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 HClO$_4$ 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\textsubscript{0.11}/C before (solid lines) and after (dash-dotted 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\textsubscript{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\textsubscript{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 mol L$^{-1}$ at 303 K.
Figure S9. TEM images of Pd/C (a) and Pd@Bi$_{0.11}$/C (b) after recyclability FAD test in 1.1 M FA + 0.8 M SF solution.
**Figure S10.** Energy profile for $\text{HCOO}^* \rightarrow \text{HCOO}_{\text{M}}^* \rightarrow \text{CO}_2 + \text{H}^*$ 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@M0.11/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(NO$_3$)$_2$) 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 Sb$^{3+}$/Sb$^{0}$ (Pb$^{2+}$/Pb$^{0}$) is lower than that of Bi$^{3+}$/Bi$^{0}$, the addition of ascorbic acid serves to facilitate the reduction of Sb (Pb) and to suppress the hydrolysis of the cation.
Table S1. Yields of Bi deposition on Pd/C to produce Pd@Bi/C measured by ICP-AES.

<table>
<thead>
<tr>
<th>Precursor n_{Bi^{3+}}/μmol</th>
<th>Measured n_{Bi}/μmol</th>
<th>Yield / %</th>
<th>Measured n_{Bi}/n_{Pd}, ( x )</th>
</tr>
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<tbody>
<tr>
<td>1.76</td>
<td>1.77</td>
<td>100</td>
<td>0.03</td>
</tr>
<tr>
<td>3.54</td>
<td>3.58</td>
<td>101</td>
<td>0.06</td>
</tr>
<tr>
<td>4.72</td>
<td>4.47</td>
<td>95</td>
<td>0.08</td>
</tr>
<tr>
<td>7.08</td>
<td>6.38</td>
<td>90</td>
<td>0.11</td>
</tr>
<tr>
<td>9.40</td>
<td>8.07</td>
<td>86</td>
<td>0.14</td>
</tr>
<tr>
<td>14.16</td>
<td>10.88</td>
<td>77</td>
<td>0.19</td>
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Table S2. TOF\( _g \) of Catalytic formic acid dehydrogenation at 303 K with different concentration of sodium formate in 5 mL aqueous solution

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( c_{FA} )/ mol L(^{-1} )</th>
<th>( c_{SF} )/ mol L(^{-1} )</th>
<th>TOF( _g )/h(^{-1} )</th>
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</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>1.1</td>
<td>0.4</td>
<td>747</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>0.8</td>
<td>1240</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.2</td>
<td>1690</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.6</td>
<td>2060</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2.4</td>
<td>2660</td>
</tr>
<tr>
<td>Pd@Bi( _{0.11} )/C</td>
<td>1.1</td>
<td>0.4</td>
<td>1580</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>0.8</td>
<td>2370</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.2</td>
<td>3030</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>1.6</td>
<td>3560</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2.4</td>
<td>4350</td>
</tr>
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</table>
Table S3. TOF values of catalytic formic acid dehydrogenation performed over different catalysts in different conditions- a comparison with literature reports.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature/°C</th>
<th>$c_{FA}/mol\ L^{-1}$</th>
<th>$c_{SF}/mol\ L^{-1}$</th>
<th>TOF/h$^{-1}$</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Pd@Bi$_{0.11}$/C</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.1</td>
<td>0.8</td>
<td>2370 a,#</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td>4470 b,#</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td></td>
<td></td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.1</td>
<td>2.4</td>
<td>4350 a,#</td>
<td></td>
</tr>
<tr>
<td>Pd$<em>{1}$Au$</em>{1}$/72-LA</td>
<td>30</td>
<td>1.0</td>
<td>3.0</td>
<td>3583 a,*</td>
<td>S1</td>
</tr>
<tr>
<td>Pd@CN900K</td>
<td>30</td>
<td>1.0</td>
<td>3.0</td>
<td>2571 a,*</td>
<td>S2</td>
</tr>
<tr>
<td>Pd/C$_{m}$</td>
<td>60</td>
<td>1.7</td>
<td>1.7</td>
<td>7256 a,#</td>
<td>S3</td>
</tr>
<tr>
<td>Pd/N-MSC-30-two-175</td>
<td>30</td>
<td>1.0</td>
<td>2.5</td>
<td>1803 a,*</td>
<td>S4</td>
</tr>
<tr>
<td>Pd$<em>{0}$/CeO$</em>{2}$</td>
<td>25</td>
<td>0.16</td>
<td>1.4</td>
<td>1400 a,*</td>
<td>S5</td>
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<tr>
<td>PdAg@ZrO$_{2}$/C/rGO</td>
<td>60</td>
<td>1.5</td>
<td>3.75</td>
<td>4500 a,*</td>
<td>S6</td>
</tr>
<tr>
<td>(Co$<em>{9}$)Ag$</em>{0.1}$Pd$_{0.9}$/rGO</td>
<td>50</td>
<td>0.67</td>
<td>1.67</td>
<td>2739 a,*</td>
<td>S7</td>
</tr>
<tr>
<td>AuPd/n-CNS-Th-160</td>
<td>60</td>
<td>0.5</td>
<td>0.5</td>
<td>1896 a,#</td>
<td>S8</td>
</tr>
<tr>
<td>PdO/C</td>
<td>30</td>
<td>1.1</td>
<td>0.8</td>
<td>3172 b,#</td>
<td>S9</td>
</tr>
<tr>
<td>Pd-B/C</td>
<td>30</td>
<td>1.1</td>
<td>0.8</td>
<td>1184 b,#</td>
<td>S10</td>
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<tr>
<td>Pd/C</td>
<td>30</td>
<td>1.1</td>
<td>0.8</td>
<td>1815 b,#</td>
<td>S11</td>
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<tr>
<td>Pd/S1-in-K</td>
<td>25</td>
<td>2.0</td>
<td>2.0</td>
<td>856 a,*</td>
<td>S12</td>
</tr>
<tr>
<td>Au$<em>{0.67}$Pd$</em>{0.33}$/C-L-7.5</td>
<td>25</td>
<td>1.0</td>
<td>1.0</td>
<td>1153 a,*</td>
<td>S13</td>
</tr>
</tbody>
</table>

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.

*a* TOF values calculated on the complete time of gas releasing.
Detailed procedure for calculating the binding energy of H*

The Gibbs free-energy change ($\Delta G_{\text{ads}}$) of H is defined as follows:

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

where $\Delta E_{\text{ads}}$ is the adsorption energy of the atomic H on the surface, $\Delta E_{\text{ZPE}}$ is the difference in zero-point energy between the adsorbed hydrogen and hydrogen in the gas phase. $\Delta S$ 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, $\Delta S$ can be estimated by $-1/2 \times S_0$, in which $S_0$ is the standard entropy of H$_2$ with gas phase at pressure of 1 bar at 300 K. In summary, the Gibbs free-energy change ($\Delta G_{\text{ads}}$) of H can be described as

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

The $\Delta E_{\text{ads}}$ is defined as follows:

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

where the $E_{H/\text{slab}}$ is the total energy of H atom on the catalyst, $E_{\text{slab}}$ is the total energy of the slab and $E_{H_2}$ is the energy of H atom reference to the gas H$_2$. The first two terms are calculated with the same parameters. The third term is calculated by setting the isolated H$_2$ in a box of 12 Å×12 Å×12 Å.
References

(S2) Q. J. Wang, N. Tsumori, M. Kitta, Q. Xu, ACS Catal, 2018, 8, 12041-12045.