Supporting Information

Silver-decorated Palladium on Carbon Catalyst for Enhanced Ammonium Formate Dehydrogenation

Zhun Dong [a], Ahmad Mukhtar [a], Thomas Ludwig [b], Sneha A. Akhade [b], Wenda Hu [a, c], Jian Zhi Hu [a, c], Katarzyna Grubel [d], Mark Engelhard [e], Brandon C. Wood [b], Tom Autrey [d], Hongfei Lin [a]*

[a] *Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99163, United States.*

[b] *Materials Sciences Division, Lawrence Livermore National Laboratory (LLNL), Livermore, CA 94550, United States.*

[c] *Institute for Integrated Catalysis, Pacific Northwest National Laboratory (PNNL), Richland, WA 99352, United States.*

[d] *Energy and Environment Division, Pacific Northwest National Laboratory (PNNL), Richland, WA 99352, United States.*

[e] *Environmental & Molecular Sciences, Earth & Biological Sciences, Pacific Northwest National Laboratory (PNNL), Richland, WA 99352, United States.*

**Corresponding author: hongfei.lin@wsu.edu*

TOF calculation:

$$TOF = \frac{moles\ of\ H_2\ formed\ at\ a\ certain\ reaction\ time}{(total\ moles\ of\ Pd\ atom) \times\ reaction\ time} \qquad (1)$$

Where, the reaction time is 10 min; total moles of Pd is calculated from Pd loading in the catalyst.

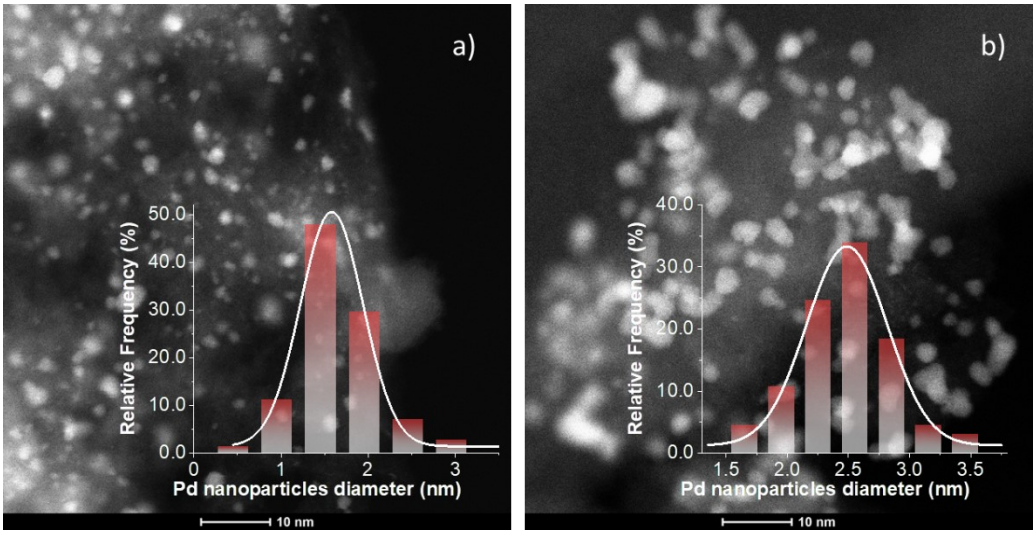

Figure S1. TEM images of a) Pd3Ag10/ACA-G, b) Pd3Ag10/ACA-C, and corresponding nanoparticles size distributions.

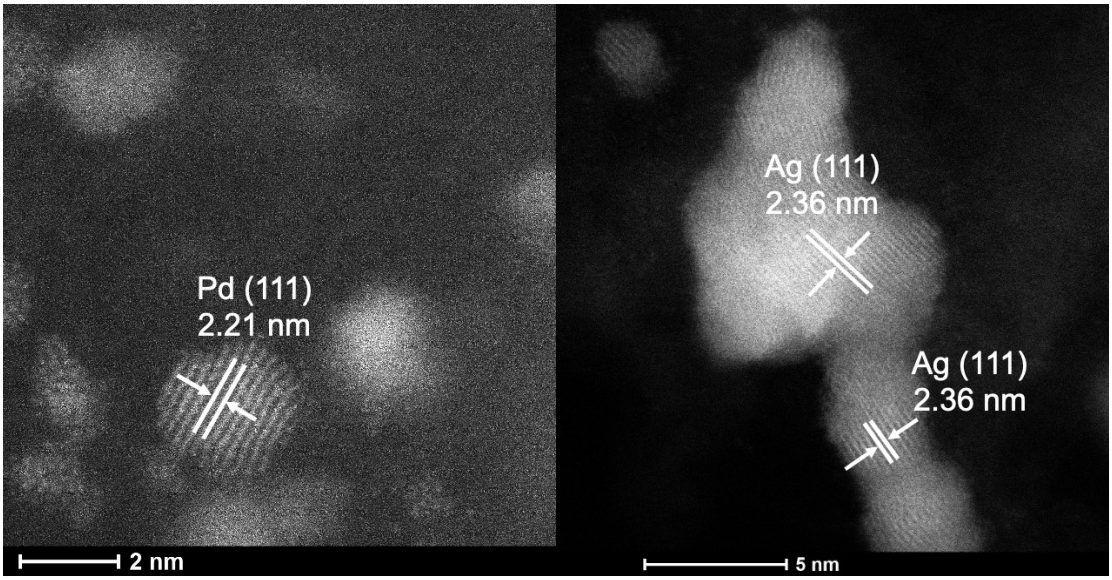

Figure S2. HAADF images for Pd3Ag10/ACA-G (Left) and Pd3Ag10/ACA-C (Right).

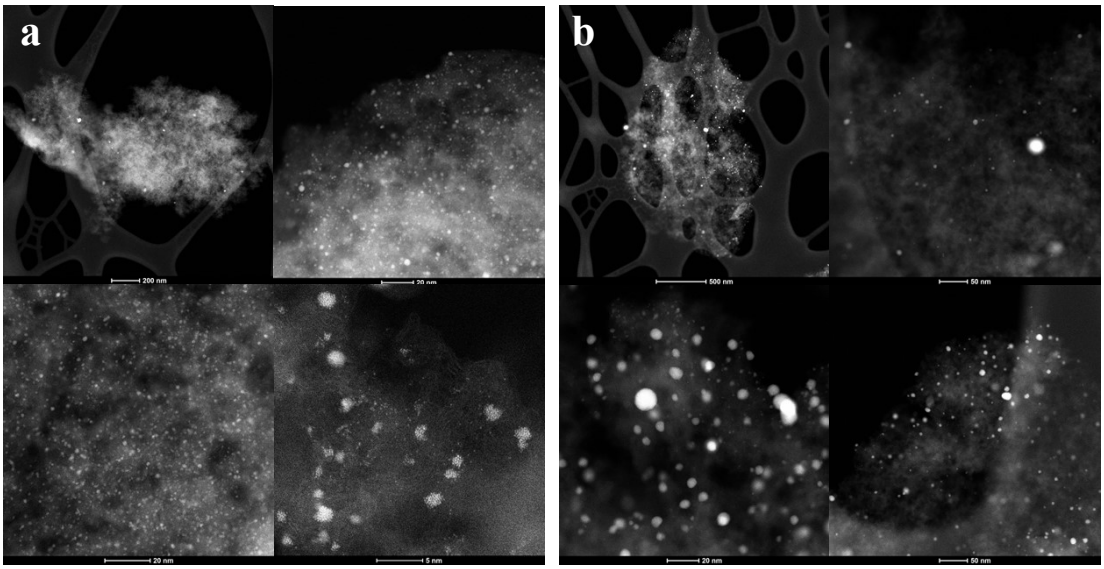

Figure S3. HAADF-STEM images of Pd5/ACA(a) and Ag3/ACA(b).

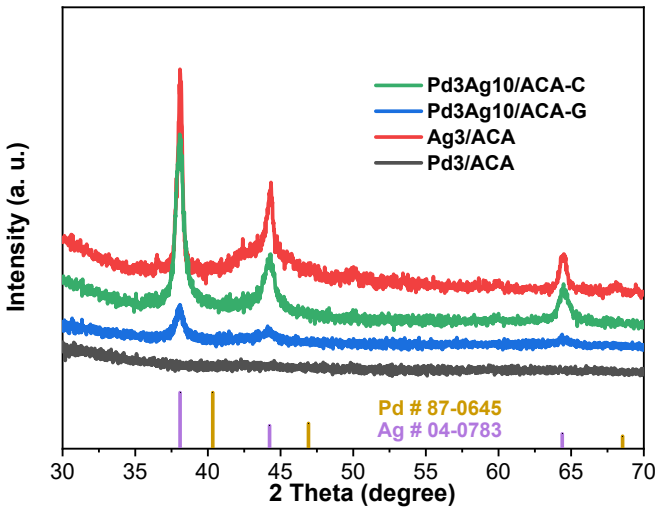

Figure S4. XRD spectra of Pd3/ACA, Ag3/ACA, Pd3Ag10/ACA-G, and Pd3Ag10/ACA-C catalyst.

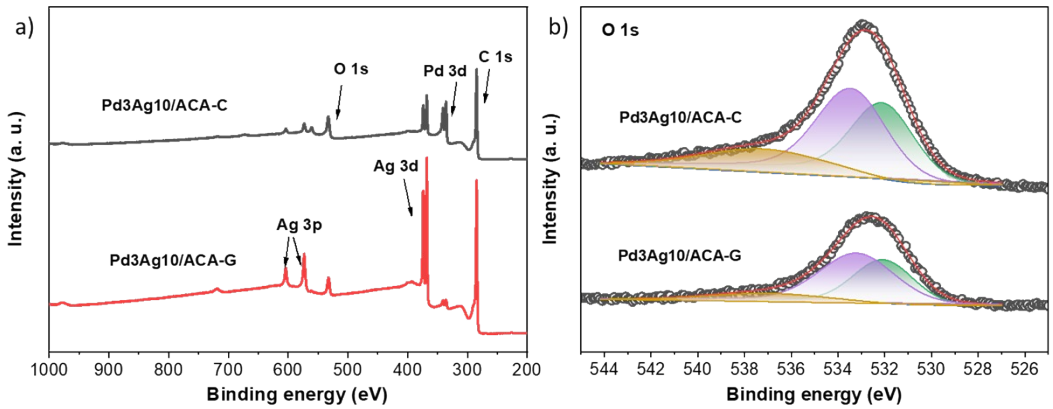

Figure S5. XPS spectra of Pd3Ag10/ACA-G and Pd3Ag10/ACA-C. A) Scan survey. B) O 1s.

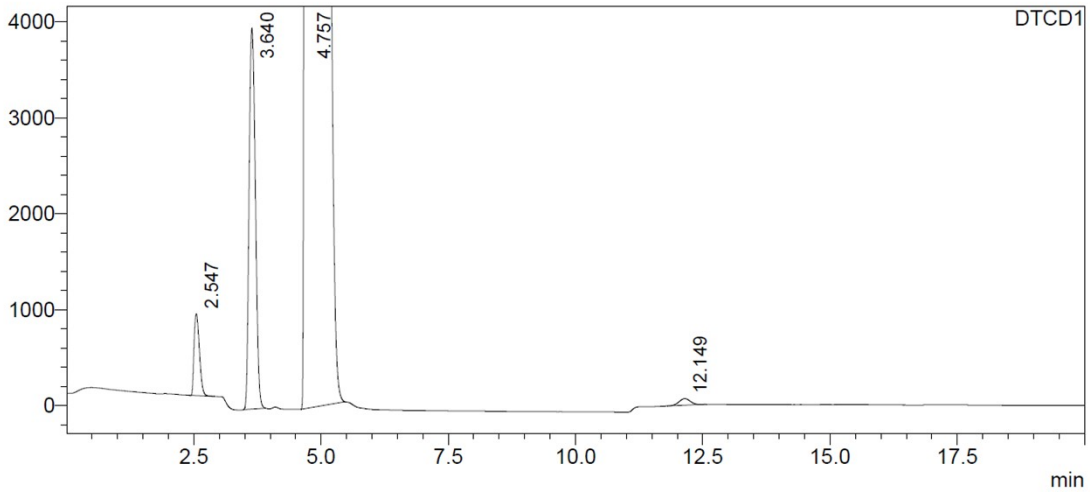

Figure S6. GC spectra of gas phase product after dehydrogenation of ammonium formate.

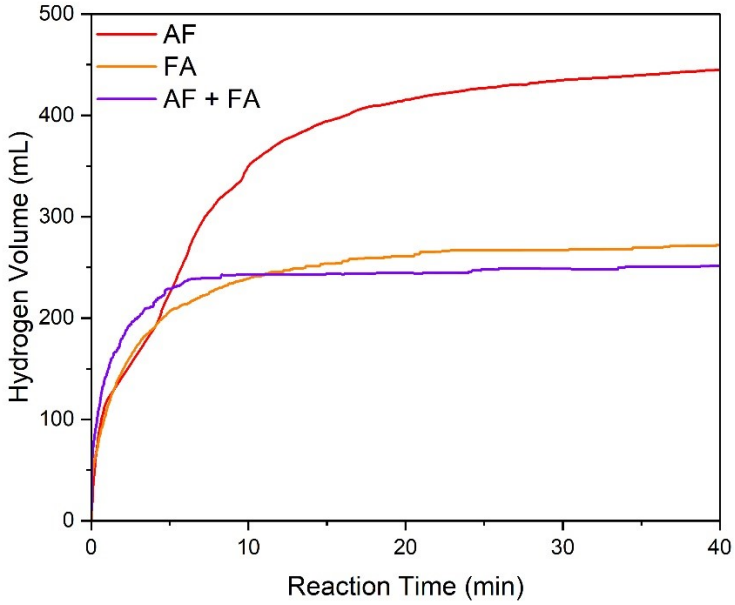

Figure S7. Dehydrogenation of ammonium formate (AF), formic acid (FA), and their mixtures (AF + FA, 50:50) over Pd3Ag10/ACA catalyst. Reaction Conditions: reactants (1M, 20 mL), Catalyst loading (50 mg), Reaction temperature (80 °C), and Stirring speed (500 rpm).

Table S1. Gas product component tested by GC-TCD.

Ret. Time	Area	Height	Gas	Calibration peak area (1 v%)	Concentration (%)
2.548	6284	854	H_2	451	99.6
3.640	34069	3970	O_2	-	-
4.757	1280681	69908	N_2	-	-
12.149	1092	69	CO_2	17645	0.4

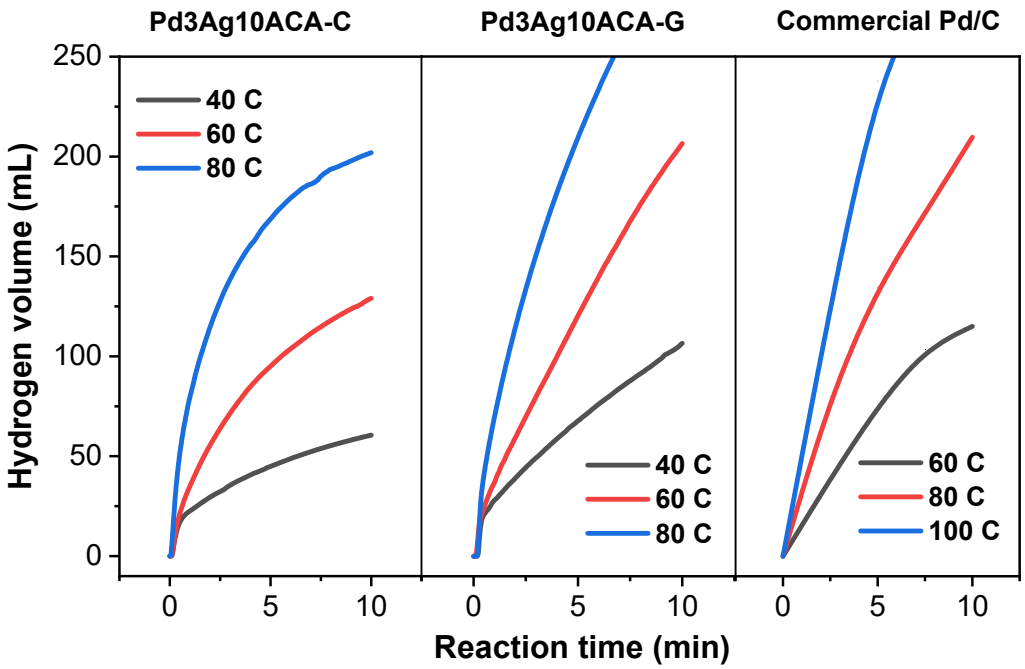

Figure S8. Comparison of the dehydrogenation activity of the commercial Pd/C, Pd3Ag10/ACA-C, and Pd3Ag10/ACA-G at different reaction temperatures.

Table S2. Calculated TOFs of Pd3Ag10/ACA-G at different temperatures

Temperature (°C)	TOF (h^{-1})
40	1799
60	3487
80	5202

Table S3. Calculated TOFs of Pd3Ag10/ACA-G during stability test.

Runs	TOF (h^{-1})
1	5202
2	4864
3	4340
4	3884
5	3242

Table S4. Pd dispersion in the catalysts of fresh Pd3Ag10/ACA-G, spent Pd3Ag10/ACA-G after 1st run, and spent Pd3Ag10/ACA-G after 3rd run and Pd and Ag loading (wt%) tested by ICP-MS.

Catalysts	Pd dispersion (%)	Pd loading (%)	Ag loading (%)
Fresh Pd3Ag10/ACA-G	21.4	3.01	9.83
After 1st run	19.2	-	-
After 3rd run	17.9	3.00	9.92

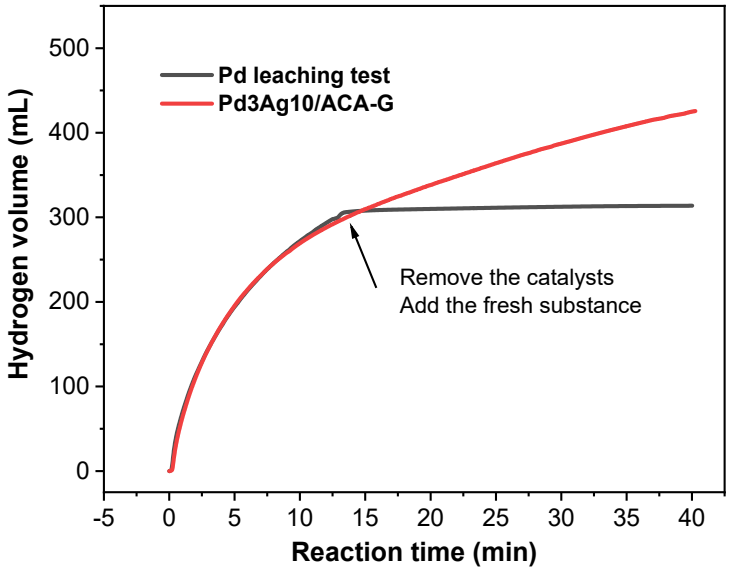

Figure S9. Hot filtration curves of formate dehydrogenation over Pd3Ag10/ACA-G. Reaction conditions: 20 mmol ammonium formate, 80 °C, 350 rpm, and 1 atm N2.

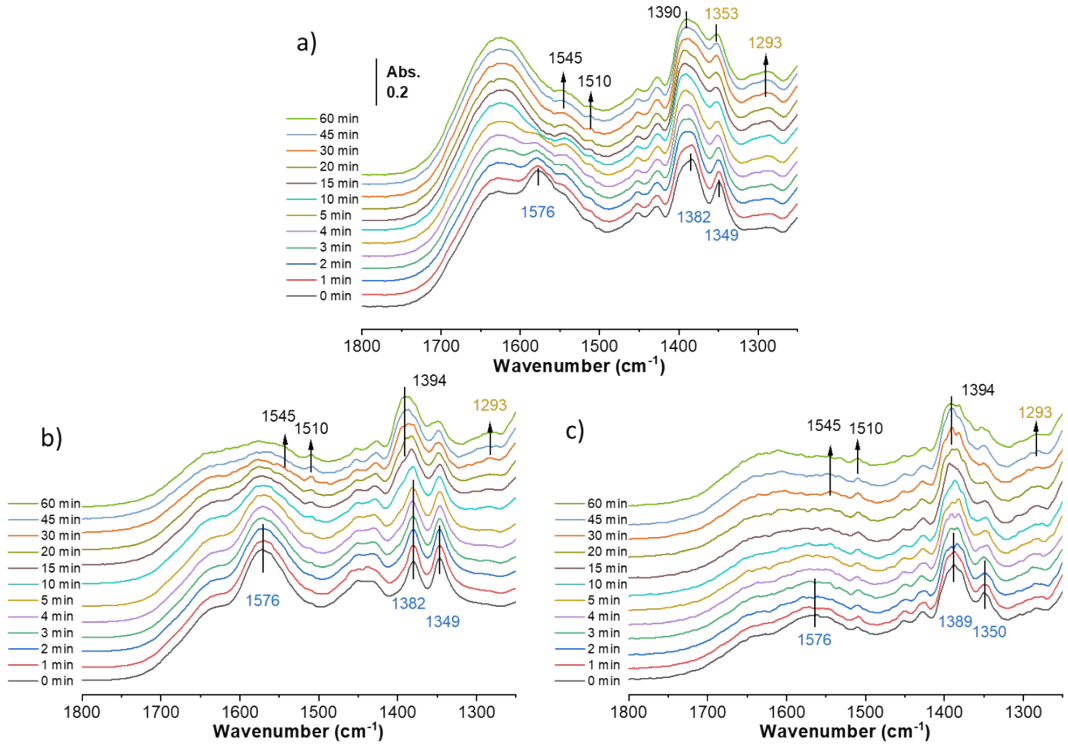

Figure S10. Selected in-situ ATR-IR spectra over Pd3Ag10/ACA-G at different temperatures A): 25 °C, B) 60 °C, and C) 80 °C, as a function of time recorded after rinsing a 2 M ammonium formate solution to the spectral cell. The reference spectrum was recorded in the air before the rinse.

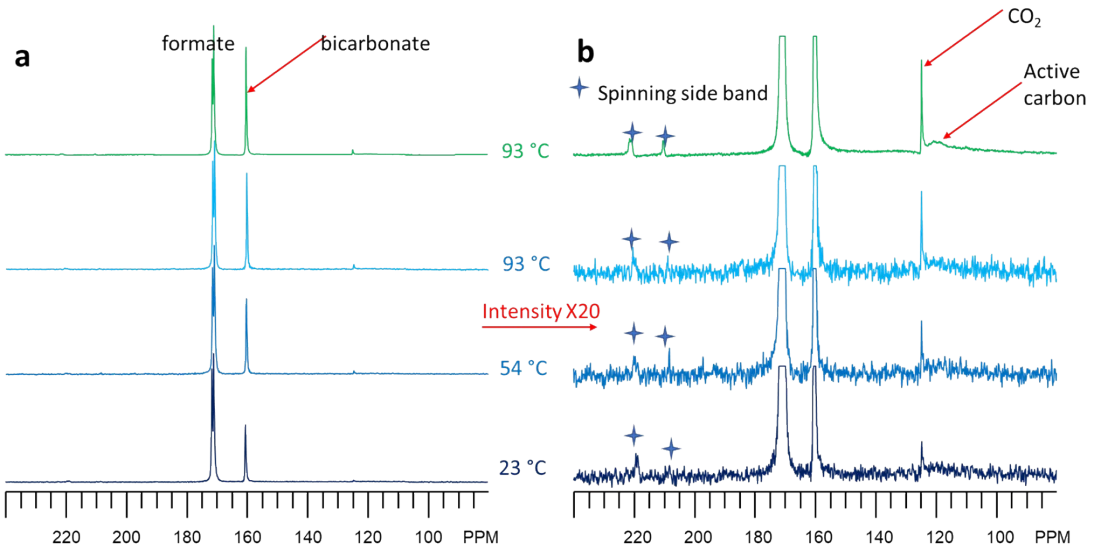

Figure S11. Operando ^{13}C single pules NMR spectra of formate to bicarbonate reaction over Pd/Ag/AC catalyst (a) full spectra at various reaction temperatures; (b) intensity vertically expanded by 20 times.

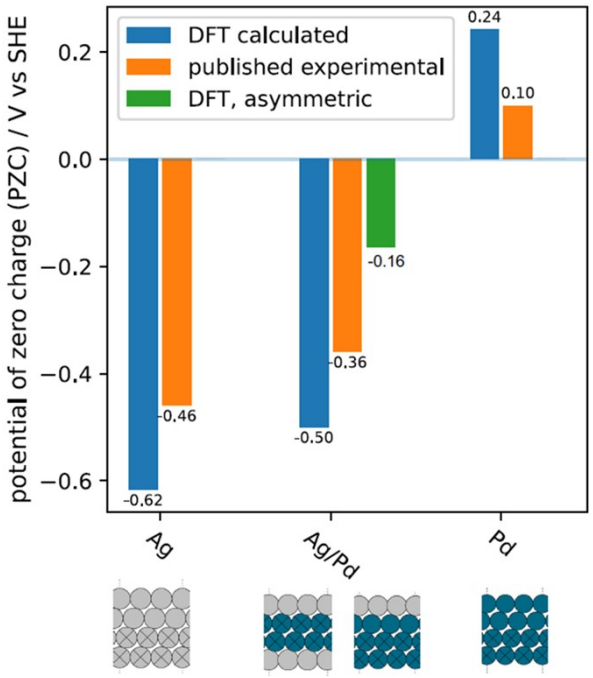

Figure S12. PZC of Pd, Ag, and Pd-Ag bimetallic surface calculated with DFT and comparison with publications.