectively.

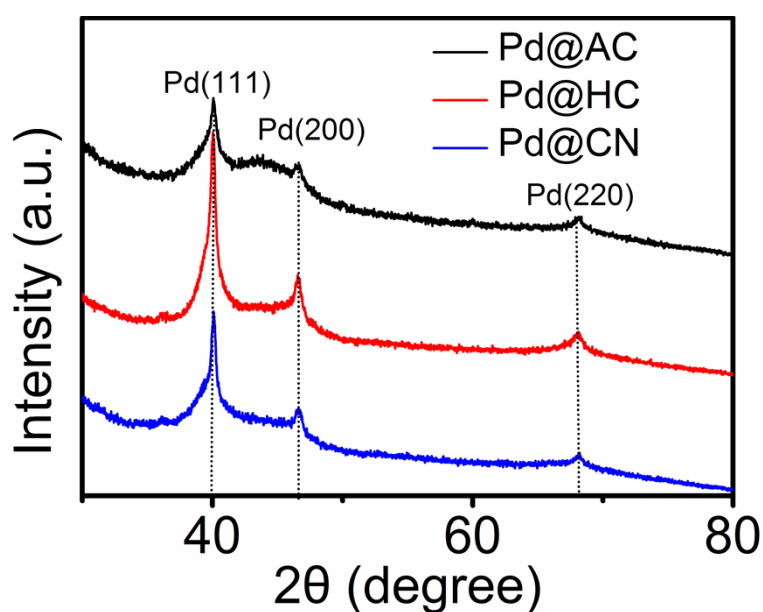
### **Electrochemical Characterization**

Electrochemical measurements were performed in a conventional three-electrode electrochemical cell by using a LK2005A electrochemical analyzer. A commercial glassy carbon (GC) electrode (5mm diameter, 0.196 cm<sup>2</sup>) was polished to a mirror-like finish and thoroughly cleaned. The preparation of the working electrode was

performed as described below: ethanol suspensions containing 500uL ethanol, 3 mg of catalyst and 50uL 5wt. % Nafion solution were obtained by ultrasonic mixing for about 20 min. The 5uL of the catalyst ink suspension thus obtained was coated onto the polished GC electrode. A saturated calomel electrode (SCE) with a double salt bridge system was used as the reference electrode and a Pt plate served as the auxiliary electrode. All potentials in this study were reported with respect to the SCE. Electrochemical activities of the catalysts were assessed by cyclic voltammetry (CVs), chronoamperometric curves, and CO stripping tests. CVs were performed in a mixed solution of 1 M C<sub>2</sub>H<sub>5</sub>OH + 1 M KOH. The electrochemically active surface area (ECSA) of the catalysts can be calculated from the reductive peak of the palladium oxides. The ECSA (m<sup>2</sup>/g<sub>Pd</sub>) of the catalysts is estimated according to the equation  $ECSA = Q / (424 * W_{Pd})$ , where  $W_{Pd}$  represents the Pd loading (μg/cm<sup>2</sup>) on the electrode, Q is the total charge (μC) of reducing Pd oxides, and 424 is the palladium's conversion factor.<sup>3</sup> CO-stripping voltammetry measurements were performed according to previous reported procedure.<sup>4</sup> N<sub>2</sub> was bubbled through all the solution for 30 min to remove the dissolved O<sub>2</sub> prior to the electrochemical measurements (scan rate: 50 mV s<sup>-1</sup>). All electrochemical measurements were carried out at 25°C.

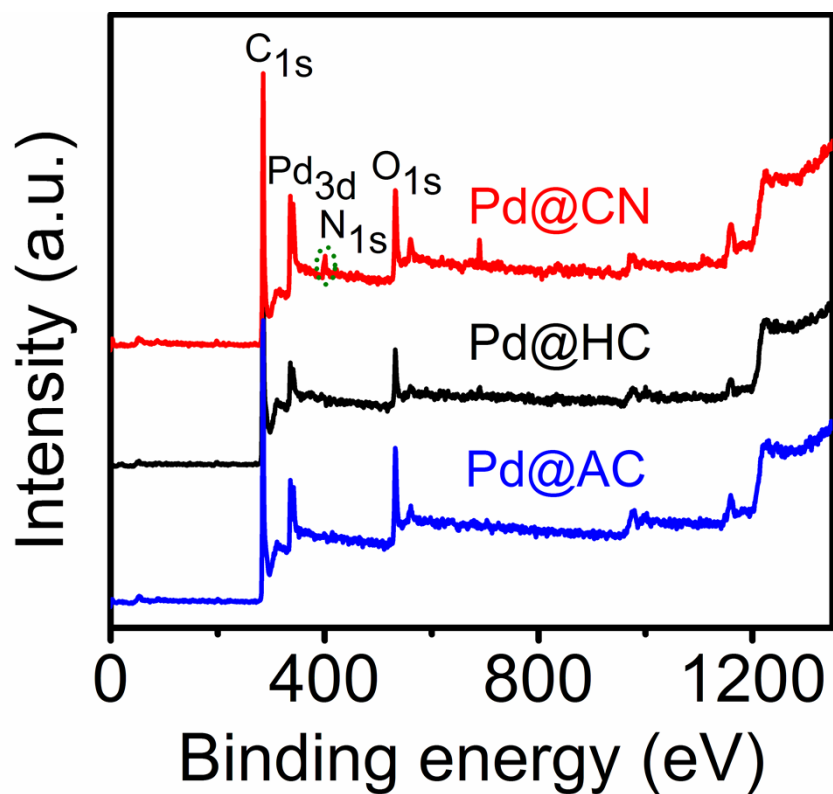


**Fig. S1.** CVs of Pd@AC, Pd@HC, and Pd@CN in 1 M CH<sub>3</sub>OH + 1 M KOH solution at a scan rate of 50 mV/s. (The current density is normalized to per unit mass of Pd).

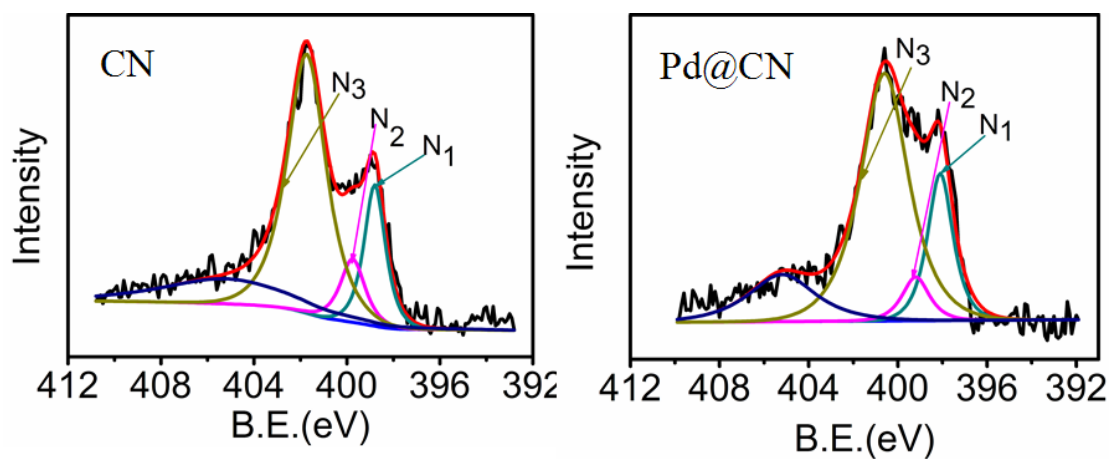


**Fig. S2.** XRD patterns of Pd@AC, Pd@HC, and Pd@CN.

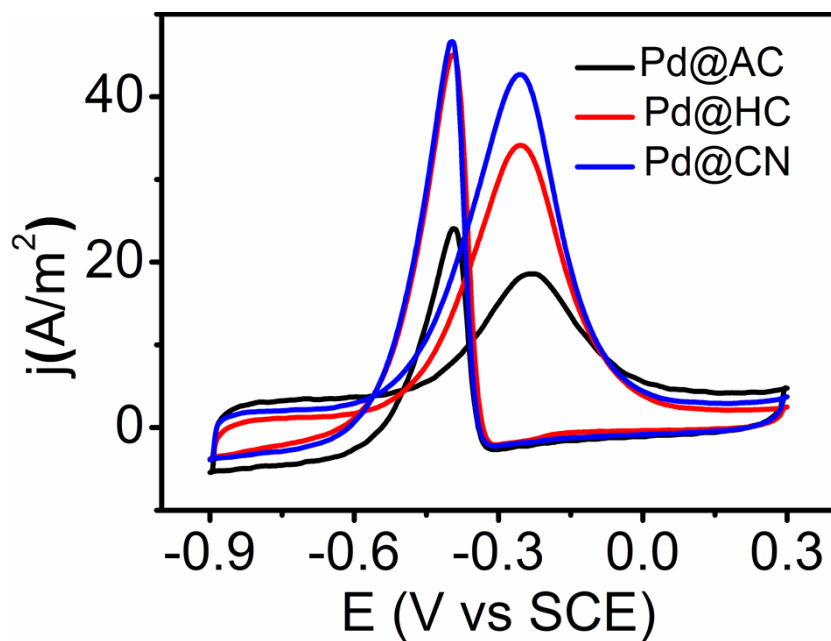
All catalysts exhibit similar diffraction peaks of (111), (200), (220) planes corresponding to a face centered cubic crystal structure, indicating similar metal morphology structure.



**Fig. S3.** The survey X-ray photoelectron spectroscopies of Pd@AC, Pd@HC, and Pd@CN.



**Fig. S4.** The deconvoluted  $N_{1s}$  XPS of CN and Pd@CN ( $N_1$ : pyridic-N,  $N_2$ : pyrrolic-N and  $N_3$ : quaternary-N).



**Fig. S5.** CVs of Pd@AC, Pd@HC, and Pd@CN in 1 M C<sub>2</sub>H<sub>5</sub>OH + 1 M KOH solution at 50mV/s. (The surface area normalized activity based the electrochemical surface area of Pd).

**Table S1.** The structure parameters of supports and the properties of catalysts.

samples	D <sub>p</sub> (nm)	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	samples	ECSA (m <sup>2</sup> g <sup>-1</sup> ) I <sub>Pd</sub>	D <sub>Pd</sub> (nm)
AC	4	0.64	899	Pd@AC	28.20	3.79
HC	34	0.9	115	Pd@HC	38.6	3.52
CN	8	0.75	324	Pd@CN	53.7	3.40

D<sub>p</sub>: pore diameter    V<sub>p</sub>: pore volume    D<sub>Pd</sub>: metal particle size

**Table S2.** Pd<sub>3d</sub> XPS analysis datas of Pd@AC, Pd@HC, and Pd@CN.

Sample	Pd <sup>0</sup> (Pd <sub>3d3/2</sub> )		Pd <sup>2+</sup> (Pd <sub>3d5/2</sub> )		The percentage of Pd <sup>0</sup>
	B. E. (ev)		B. E. (ev)		
Pd@AC	335.9	341.0	337.3	342.3	55.5%
Pd@HC	335.9	341.0	337.4	342.3	60.6%
Pd@CN	336.5	341.7	338.2	343.6	70.0%

**Table S3.** The binding energies of the three types of nitrogen for CN and Pd@CN.

sample	N <sub>1</sub>	N <sub>2</sub>	N <sub>3</sub>
	B. E. (ev)	B. E. (ev)	B. E. (ev)
CN	398.8	399.7	401.7
Pd@CN	398.1	399.2	400.6

## References

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