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Nanoporous Pd Alloys with Compositionally Tunable Hydrogen Storage Properties Prepared by Nanoparticle Consolidation

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Supplemental Information

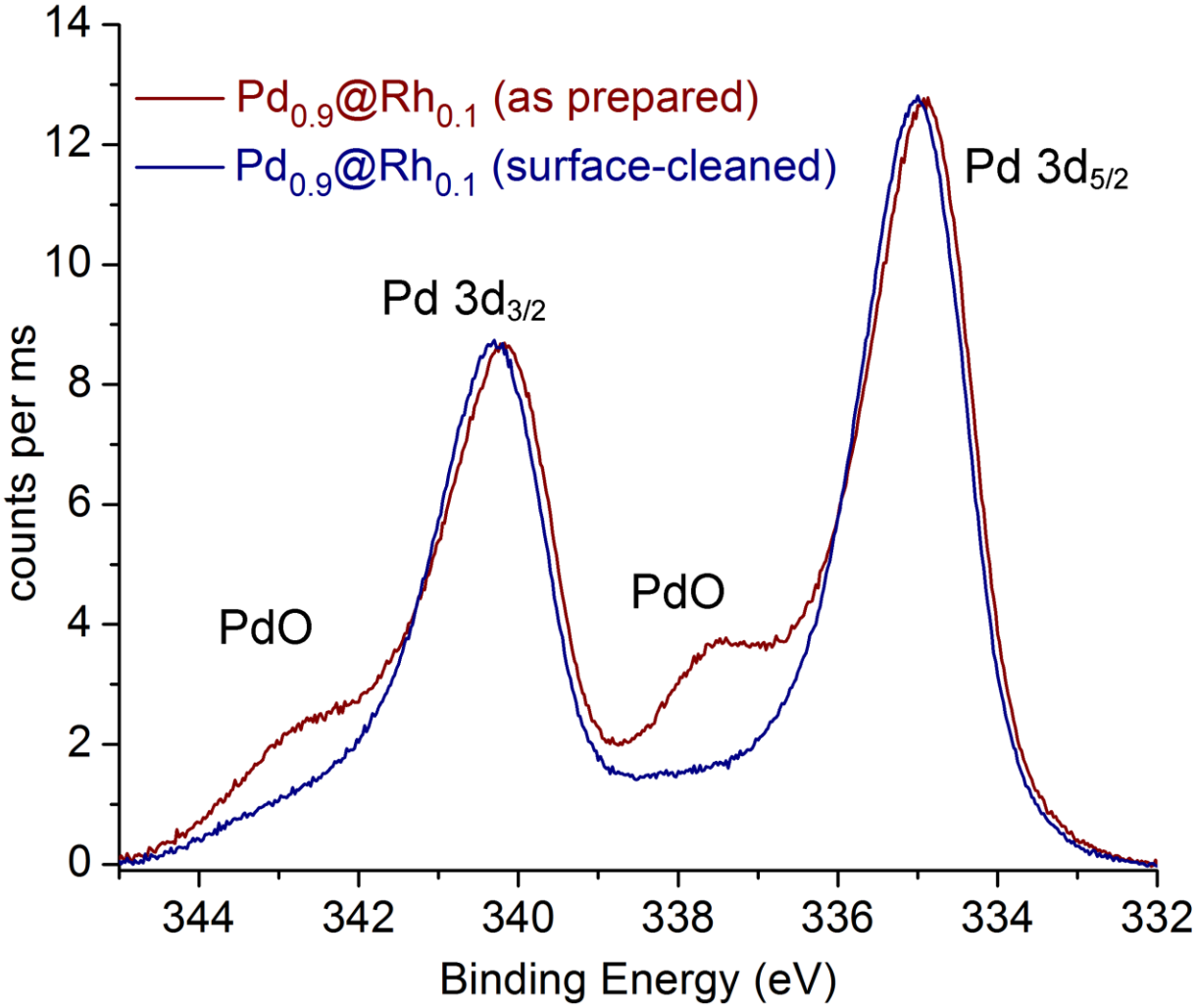

Figure S1. XPS spectra of nanoporous $Pd_{0.9}Rh_{0.1}$ before after exposure to 1 Torr H_2 gas at room temperature to remove surface PdO.

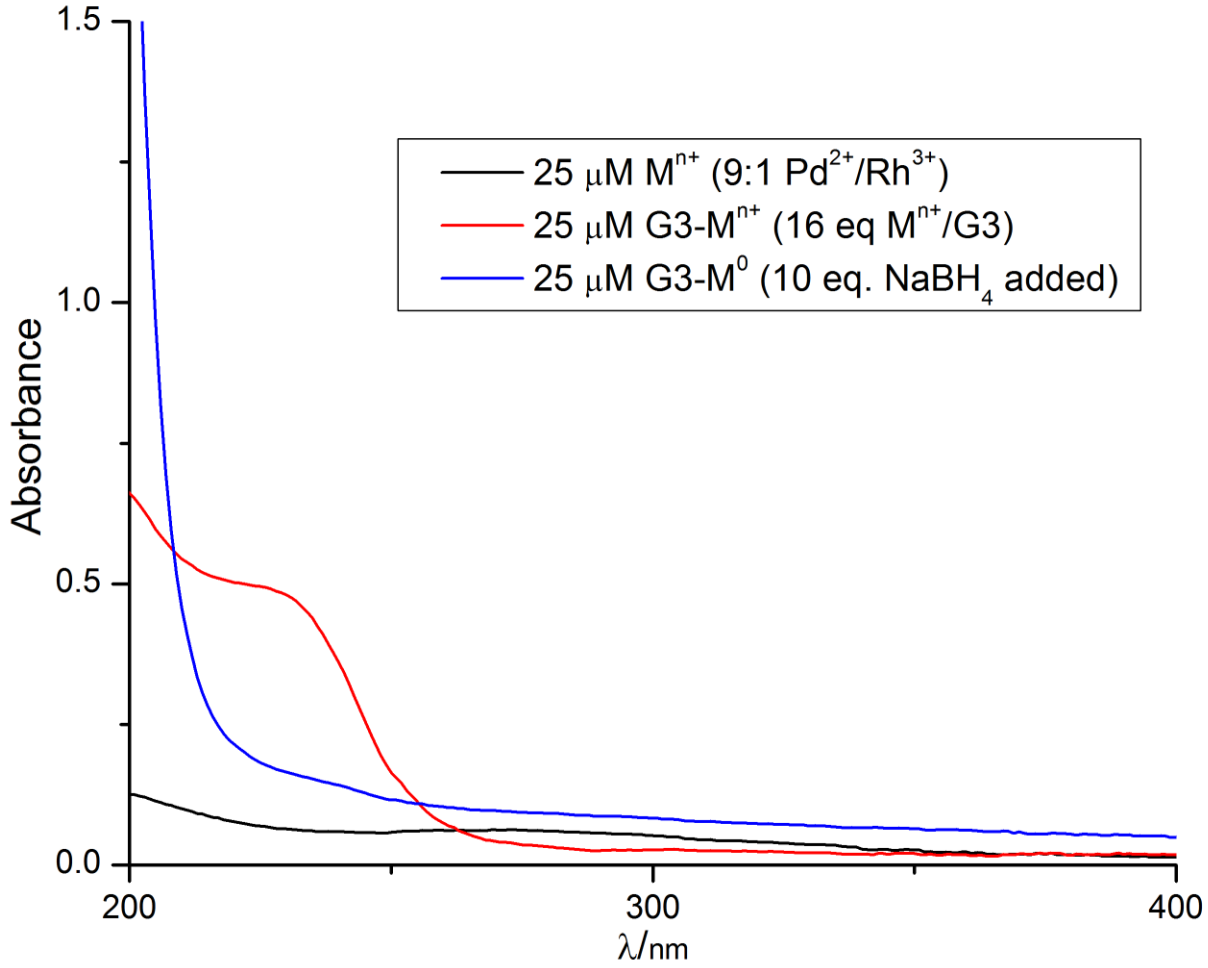

Figure S2. UV/vis traces of a 9:1 mixture of K_2PdCl_4 and $RhCl_3$ (black), this metal salt ratio added to 1.6 μm G3-PAMAM dendrimer (red), and the metal salt/dendrimer mixture after reduction by 10 equivalents of $NaBH_4$ (blue)

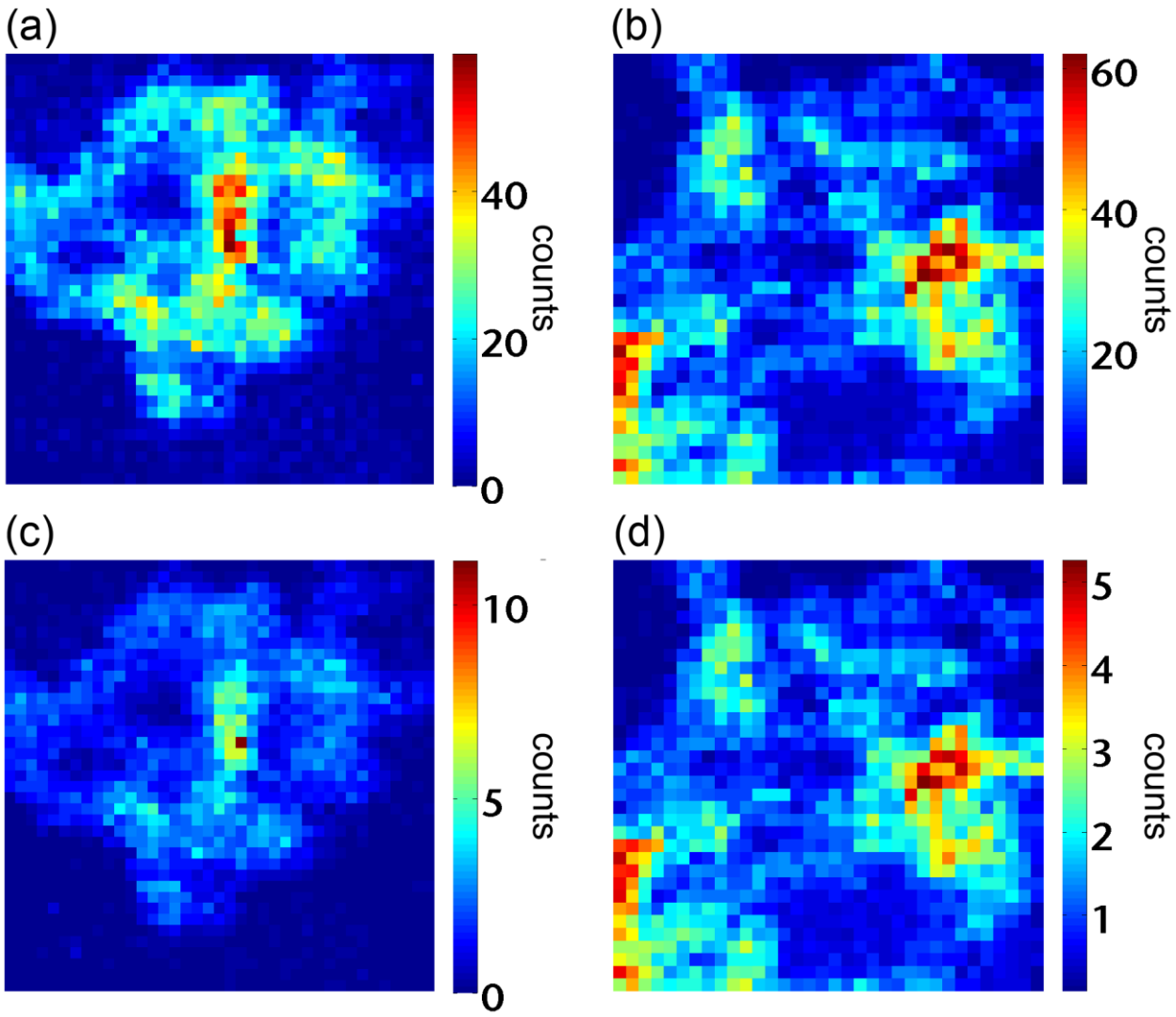

Figure S3. Total STEM-EDS counts for Pd ((a) and (b)) and Rh ((c) and (d)) for $Pd_{0.9}Rh_{0.1}$ and $Pd_{0.9}@Rh_{0.1}$, respectively, corresponding to STEM images and spectral images in Figure 4. Summed Rh counts were 1.64×10^3 and 1.49×10^3 for $Pd_{0.9}Rh_{0.1}$ and $Pd_{0.9}@Rh_{0.1}$, respectively. Summed Pd counts were 1.55×10^4 and 1.66×10^4 for $Pd_{0.9}Rh_{0.1}$ and $Pd_{0.9}@Rh_{0.1}$, respectively.

Table S1. Rh fraction obtained from elemental analysis of $Pd_{0.9}Rh_{0.1}$ (alloy) and $Pd_{0.9}@Rh_{0.1}$ (core/shell) using several techniques

	$Pd_{0.9}Rh_{0.1}$ atom % Rh (±)	$Pd_{0.9}@Rh_{0.1}$ atom % Rh (±)
SEM-EDS	9.5 (0.5)	9.9 (0.5)
TEM-EDS (Large)*	9.2 (0.2)	7.6 (0.3)
TEM-EDS (Small 1)*	9.3 (0.4)	10.9 (0.3)
TEM-EDS (Small 2)*	9.5 (0.2)	7.4 (0.2)
TEM-EDS (Small 3)*	9.1 (0.2)	5.9 (0.2)
TEM-EDS (Small 4)*	9.2 (0.3)	6.2 (0.3)
TEM-EDS (Small 5)*	9.5 (0.2)	5.1 (0.2)
TEM-EDS (Small 6)*	9.4 (0.2)	10.5 (0.2)
Reactant	10.0	10.0

*Quantitated using standardless quantification available in the Oxford EDS system, using Pd and Rh K lines

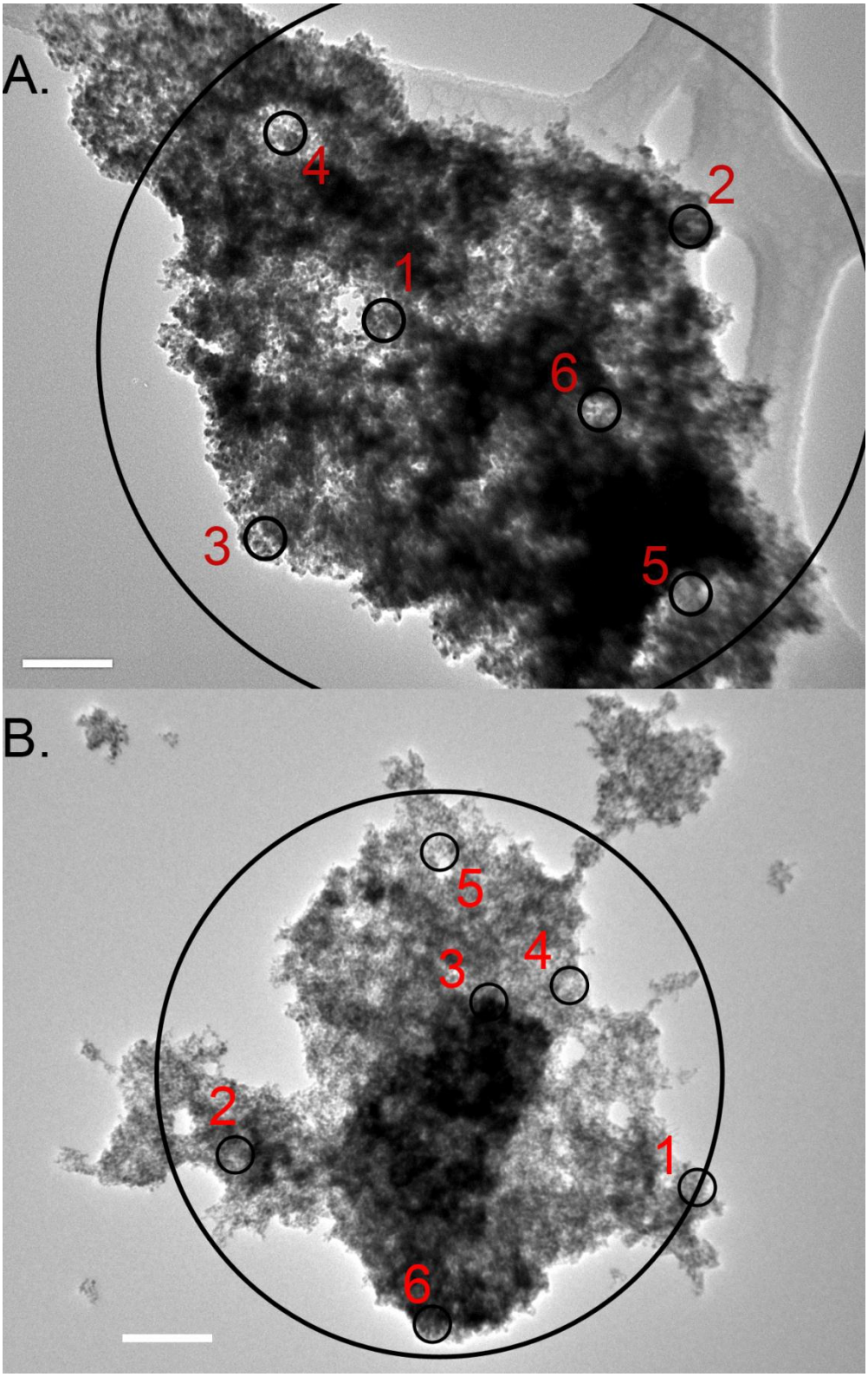

Figure S4. TEM-EDS for $Pd_{0.9}Rh_{0.1}$ (A) and $Pd_{0.9}@Rh_{0.1}$ (B) corresponding to the values in Table S1. Scale bars are calibrated to 100 nm.

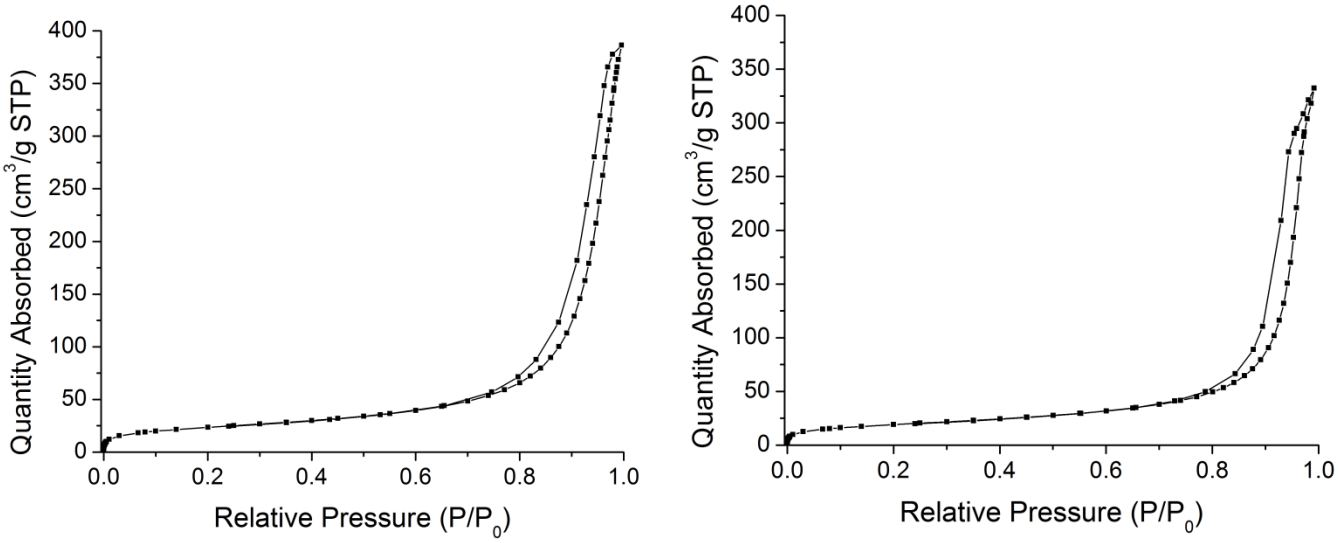

Figure S5. Nitrogen absorption isotherms (77 K) for $Pd_{0.9}Rh_{0.1}$ (left) and $Pd_{0.9}(Rh_{0.1})$

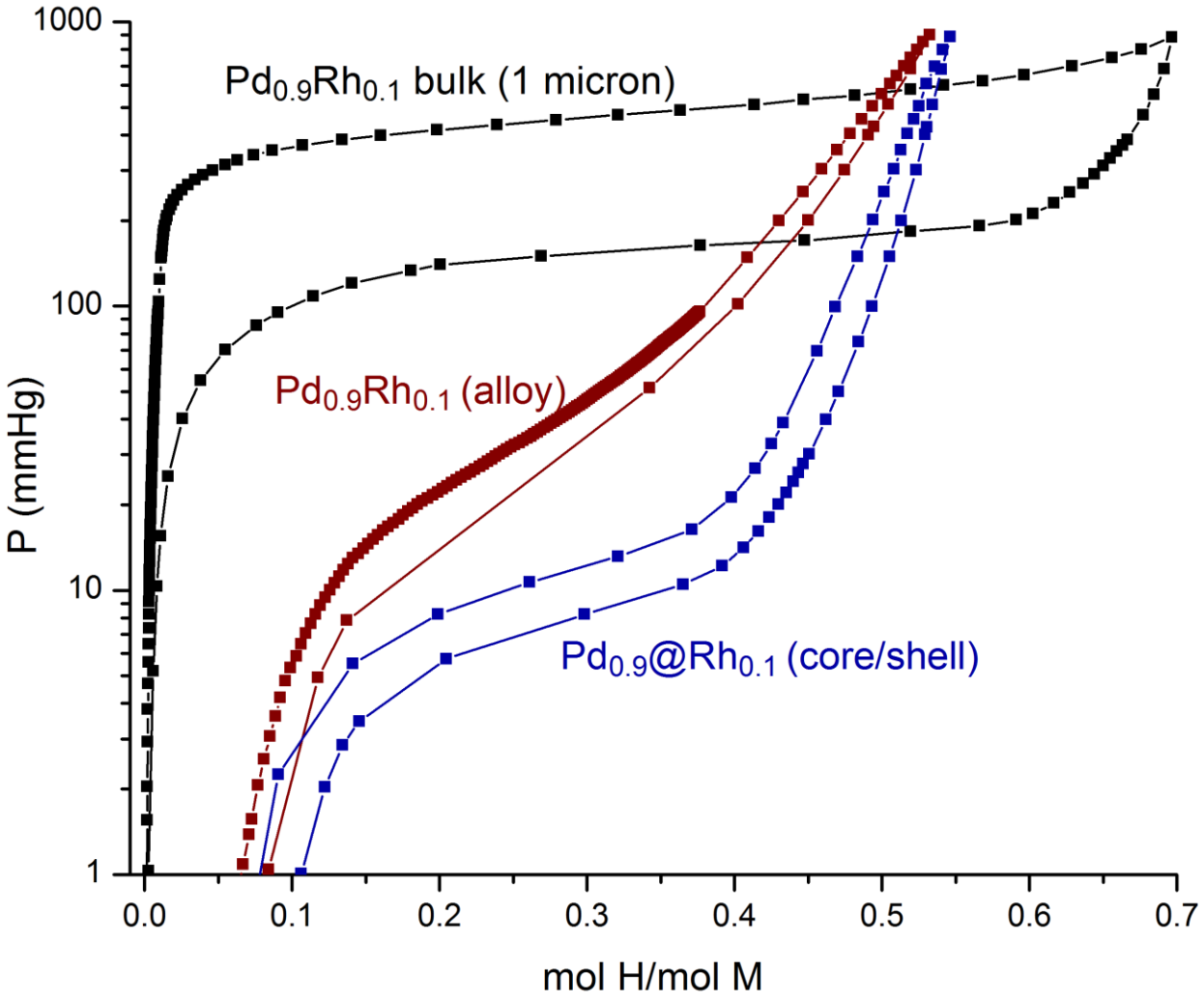

Figure S6. Full hydrogen storage isotherms (298K) of $Pd_{0.9}Rh_{0.1}$ (alloy) and $Pd_{0.9}@Rh_{0.1}$ (core/shell) along with bulk $Pd_{0.9}Rh_{0.1}$ alloy for comparison.

Table S2. Parameters used for Rietveld refinement of $Pd_{0.9}Rh_{0.1}$ (alloy) and crystallite size determination

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
40.050640	12607(66)	1.870181	2.24947	100.00
46.592790	4450(20)	1.913021	1.94772	35.30
68.045620	2334(10)	2.119664	1.37671	18.51
82.021390	2626(14)	2.327940	1.17388	20.83
86.535150	904(16)	2.412352	1.12386	7.17
104.660400	335(13)	2.874154	0.97316	2.66
119.229000	1191(16)	3.472460	0.89295	9.45
124.521900	1113(17)	3.773746	0.87032	8.83

Table S3. Parameters used for Rietveld refinement of $Pd_{0.9}@Rh_{0.1}$ (core/shell) and crystallite size determination

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
39.829780	18605.840000	1.973507	2.26144	100.00
46.336970	6648.706000	2.018240	1.95787	35.73
67.660650	3640.415000	2.233531	1.38360	19.57
81.533850	3613.431000	2.449668	1.17966	19.42
86.009870	1207.373000	2.537004	1.12937	6.49
103.949300	435.284700	3.011856	0.97786	2.34
118.303900	1655.830000	3.618707	0.89723	8.90
123.495100	1415.281000	3.920254	0.87447	7.61

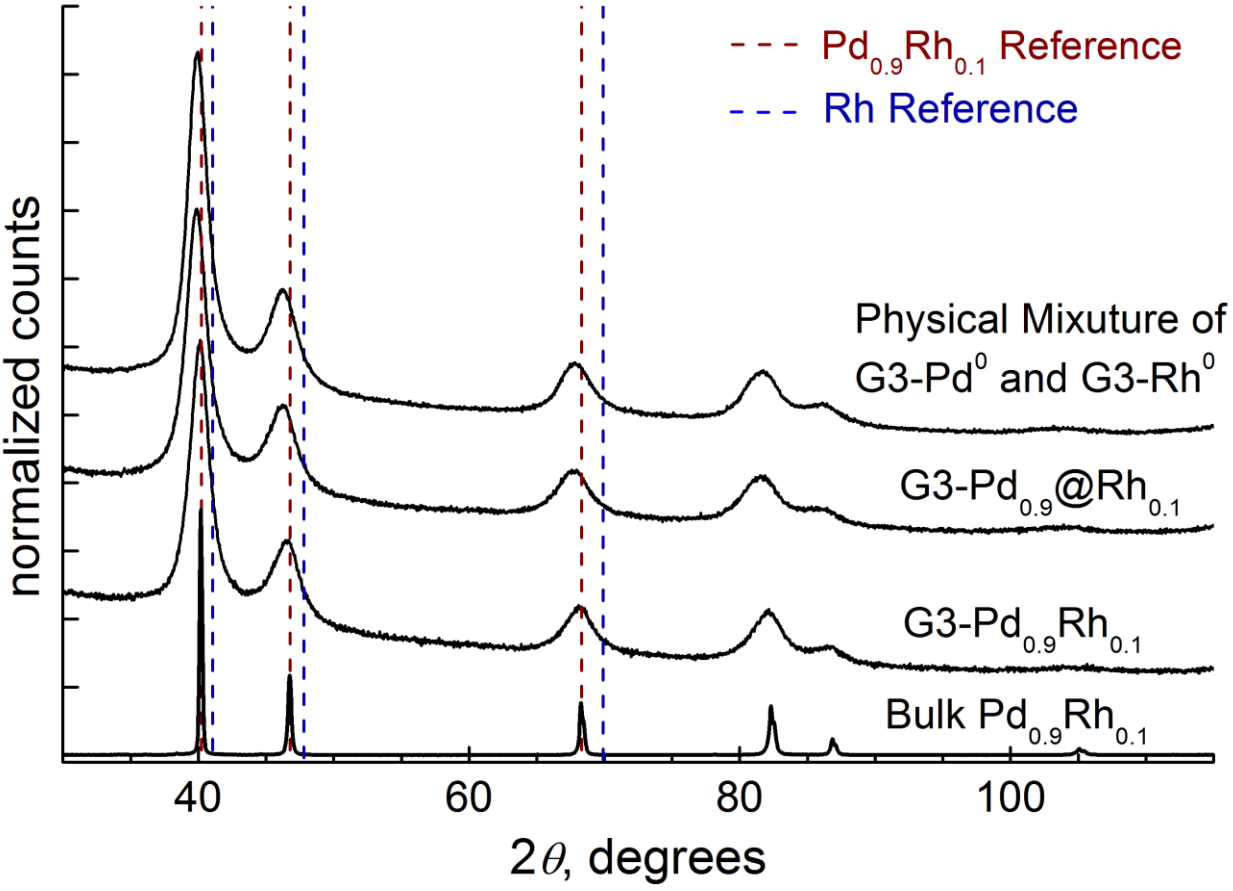

Figure S7 Powder XRD patterns for nanoporous alloy (Pd0.9Rh0.1), core/shell (Pd0.9@Rh0.1), and bulk Pd0.9Rh0.1 Pd/Rh materials. Reference positions for the [111], [002] and [022] planes are shown from left to right, respectively. Top plot is a physical mixture of pure Pd and pure Rh in 9:1 ratio.

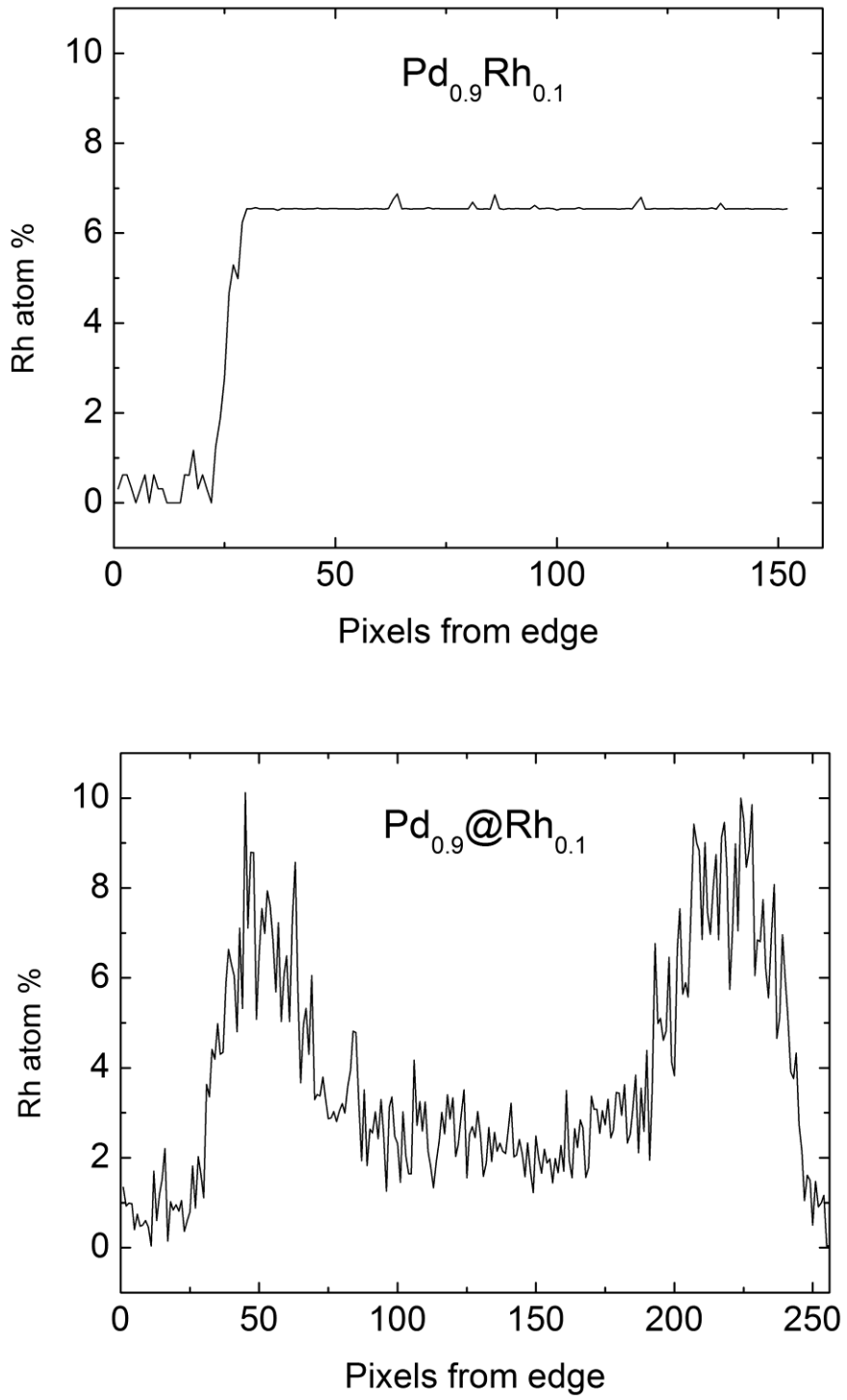

Figure S8. Quantitative line scans showing the variation of atom % Rh across the particles in Figure 5 for and $Pd_{0.9}Rh_{0.1}$ (alloy, top) and $Pd_{0.9}@Rh_{0.1}$ (core/shell, bottom).

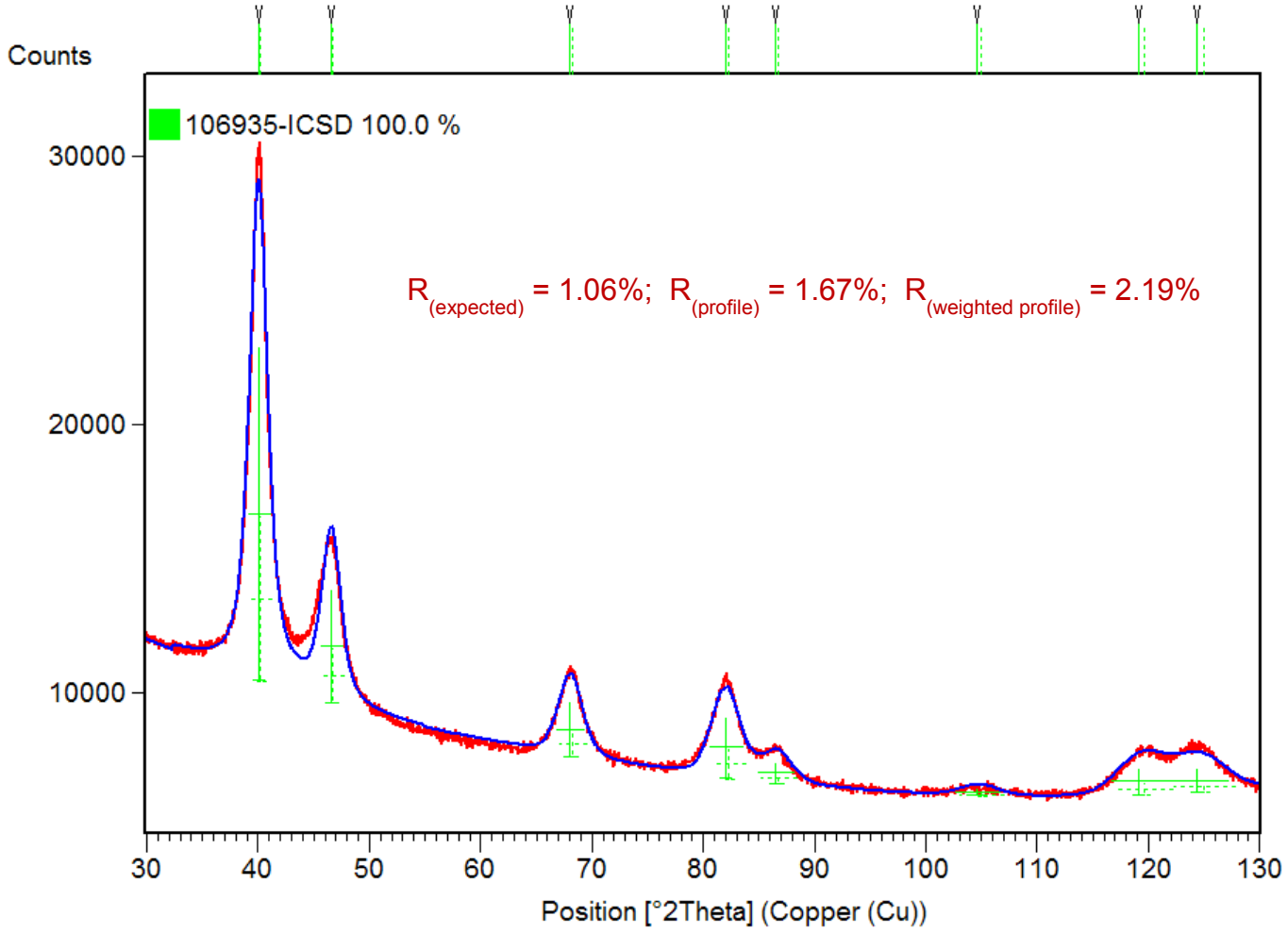

Figure S9. Reitveld refinement of the $Pd_{0.9}Rh_{0.1}$ XRD pattern used to determine crystallite size.

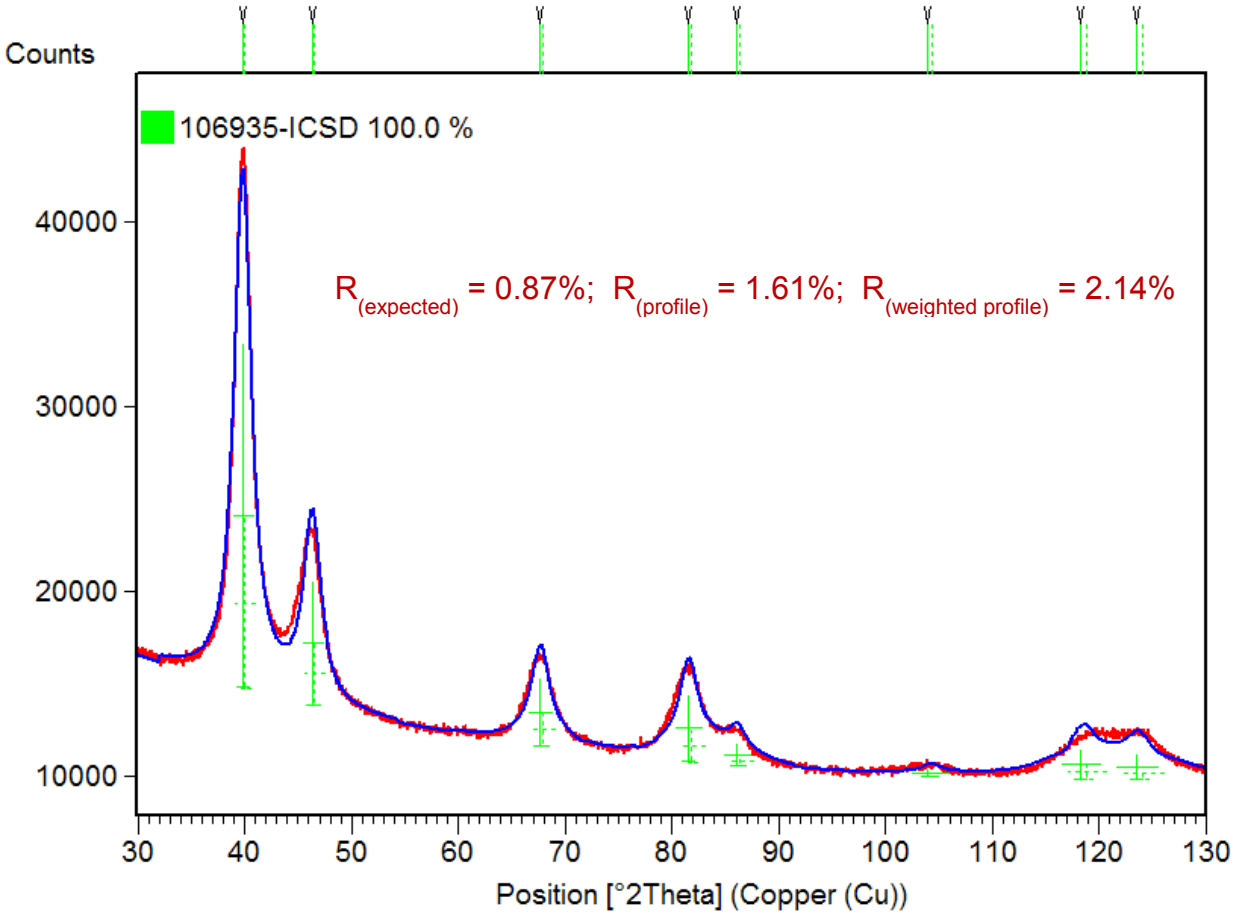

Figure S10. Reitveld refinement of the $Pd_{0.9}@Rh_{0.1}$ XRD pattern used to determine crystallite size.