

## **Electronic property-dependent activity and durability in Pd/C catalyzed hydrogenation of benzoic acid**

Ke Xu,<sup>#a</sup> Yu Sun,<sup>#a</sup> You Wang,<sup>a,b</sup> Bing Du,<sup>c</sup> Xiaolong Li,<sup>c</sup> and Sai Zhang<sup>\*a,b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, 710072 Xi'an, China

<sup>b</sup> Research & Development Institute of Northwestern Polytechnical University in Shenzhen, 518057 Shenzhen, China

<sup>c</sup> Shaanxi Rock New Material Co., Ltd, 721013 Baoji, China

<sup>#</sup> These authors contributed equally to this work.

Email: [zhangsai1112@nwpu.edu.cn](mailto:zhangsai1112@nwpu.edu.cn)

## Experimental detail

### Synthesis of Pd/C-H<sub>2</sub>O<sub>2</sub>, Pd/C-50 and Pd/C-150 catalysts

The commercial Pd/C catalysts (Batch number: D5H2B) were obtained from Shannxi Rock New Materials Co., Ltd. and washed three times alternately by ethanol and water. The loading of Pd in Pd/C was 5.0 wt.%.

The Pd/C-H<sub>2</sub>O<sub>2</sub> catalysts were treated by 30 wt.% H<sub>2</sub>O<sub>2</sub> solution. Typically, 100 mg of the commercial Pd/C catalysts were dispersed in a 25 mL of deionized water and 2.5 mL H<sub>2</sub>O<sub>2</sub> solution (30 wt.%), and then stirred at room temperature for 1 h. After the oxidation process, the Pd/C-H<sub>2</sub>O<sub>2</sub> catalysts were washed with H<sub>2</sub>O for three times and dried at 60 °C.

The commercial Pd/C catalysts were treated in 5% H<sub>2</sub>/Ar at 50°C and 150°C for 2 h, respectively, to yield the Pd/C-50 and Pd/C-150 catalysts.

### Catalyst Characterization

High-resolution TEM (HRTEM) images and element dispersive spectroscopy (EDS) images were recorded by a JEOL JEM-2100F with electron acceleration energy of 200 kV. High-angle annular dark field scanning TEM (HAADF-STEM) images were taken by JEOL 200F TEM operated at 200 keV, which was equipped with a probe spherical aberration corrector. All measured binding energies were calibrated with the C 1s peak (284.6 eV). The d-band electron structures of various catalysts were characterized by high-resolution valence-band (VB) XPS analysis.

### Catalytic Reaction

For a typical hydrogenation of benzoic acid (BA), 20 mg of catalyst and 2 mmol of BA were added to 3 mL of isopropanol in 8 mL glass tube. Then, the glass tube was transferred into the autoclave equipped with a pressure system. After purging with 1 MPa H<sub>2</sub> for three times, the hydrogenation was performed at 100°C for a given time. The products were analyzed by gas chromatography (GC, Agilent 7890B).

The BA (A) conversion is defined by:

$$Conv.A\% = \frac{n_A - n_A'}{n_A} \times 100 \quad (1)$$

The reaction rate was calculated as:

$$r = \frac{n_A \times (1 - Conv.A)/V}{t} \quad (2)$$

Where  $n_A$  is the molar amount of BA added in the reaction system;  $n_A'$  the molar amount of BA in the reaction system after the reaction;  $Conv.A$  is the conversion of substrates at the reaction of  $t$ ;  $V$  is the volume of reaction solution;  $t$  is reaction time, h.

### Stability test

Typically, 20 mg of catalysts and 2 mmol of BA were added into 3 mL of isopropanol in 10 mL glass bottle. The glass bottle with mixture was transferred to 500 mL of autoclave, which was purged with 1 MPa H<sub>2</sub> for three times. Subsequently, the reactions were carried out at 100°C for 6 h and 1 MPa H<sub>2</sub>. After the reaction, the liquid phase was analyzed using gas chromatograph (Agilent 7890B).

The Pd/C catalyst was centrifuged from the reaction solution and washed three times with isopropanol. Then, 0.5 mL H<sub>2</sub>O<sub>2</sub> solution (30 wt.%) were added and stirred at room temperature for 1 h. Finally, the separated H<sub>2</sub>O<sub>2</sub> treated Pd/C catalysts was used for the next cycles under the same reaction conditions.

### XPS analysis

X-ray photoelectron spectroscopy (XPS) spectra were carried out by Thermo Fisher Scientific K-Alpha. The signals of Pd<sup>0</sup>, Pd<sup>2+</sup> and Pd<sup>4+</sup> of various catalysts were assigned by the NIST XPS Database (<https://srdata.nist.gov/xps/selectEnergyType.aspx>). The XPS peak of Pd 3d peaks were corrected by the C 1s peaks (binding energy of 284.6 eV). During the fitting process, the peak shape is fitted by Gaussian-Lorentzian with ratio GL of 30%. The FWHM of Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> is consistent. The binding energy difference between Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> is 5.3eV, and the area ratio of Pd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> is 3:2. The respective peak shifts of Pd<sup>0</sup>, Pd<sup>2+</sup> and Pd<sup>4+</sup> were listed in the Table S1.

**Table S1.** Summary of the assigned binding energy of Pd<sup>0</sup>, Pd<sup>2+</sup> and Pd<sup>4+</sup>.

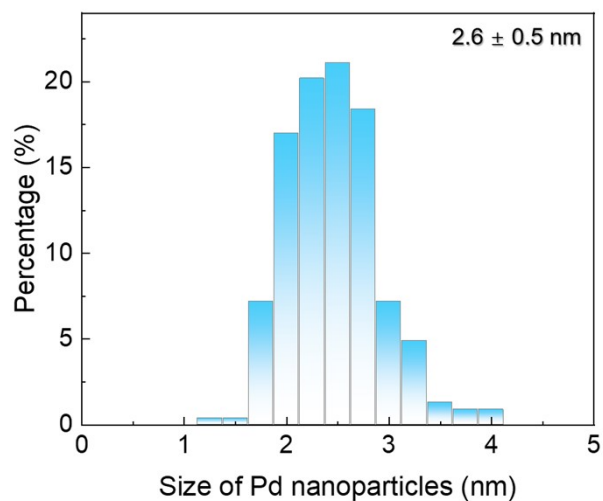
	<i>3d<sub>5/2</sub></i>			<i>3d<sub>3/2</sub></i>		
	Pd <sup>0</sup>	Pd <sup>2+</sup>	Pd <sup>4+</sup>	Pd <sup>0</sup>	Pd <sup>2+</sup>	Pd <sup>4+</sup>
Binding energy (eV)	335.3 ± 0.1	337.3 ± 0.1	338.1 ± 0.1	340.8 ± 0.1	342.6 ± 0.1	343.4 ± 0.1

## DFT

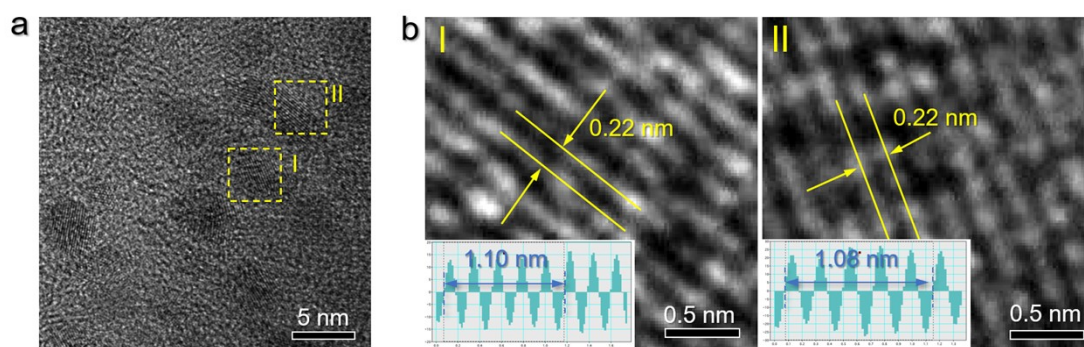
The first principle calculations are performed by Vienna Ab initio Simulation Package(VASP)<sup>1</sup> with the projector augmented wave (PAW) method<sup>2</sup>. The exchange-functional is treated using the Perdew-Burke-Ernzerhof (PBE)<sup>3</sup> functional, in combination with the DFT-D3 correction<sup>4</sup>. The cut-off energy of the plane-wave basis is set at 400 eV. For the optimization of both geometry and lattice size, the Brillouin zone integration is performed with 2\*2\*1 Monkhorst-Pack<sup>5</sup> kpoint sampling. The self-consistent calculations apply a convergence energy threshold of 10<sup>-5</sup> eV. The equilibrium geometries and lattice constances are optimized with maximum stress on each atom within 0.02 eV/Å.

## Reference:

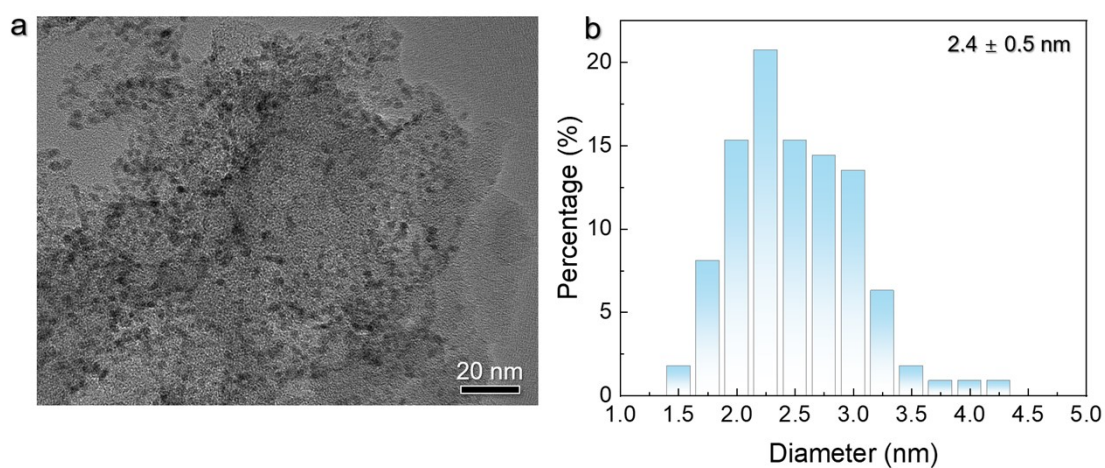
1. J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
2. G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758.
3. J.P. Perdew, K. Burke, M. Ernzerhof, Phy. Rev. Lett. 77 (1996) 3865.
4. S. Grimme, J. Antony, S. Ehrlich, and S. Krieg, J. Chem. Phys. 132, 154104 (2010).
5. H. J. Monkhorst, J. D. Pack, Phys. Rev. B 1976, 13, 5188.



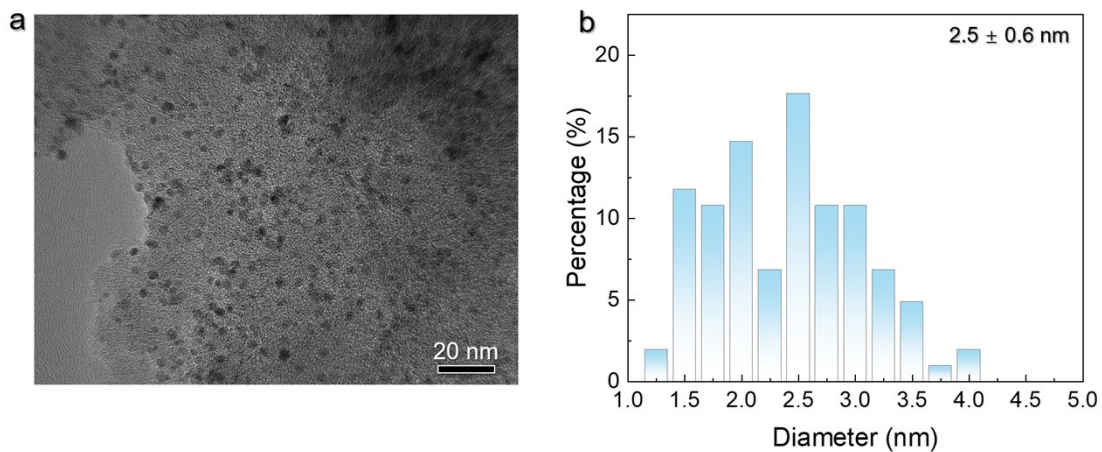
**Figure S1.** Size distribution of Pd nanoparticles for the Pd/C catalysts.



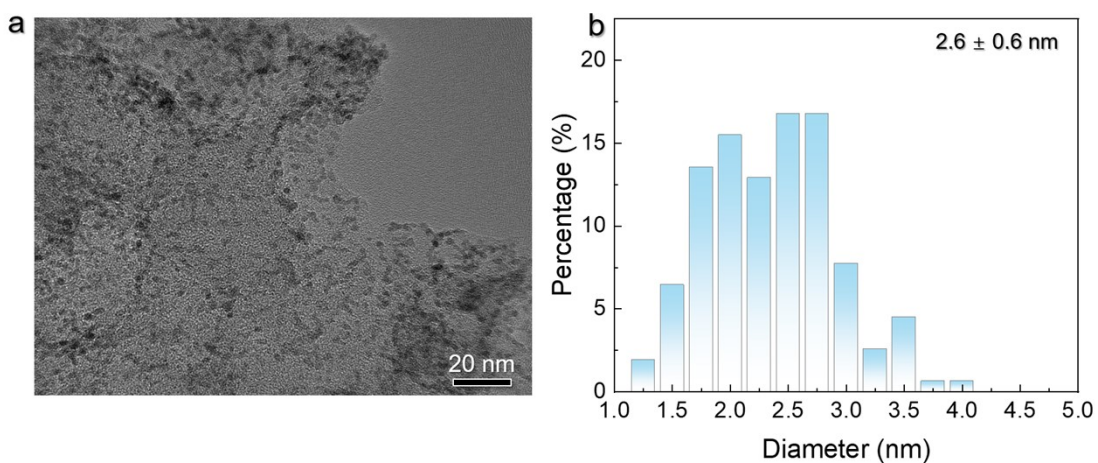
**Figure S2.** (a) HRTEM image of the Pd/C catalysts. (b) Fast Fourier transform pattern of the selected yellow area.



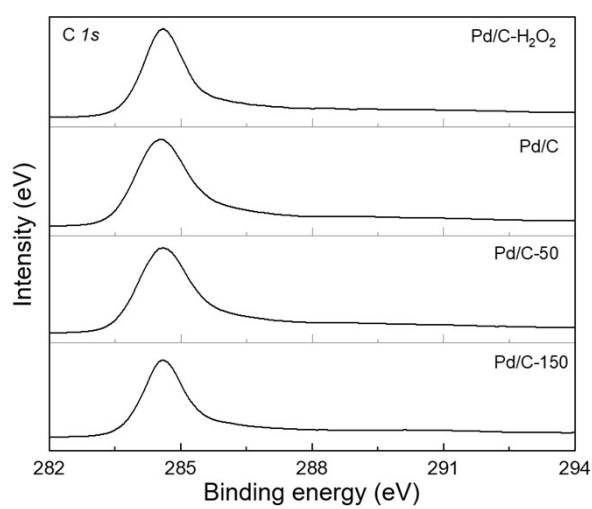
**Figure S3.** (a) TEM image and (b) size distribution of Pd nanoparticles for the Pd/C-50 catalysts.



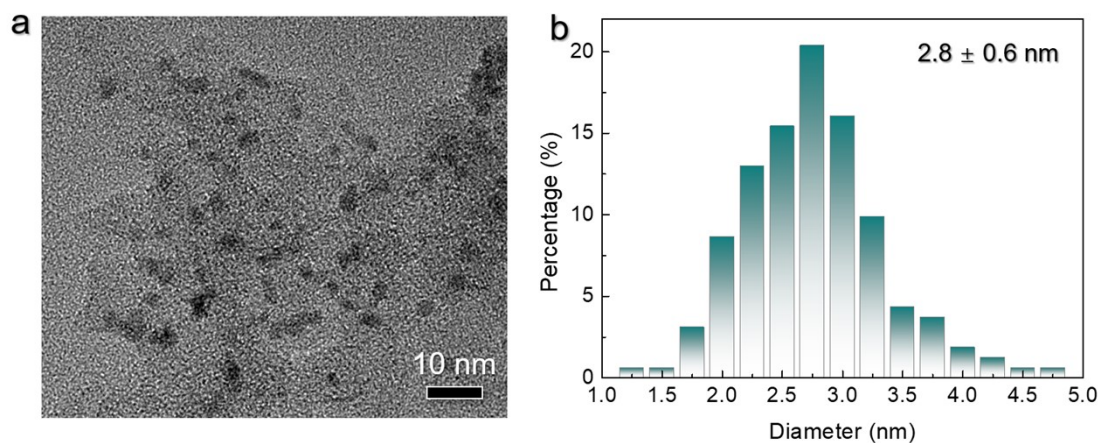
**Figure S4.** (a) TEM image and (b) size distribution of Pd nanoparticles for the Pd/C-100 catalysts.



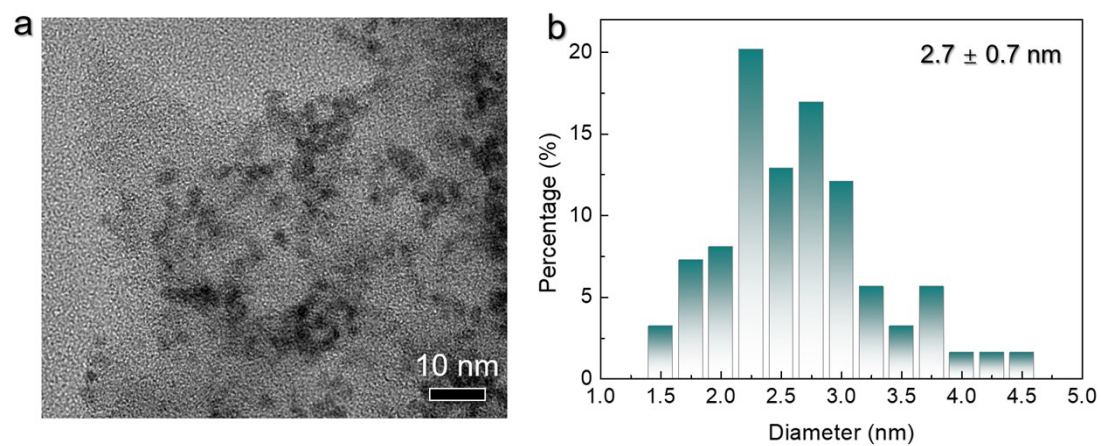
**Figure S5.** (a) TEM image and (b) size distribution of Pd nanoparticles for the Pd/C-H<sub>2</sub>O<sub>2</sub> catalysts.



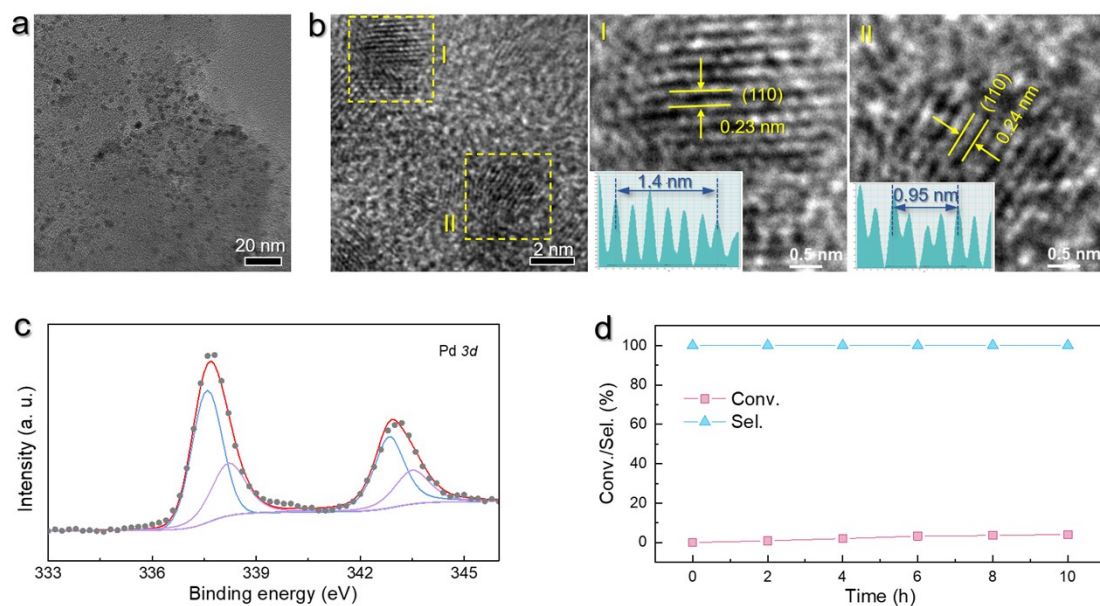
**Figure S6.** C 1s peaks of various catalysts.



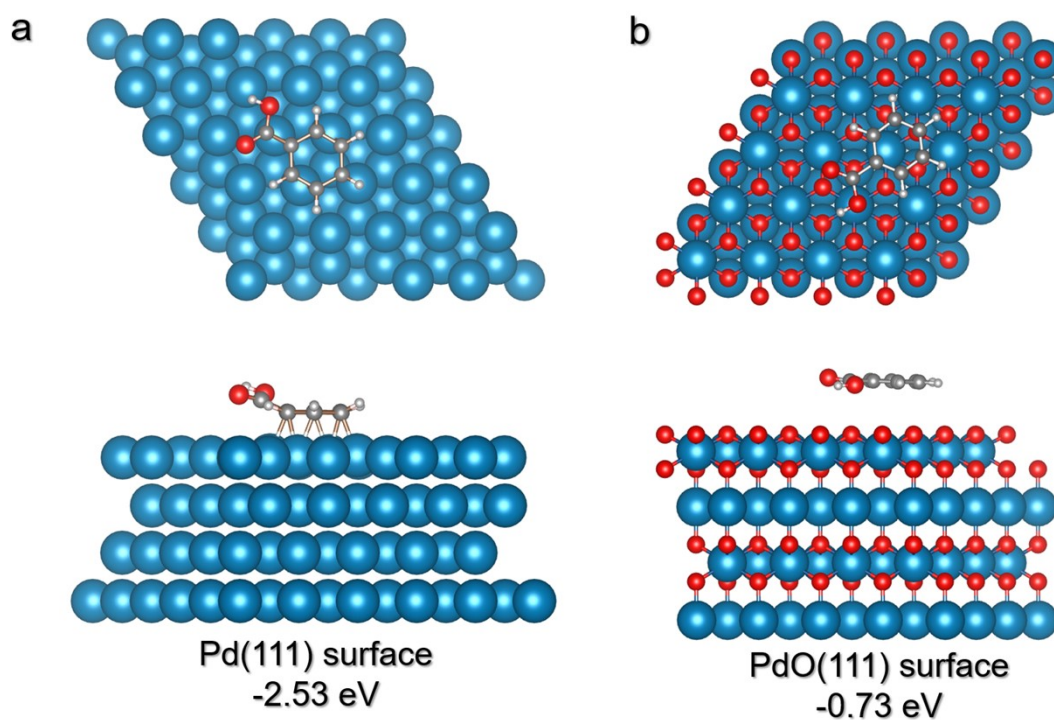
**Figure S7.** (a) TEM image and (b) size distribution of Pd nanoparticles for the used Pd/C catalysts without treatment.



**Figure S8.** (a) TEM image and (b) size distribution of Pd nanoparticles for the used Pd/C catalysts after H<sub>2</sub>O<sub>2</sub> treatment.



**Figure S9.** (a) TEM and (b) HRTEM images of the PdO/C catalysts. (c) XPS analysis of Pd 3d peak of the PdO/C catalysts. (d) Catalytic performance of BA hydrogenation catalyzed the PdO/C catalysts. **Reaction conditions:** BA (2 mmol), PdO/C (20 mg), isopropanol (3 mL), 100 °C and 1 MPa H<sub>2</sub>.



**Figure S10.** Adsorption configuration of benzoic acid molecule on (a) Pd(111) and (b) PdO(111) surface.