Supporting Information

Unexpected Compositional and Structural Modification of $CoPt_3$ Nanoparticles by Extensive Surface Purification

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Coordination numbers analysis: Figure 1S shows the calculated average coordination numbers (N_{PtPt} and N_{PtCo}) for a core/shell NP with Pt metallic core and a $CoPt_3$ alloy shell. Vertical red and blue bars indicate the range of consistence between theoretical and EXAFS results. From these figures it is clear that using the Pt/$CoPt_3$ model, it is impossible to find a region of the core radius to fulfill experimental data on coordination numbers.

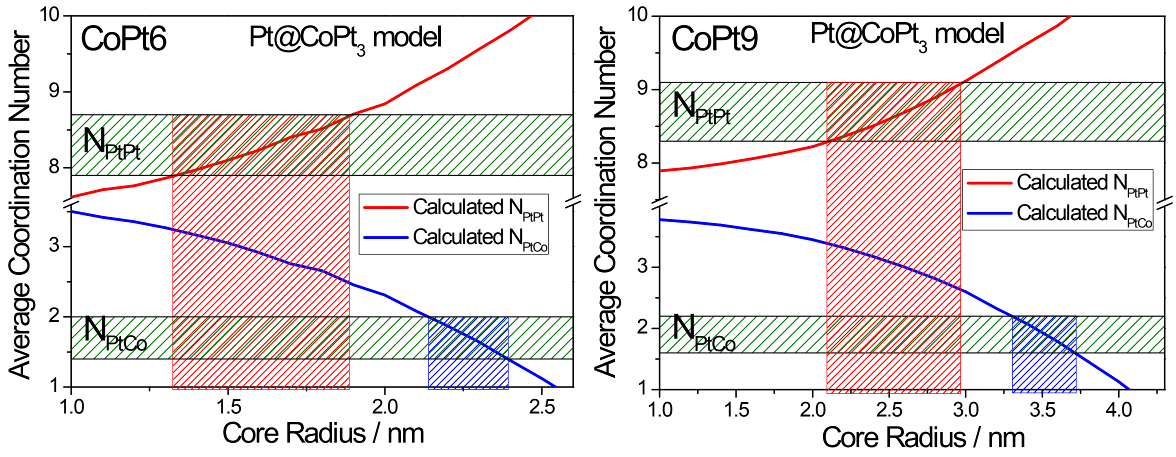

Figure S1. *Pt/$CoPt_3$ core/shell model: calculated average coordination numbers N_{PtPt} (red line) and N_{PtCo} (blue line) as function of Pt core radius for 5.9 nm and 9.3 nm NPs (left and right images, respectively). The green horizontal bars represent the average coordination numbers obtained by the EXAFS fits, and the vertical red and blue bars indicate the region of the core radius for the matching between theoretical and EXAFS values of the N_{PtPt} and N_{PtCo}.*

Figure S2 shows the calculated average coordination numbers (N_{PtPt} and N_{PtCo}) for a random distribution of Pt and Co atoms in a *fcc* structure. For both samples we used the Pt/Co ratios obtained from the fits of the corresponding fluorescence spectra. Vertical black lines indicate the average particle radius obtained by the analysis of TEM images. For these radii the calculated average coordination numbers do not match to the estimates of the EXAFS fits.

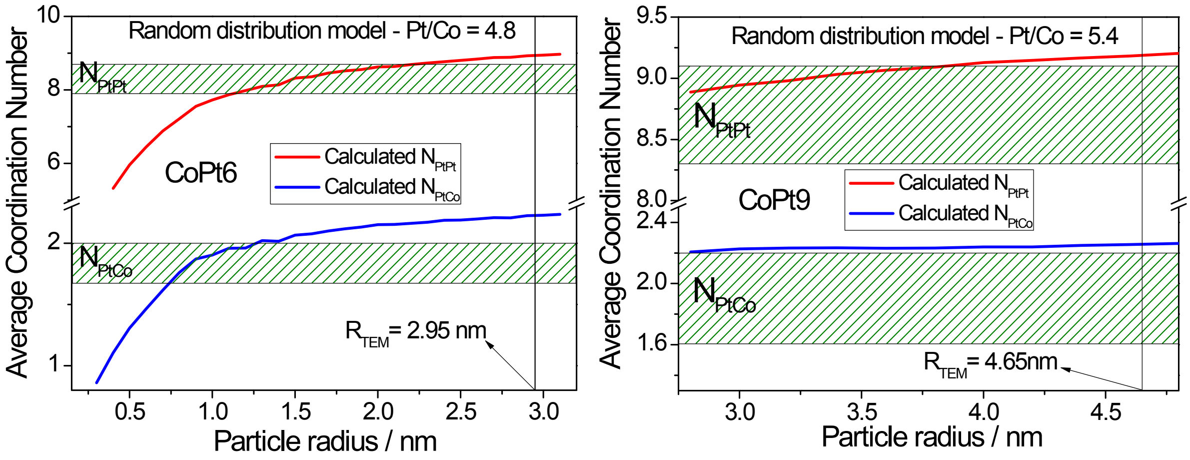

Figure S2. *Calculated average coordination numbers N_{PtPt} (red line) and N_{PtCo} (blue line) as function of core radius for a random distribution of Pt and Co atoms, with the Pt/Co ratio obtained by fluorescence measurements for 5.9 nm and 9.3 nm NPs (left and right images, respectively). The green horizontal bars represent the average coordination numbers obtained by the EXAFS fits, and the vertical black line indicates the particle average radius obtained by TEM.*

Co K-edge XANES analysis: Co K-edge XANES technique is a sensible tool to identify Co species in small crystalline domains.[1] Figure S3 presents the Co K-edge absorption spectra of the 9.3 nm $CoPt_3$ NPs before and after extensive purification, as well as spectra corresponding to metallic Co, CoO, Co_3O_4 and $CoPt_3$ reference samples. The absorption edge at 7709 eV corresponds to the electronic transition from 1s to 3d states, whereas the maximum at the white line at 7725 eV is due to electronic transition from 1s to 4p.[2] The XANES spectra of $CoPt_3$ alloy reference compound and extensively purified $CoPt_3$ NP samples revealed the same characteristic feature at the edge and the two main resonances at 7709 and 7725 eV, and a third one at 7750 eV (in both energy and intensity). On the contrary, the spectrum of as-synthetized $CoPt_3$ sample is noticeably different than that of extensively purified NPs. The Co K-edge EXAFS study on as-synthetized $CoPt_3$ NP indicate the presence of additional coordination shells for Co with Co-Co and Co-O contributions (Figure S3b, Table S1) that is consistent with the presence of oxidized Co atoms at the surface of the as-synthetized NPs.

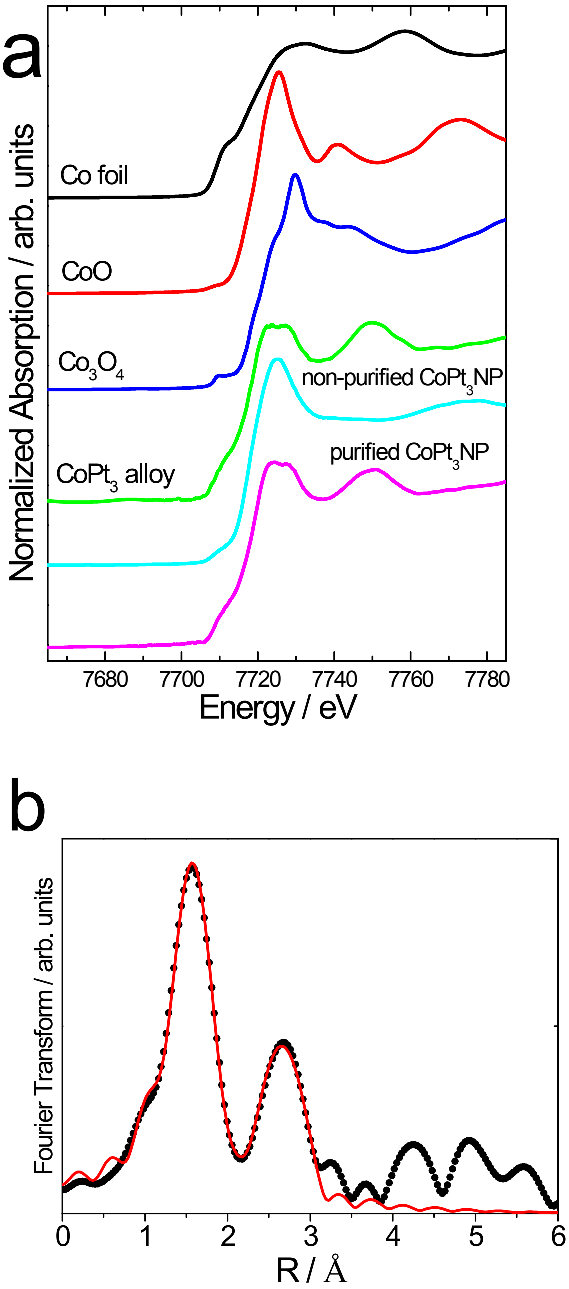

Figure S3. a) Co K-edge XANES spectra 9 nm $CoPt_3$ NP before and after purification, compared with metallic Co foil, CoO, Co_3O_4 and $CoPt_3$ reference compounds. b) Experimental Fourier transform of the EXAFS oscillations at the Co-K edge (dotted line) and the corresponding fits (red line) for non-purified $CoPt_3$ sample (corresponding data and fittings for purified sample are showed in Figure 2 and Table 1 respectively in the manuscript.

Coordination shell	**Non-purified $CoPt_3$ NP sample**	
	Average Coordination number N	**Interatomic distance R (Å)**
Co - O	2.8_4	2.04_1
Co - Co	1.2_4	3.07_3
Co - Pt	3.3_8	2.68_3

Table S1. Structural parameters obtained from the EXAFS fits at the Co-K edge for non-purified CoPt$_3$ NPs. Subscript number represent the error in the last digit.

References:

1 - Wei-Feng Huang, Qian Zhang, Dong-Feng Zhang, Jing Zhou, Cheng Si, Lin Guo, Wang-Sheng Chu, and Zi-Yu Wu. J. Phys. Chem. C 2013, 117, 6872−6879.

2 - Zhang, G.; Wu, Z.; Li, A.; Wang, Y.; Zhang, J.; Abbas, M.; Hu, R.; Ni, X.; Tong, Y.; Hu, Y. Phys. Rev. B 2004, 69, 115405; Lai, F.-J.; Sarma, L. S.; Chou, H.-L.; Liu, D.-G.; Hsieh, C.-A.; Lee, J.-F.; Hwang, B.-J. J. Phys. Chem. C 2009, 113, 12674−12681.

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