

Supporting Information

Greatly changed performance of metal Pd catalyst by a rather easily formed and removed species–PdH_x

Hongxu Yan, Yunyi Liu, Tao Zhang, Ze Jin, Ming Wang, Ying Peng Xie and Hongfan Guo*

Content

1. Supporting Figures and Tables for Pd colloids that inspire this work

Figures S1-S6 and Table 1

2. Supporting Figures for SiO₂-supported Pd catalysts that verify the catalytic performance of various Pd species in the metal Pd catalysts

Figures S7-S14

Supporting references

1 Supporting Figures and Tables for Pd colloids that inspire this work

Figures S1-S6 and Table 1

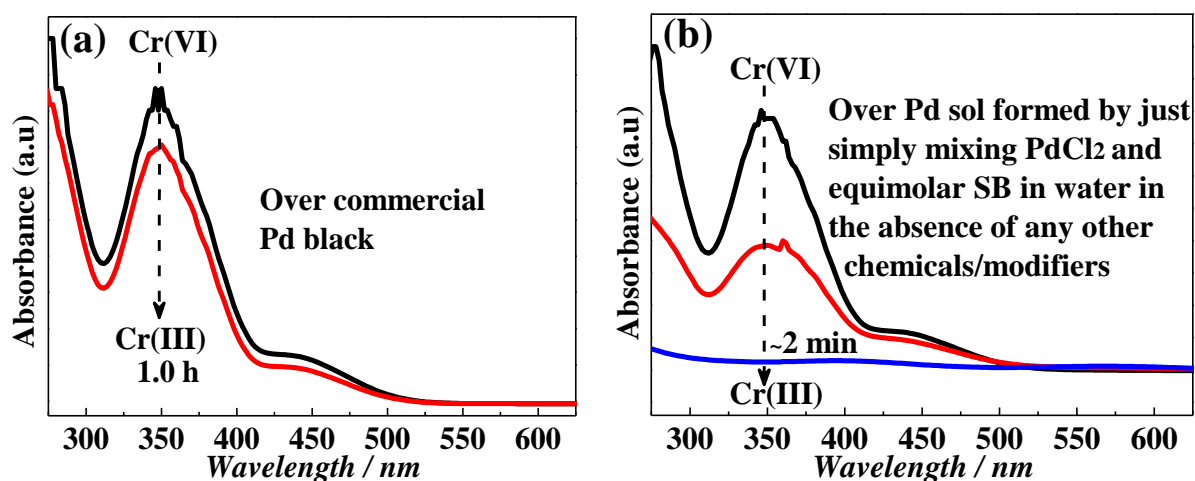


Figure S1. UV-vis spectra for the reduction of Cr(VI) ($\text{Cr}_2\text{O}_7^{2-}$) with FAD over Pd black and Pd sol. Reaction conditions: 20 °C; 2.5 ml of 0.1 mM Pd sols aqueous solution (i.e., 2.5×10^{-4} mmol Pd); the molar amount of Pd for *Pd black* was the same as that for Pd sols; 0.04 mmol Cr(VI) (i.e., 0.02 mmol $\text{K}_2\text{Cr}_2\text{O}_7$); Experimental Section 1.2 for more details.

Comments for Figure S1: As commercial Pd black was frequently used as a reference or evaluation catalyst in some previous reports,^[S1,S2] in this work the reduction of Cr(VI) was also performed over Pd black as a reference. It's worth noting that the Pd sol, formed just by simply mixing PdCl_2 and equimolar SB in water in the absence of any other chemicals/modifiers, gives a much shorter reaction time (~2 min for a full reduction of all the Cr(VI)) than Pd black that just obtains a ~20 % conversion in 1.0 h. This indicates that the Pd sol possesses excellent activity.

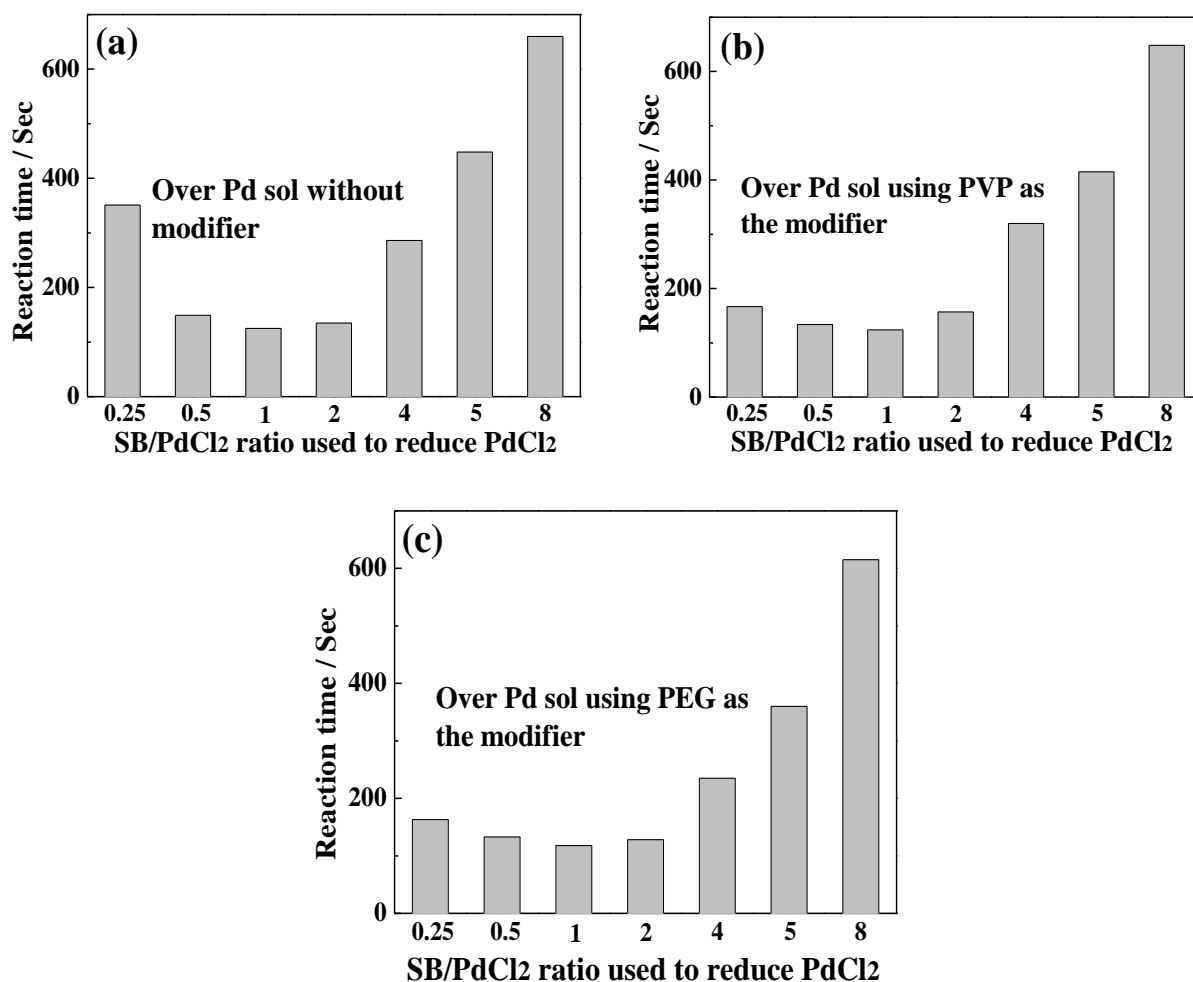


Figure S2. Influence of SB/PdCl₂ molar ratio on the catalytic activity of the Pd sols formed by reducing PdCl₂ with SB in water. Reaction time in the figures means the time for the complete reduction of all the Cr(VI). Reaction conditions are the same as those of Figure S1.

Comments for Figure S2: Figures S2 shows that the amount of SB used to synthesize metal Pd is a critical parameter in determining the catalytic activity. The suitable SB/PdCl₂ ratio is ~1 for all the Pd sols no matter with a modifier or without. The sols prepared with this ratio give much higher TOF values than the reported Pd catalysts (Table S1). When the used SB/PdCl₂ ratio is above 2, the obtained Pd catalysts exhibit markedly decreased activity.

Table S1 Turnover frequency (TOF) values in the catalytic reduction of Cr(VI) over different Pd catalysts

Entry	Pd catalyst used	TOF value (min ⁻¹) ^a	Reaction temperatre	Ref.
1	Pd sols shown in Figures S2	Up to ~ 40	20 °C	This work
2	Amino-functionalized Pd nanowires	1.42	r.t. ^b	[S1]
3	Pd nanotetrapods synthesized by the assistance of arginine in the presence of PVP	4.23	50 °C	[S2]
4	Pd nanoparticles (NPs) on amine-functionalized SiO ₂	2.53	r.t. ^b	[S3]
5	Pd NPs on amine-functionalized SiO ₂	4.33	35 °C	[S3]
6	Pd NPs on amine-functionalized SiO ₂	6.06	45 °C	[S3]
7	Pd NPs on polyethyleneimine/polyvinyl alcohol nanofibers	2.32	50 °C	[S4]
8	Pd/Pt NPs on procyanidin-grafted eggshell membrane	1.66	45 °C	[S5]

^aTOF value is calculated as $\text{Cr}_2\text{O}_7^{2-}/(\text{Pd}_{\text{mol}} \times \text{reaction time})$; ^br.t.: Room temperature (25 °C).

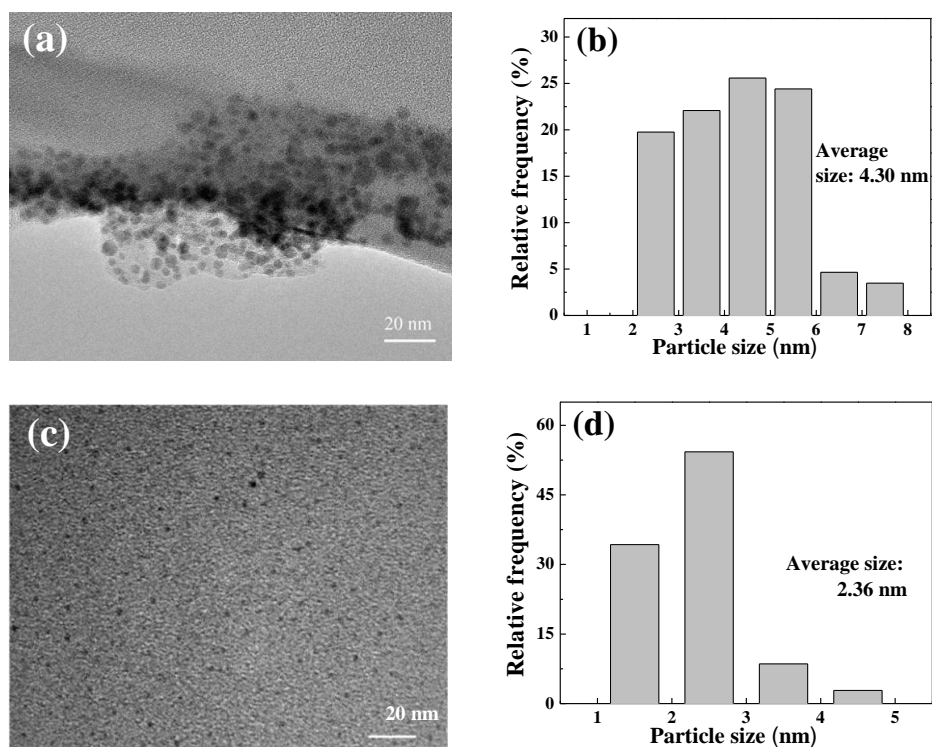


Figure S3. HRTEM images and particle size distribution of the Pd sols using PVP as the modifier prepared with: (a, b) SB/PdCl₂ = 1/1; (c, d) SB/PdCl₂ = 5/1.

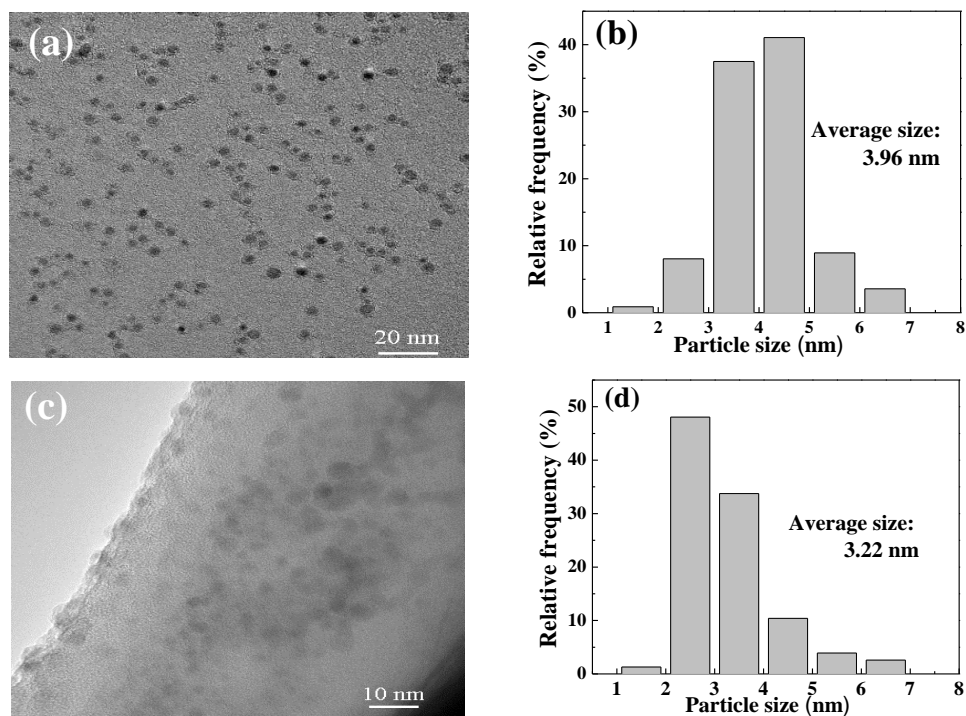


Figure S4. HRTEM images and particle size distribution of the Pd sols using PEG as the modifier prepared with: (a, b) SB/PdCl₂ = 1/1; (c, d) SB/PdCl₂ = 8/1.

Comments for Figures S3 and S4: HRTEM analyses demonstrate that the reason for the decreased catalytic activity due to the use of more SB in the catalyst synthesis (SB/PdCl₂ ratio

above 2 as shown in Figures S2) might not be simply explained by the increase in the particle size of the Pd sols. For example, as shown in Figure S3, when PVP is used as the modifier, the Pd sol prepared with SB/PdCl₂=5 shows a much smaller particle size (2.36 nm; Figure S3d) than that prepared with SB/PdCl₂=1 (4.30 nm; Figure S3b). Moreover, in the case of using PEG as the modifier, the Pd sols prepared with SB/PdCl₂=1 and 8 have very different activity (Figure S2c), but their particle sizes are very similar, 3.96 nm verse 3.22 nm (Figure S4). Of course, in some reported work larger particle size is shown to give higher activity for some catalytic reactions.^[S6] However, the Pd sol prepared with PEG and SB/PdCl₂=8 (3.22 nm; Figure S4d) shows a larger particle size but a lower activity than that prepared with PVP and SB/PdCl₂=5 (2.36 nm; Figure S3d). All the above observations indicate that there are no obvious relations between catalytic activity and particle size.

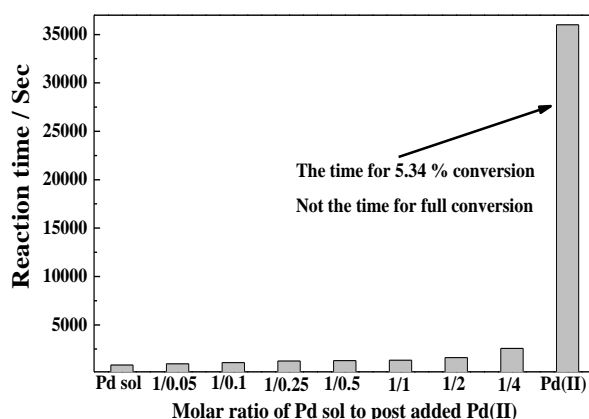


Figure S5. Influence of adding Pd(II) on the catalytic activity of the Pd sol prepared with high SB/PdCl₂ ratio. In each catalytic test, the used total molar amount of elemental Pd remained constant; Pd sol was prepared by reducing PdCl₂ with 8 equivalents of SB; PdCl₂ was used as the source of Pd(II). Note: Before the addition of Pd(II) to Pd sol, the Pd sol and a small amount of FA were first mixed together for thoroughly decomposing the possible residual SB in the Pd sol (SB is not stable in the presence of an acid), in case of the reduction of the post added Pd(II).

Comments for Figure S5: The decreased catalytic activity due to the use of high SB/PdCl₂ ratio in the catalyst synthesis is possibly attributed to the decreased content of Pd(II) that serves as the active phase. To examine this possibility, different amounts of Pd(II) were added to the Pd catalyst prepared with high SB/PdCl₂ ratio, respectively. The catalytic results in Figure S5 show a decreasing activity with an increasing amount of the post added Pd(II). Particularly, pure Pd(II) exhibits a neglectable activity. These results ambiguously suggest that Pd(0) acts as the active phase, instead of Pd(II) (further confirmed later). In Figure S5 it

seems that “whether Pd(0) exists” is more critical than “how much the Pd(0)/Pd(II) ratio is”, that is, Pd(0) likes an initiator. The reason is possibly as follows: Pd(0) can decompose FA into reactive hydrogen species that not only reduce Cr(VI) to Cr(III) but also reduce Pd(II) to the catalytically active Pd(0); while only Pd(II) has the difficulty in producing active hydrogen species.

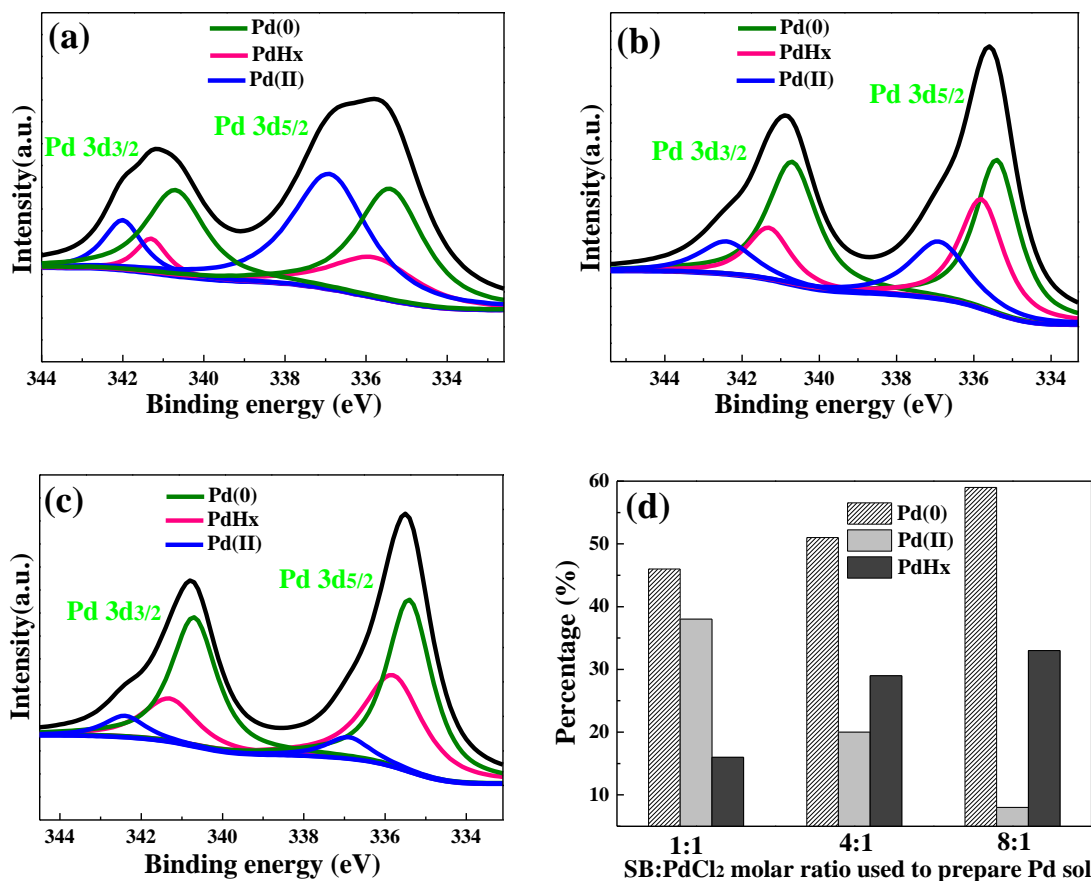


Figure S6. (a-c) High resolution Pd 3d XPS spectra of the Pd sols prepared with SB/PdCl₂ molar ratio of (a) 1:1, (b) 4:1 and (c) 8:1. (d) Percentage of Pd(0), Pd(II) and PdH_x species in different Pd sols. PEG is used as the modifier.

Comments for Figure S6: From Figures S6a-S6c it can be seen that the deconvolution of Pd 3d XPS spectrum gives the peaks of three different Pd species, attributable to Pd(0), PdH_x and Pd(II), respectively.^[S7-S9] Moreover, the more the SB is used, the higher the percentage of PdH_x is in the obtained Pd catalysts (Figure S6d). Based on the fact that the high SB/PdCl₂ ratios cause the decrease in the catalytic activity, it is hypothesized that PdH_x poisons the present catalytic reaction.

2 Supporting Figures for SiO₂-supported Pd catalysts that verify the catalytic performance of various Pd species in the metal Pd catalysts

Figures S7-S14

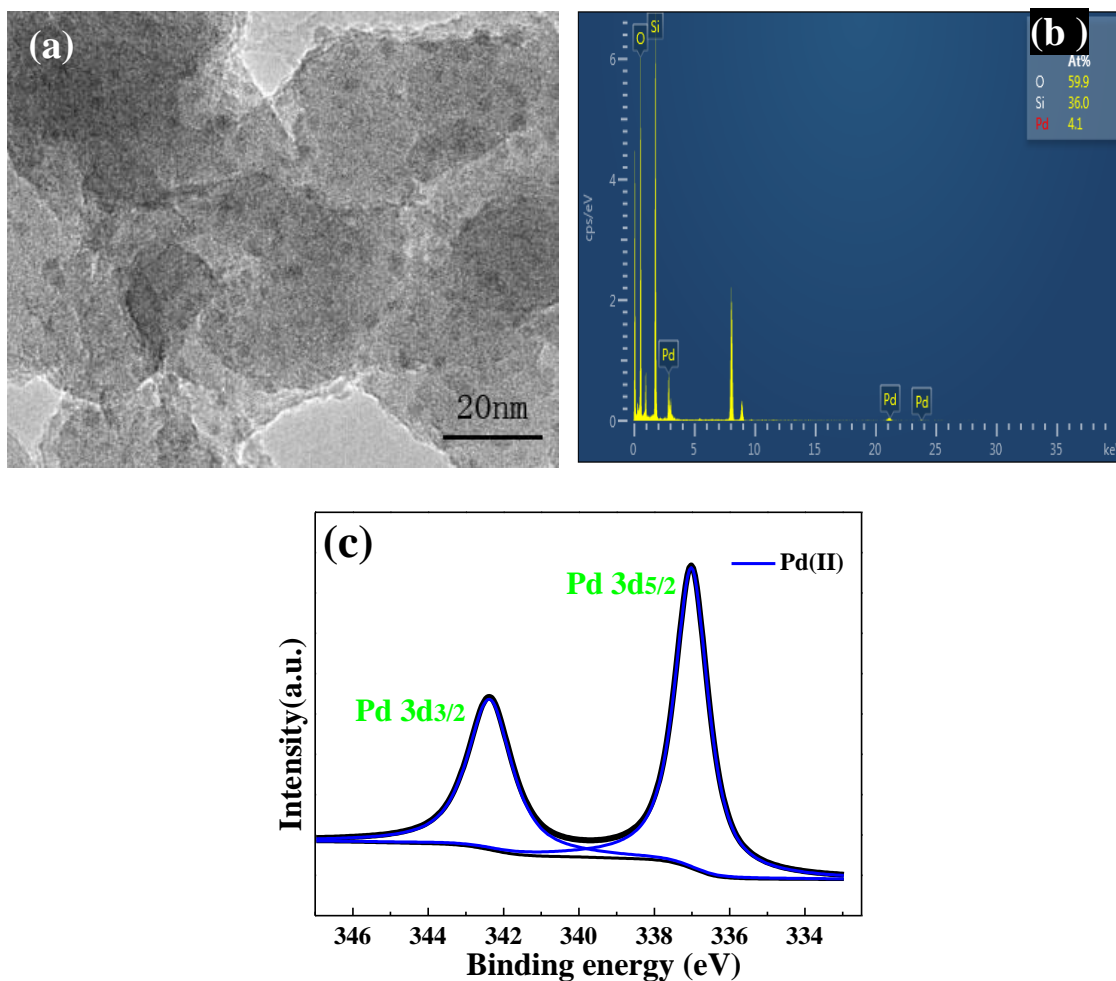


Figure S7. (a) HRTEM image, (b) EDS spectrum, and (c) high resolution Pd 3d XPS spectrum of PdO₂ catalyst.

Comments for Figure S7c: In the XPS spectrum of PdO₂ catalyst, only the peak of Pd(II) can be fitted out, indicating that the elemental Pd exists only as PdO.

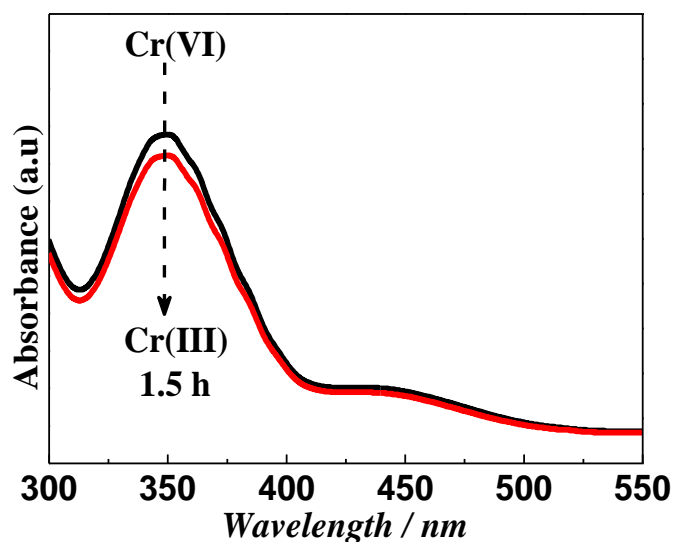


Figure S8. UV-vis spectra for the reduction of Cr(VI) ($\text{Cr}_2\text{O}_7^{2-}$) with FAD over PdO_2 catalyst.

Comments for Figure S8: From Figure S8 it can be seen that PdO_2 exhibits neglectable activity, as there is no obvious change in the characteristic peak of $\text{Cr}_2\text{O}_7^{2-}$ at 350 nm^[S2] after 1.5 h.

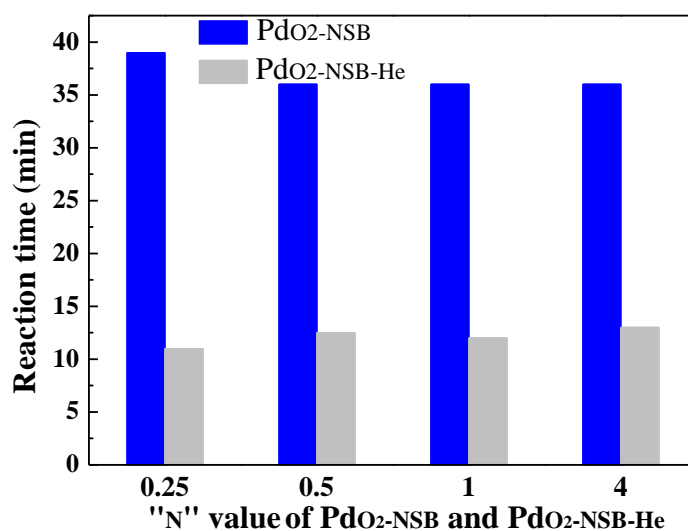


Figure S9. Effect of different catalyst treatments on the catalytic activity for the Cr(VI) reduction by FAD. Reaction conditions are the same as those of Figure 1. Note: reaction time in the figure refers to the time for a full reduction of all the Cr(VI).

Comments for Figure S9: Figure S9 shows that the catalytic activity of $\text{PdO}_2\text{-NSB}$ is not obviously affected by its “N” value, which is different from the observation obtained from Pd

sols whose activity is greatly affected by SB amount (Figure S2). The definite reasons are unknown. Possibly, SB can access each Pd atom of the dissolved PdCl₂ in the synthesis of Pd sols; while in the reduction of SiO₂-supported PdO₂ for preparing PdO₂-NSB, SB mainly reacts through the Pd atoms near the surface of the existing Pd particles on the SiO₂, and thus the use of a small amount of SB can cause the production of enough PdH_x on the surface of the Pd particles.

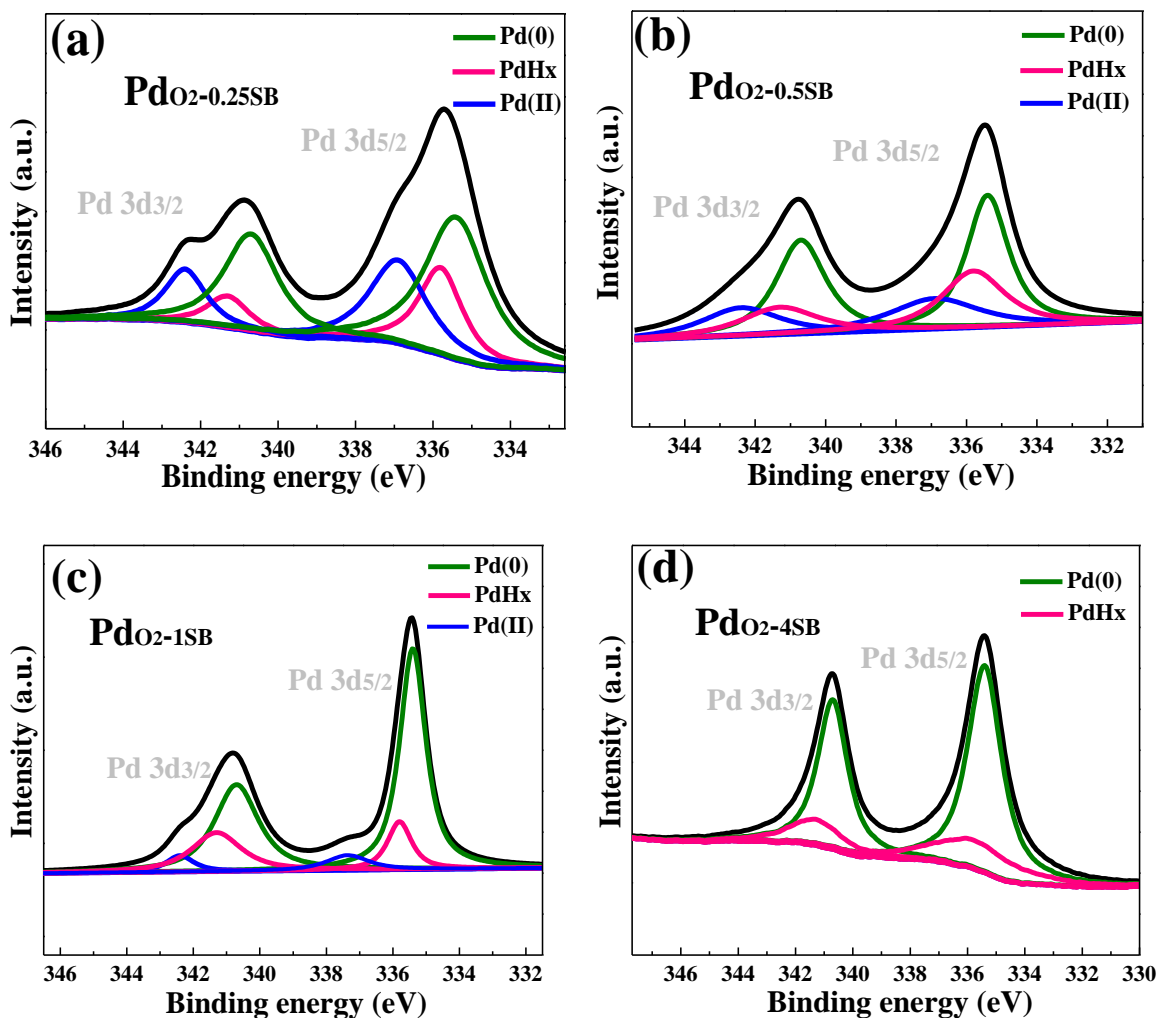


Figure S10. High resolution Pd 3d XPS spectra of PdO_{2-NSB} catalysts.

Comments for Figure S10: Figure S10 shows that the peak of PdH_x species is very obvious in the deconvolution of Pd 3d XPS spectra of PdO_{2-NSB} catalysts, indicating that a noticeable amount of PdH_x species exist in PdO_{2-NSB} catalysts. In addition, the content of Pd(II) decreases with the increase in the “*N*” value of PdO_{2-NSB} catalysts. The Pd(II) phase even can vanish when the “*N*” value is high (Figure S10d). The contents of Pd(0), Pd(II) and PdH_x species are summarized in Figure 1c.

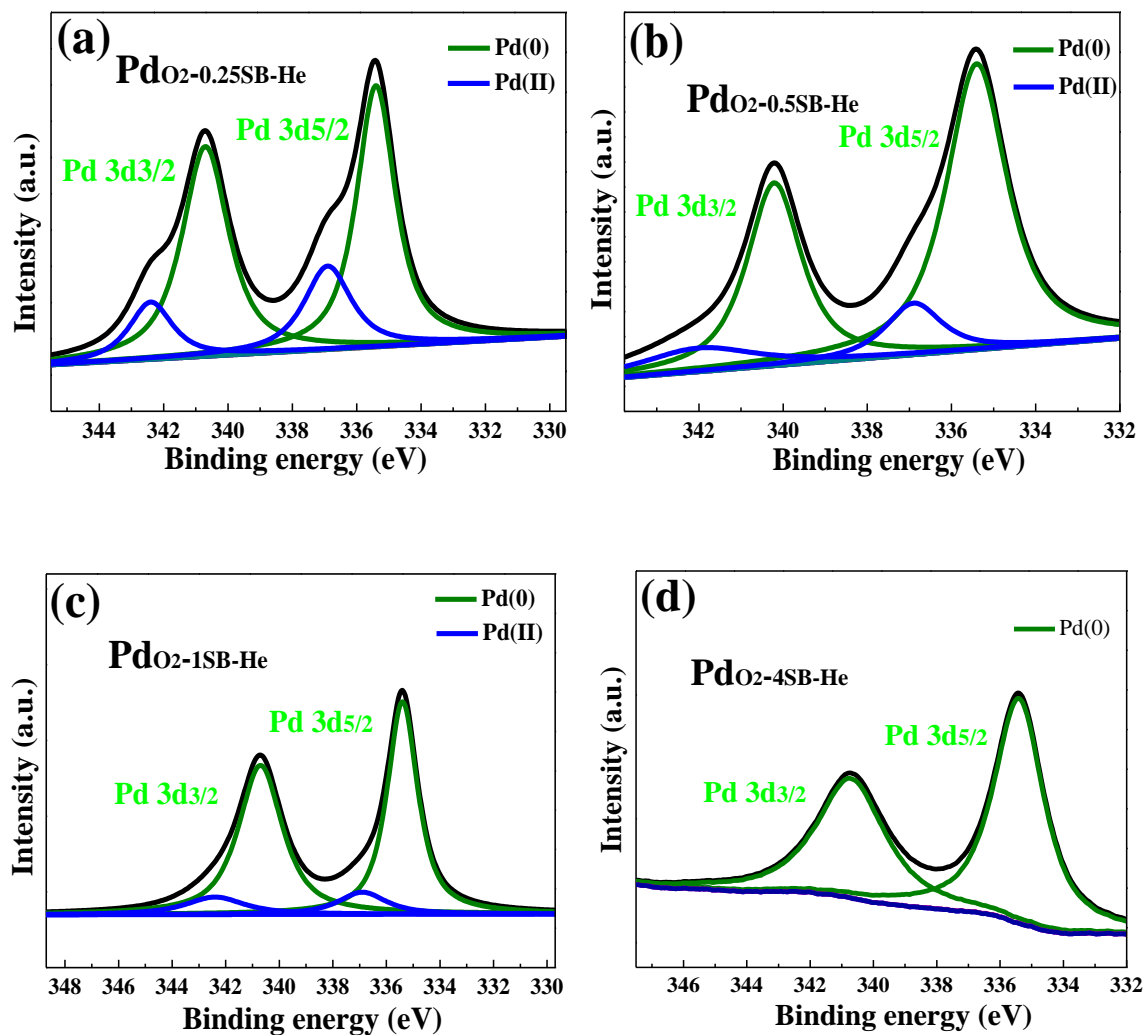


Figure S11. High resolution Pd 3d XPS spectra of PdO₂-NSB-He catalysts obtained from heat treating PdO₂-NSB at 200 °C in helium for 10 min.

Comments for Figure S11: No peaks of PdH_x species can be fitted out in the XPS spectra, indicating that PdO₂-NSB-He catalysts only consist of Pd(0) and Pd(II) phases. The percentage of Pd(0) and Pd(II) species in PdO₂-NSB-He catalysts is summarized in Figure 2.

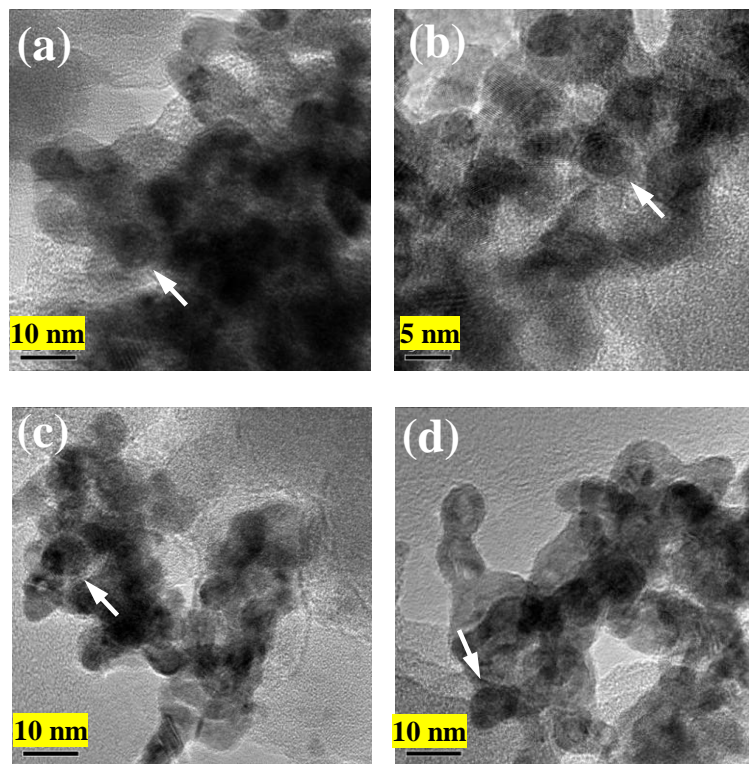


Figure S12. HRTEM images of (a) Pd_{O₂-0.25SB}, (b) Pd_{O₂-0.25SB-He}, (c) Pd_{O₂-4SB}, and (d) Pd_{O₂-4SB-He} catalysts.

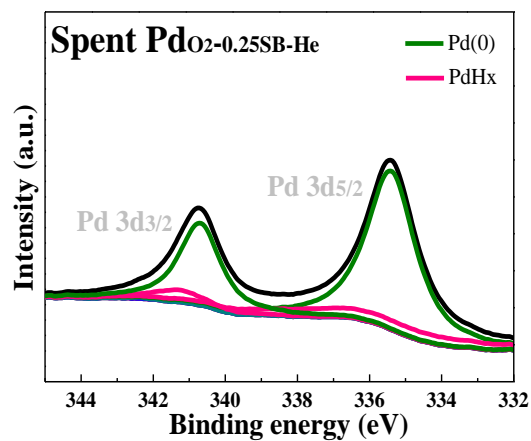


Figure S13. High resolution Pd 3d XPS spectrum of the Pd_{O₂-0.25SB-He} catalyst after the catalytic reduction of Cr(VI) by FAD.

Comments for Figure S13: Figure S13 shows that Pd(II) phase in Pd_{O₂-0.25SB-He} catalyst vanishes after catalytic Cr(VI) reduction. However, before use there is ~25 % Pd(II) in Pd_{O₂-0.25SB-He} catalyst, as shown in Figures S11a and 2. These observations indicate that Pd(II) can be reduced to Pd(0) during the catalytic reduction of Cr(VI).

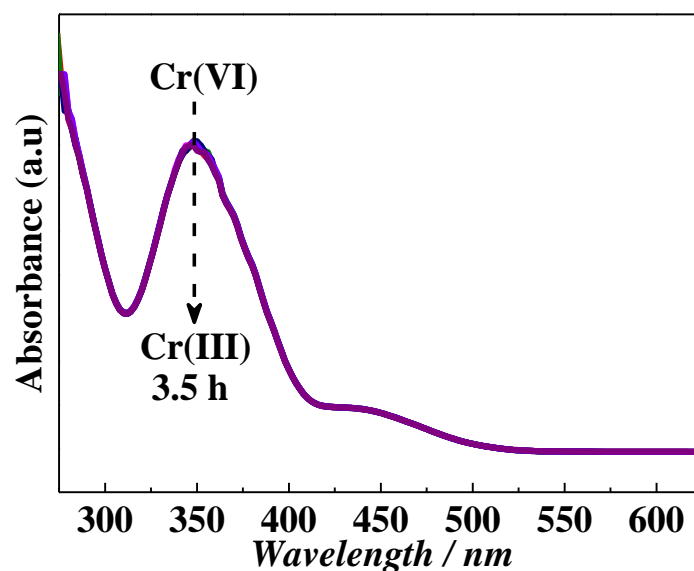


Figure S14. UV-vis spectra of the reduction of Cr(VI) ($\text{Cr}_2\text{O}_7^{2-}$) with FA in the absence of any catalyst.

Comments for Figure S14: Figure S14 shows that in the absence of a catalyst the characteristic absorption peak of Cr(VI) at 350 nm ^[S2] remains almost unchanged over 3.5 h, which confirms that the Cr(VI) reduction with FA cannot proceed without a catalyst.

Supporting references

[S1] L. Wei, R. Gu, J. Lee. *Appl. Catal. B* **2015**, 176-177, 325-330.

[S2] G. Fu, X. Jiang, R. Wu, S. Wei, D. Sun, Y. Tang, T. Lu, Y. Chen. *ACS Appl. Mater. Interfaces* **2014**, 6, 22790-22795.

[S3] M. Celebia, M. Yurderia, A. Buluta, M. Kayab, M. Zahmakiran. *Appl. Catal. B* **2016**, 180, 53-64.

[S4] Y. Huang, H. Ma, S. Wang, M. Shen, R. Guo, X. Cao, M. Zhu, X. Shi. *ACS Appl. Mater. Interfaces* **2012**, 4, 3054-3061.

[S5] M. Liang, R. Su, W. Qi, Y. Zhang, R. Huang, Y. Yu, L. Wang, Z. He. *Ind. Eng. Chem. Res.* **2014**, 53, 13635-13643.

- [S6]C. Yang, J. H. Meldon, B. Lee, H. Yi. *Catal. Today* **2014**, 233, 108-116.
- [S7]C. Huan, L. Ma, D. Lü, Y. Zheng, L. Ji, X. Li. *J. Inorg. Mater.* **2013**, 28(10), 1072-1078.
- [S8]C. Huan, L. Ma Lei, L. Ji, Y. Zheng, X. Li. *J. Chem. Eng. Chin. Uni.* **2013**, 5, 811-817.
- [S9]L. Yan, X. Liu, Y. Fu. *RSC Adv.* **2016**, 6, 109702-109705.