

## Enhancing the selectivity of Pd/C catalyst for the direct synthesis of H<sub>2</sub>O<sub>2</sub> by HNO<sub>3</sub> pretreatment

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Table S1. Catalytic performances of the original and H<sub>2</sub> reduced Pd/C-A% series catalysts.

Catalyst	Pd content <sup>a</sup> (wt%)	H <sub>2</sub> O <sub>2</sub> selectivity (%)	H <sub>2</sub> conversion (%)	H <sub>2</sub> O <sub>2</sub> productivity <sup>b</sup> (mol H <sub>2</sub> O <sub>2</sub> /kg <sub>cat</sub> ·h)
Pd/C-0%	0.98	64	22	70
Pd/C-2%	1.02	68	17	57
Pd/C-5%	0.98	70	15	49
Pd/C-10%	0.96	84	10	44
Pd/C-20%	0.93	90	8	36
Pd/C-0%T <sup>c</sup>	0.99	46	18	39
Pd/C-2%T <sup>c</sup>	1.01	46	12	27
Pd/C-5%T <sup>c</sup>	1.02	49	9.2	21
Pd/C-10%T <sup>c</sup>	0.99	52	7.6	16
Pd/C-20%T <sup>c</sup>	0.95	50	4.5	12
Pd/C-0%H <sup>d</sup>	/	/	/	2.9
Pd/C-2%H <sup>d</sup>	/	/	/	2.8

<sup>a</sup> Pd content was tested by ICP-MS. <sup>b</sup> H<sub>2</sub>O<sub>2</sub> synthesis experiment conditions: H<sub>2</sub>:O<sub>2</sub>:N<sub>2</sub> = 9:18:33 (total flow rate 60 ml/min), 80 ml H<sub>2</sub>O and 20 ml ethanol, 1 ml 10 wt% H<sub>2</sub>SO<sub>4</sub> and 1ml 0.1 mol/L KBr, 25 °C, atmosphere, 2000 rpm, 1h. <sup>c</sup> 400 °C H<sub>2</sub> reduced Pd/C-A% series catalysts. H<sub>2</sub> 20 ml/min, N<sub>2</sub> 20 ml/min, ramp 5 °C/min, 5 h. H<sub>2</sub> was fed along with N<sub>2</sub> at ambient temperature. <sup>d</sup> 400 °C H<sub>2</sub> reduced Pd/C-A% series catalysts. H<sub>2</sub> 20 ml/min, N<sub>2</sub> 20 ml/min, ramp 5 °C/min, 5 h. H<sub>2</sub> was fed when the temperature rose to 400 °C in N<sub>2</sub> atmosphere.

Table S2. Catalytic performances of N<sub>2</sub>-calcinated Pd/C-0% series catalysts.

Catalyst	H <sub>2</sub> O <sub>2</sub> selectivity (%)	H <sub>2</sub> conversion (%)	H <sub>2</sub> O <sub>2</sub> productivity (mol H <sub>2</sub> O <sub>2</sub> /kg <sub>cat</sub> ·h)
Pd/C-0%	64	22	70
Pd/C-250	65	15	48
Pd/C-300	57	13	38
Pd/C-350	58	6.9	23
Pd/C-400	/	< 2	3.1

Catalyst prepared by calcinating Pd/C-0% in N<sub>2</sub> at different temperatures. E.g. Pd/C-250 the number “250” means this catalyst was prepared by calcinating Pd/C-0% in N<sub>2</sub> at 250 °C for 5 h.

Table S3. Pd content in the fresh and spent catalyst.

Catalyst	Fresh catalyst (wt%)	Spent catalyst (wt%)	Solution (mg/L)
Pd/C-0%	0.98	1.01	< 0.02
Pd/C-2%	1.02	0.99	< 0.02
Pd/C-5%	0.98	0.96	< 0.02
Pd/C-10%	0.96	0.98	< 0.02
Pd/C-20%	0.93	0.95	< 0.02

Pd content was tested by ICP-MS.

Table S4. H<sub>2</sub>O<sub>2</sub> decomposition and hydrogenation capacities of the HNO<sub>3</sub>-pretreated and N<sub>2</sub>-calculated activated carbons.

Material	H <sub>2</sub> O <sub>2</sub> decomposition rate (mol	H <sub>2</sub> O <sub>2</sub> hydrogenation rate (mol
	H <sub>2</sub> O <sub>2</sub> /kg <sub>cat</sub> ·h)	H <sub>2</sub> O <sub>2</sub> /kg <sub>cat</sub> ·h)
AC-0%	11	23
AC-2%	10	21
AC-5%	10	19
AC-10%	9.5	21
AC-20%	9.8	20
AC-2%C	11	20
AC-5%C	12	22
AC-10%C	11	22
AC-20%C	13	23

E.g. AC-2%C: 400 °C N<sub>2</sub> calcinated AC-2%, so do the others. H<sub>2</sub>O<sub>2</sub> decomposition experiment conditions: N<sub>2</sub> flow rate 60 ml/min, 100 ml 0.5 wt% H<sub>2</sub>O<sub>2</sub>, 1 ml 10 wt% H<sub>2</sub>SO<sub>4</sub>, 1ml 0.1 mol/L KBr, 25 °C, atmosphere, 2000 rpm, 1h. H<sub>2</sub>O<sub>2</sub> hydrogenation reaction conditions: H<sub>2</sub>:N<sub>2</sub> = 9:51 (total flow rate 60 ml/min), 100 ml 0.5 wt% H<sub>2</sub>O<sub>2</sub>, the other conditions were same as H<sub>2</sub>O<sub>2</sub> decomposition experiment.

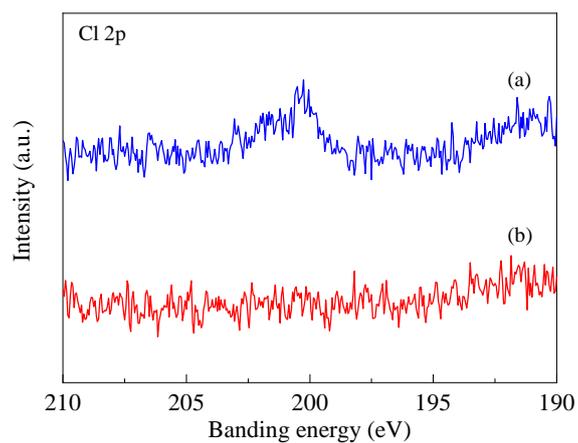


Fig. S1. Cl 2p XPS spectra of HCl treated AC and 400 °C N<sub>2</sub> calcinated AC. (a) Water rinsed AC after HCl pretreatment, (b) 400 °C N<sub>2</sub> calcinated (a).

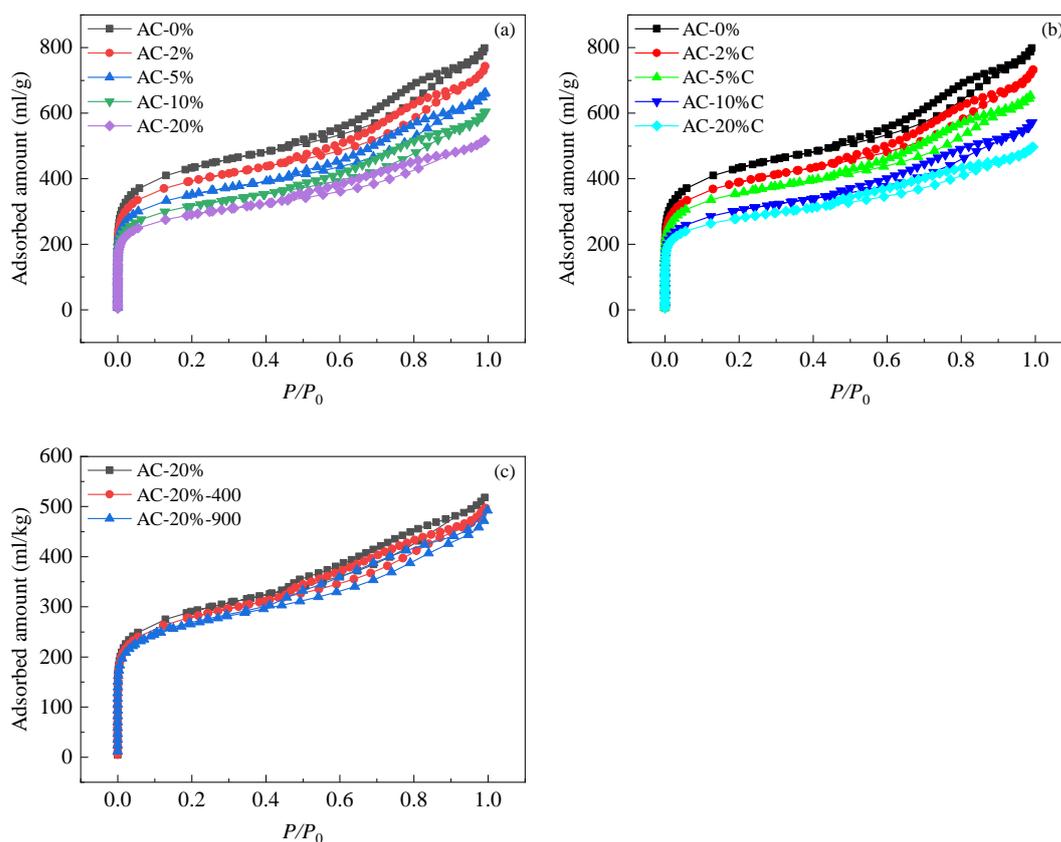


Fig. S2. N<sub>2</sub> adsorption-desorption isotherms of activated carbons. (a) HNO<sub>3</sub>-pretreated AC; (b) 400 °C N<sub>2</sub> calcinated (a); (c) N<sub>2</sub> calcinated AC-20%.

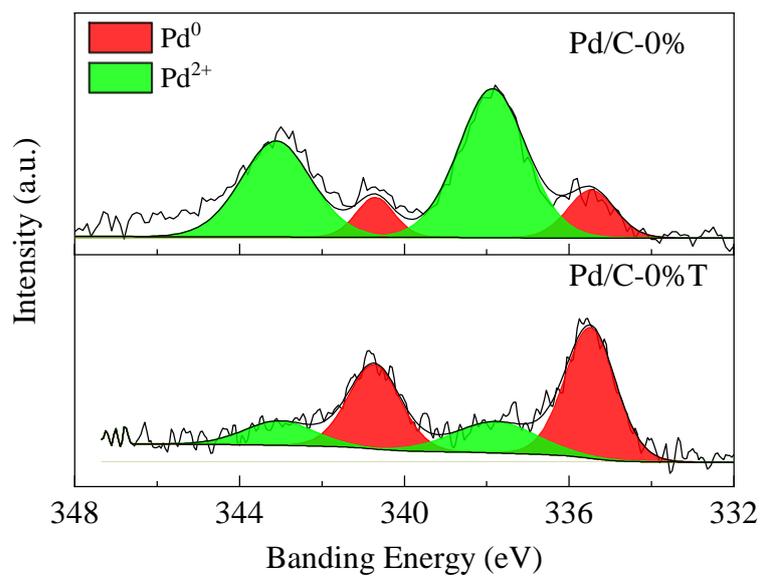


Fig. S3. Pd 3d XPS spectra of the original and H<sub>2</sub> reduced Pd/C-0%. Pd/C-0%T: 400 °C H<sub>2</sub> reduced Pd/C-0%. H<sub>2</sub> 20 ml/min, N<sub>2</sub> 20 ml/min, ramp 5 °C/min, 5 h. H<sub>2</sub> was fed along with N<sub>2</sub> at ambient temperature.

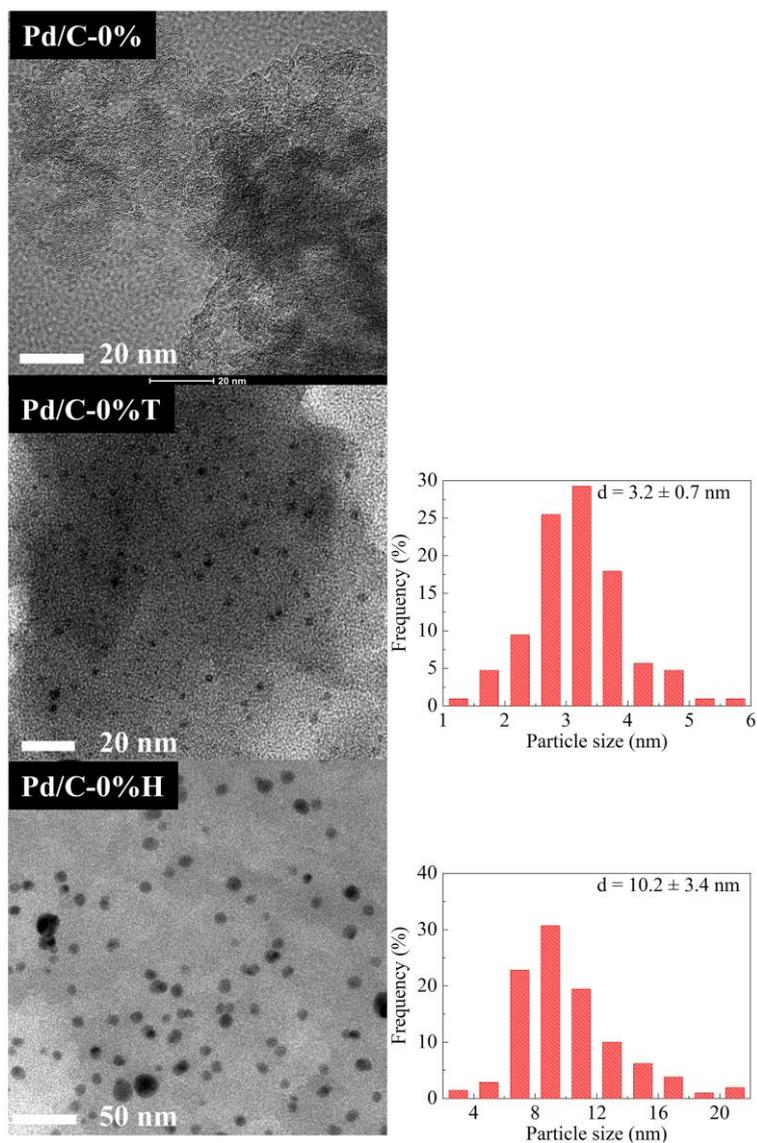


Fig. S4. TEM micrographs of the original and H<sub>2</sub> reduced Pd/C-0%. Pd/C-0%-T: 400 °C H<sub>2</sub> reduced Pd/C-0%. H<sub>2</sub> 20 ml/min, N<sub>2</sub> 20 ml/min, ramp 5 °C/min, 5 h. H<sub>2</sub> was fed along with N<sub>2</sub> at ambient temperature. Pd/C-0%-H: 400 °C H<sub>2</sub> reduced Pd/C-0%. H<sub>2</sub> 20 ml/min, N<sub>2</sub> 20 ml/min, ramp 5 °C/min, 5 h. H<sub>2</sub> was fed when the temperature rose to 400 oC in N<sub>2</sub> atmosphere.

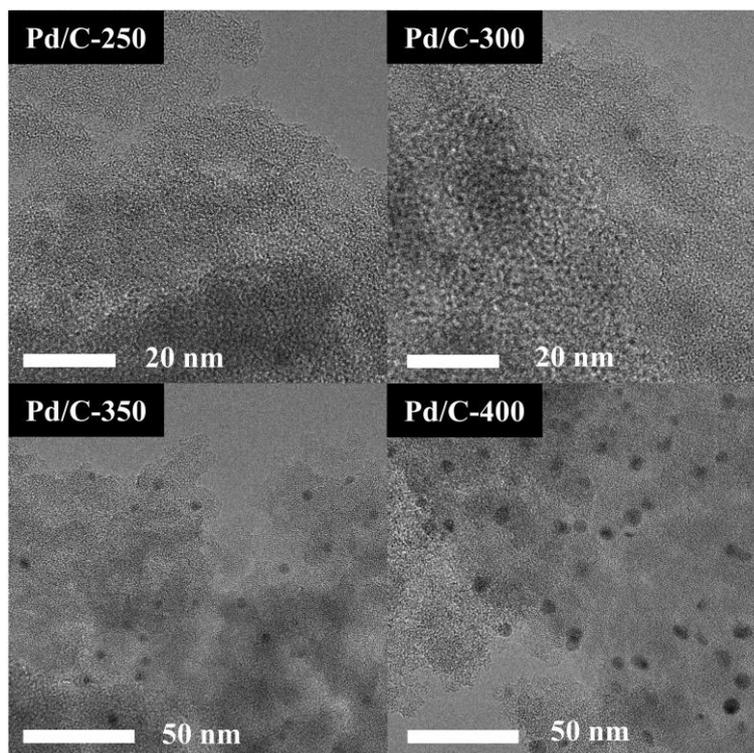


Fig. S5. TEM micrographs of the N<sub>2</sub>-calcinated Pd/C-0% series catalysts. The suffix number means the N<sub>2</sub> calcination temperature.