Insight into the size effect of Pd nanoparticles on the catalytic reduction of nitrite in water over Pd/C catalysts

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1. Experimental section

Catalysis preparation:

Carbon-supported Pd nanoparticles range from 2 to 8 nm were synthesized by a liquid phase $NaBH_4$ reduction method using $PdCl_2$ as the precursor and sodium citrate as a stabilizing agent according to the previous reports with a slight modification[1, 2]. The particle size of Pd nanoparticles was controlled by varying the experimental factors including the ratio of $PdCl_2$ to sodium citrate and the reduction temperature. The detailed procedure for the Cat.1 Pd/C catalyst synthesis was as follows: 0.2 mmol $PdCl_2$ (dissolved in HCl solution) and 1.6 mmol $C_6H_5O_7Na_3$ were dissolved into 400 ml water, and then 400 mg pretreated Vulcan XC-72R carbon black (Carbot corp.) was added, and stirred for 5 min follow by sonicated for 30 min. 50 ml of freshly prepared 0.1 mol $NaBH_4$ solution was added into the suspension dropwise with a constant flow rate of 1.0 ml/min under vigorous stirring at 3 °C for 8 h. Then, the black suspension was filtered, and washed with deionized water and ethanol several times to remove the $C_6H_5O_7Na_3$ weakly absorbed on Pd nanoparticle surface. The obtained as-prepared catalysts were then dried overnight follow by in a vacuum oven at 40 °C for 12 h. The detailed preparation conditions of other size Pd/C catalyst was summarized in **Table S1**.

Table S1 Synthesis for the 2~8 nm Pd/XC-72R catalysts.

Catalyst samples	XC72R (mg)	$PdCl_2$ (mmol)	$C_6H_5O_7Na_3$ (mmol)	$PdCl_2/C_6H_5O_7Na_3$ ratio	Temperature (°C)	Time (h)
Cat.1	400	0.2	1.6	1:8	3	8
Cat.2	400	0.2	1.6	1:8	25	8
Cat.3	400	0.2	1.6	1:8	60	8
Cat.4	400	0.2	0.6	1:3	25	8
Cat.5	400	0.2	0.4	1:2	25	8
Cat.6	400	0.2	0	--	25	8

18~22 nm Pd/C catalysts were synthesized using a modified double-solvent method[3]. 0.2 mmol $Pd(NO_3)_2$ (dissolved dilute HNO_3 solution, hydrophilic solvent) was dispersed into 100 ml n-Butyl alcohol (hydrophobic solvent). And then 400 mg pretreated Vulcan XC-72R carbon black (Carbot corp.) was added under vigorous stirring at room temperature overnight. The black samples were then filtered and wash with 500 ml deionized water and 500 ml ethanol, respectively. After dried under 80 °C for 12 h, the samples were activated by 20%H_2/Ar at a certain temperature and flow rate described in **Table S2**.

Table S2 Synthesis for the 18~22 nm Pd/XC-72R catalysts.

Catalyst samples	XC72R (mg)	$Pd(NO_3)_2$ (mmol)	20%H_2/Ar flow rate (ml/min)	Temperature (°C)	Time (h)
18.2 nm	400	0.2	100	300	3
22.1 nm	400	0.2	100	550	3

Pd-^{int}Li/C and Pd-^{int}B/C catalysts were synthesized according to the previous reports with a slight modification[3, 4]. Pd-intLi/C catalyst:100 mg cat.8 Pd/C catalyst and 70 mg of $C_2H_3O_2Li\cdot 2H_2O$ was placed in a agate mortar and grinded for 10 min until a homogeneous mixture of the two powders was obtained. The mixture powder was then transferred into a three-necked round bottom flask and heated at 250 ^oC for 2 h under N_2 atmosphere, after natural cooling, the as-synthesized Pd-intLi/C catalyst was washed using 200 ml deionized water and 400 ml ethanol, and then dried at 40 ^oC for 12 h under vacuum. Pd-^{int}B/C catalyst: 100 mg Cat. 8 Pd/C catalyst was placed in a three-neck round bottom flask equipped with nitrogen inlet and outlet switch. The catalyst was purged firstly with nitrogen gas for 5 h to remove the oxygen and moisture, avoiding the oxidized of the $BH_3\cdot THF$. And then 2 ml of $BH_3\cdot THF$ (1 M) solution was added into the flask under nitrogen gas. The resultant suspension was heated to 40ºC to evaporate the solvent. And then the flask was heated at 200 ^oC for 1 h. After cooling to room temperature, the as-synthesized Pd-^{int}B/C catalyst was washed with water (200 mL) and ethanol (400mL) before dried overnight under vaccum.

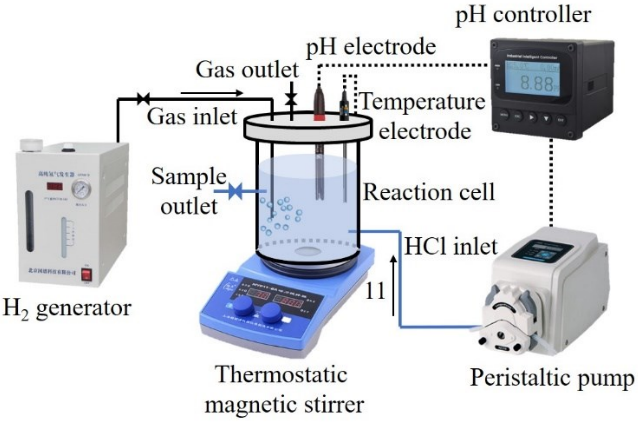

Fig. S1 Schematic diagram of homemade catalytic reaction system

The catalytic NO_2^- reduction tests were performed in a 100 ml homemade, sealed semi-batch reactor with a gas inlet and outlet. The reaction temperature and stirring rate were controlled by a water bath equipped with a magnetic stirring, and the pH of the solution was maintained at 5.5 ± 0.2 with 0.05 M HCl by a pH-stat. At appropriate time intervals, samples of the reaction mixture were withdrawn from the sample outlet and filtered with 0.45 μm membrane for subsequent analysis.

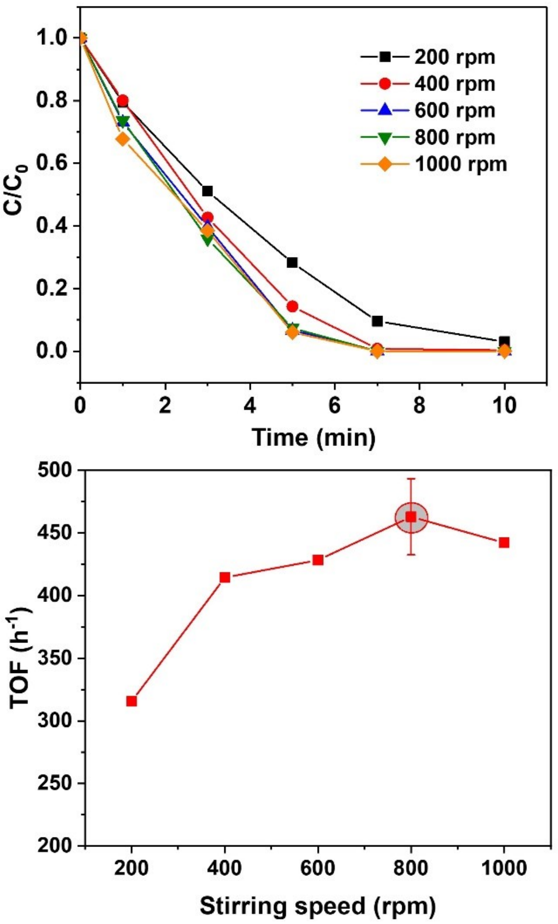

Fig. S2 Influence of stirring speed on the catalytic nitrite reduction.

Stirring speed has a significant effect on the mass diffusion rate, which seriously interferes the activity analysis of catalyst. **Fig.S2** shows that the TOF maintained at a relatively stable value when the stirring speed more than 600 rpm. In this study, 800 rpm of stirring speed was selected for all the catalytic experiments to avoid the influence of the stirring speed.

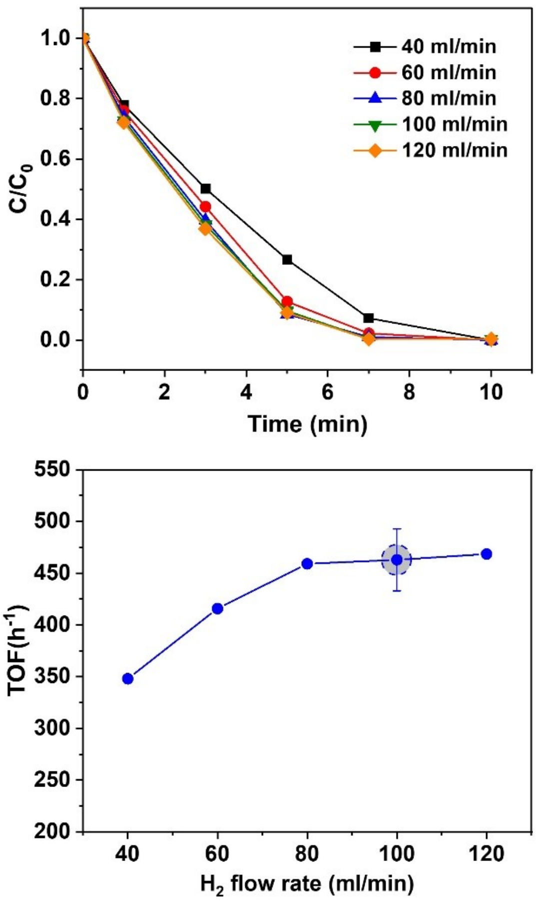

Fig. S3 Influence of H_2 flow rate on the catalytic NO_2- reduction

The influence of H_2 flow rate on the catalytic NO_2^- reduction is shown in **Fig.S3**. It can be seen that the TOF increased from ca. 350 to 460 h^{-1} following the increase of H_2 flow rate from 40 to 80 ml/min, and then the TOF tended to keep constant when the H_2 flow rate greater than 80 ml/min. In this study, 100 ml/min of H_2 flow rate was selected for all the catalytic experiments to avoid the influence.

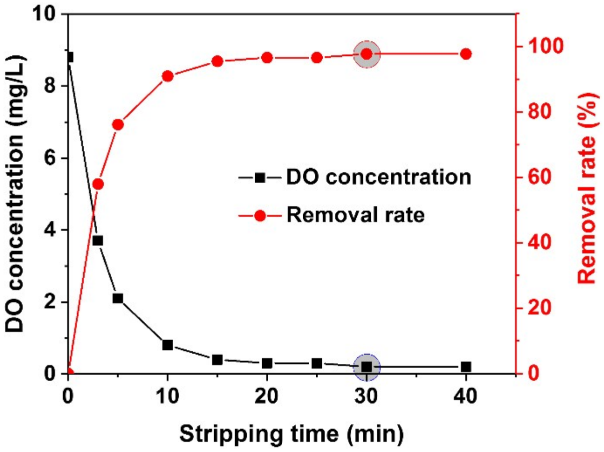

Fig. S4 DO concentration as a function of H_2 stripping time. (H_2 flow rate: 50 ml/min, Temperature: 25 °C)

In order to eliminate the influence of DO, a H_2 stripping was used to remove the DO from water prior the catalytic experiments. **Fig.S4** shows that the DO concentration quickly decreased when the stripping time less than 5 min, and then the DO concentration slowly lower with the stripping time. The DO removal rate was greater than 95% at the stripping time of 20 min. In this study, a H_2 stripping time of 30 min was selected in all the catalytic nitrite reduction experiments.

2. Results and discussion section

Table S3 ICP-AES analysis of the catalysts.

Catalyst	Pd loading (%)	Li loading (%)	B loading (%)	Relative error
Cat.1	4.92	--	None[a]	-1.54
Cat.2	5.07	--	None	1.46
Cat.3	5.02	--	None	0.41
Cat.4	4.91	--	None	-1.82
Cat.5	4.99	--	None	-0.14
Cat.6	4.92	--	None	-1.66
Cat.7	5.06	--	None	1.10
Cat.8	5.08	--	None	1.66
Pd-^{int}Li/C	5.04	0.08	None	0.74
Pd-^{int}B/C	5.06	None	0.17	1.12

a: lower than the detection limits

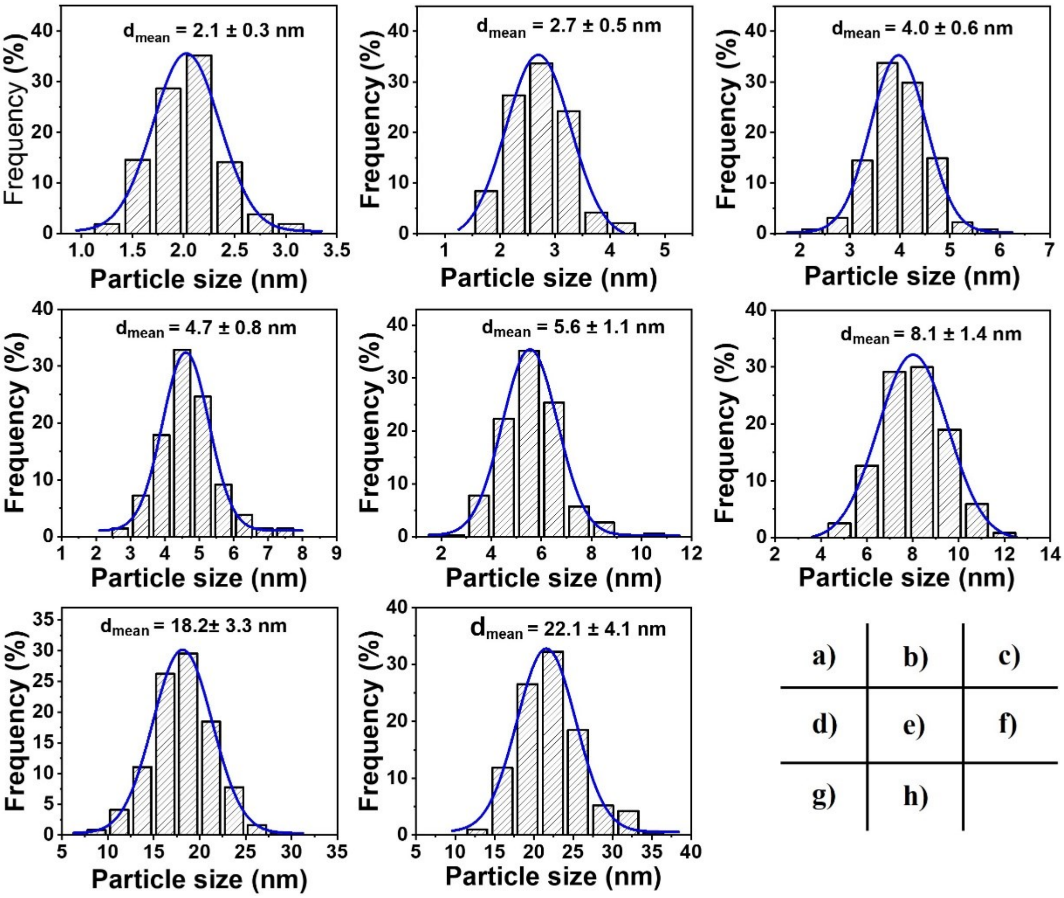

Fig. S5 Corresponding Pd particle size distributions of the a) Cat.1, b) Cat.2, c) Cat.3, d) Cat.4, e) Cat.5, f) Cat.6, g) Cat.7, and h) Cat.8 Pd/C catalyst, respectively.

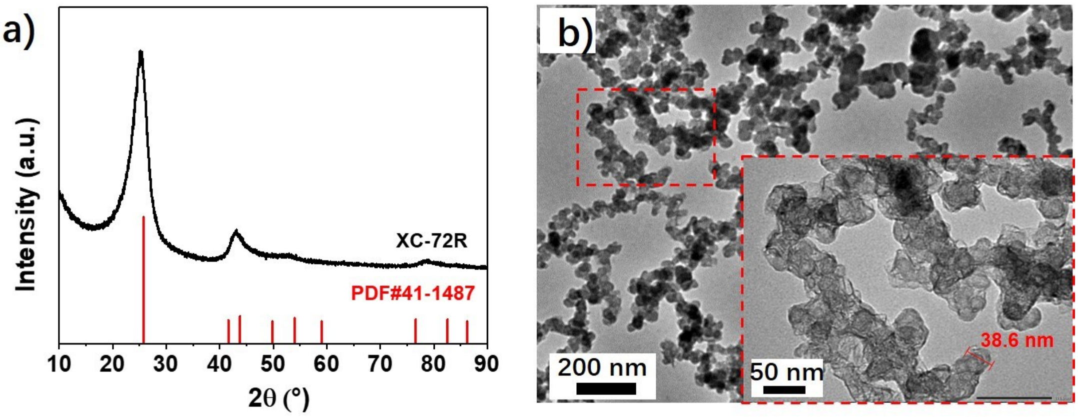

Fig. S6 a) XRD pattern of XC-72R support, and b) TEM image of fresh XC-72R support.

The TEM image shown that the fresh XC-72R support were well dispersion and exhibited a spherical or ellipsoidal morphology. The average sizes of the XC-72R was ca. 30~40 nm.

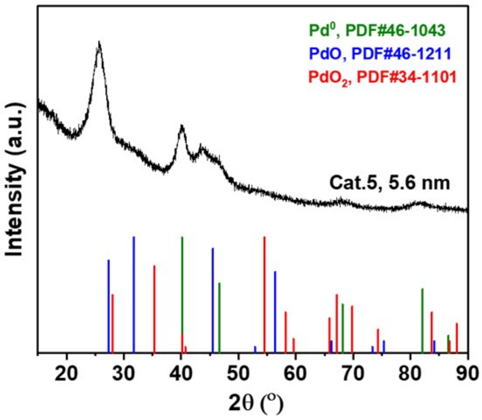

Fig. S7 Comparison of between the XRD spectrum of 5.6 nm Pd/C catalyst and the standard diffractions of the Pd, PdO, and PdO_2.

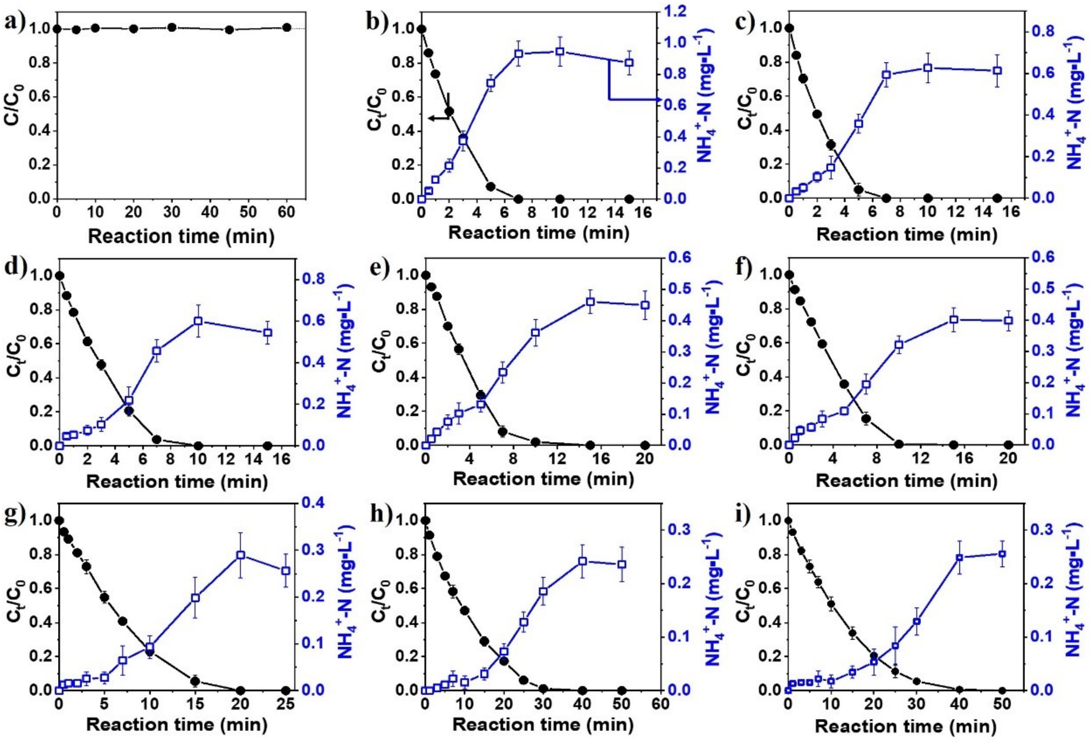

Fig.S8 Catalytic nitrite reduction performances over the Pd/C catalysts. a) no catalyst, b) Cat.1, c) Cat.2, d) Cat.3, e) Cat.4, f) Cat.5, g) Cat.6, h) Cat.7, and i) Cat.8 Pd/C catalyst, respectively. (Initial concentration: C_0=14.0 mg/L as N, pH: 5.5±0.5, Temperature: T=25℃, catalyst concentration: C_{cat}=0.1 g/L, H_2 flow: Q_{H2}=100 ml/min)

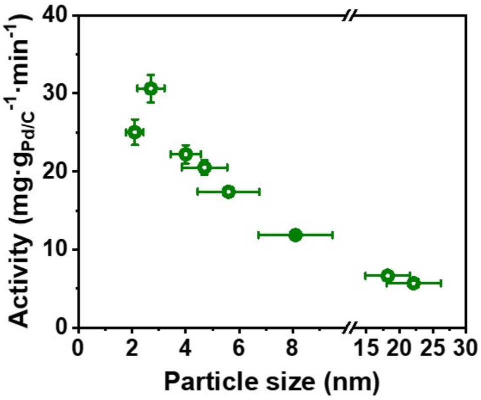

Fig. S9 The Pd/C mass catalytic activities.

As shown in above Fig. S8, the mass catalytic activities ($A_{mass,\ Pd/C}$) of the Pd/C catalysts were also calculated using the Pd/C concentration (including the support), and the values of the A_{mass} were 25.02, 30.60, 22.19, 20.49, 17.39, 11.84, 6.65, and 5.68 mg·$g_{Pd/C}^{-1}$·min^{-1} for the 2.1, 2.7, 4.0, 4.7, 5.6, 8.1, 18.2, and 22.1 nm Pd catalysts, respectively. The variation trend of the $A_{mass,\ Pd/C}$ against to the Pd nanoparticle size was consistent with the $A_{mass,\ Pd}$ that calculated using Pd concentration (excluding the support, **Fig. 3** a)) because of the similar Pd loading rate of the Pd/C catalysts (**Table S3**).

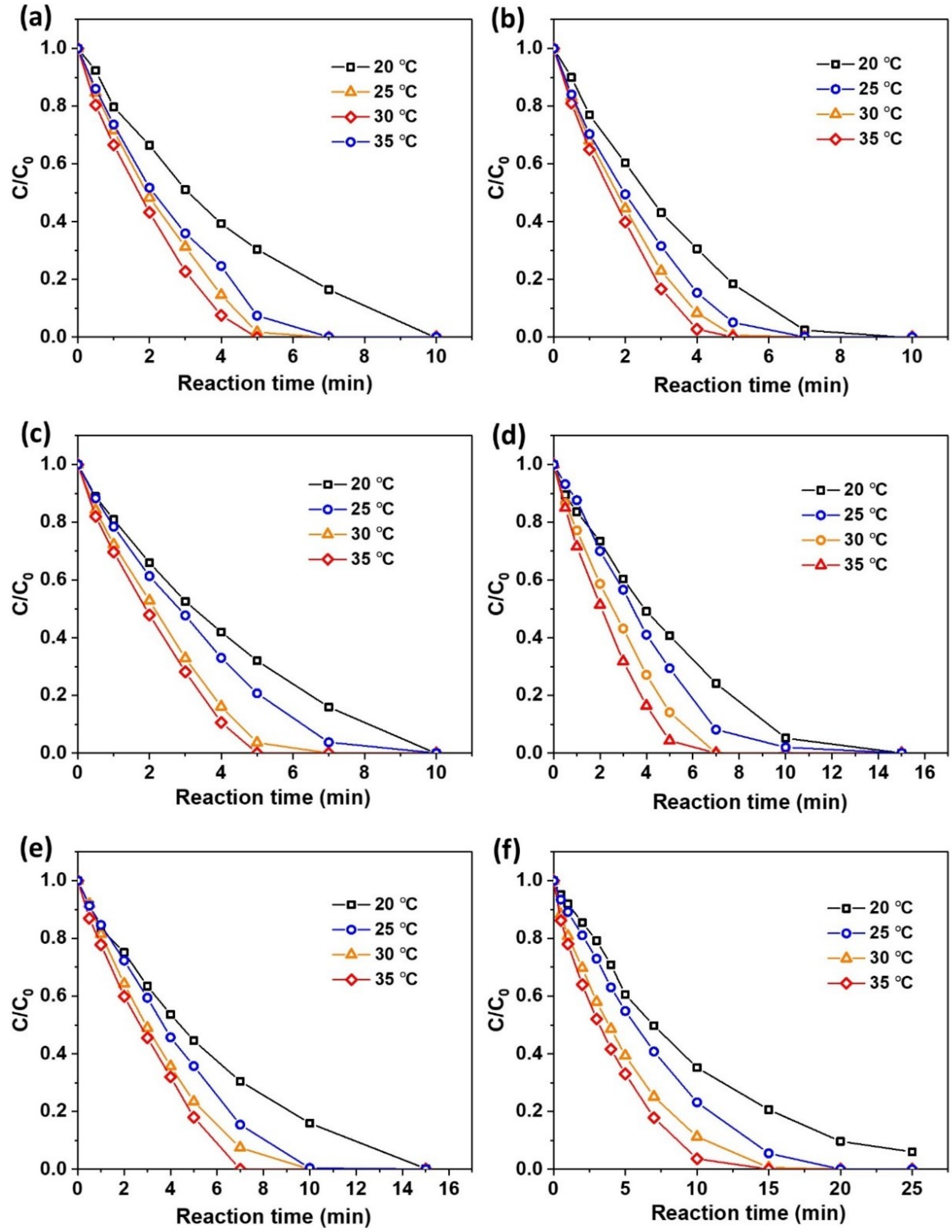

Fig. S10 Effect of reaction temperature on catalytic nitrite reduction over (a) Cat.1, (b) Cat.2, (c) Cat.3, (d) Cat.4, (e) Cat.5, and (f) Cat.6 Pd/C catalysts. (Initial concentration: C_{NO2-}=14.0 mg/L as N, C_{NH4+}=1.0 mg/L as N, pH value: 5.5±0.5, catalyst concentration: C_{Cat}=0.1 g/L, H_2 flow: Q_{H2}=100 ml/min)

As shown in **Fig. S10**, for all the Pd/C catalysts, the nitrite catalytic reduction rate exhibited an increase following an increase of reaction temperature.

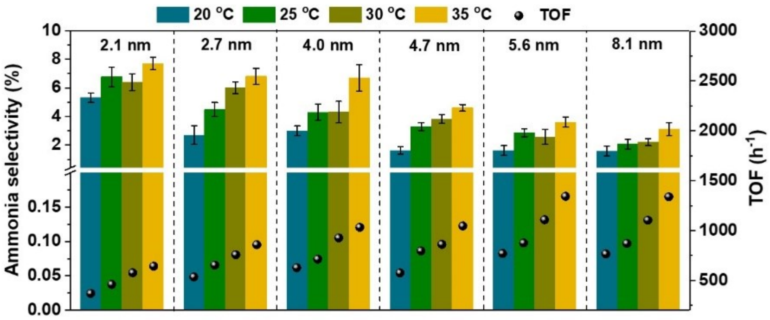

Fig. S11 Corresponding TOF and ammonia selectivity of Pd/C catalyst with different sizes under 20, 25, 30, and 35^{o}C, respectively.

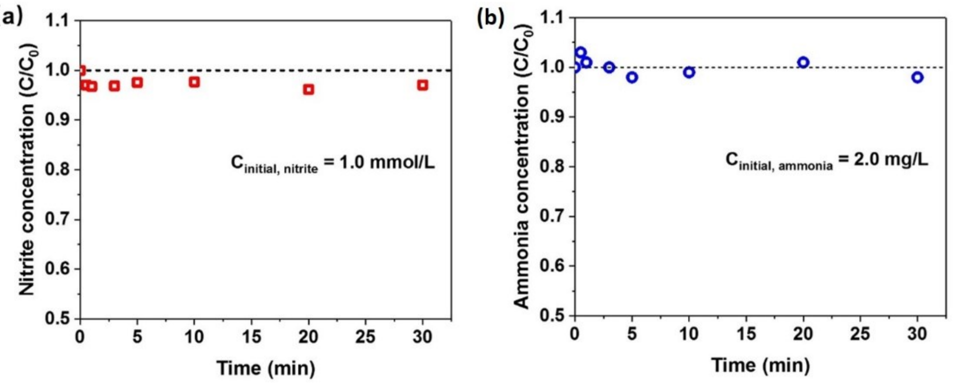

Fig. S12 The adsorption behavior of nitrite and ammonia by Cat.1 Pd/C catalysts (Initial concentration: C_{NO2-}=14.0 mg/L as N, C_{NH4+}=1.0 mg/L as N, pH value: 5.5±0.5, Temperature: T=25°C, catalyst concentration: $C_{Cat.1}$=0.1 g/L)

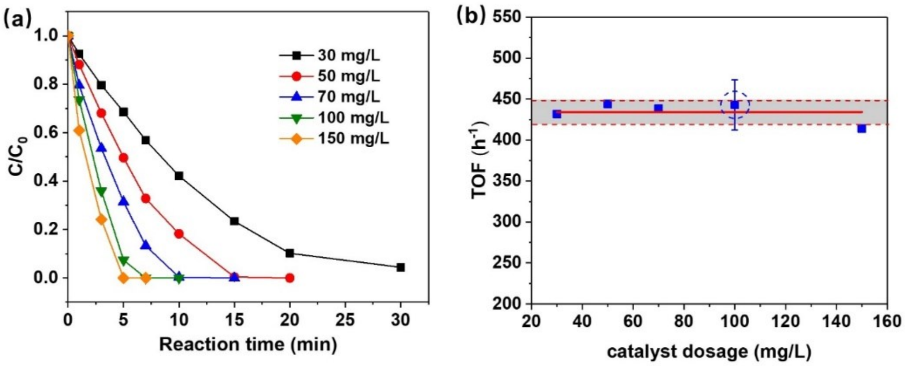

Fig. S13 Catalytic nitrite reduction performance over Cat.1 Pd/C catalyst. The wine-red dash lines with gray areas represent the standard deviation σ at a 95% confidence level. (Initial concentration: C_{NO2-}=14.0 mg/L as N, C_{NH4+}=1.0 mg/L as N, pH value: 5.5±0.5, Temperature: T=25°C, catalyst concentration: $C_{Cat.1}$=0.1 g/L, H_2 flow: Q_{H2}=100 ml/min)

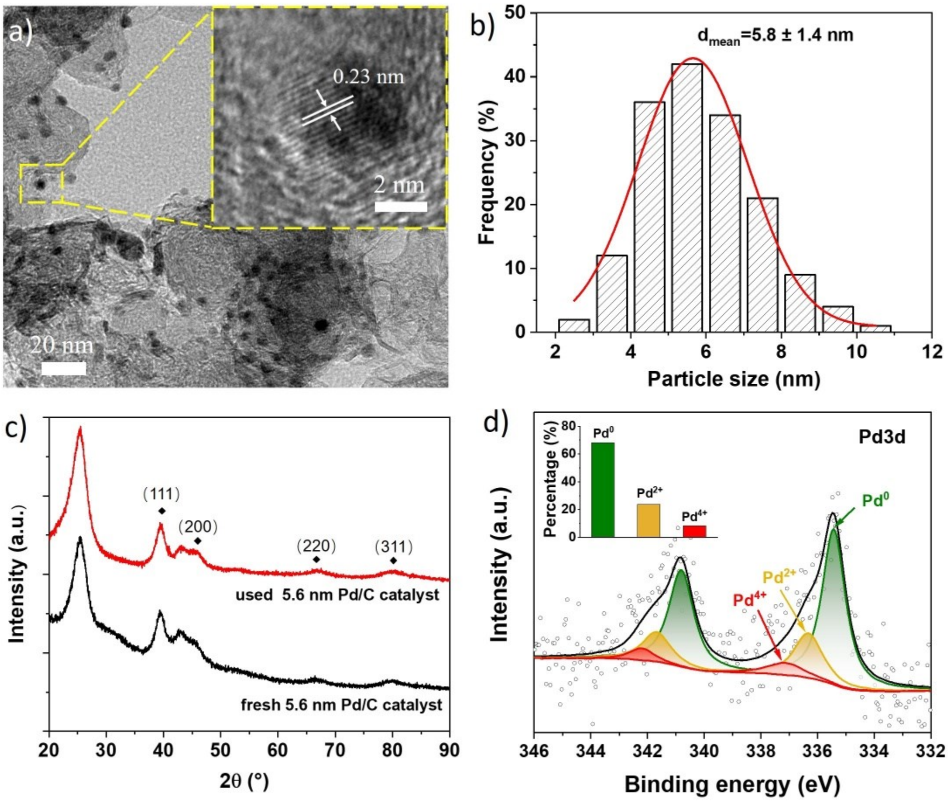

Fig. S14 Characterizations of the used 5.6 nm Pd/C catalyst, a) TEM and HR-TEM images, b) Pd particle size distribution, c) XRD spectra, and d) XPS spectra and proportion of Pd^0, Pd^{2+}, and Pd^{4+}.

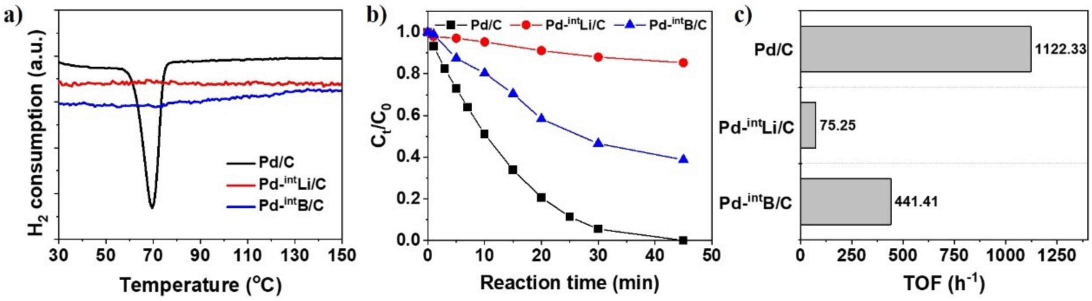

Fig. S15 a) TPR profiles, b) catalytic nitrite reduction performances and c) intrinsic activity (TOF) of the 22.1 nm Pd/C, Pd-^{int}Li/C, and Pd-^{int}B/C catalysts. (Initial concentration: C_{NO2-} =14.0 mg/L as N, C_{NH4+}=1.0 mg/L as N, pH value: 5.5±0.5, Temperature: T=25℃, catalyst concentration: $C_{Cat.1}$=0.1 g/L, H_2 flow: Q_{H2}=100 ml/min)

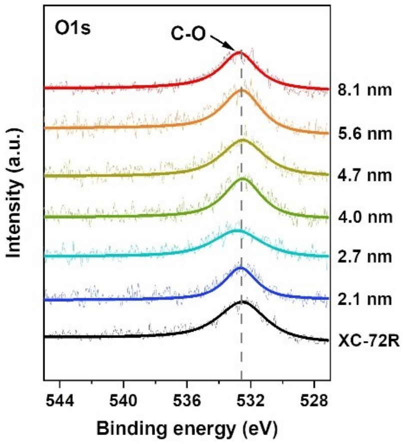

Fig. S16 O1s spectra of the fresh XC-72R support and the catalysts (2.1 to 8.1 nm).

As shown in Fig. S16, all the Pd/C catalysts and fresh XC-72R support exhibited nearly identical O1s spectra at around 532.5 eV, corresponding to the C-O bonds of the oxidized graphene, and no significant O1s spectra for the Pd-O (530.5 eV) can be found[5, 6].

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