

Probing Compositional Variation within Hybrid Nanostructures

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Supporting Information

Metal nanoparticle control samples

Control samples were prepared in the absence of CdS nanorods to gain a better understanding of how the nanorod substrate influences the binary metal nanoparticle structure. The nanoparticles in Figure S1 were synthesized according to the method described previously,²⁴ although without the addition of CdS nanorods.

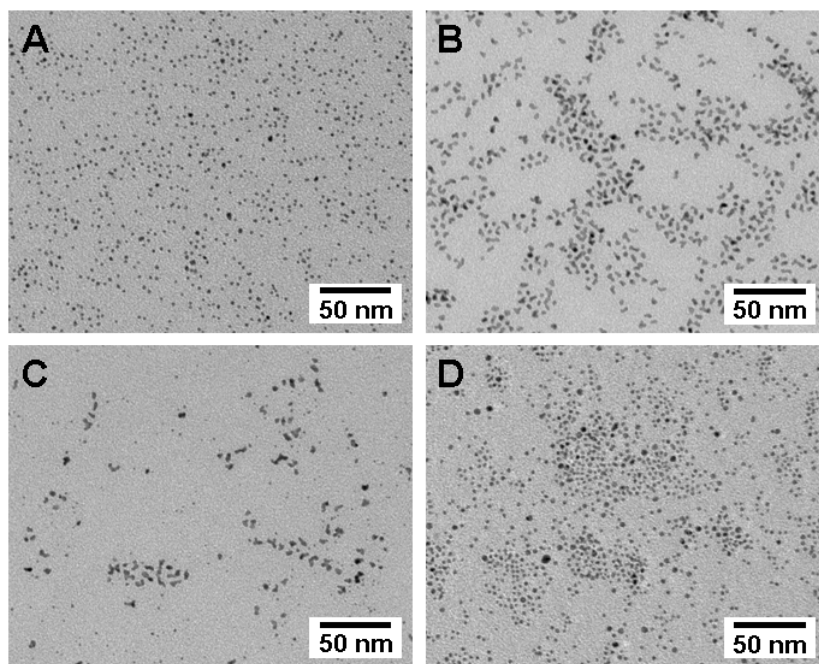


Figure S1. Control samples prepared by (A) the co-reduction of $\text{Co}(\text{OAc})_2$ with $\text{Pt}(\text{acac})_2$ in the absence of CdS nanorods, (B) reduction of $\text{Pt}(\text{acac})_2$ to give pure Pt seeds, (C) co-reduction of $\text{Co}(\text{OAc})_2$ with $\text{Pt}(\text{acac})_2$ in the presence of the pre-formed Pt seeds, and (D) co-reduction of $\text{Ni}(\text{OAc})_2$ with $\text{Pt}(\text{acac})_2$ without CdS rods.

K-space EXAFS spectra

For each sample (PtCo nanoparticles alone, Low Co hybrid, and High Co hybrid), EXAFS spectra were acquired at both the Pt L_3 -edge and the Co K-edge. The EXAFS spectra were first calibrated with appropriate elemental standards, then the pre-edge background was subtracted and the post-edge absorption was normalized. The k^2 -weighted spectra were extracted and then Fourier-transformed with a Kaiser-Bessel window to real (R) space. For the Pt L_3 -edge spectra, the fitting k -range was $2.8\text{-}11.2 \text{ \AA}^{-1}$, and the R-range was $1.8\text{-}4.6 \text{ \AA}$. For the Co K-edge spectra, the fitting ranges depended on the sample being analyzed. For the PtCo NPs alone, the k -range was $2.4\text{-}10.2 \text{ \AA}^{-1}$, and the R-range was $1.8\text{-}4.0 \text{ \AA}$. For each hybrid structure, the k -range was $2.2\text{-}8.4 \text{ \AA}^{-1}$, and the R-range was $1.2\text{-}4.0 \text{ \AA}$. The k -space spectra are shown in Figure S2.

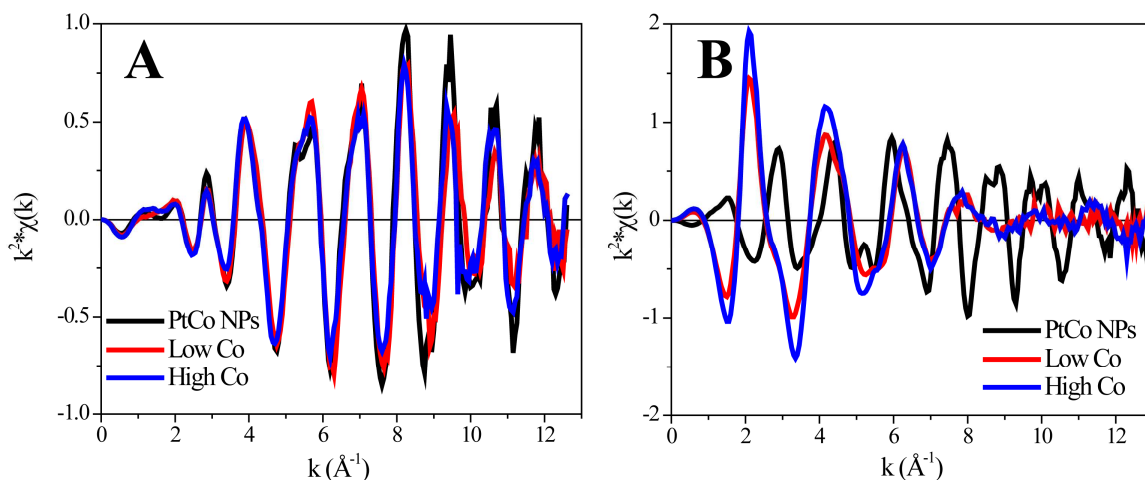


Figure S2. K-space EXAFS spectra of both hybrid samples and the free PtCo nanoparticles at the (A) Pt L_3 -edge and (B) Co K-edge. There is significant damping in the Co K-edge EXAFS of the hybrid samples that is not present in any other spectrum which implies a higher degree of disordered cobalt in the system.

Model Lattices

For the EXAFS fitting, a variety of model lattices were constructed to simulate theoretical EXAFS spectra for comparison to the experimental data. For the Pt L_3 -edge spectra, two different model lattices were compared. Both of them use the face-centered cubic (fcc) dimensions of pure Pt metal ($a = 3.92 \text{ \AA}$). The first model is simply the pure Pt lattice. This model lattice is called “All Pt”. The second model replaces a certain percentage of the Pt atoms with Co atoms, with the percentage reflecting the atomic ratios determined by EDX spectroscopy. This model lattice is called “Alloy”. The example lattices are shown pictorially in Figure S3, and the results of fitting with each model for the Pt EXAFS spectra can be seen in Table S1.

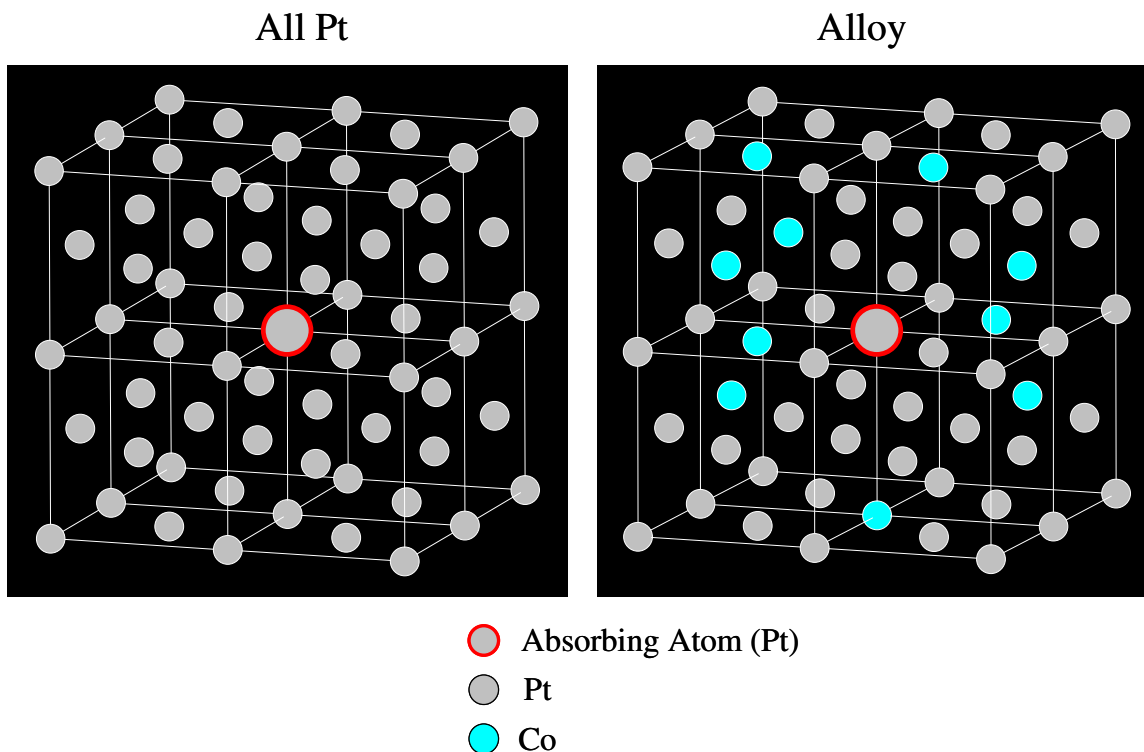


Figure S3. Cartoon representation of each model lattice used for fitting of the Pt L₃-edge EXAFS spectra. The Alloy model has Co atoms substituted for Pt atoms at a level commensurate with EDX elemental analysis data (the Low Co Pt:Co ratio is shown above, with Pt:Co = 3:1). Each coordination shell contains the proportionate number of Co atoms (e.g., the first shell, with 12 nearest neighbors, has 9 Pt atoms and 3 Co atoms). The placement of the Co atoms within a shell was random, and there was no statistically significant change in fitting parameters when Co atoms were moved within a shell.

Sample	Alloy			All Pt		
	PtCo NPs	Low Co Hybrid	High Co Hybrid	PtCo NPs	Low Co Hybrid	High Co Hybrid
<i>R</i> -factor	0.0049	0.0198	0.0089	0.0327	0.0613	0.0342
NN (Å)	2.751±0.002 (Pt) 2.660±0.089 (Co)	2.731±0.018 (Pt) 2.622±0.127 (Co)	2.739±0.010 (Pt) 2.633±0.116 (Co)	2.737±0.007	2.724±0.048	2.740±0.031
σ^2 (10 ⁻³ Å ²)	5.48±0.86 (Pt) 4.62±2.18 (Co)	8.34±1.29 (Pt) 5.63±2.62 (Co)	6.96±1.09 (Pt) 11.60±7.37 (Co)	6.11±1.05	9.18±1.55	7.94±1.10

Table S1. Comparison of fitting results for all Pt EXAFS spectra between the “Alloy” and “All Pt” model lattices. The *R*-factor is the fractional misfit, NN represents the nearest-neighbor distance, and σ^2 is the mean-square displacement of the scattering atoms. For all samples, fitting with the “All Pt” model lattice results in worse *R*-factors, greater σ^2 values, and larger overall uncertainties in each variable.

For the Co K-edge, the hybrid samples used two model lattices. In addition to the “Alloy” model described above, the model lattice CoO (rock salt structure, space group = $Fm3m$) was also considered (The free-standing PtCo nanoparticles only required the use of the “Alloy” model). Successful fitting of the hybrid samples required both model lattices to be used simultaneously, i.e., two different Co environments had to be considered. Using only one of the two model lattices alone gave no convergence of the theoretical EXAFS with the experimental data, as shown in Table S2.

Sample	Alloy + CoO		CoO Only	
	Low Co Hybrid	High Co Hybrid	Low Co Hybrid	High Co Hybrid
R-factor	0.0112	0.0066	0.1092	0.0767
NN (Å)	2.062 ± 0.063 (O) 2.643 ± 0.106 (Co/Pt) ^a	2.053 ± 0.072 (O) 2.653 ± 0.097 (Co/Pt) ^a	1.718 ± 0.407 (O) 2.430 ± 0.575 (Co)	1.692 ± 0.433 (O) 2.393 ± 0.613 (Co)
σ^2 (10^{-3} Å ²)	8.60 ± 5.98 (O) 8.98 ± 7.09 (Co/Pt) ^a	8.15 ± 5.30 (O) 4.22 ± 2.64 (Co/Pt) ^a	78.3 ± 58.2 (O) 58.9 ± 66.3 (Co)	120.7 ± 284.3 (O) 103.7 ± 194.2 (Co)
S_0^2	0.901	0.887	0.692	1.435

(a) Due to fitting constraints from using two models simultaneously, the Co and Pt atoms were fit with the same variable in these cases.

Table S2. Comparison of fitting results of the Co EXAFS spectra for each hybrid sample. The parameters on the left side of the table are obtained by using the combination of the “Alloy” and “CoO” model lattices in fitting, while those parameters on the right result from fitting only with the “CoO” model lattice. The R-factor is the fractional misfit, NN represents the nearest-neighbor distance, σ^2 is the mean-square displacement of the scattering atoms, and S_0^2 is the passive electron-reduction factor, which typically ranges between 0.85-0.95 for good-quality fits. Using only the “CoO” model results in poor fitting, giving higher R-factors and uncertainties in variables, as well as nonsensical meanings for certain parameters (e.g., the extraordinarily higher σ^2 values). Similarly poor fits are obtained if only the “Alloy” model lattice is used instead of only the “CoO” model lattice.

Room Temperature Magnetization Measurements

In addition to the magnetization measurements conducted at low temperature (Figure 5, main section), we also conducted field-dependent measurements at room temperature, as shown in Figure S4.

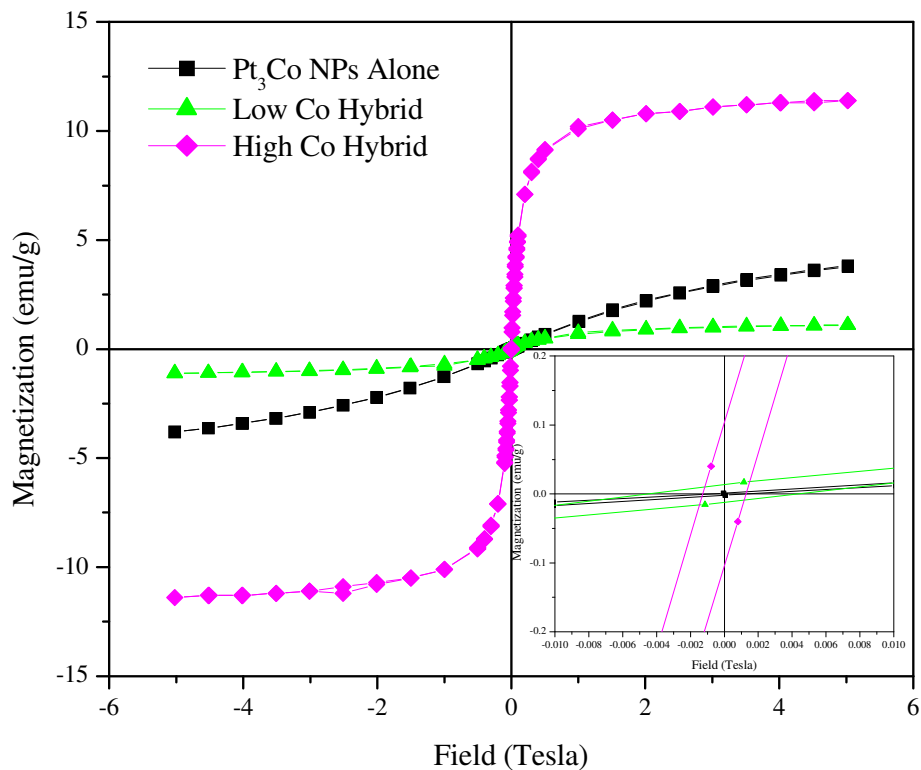


Figure S4. Room-temperature field-dependent magnetization of free-standing PtCo nanoparticles and the low and high Co hybrid samples.

At room temperature, the free-standing PtCo nanoparticles lose all traces of hysteresis, which is consistent with superparamagnetic behavior above the blocking temperature. The hybrid samples, meanwhile, show a trace amount of hysteresis still present at room temperature. In addition, both hybrid samples show a greater degree of saturation at high magnetic field when compared to the low temperature measurement.