Supporting Information

Design of Atomically Precise Au₂Pd₆ Nanoclusters for Boosting Electrocatalytic Hydrogen Evolution on MoS₂

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Reference

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Fig. S1. Optical absorption spectrum of Au2Pd6 NC.

Fig. S2. (A) The one way of one S atom linked to two Pd atoms and one Au atom, (B) the another way of one S atom linked to two Au atoms and one Pd atom, (C) The distance of Au-S, and Pd-S in the Au2Pd6 NC. (Color labels: yellow = Au, blue = Pd,
Fig. S3. The distances between Pd atoms in the two triangular Pd₃ units of Au₂Pd₆ NC. From Fig. S3, the Pd-Pd distances in the Pd₃ units were 2.772 Å, 2.776 Å, 2.800 Å. The distances between Pd₃-Pd₆ and Pd₂-Pd₄ were 7.224 Å, the distances between Pd₁-Pd₄ and Pd₃-Pd₅ were 6.080 Å, and the distances between Pd₂-Pd₅ and Pd₁-Pd₆ were 8.199 Å. The quadrangles of Pd₂Pd₃Pd₆Pd₄, Pd₁Pd₃Pd₅Pd₄, and Pd₂Pd₁Pd₆Pd₅ were parallelogram, which means that the two triangular Pd₃ units were paralleled.
Fig. S4. The distances between the Au and Pd atoms in the Au$_2$Pd$_6$ metal core of Au$_2$Pd$_6$ NC. In the Au$_2$Pd$_6$ core, the distance between Au$_1$-Au$_2$ was 3.088 Å, which is greatly larger than the bulk Au-Au distance (2.88 Å). The Au-Pd distances in the Au$_2$Pd$_6$ core were 3.001 Å, 3.096 Å, 3.150 Å, respectively.
The angles of Au and Pd atoms in the Au$_2$Pd$_6$ metal core of Au$_2$Pd$_6$ NC. The angles of Pd$_1$-Au$_1$-Pd$_4$ and Pd$_3$-Au$_2$-Pd$_5$ were 171.30 °, the angles of Pd$_1$-Pd$_3$-Au$_1$ and Au$_2$-Pd$_4$-Pd$_5$ were 60.47 °, and the angles of Pd$_3$-Au$_1$-Au$_2$ and Au$_1$-Au$_2$-Pd$_4$ were 59.51°, which means that the quadrangle of Pd$_1$Pd$_3$Au$_1$Au$_2$Pd$_4$Pd$_5$ was twisty.
Fig. S6. (A) TEM image and (B) XRD pattern of MoS$_2$.

Fig. S7. XRD pattern of Au$_2$Pd$_6$/MoS$_2$.

Fig. S8. (A) UV-vis and (B) MALDI-MS spectra of Pd$_3$ NC. Inset of (A): crystal structure of Pd$_3$ NC (blue = Pd, deep yellow = P, reseda = Cl). Fig. S8A shows the UV-vis spectrum of Pd$_3$ NC, in which the peaks at 340, 418, and 485 nm are fingerprints of Pd$_3$ NC. The X-ray structure of Pd$_3$ NC (Fig. S8A, inset) comprises a
triangular Pd₃ unit protected by three –PPh₃, three –PPh₂, and one Cl atom. Fig. S8B shows the matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) of Pd₃ NC with the molecular ion peak at ~1511.8 Da (theoretical Mᵦ = 1511.05).

Fig. S9. (A) UV-vis and (B) MALDI-MS spectra of Au₂ complex. Inset of (A): simulated diagram of Au₂ complex crystal structure (yellow = Au, purple = P, pink = Cl). The UV–vis spectrum of Au₂ showed one peak at 330 nm (Fig. S9A). Fig. S9B showed the matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) of Au₂ with the molecular ion peak at ~780.87 (theretical [M-2Cl+2H]ᵦ=780.155).

Fig. S10. Exchange current density of various samples calculated using extrapolation methods.
Fig. S11. Cyclic voltammograms (0.3-0.4 V) recorded in 0.5 M H₂SO₄ for (A) Au₂Pd₆/MoS₂, (B) Au₂-Pd₃/MoS₂, (C) Pd₃/MoS₂, (D) Au₂/MoS₂ and (E) MoS₂.
Fig. S12. Cyclic voltammograms (−0.1−0.6 V) recorded in pH = 7 phosphate buffer, scan rate: 50 mV/S.

Fig. S13. Calculated turnover frequencies for MoS$_2$ and various NCs modified MoS$_2$. 
Fig. S14. (A) XRD pattern, (B) TEM image, (C) Mo 3d, (D) S 2p, (E) Au 4f, and (F) Pd 3d XPS spectra of $\text{Au}_2\text{Pd}_6/\text{MoS}_2$ after long-time durability test.
Fig. S15. Pd 3d XPS spectra of Pd$_3$ and Pd$_3$/MoS$_2$.

Fig. S16. Raman spectra of MoS$_2$, Pd$_3$/MoS$_2$ and Au$_2$Pd$_6$/MoS$_2$, the inset shows the schematic illustrations of the oscillating modes of $E^{1}_{2g}$ and $A_{1g}$, respectively. Atom color code: green, Mo; yellow, S.
**Fig. S17.** Different H adsorption sites in (A) Au₂Pd₆ NC system and (B) Au₂Pd₆/MoS₂ system. Yellow ball: S, purple ball: Mo, blue ball: Pd, orange ball: Au, pink ball: P, green ball: H.

**Fig. S18.** The optimal H adsorption position in defect-free MoS₂, the corresponding $\Delta G_{\text{H}}^\ast$ is 1.83 eV. Yellow ball: S, purple ball: Mo, green ball: the adsorption H.
Fig. S19. The specific position of the other two sites with the appropriate $\Delta G_{\text{H}^*}$ in Au$_2$Pd$_6$/MoS$_2$ system. Yellow ball: S, purple ball: Mo, blue ball: Pd, orange ball: Au, pink ball: P, green ball: H, red ball: the adsorption H.

Fig. S20. H adsorption configuration (site 4) in the Au$_2$Pd$_6$ NC (from different orientations) with best $\Delta G_{\text{H}^*}$ value. Yellow ball: S, blue ball: Pd, orange ball: Au, pink ball: P, green ball: H, red ball: the adsorption H.
Fig. S21. Different H adsorption sites in (A) Pd$_3$ NC system and (B) Pd$_3$/MoS$_2$ system. Yellow ball: S, purple ball: Mo, blue ball: Pd, pink ball: P, dark green ball: Cl, green ball: H.

Fig. S22. Different H adsorption sites in (A) Au$_2$ NC system and (B) Au$_2$/MoS$_2$ system. Yellow ball: S, purple ball: Mo, orange ball: Au, pink ball: P, dark green ball: Cl, brown ball: C, green ball: H.
Fig. S23. The density of states of Au, Pd, S and P atoms in the Au$_2$Pd$_6$/MoS$_2$ system.

Fig. S24. The charge deformation density of Au$_2$Pd$_6$/MoS$_2$ system. The charge density of Au$_2$Pd$_6$ NC is decreased, while the charge density of MoS$_2$ is increased, it indicates the charge transfer from NC to MoS$_2$. 
Table S1. Electrochemical Parameters of bare MoS$_2$ and various NCs modified MoS$_2$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Overpotential at 10 mA/cm$^2$ (mV)</th>
<th>Current density at 400 mV (mA/cm$^2$)</th>
<th>Tafel slope (mV/dec)</th>
<th>Exchange capacitance (mF/cm$^2$)</th>
<th>Double layer capacitance (µF/cm$^2$)</th>
<th>Charge transfer resistance (Ω)</th>
<th>Series resistance (Ω)</th>
<th>The number of active sites (×10$^3$ mol/g)</th>
<th>TOF 400 (nm) at 1 mV</th>
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<tbody>
<tr>
<td>MoS$_2$</td>
<td>218</td>
<td>355</td>
<td>20.5</td>
<td>97</td>
<td>2.04</td>
<td>5.69</td>
<td>403</td>
<td>14.13</td>
<td>1.673</td>
</tr>
<tr>
<td>Au/MoS$_2$</td>
<td>180</td>
<td>319</td>
<td>30.1</td>
<td>94</td>
<td>3.89</td>
<td>11.65</td>
<td>329</td>
<td>10.42</td>
<td>2.425</td>
</tr>
<tr>
<td>Pd/MoS$_2$</td>
<td>148</td>
<td>283</td>
<td>53.7</td>
<td>88</td>
<td>7.58</td>
<td>22.48</td>
<td>181</td>
<td>6.82</td>
<td>3.373</td>
</tr>
<tr>
<td>Au$_x$Pd$_y$/MoS$_2$</td>
<td>141</td>
<td>273</td>
<td>61.7</td>
<td>86</td>
<td>8.31</td>
<td>24.71</td>
<td>178</td>
<td>6.45</td>
<td>3.472</td>
</tr>
<tr>
<td>Au$_x$Pd$_y$/MoS$_2$</td>
<td>127</td>
<td>232</td>
<td>91</td>
<td>67</td>
<td>9.88</td>
<td>32.08</td>
<td>163</td>
<td>6.08</td>
<td>4.02</td>
</tr>
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</table>

Table S2. Comparison of HER performance of MoS$_2$-based catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Overpotential at 10 mA/cm$^2$ (mV)</th>
<th>Current density at 400 mV (mA/cm$^2$)</th>
<th>Tafel slope (mV/dec)</th>
<th>Exchange current density (µA/cm$^2$)</th>
<th>Double layer capacitance (mF/cm$^2$)</th>
<th>Charge transfer resistance (Ω)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>218</td>
<td>355</td>
<td>20.5</td>
<td>97</td>
<td>2.04</td>
<td>5.69</td>
<td>403</td>
</tr>
<tr>
<td>Au$_x$Pd$_y$/MoS$_2$</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>127</td>
<td>232</td>
<td>91</td>
<td>67</td>
<td>9.88</td>
<td>32.08</td>
<td>163</td>
</tr>
<tr>
<td>Au$_x$Pd$_y$/MoS$_2$</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>200</td>
<td>280</td>
<td>59.3</td>
<td>79.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MoS$_2$/Au 39.5 mol %</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>-</td>
<td>350</td>
<td>22.62</td>
<td>56.97</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MoS$_2$/Au (dark)</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>220</td>
<td>-</td>
<td>28</td>
<td>86</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P. MoS$_2$/Au</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>-</td>
<td>279</td>
<td>68.8</td>
<td>0.921</td>
<td>1.6</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>Se-doped MoS$_2$</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>140</td>
<td>275</td>
<td>42.7</td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt-MoS$_2$</td>
<td>0.1 M H$_2$SO$_4$</td>
<td>-</td>
<td>150</td>
<td>27</td>
<td>96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt/MoS$_2$-80</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>31</td>
<td>90</td>
<td>-</td>
<td>52</td>
<td>12.8</td>
<td>8</td>
<td>7</td>
</tr>
</tbody>
</table>

Note: $^a$ The numerical value was calculated from the figure in the reference.
Table S3. The Gibbs free energy of hydrogen adsorption on different sites in Au$_2$Pd$_6$ NC system.

<table>
<thead>
<tr>
<th>Site in Figure S17A</th>
<th>$\Delta G_H^\ast$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.32718</td>
</tr>
<tr>
<td>2</td>
<td>-1.3483</td>
</tr>
<tr>
<td>3</td>
<td>-1.14434</td>
</tr>
<tr>
<td>4</td>
<td>-0.03647</td>
</tr>
<tr>
<td>5</td>
<td>-2.22077</td>
</tr>
<tr>
<td>6</td>
<td>-0.59976</td>
</tr>
<tr>
<td>7</td>
<td>-2.56855</td>
</tr>
<tr>
<td>8</td>
<td>-0.87684</td>
</tr>
<tr>
<td>9</td>
<td>-3.06807</td>
</tr>
<tr>
<td>10</td>
<td>-2.21782</td>
</tr>
<tr>
<td>11</td>
<td>-1.41258</td>
</tr>
<tr>
<td>12</td>
<td>-1.4237</td>
</tr>
</tbody>
</table>

The calculated $\Delta G_H^\ast$ on different sites in Au$_2$Pd$_6$ NC system show that the best H adsorption site is site 4 in Fig. S17A and Fig. S20, the $\Delta G_H^\ast$ on this site is -0.04 eV.
**Table S4.** The Gibbs free energy of hydrogen adsorption on different sites in Au$_2$Pd$_6$/MoS$_2$ system.

<table>
<thead>
<tr>
<th>Site in Figure S17B</th>
<th>$\Delta G_H^*$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.149833</td>
</tr>
<tr>
<td>2</td>
<td>0.4319</td>
</tr>
<tr>
<td>3</td>
<td>0.295432</td>
</tr>
<tr>
<td>4</td>
<td>-0.01148</td>
</tr>
<tr>
<td>5</td>
<td>0.022313</td>
</tr>
<tr>
<td>6</td>
<td>-0.02848</td>
</tr>
</tbody>
</table>

The calculated $\Delta G_H^*$ on different sites in Au$_2$Pd$_6$/MoS$_2$ system show that the best H adsorption site is site 4 in Fig. S17B and Fig. 5A, the $\Delta G_H^*$ on this site is -0.01 eV. Meanwhile, site 5 and site 6 also have an appropriate $\Delta G_H^*$, which is 0.02 and -0.03 eV, respectively. The site position is detailedly shown in Fig. S19.

**Table S5.** The Gibbs free energy of hydrogen adsorption on different sites in Pd$_3$ NC system.

<table>
<thead>
<tr>
<th>Site in Figure S21A</th>
<th>$\Delta G_H^*$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.418051</td>
</tr>
<tr>
<td>2</td>
<td>0.72283</td>
</tr>
<tr>
<td>3</td>
<td>1.875788</td>
</tr>
</tbody>
</table>
Table S6. The Gibbs free energy of hydrogen adsorption on different sites in Pd₃/MoS₂ NC system.

<table>
<thead>
<tr>
<th>Site in Figure S21B</th>
<th>ΔG_{H₂}^*(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00724</td>
</tr>
<tr>
<td>2</td>
<td>0.961975</td>
</tr>
<tr>
<td>3</td>
<td>0.391343</td>
</tr>
<tr>
<td>4</td>
<td>0.993066</td>
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</table>

Table S7. The Gibbs free energy of hydrogen adsorption on different sites in Au₂ NC system.

<table>
<thead>
<tr>
<th>Site in Figure S22A</th>
<th>ΔG_{H₂}^*(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.733362</td>
</tr>
<tr>
<td>2</td>
<td>1.560567</td>
</tr>
<tr>
<td>3</td>
<td>2.279025</td>
</tr>
<tr>
<td>4</td>
<td>1.709955</td>
</tr>
<tr>
<td>5</td>
<td>1.705191</td>
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</table>

Table S8. The Gibbs free energy of hydrogen adsorption on different sites in Au₂/MoS₂ system.

<table>
<thead>
<tr>
<th>Site in Figure S22B</th>
<th>ΔG_{H₂}^*(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.727127</td>
</tr>
<tr>
<td>2</td>
<td>1.55778</td>
</tr>
<tr>
<td>3</td>
<td>2.241595</td>
</tr>
<tr>
<td>4</td>
<td>1.721984</td>
</tr>
<tr>
<td>5</td>
<td>1.686808</td>
</tr>
</tbody>
</table>
References


