Supporting Information

When a Metastable Oxide Stabilizes at Nanoscale: Wurtzite CoO Formation upon Dealloying of PtCo Nanoparticles

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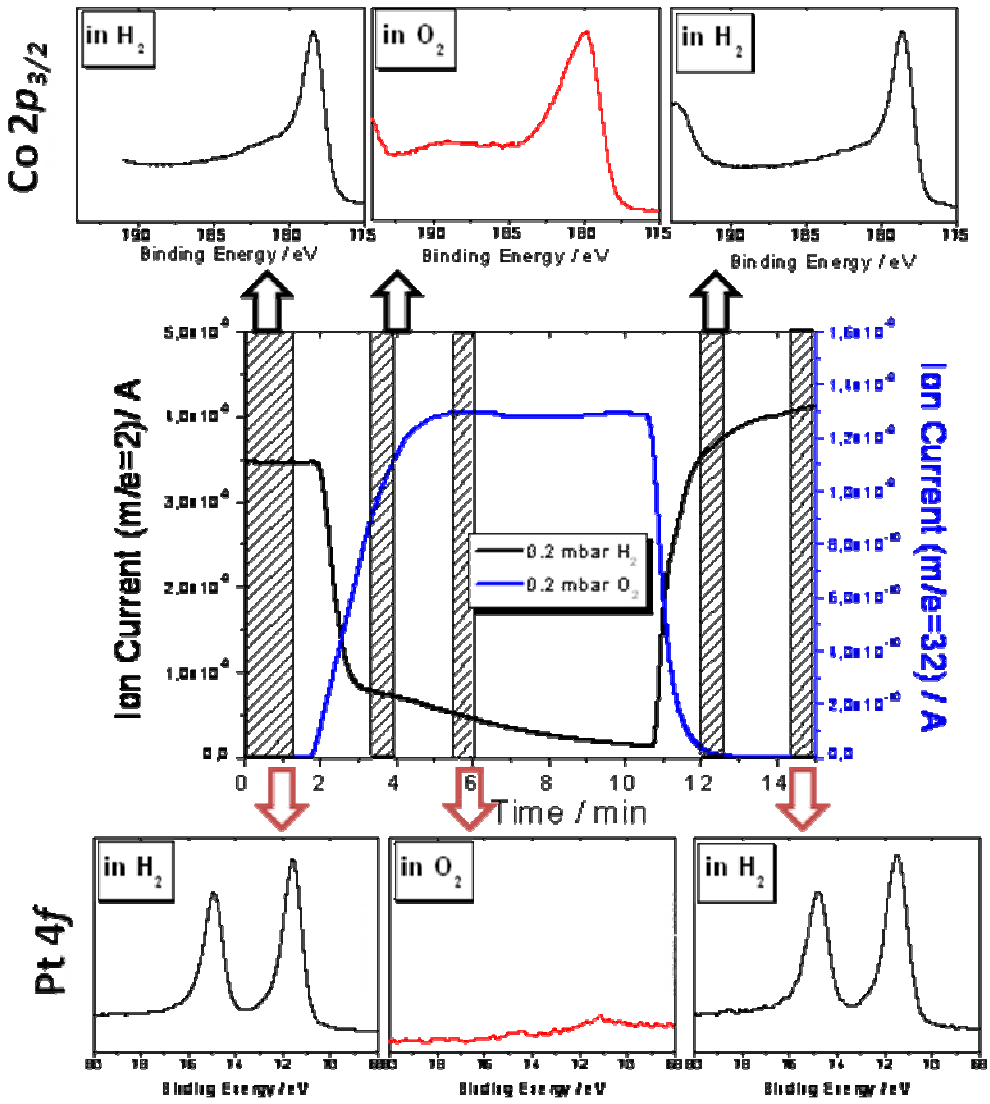

Figure S1. Real-time experiment showing the evolution of Co $2p_{3/2}$ (*top*) and Pt 4f (*bottom*) spectra from the PtCo foil in response to the changes of the gas atmosphere in the experimental cell. The *on-line* mass spectrometry signal for O_2 and H_2 and the periods of photoemission spectra acquisition are showed in the central diagram. The total gas pressure and the temperature were kept constant at 0.2 mbar and 520 K respectively.

Section S2

The depth distribution of Pt and Co over the first few atomic layers was investigated by non-destructive depth profile. Four different information depths were collected and evidently, the contribution of surface components is less as the electron kinetic energy increases. The relative Pt 4f/Co 2p atomic ratio was normalized to the photon flux and the experimental photo-ionization cross-section. The cross sections used for the calculations were based on experimental reference data on pure Pt and Co NPs samples of similar sizes (ca. 3 nm) recorded under similar condition in the same experimental setup, and not on the usually employed theoretically calculated sensitivity factors given in ref. [1]. This was mainly due to the fact that differences in the size and shape of the NPs as well as in the level of surface adsorbed carbon species are not taken into account in the theoretically calculated sensitivity factors, although might have an significant effect to the photoelectron signal. By using reference experimental values the above mentioned effects are less influential. In order to avoid complications due to the unspecified level of surface contamination and shape/size effects to the photoemission spectra intensities, only the relative evolution of the Pt/Co ratios to their initial value will be considered here.

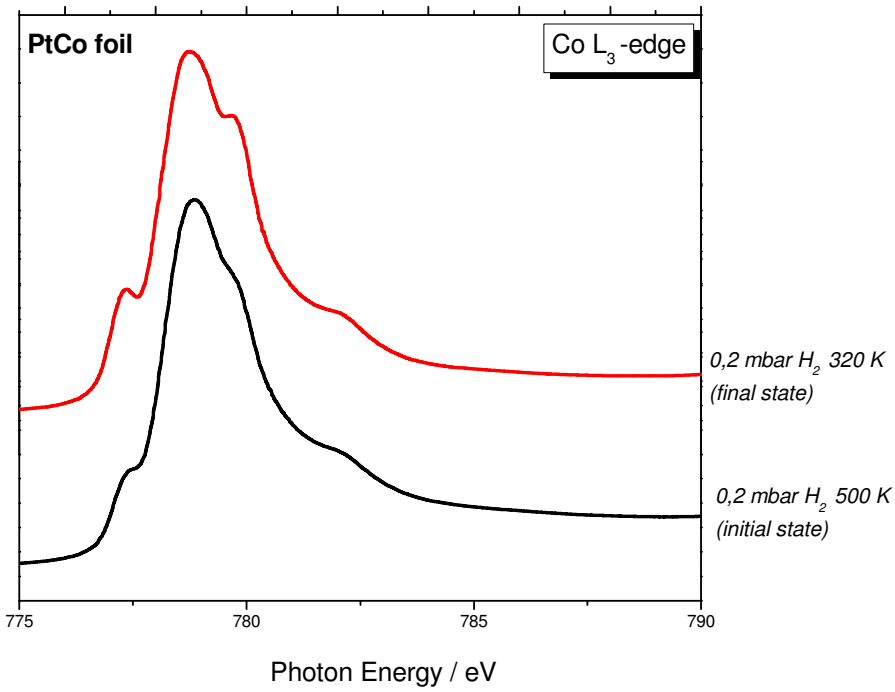

Figure S3. The Co L3 NEXAFS spectra from the PtCo alloy recorded in 0.2 mbar H2 initially at 500 K and then after cooling at 320 K. The slight differences in the spectra shape indicate modification of the cobalt electronic structure which is related to the temperature decrease.

Section S4

Platinum-cobalt nanoparticles (PtCo NPs) were prepared following the low energy cluster beam deposition technique (LECBD) [2]. In particular, NPs were prepared in the gas phase from a PtCo target (stoichiometry 1:1) using a laser vaporization clusters source apparatus, equipped with a quadrupolar electrostatic deviator that allows mass-selection of cations before deposition onto a Si substrate covered by a 10 nm thick amorphous carbon layer in ultra high vacuum conditions [3, 4]. The PtCo clusters size probability density follows a Gaussian shape distribution with a median diameter *Dm*=3 nm as derived from TEM measurements (fig. S5). In previous work it was shown that the PtCo-clusters' shape is a perfect truncated octahedron [5]. After preparation, the samples were stored in inert atmosphere and then briefly exposed to air upon transferring to the experimental chamber. The PtCo foil (bulk stoichiometry 1:1) was prepared by conventional metallurgy and x-ray diffraction showed that PtCo was a single-phase fcc solid solution. Before introduced in the experimental chamber the sample was sonicated in methanol for 15 min.

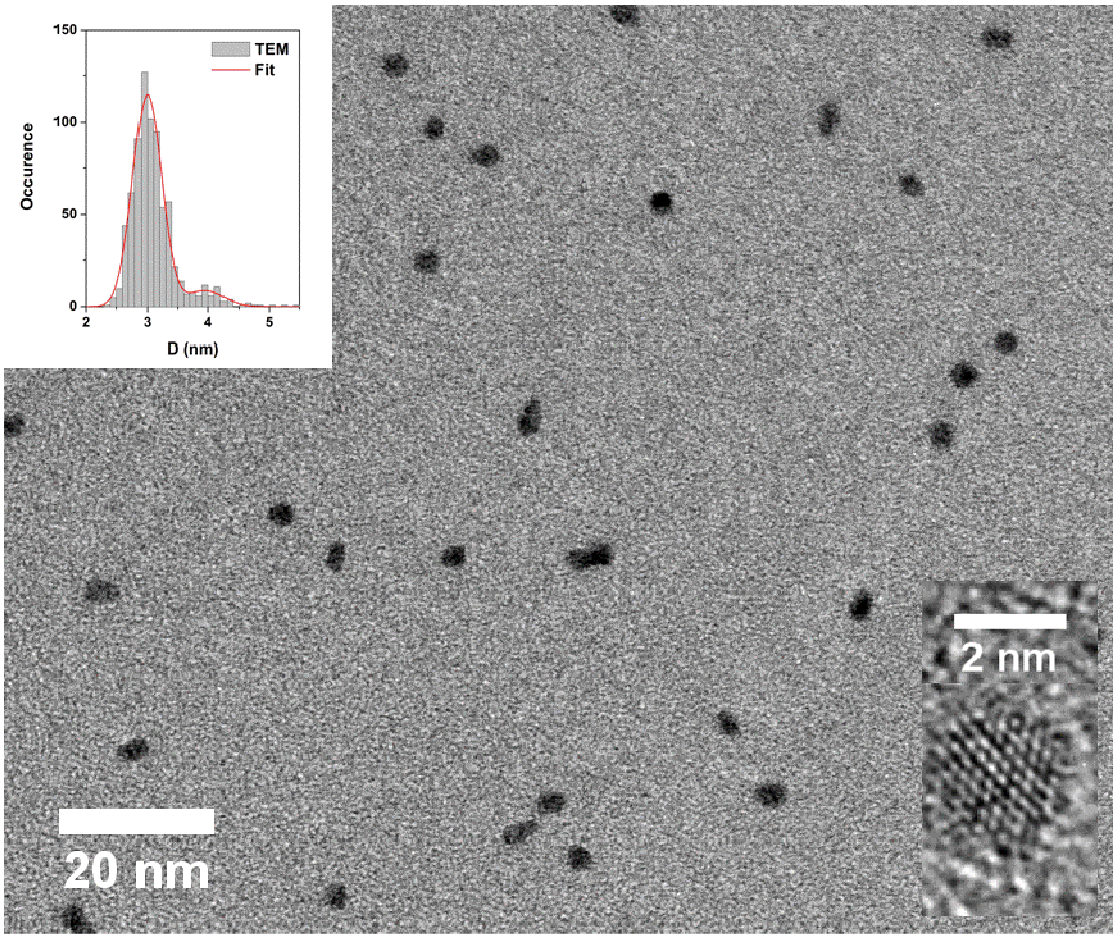

Figure S4. TEM image of PtCo clusters prepared by LECBD method and the corresponding size distribution (*up left corner*). Characteristic high resolution TEM image of a 2nm PtCo particle just after deposition (*down right image*).

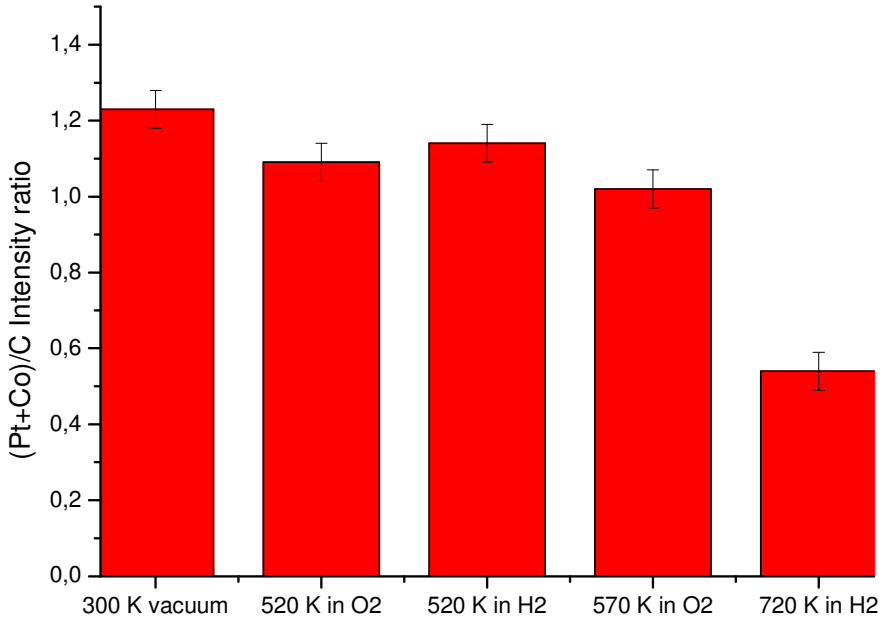

Figure S5. The (Pt 4f + Co 2p)/C 1s intensity ratio derived by APPES measurements under various conditions. In case of particles agglomeration due to high temperature (720 K) annealing a significant drop of this ratio is observed. The stability of amorphous carbon supported PtCo nanoparticles upon annealing has been also previously confirmed by TEM image analysis[6]

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Supporting information references

[1] Yeh, J.J.; Lindau, I. Atomic Subshell Photoionization Cross-Sections and Asymmetry Parameters - 1 Less-Than-or-Equal-to Z Less-Than-or-Equal-to 103 *At. Data Nucl. Data Tables* **1985**, *32*, 1-155.

[2] A. Perez, V. Dupuis, J. Tuaillon-Combes, L. Bardotti, B. Prevel, E. Bernstein, P. Mélinon, L. Favre, A. Hannour, and M. Jamet, Adv. Eng. Mater. 7, (2005) 475

[3] D. Tainoff, L. Bardotti, F. Tournus, G. Guiraud, O. Boisron, and P. Mélinon, *J. Phys. Chem. C*, 2008, 112 (17), 6842

[4] A. Tamion, C. Raufast, E. Bonet, V. Dupuis, T. Fournier, T. Crozes, E. Bernstein, W. Wernsdorfer *J. Mag. Mag. Mat.*, 2010, 622 *1315*

[5]F. Tournus, S. Rohart, and V. Dupuis, IEEE Trans. Magn. 44 (2008) 3201.

[6] F. Tournus, A. Tamion, N. Blanc, A. Hannour, L. Bardotti, B. Prével, P. Ohresser, E. Bonet, T. Epicier, V. Dupuis, Phys Rev. B 77 144411 (2008)