Supporting Information for

Mechanistic Analysis Guided Pd-Based Catalysts for Efficient Hydrogen Production from Formic Acid Dehydrogenation

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Figure S1. Cyclic voltammograms displaying hydrogen adsorption-desorption for Pd/C and Pd@Bi_{0.11}/C in 0.1 M HClO₄ at 10 mV s⁻¹.



Figure S2. XRD patterns of Pd/C and Pd@Bi_{0.11}/C before and after 3 cycles of catalytic FAD in 1.1 M FA + 0.8 M SF solution.



Figure S3. XAFS spectra obtained on Pd/C and Pd@Bi_{0.11}/C before (solid lines) and after (dashdotted lines) being immersed in 1.1 M FA + 0.8 M SF solution for 40 min.



Figure S4. (a) High resolution HAADF-STEM image of $Pd@Bi_{0.11}/C$ after recyclability test. (b) HAADF survey image of targeted nanoparticles for the EDS line scan analysis (c) Integrated EDS spectrum of the line scan. (d) Elemental distribution of Pd (blue) and Bi (red) on Pd@Bi_{0.11} nanoparticles by EDS line scan analysis.



Figure S5. Gas chromatograms obtained using a FID for the gas released from the 1.1 M FA + 0.8 M SF solution in the presence of the $Pd@Bi_{0.11}/C$ catalyst.



Figure S6. Time course of gas evolution from 5 mL of 1.1 M FA + 0.8 M SF solution in the presence of 80 mg of Pd@Bi_x/C at 303 K with different Bi/Pd molar ratio x.



Figure S7. Time course of gas evolution from 5 mL of 1.1 M FA + n M SF solution with 80 mg of Pd@Bi_{0.11}/C (a) and Pd/C (b) catalysts at 303 K with varying concentrations of sodium formate.



Figure S8. The plot of global TOF at Pd/C for the hydrogen production as a function of formate concentration in mixed formic acid-formate solutions with formic acid controlled to be $1.1 \text{ mol} \text{ L}^{-1}$ at 303 K.









Figure S10. Energy profile for $HCOO_B^* \rightarrow HCOO_M^* \rightarrow CO_2 + H^*$ on Pd(111)-(3x3)-Bi.



Figure S11. Time course of gas evolution from 5 mL of 1.1 M FA + 0.8 M SF solution over 80 mg of Pd@ $M_{0.11}$ /C catalysts at 303 K. The synthetic scheme of Pb and Sb deposition on Pd/C is slightly different from that of Bi. The Sb precursor antimony potassium tartrate (or the Pb precursor Pb(NO₃)₂) was mixed with 5 mL of 0.2 M ascorbic acid solution, before being added into the Pd/C suspension. Since the standard electrode potential of Sb³⁺/Sb⁰ (Pb²⁺/Pb⁰) is lower than that of Bi³⁺/Bi⁰, the addition of ascorbic acid serves to facilitate the reduction of Sb (Pb) and to suppress the hydrolysis of the cation.

Precursor n_{Bi}^{3+} / µmol	Measured $n_{Bi}/\mu mol$	Yield / %	Measured n_{Bi}/n_{Pd} , x
1.76	1.77	100	0.03
3.54	3.58	101	0.06
4.72	4.47	95	0.08
7.08	6.38	90	0.11
9.40	8.07	86	0.14
14.16	10.88	77	0.19

Table S1. Yields of Bi deposition on Pd/C to produce Pd@Bi_x/C measured by ICP-AES.

Table S2. TOF_{g} of Catalytic formic acid dehydrogenation at 303 K with different concentration of sodium formate in 5 mL aqueous solution

Catalyst	c_{FA} / mol L ⁻¹	c_{SF} / mol L ⁻¹	TOFg/h ⁻¹	
	1.1	0.4	747	
Pd/C	1.1	0.8	1240	
	1.1	1.2	1690	
	1.1	1.6	2060	
	1.1	2.4	2660	
Pd@Bi _{0.11} /C	1.1	0.4	1580	
	1.1	0.8	2370	
	1.1	1.2	3030	
	1.1	1.6	3560	
	1.1	2.4	4350	

Catalyst	Temperature/ºC	$c_{FA}/mol L^{-1}$	$c_{SF}/mol L^{-1}$	TOF/h ⁻¹	Reference
Pd@Bi _{0.11} /C	30		0.8	2370 ^{a,#} 4470 ^{b, #}	This work
	40	. 1.1		4100 ^{a,#}	
	50			6940 ^{a,#}	
	60			11500 ^{a,#}	
	30	1.1	2.4	4350 ^{a,#}	
Pd ₁ Au ₁ /72-LA	30	1.0	3.0	3583 ^{a,*}	S1
Pd@CN900K	30	1.0	3.0	2571 ^{a,*}	S2
Pd/C_m	60	1.7	1.7	7256 ^{a, #}	S3
Pd/N-MSC-30-two- 175	30	1.0	2.5	1803 ^{a,*}	S4
Pd ⁰ /CeO ₂	25	0.16	1.4	1400 ^{a,*}	S5
PdAg@ZrO ₂ /C/rGO	60	1.5	3.75	4500 ^{a,*}	S6
(Co ₆)Ag _{0.1} Pd _{0.9} /rGO	50	0.67	1.67	2739 ^{a,*}	S7
AuPd/n-CNS-Th- 160	60	0.5	0.5	1896 ^{a, #}	S8
PdO/C	30	1.1	0.8	3172 ^{b, #}	S9
Pd-B/C	30	1.1	0.8	1184 ^{b, #}	S10
Pd/C	30	1.1	0.8	1815 ^{b, #}	S11
Pd/S1-in-K	25	2.0	2.0	856 ^{a,*}	S12
Au _{0.67} Pd _{0.33} /C-L-7.5	25	1.0	1.0	1153 a,*	S13

Table S3. TOF values of catalytic formic acid dehydrogenation performed over different catalysts in different conditions- a comparison with literature reports.

High-performance Pd-based catalysts without modification of alkaline functioning groups are listed here for comparison.

^a TOF values calculated on total metal atoms.

^b TOF values calculated on surface metal sites or active sites.

[#] Initial TOF values calculated on initial time or initial conversion of FA.

* TOF values calculated on the complete time of gas releasing.

Detailed procedure for calculating the binding energy of H*

The Gibbs free-energy change (ΔG_{ads}) of H is defined as follows

$$\Delta G_{ads} = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S$$

where ΔE_{ads} is the adsorption energy of the atomic H on the surface, ΔE_{ZPE} is the difference in zero-point energy between the adsorbed hydrogen and hydrogen in the gas phase. ΔS is the entropy change of one H atom from the absorbed state to the gas phase. Since the H atom is binding on the surface, the entropy of the adsorbed hydrogen can be negligible. Therefore, the ΔS can be estimated by $-1/2 \times S_0$, in which S_0 is the standard entropy of H₂ with gas phase at pressure of 1 bar at 300 K. In summary, the Gibbs free-energy change (ΔG_{ads}) of H can be described as

$$\Delta G_{ads} = \Delta E_{ads} + \Delta E_{ZPE} + 0.065 eV$$

The ΔE_{ads} is defined as follows:

$$\Delta E_{ads} = E_{H/slab} - (E_{slab} + \frac{1}{2}E_{H_2})$$

where the $E_{H/slab}$ is the total energy of H atom on the catalyst, E_{slab} is the total energy of the slab and E_{H} is the energy of H atom reference to the gas H₂. The first two terms are calculated with the same parameters. The third term is calculated by setting the isolated H₂ in a box of 12 Å×12 Å×12 Å.

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