Supporting Information:

Noble-Transition Metal Nanoparticles Breathing in Reactive Atmosphere

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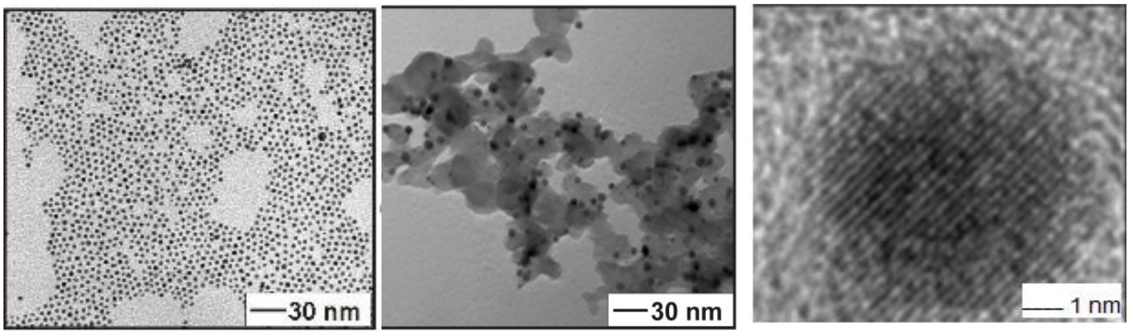


(A) (B) (C)

Figure S1. Representative TEM images of as prepared (A) and carbon supported $Pt_{25}Ni_{16}Co_{59}$ NPs with an average size of 5 ±0.5 nm (B). HRTEM image of a typical nanoparticle (C). Note the "±" deviations from the average particles size are half widths at full maximum of the gaussian-like distribution of sizes extracted from populations of a few hundred particles sampled by a few TEM images.

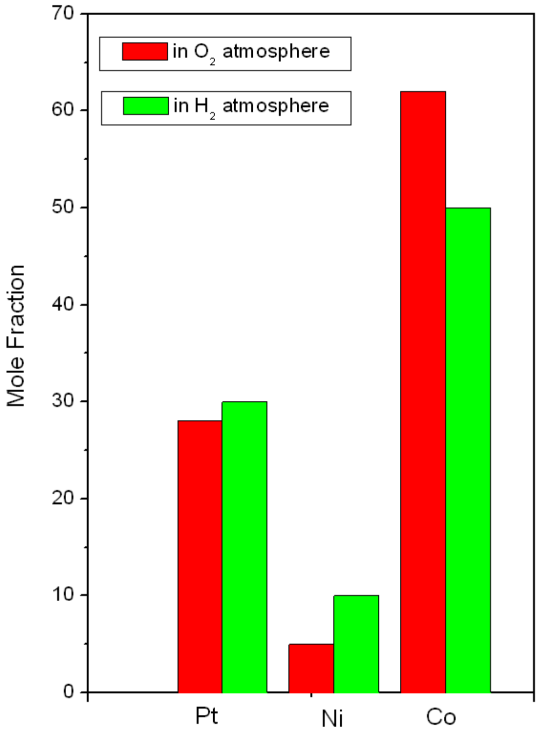
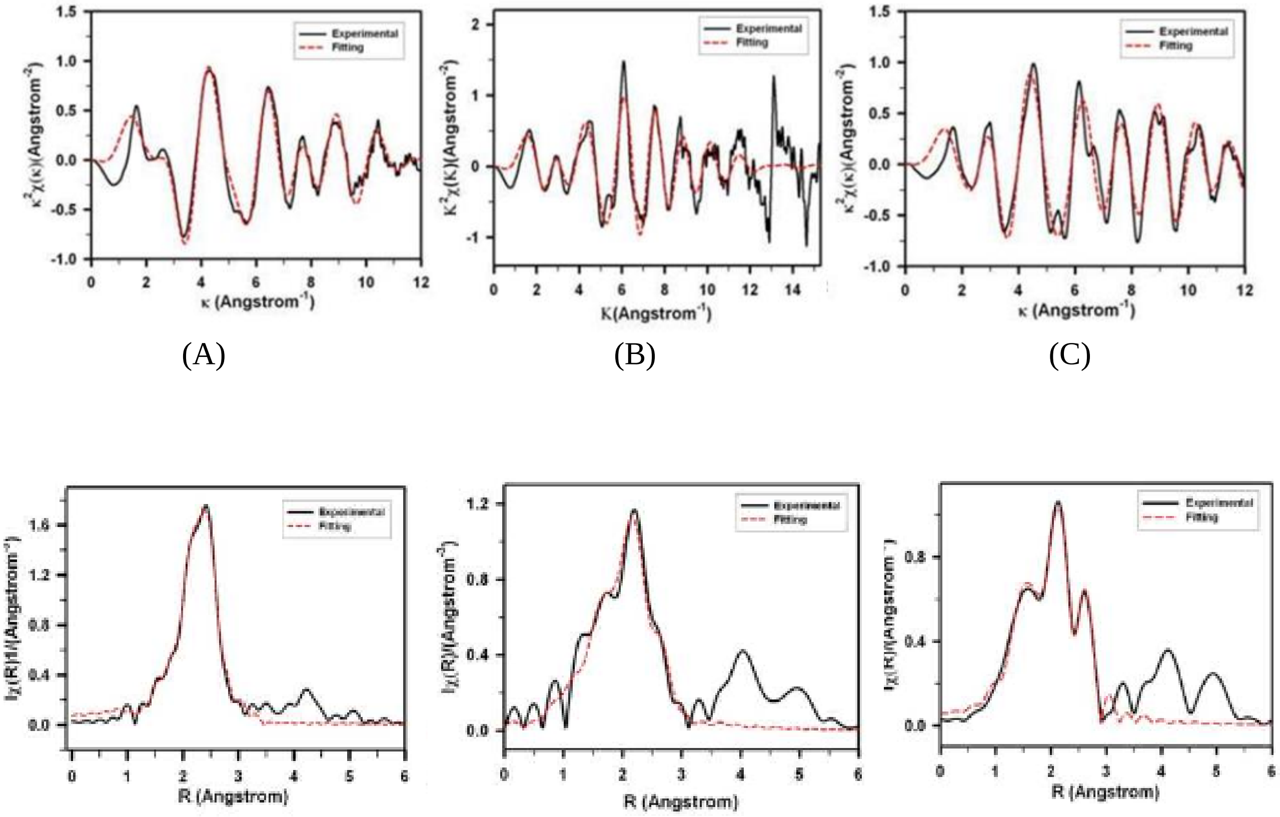


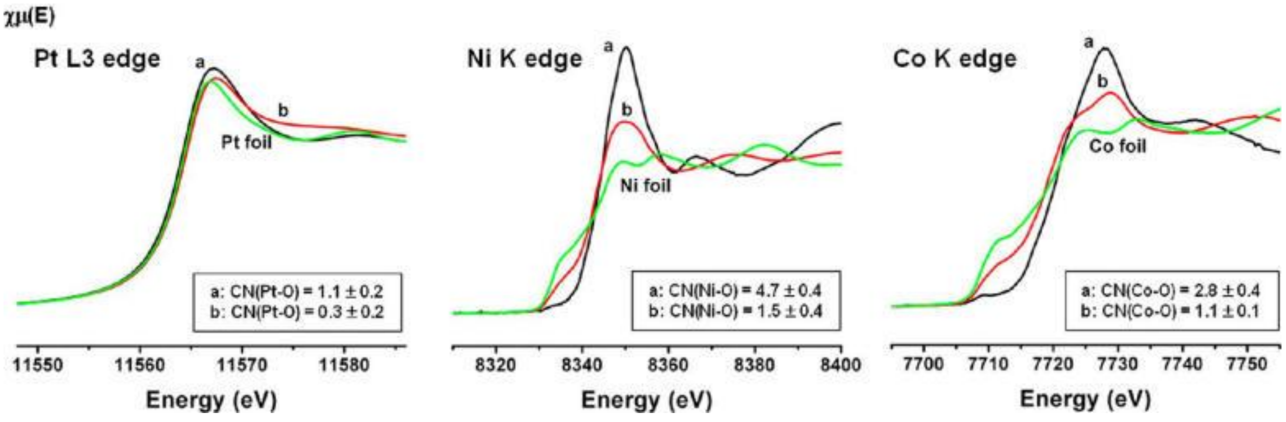
Figure S2. XPS determined relative surface composition of $Pt_{25}Ni_{16}Co_{59}$ NPs treated in reducing (red) and oxidizing (green) atmosphere as described in the paper. Note the abundance of Noble Metal (Pt) species close to the NP's surface hardly changes while that of the TM species changes a bit with the different gas environments. The results show that the particular NM-TM NPs undergo a moderate surface chemistry change only with changing the reactive gas atmosphere.



(A) (B) (C)

(D) (E) (F)

Figure S3. Pt L_3 (A), Ni (B) and Co K edges (C) $\chi(k)$ data (solid line) and the respective fitting plots (broken line in red). Original magnitude (solid line) Fourier transformed k^2-weighted Pt L_3 (D), Ni (E) and Co K (F) edge spectra. The spectra are from PtNiCo NP catalyst thermally treated in O_2 at 260 °C followed by treatment in H_2 atmosphere at 400 °C. The fits are used to extract the respective metal-metal and metal oxygen coordination numbers.



(A) (B) (C)

Figure S4. XANES spectra at Pt L_3 (A), Ni K (B) and Co K (C) edge spectra of PtNiCo/C NP catalyst thermally treated in O_2 at 260 ^{o}C only (a, line in black) followed by a treatment in H_2 at 400 ^{o}C (b; line in red). The reference spectra of Pt, Ni and Co metal foils (lines in green) are shown as well. The respective metal-oxygen coordination numbers are given by each XANES spectrum and also summarized in Tables S1 and S2 for convenience. As the XANES and EXAFS (Fig. S3 above) data show Pt atoms have a very low degree of oxidation as compared to Co and Ni species when the ternary NP alloy treated in O_2 atmosphere. The degree of oxidation in all metallic species drops very significantly after a subsequent treatment in H_2 atmosphere.

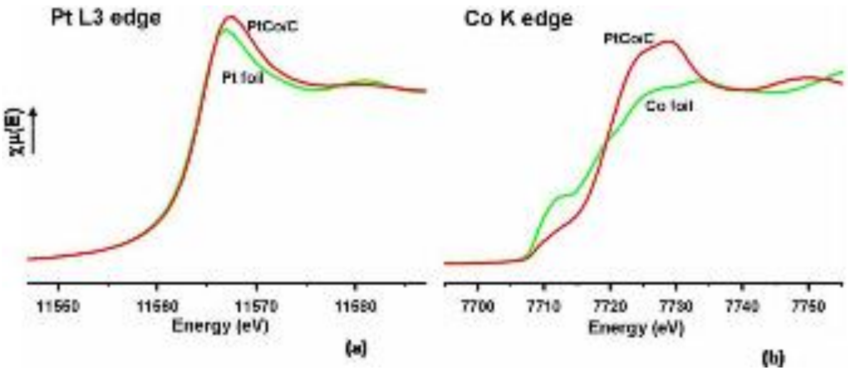


Figure S5.XANES spectra at Pt L_3 (A) and Co K (C) edge spectra of $Pt_{45}Co_{55}/C$ NP catalyst treated in O_2 atmosphere. Similarly to the case of ternary alloy (see Figs. S3 and S4 above) the amount of oxygenated Co in the NP binary alloy is quite significant while that of oxygenated Pt species – not quite. The respective metal-oxygen coordination numbers are summarized in Tables S1 and S2.

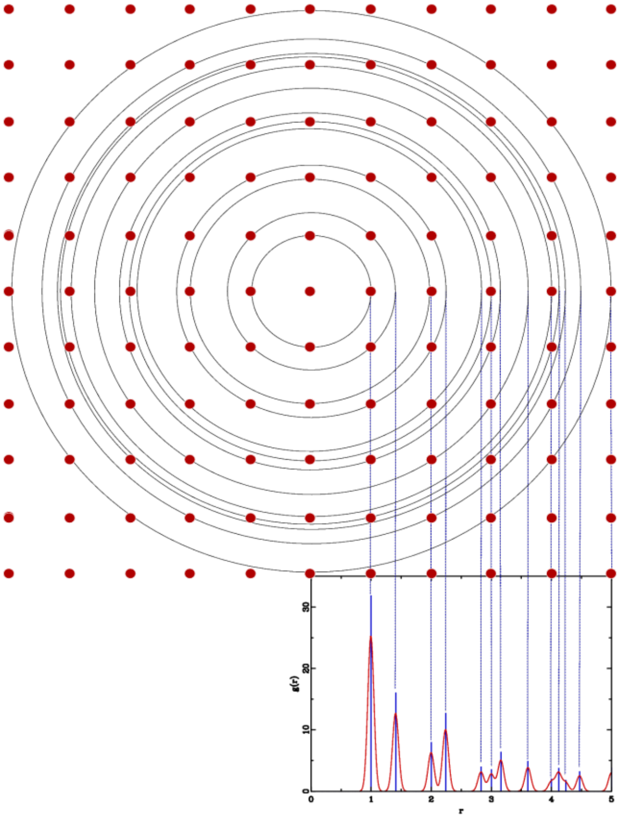


Figure S6. Relationship between the coordination spheres in materials (upper panel) and atomic Pair Distribution Functions (lower panel).

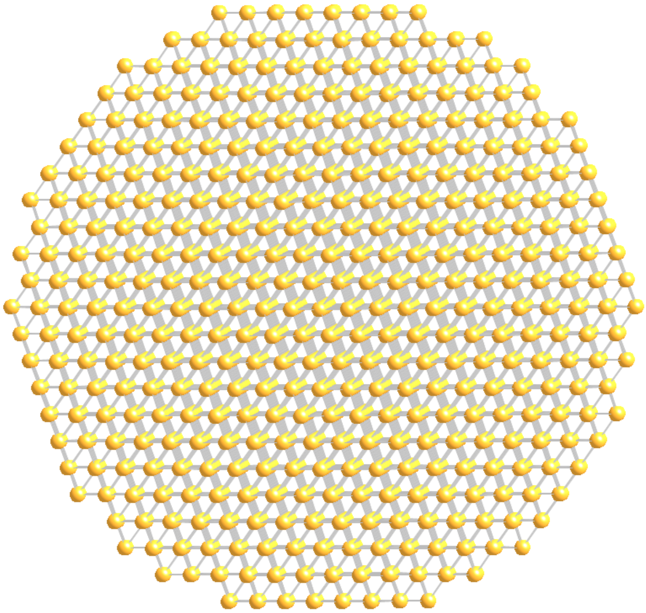


Figure S7. Pt NP of approximately 5,000 atoms as cut out from a perfect fcc lattice and used as a starting point in the reverse Monte Carlo simulations of Pt NPs treated in O_2 and H_2 atmosphere.

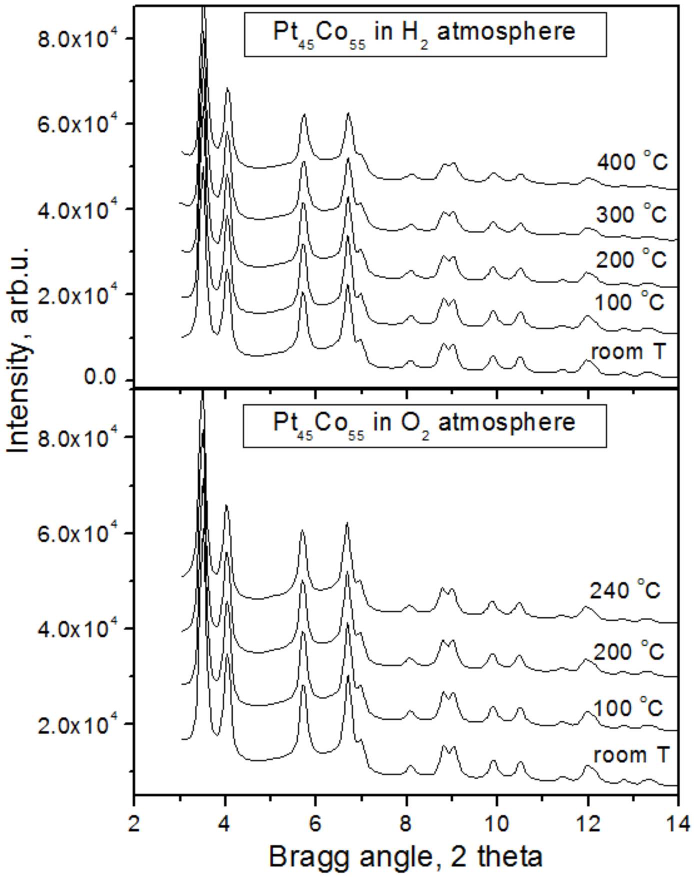


Figure S8. In situ XRD patterns for carbon supported $Pt_{45}Co_{55}$ NPs thermally treated in O_2 and H_2 atmosphere. The Bragg peaks do not change shape and width significantly when the samples are thermally treated in O_2 or H_2 atmosphere indicating no significant change in the NP morphology and size.

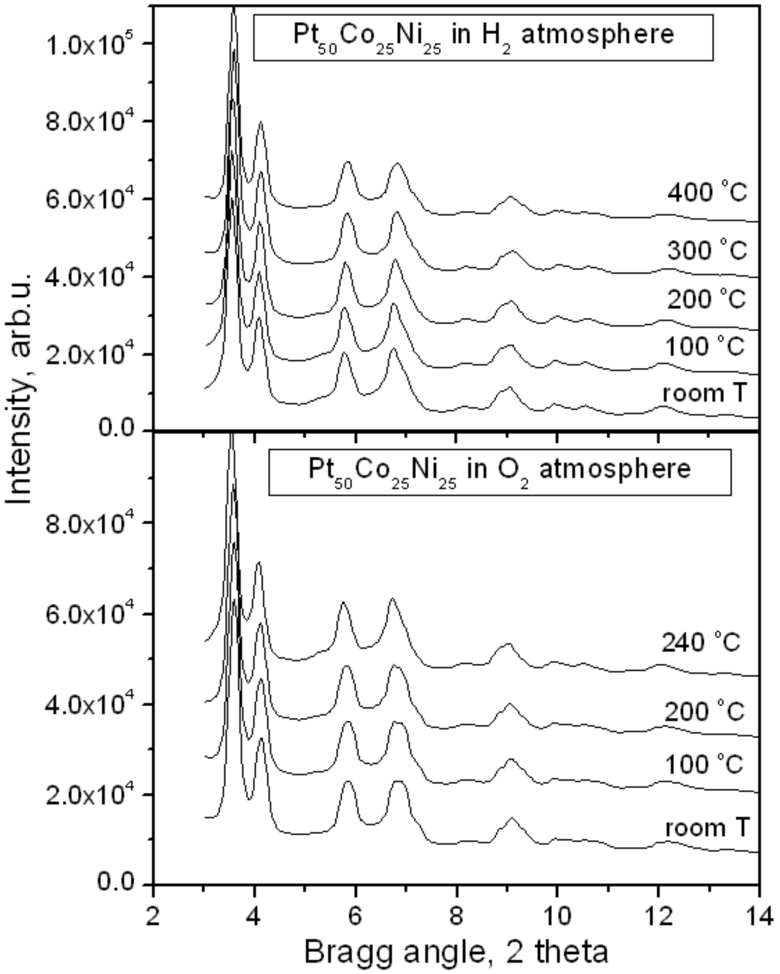


Figure S9. In situ XRD patterns for carbon supported $Pt_{50}Co_{25}Ni_{25}$ NPs thermally treated in O_2 and H_2 atmosphere. The Bragg peaks do not change shape and width significantly when the samples are thermally treated in O_2 or H_2 atmosphere indicating no significant change in the NP morphology and size.

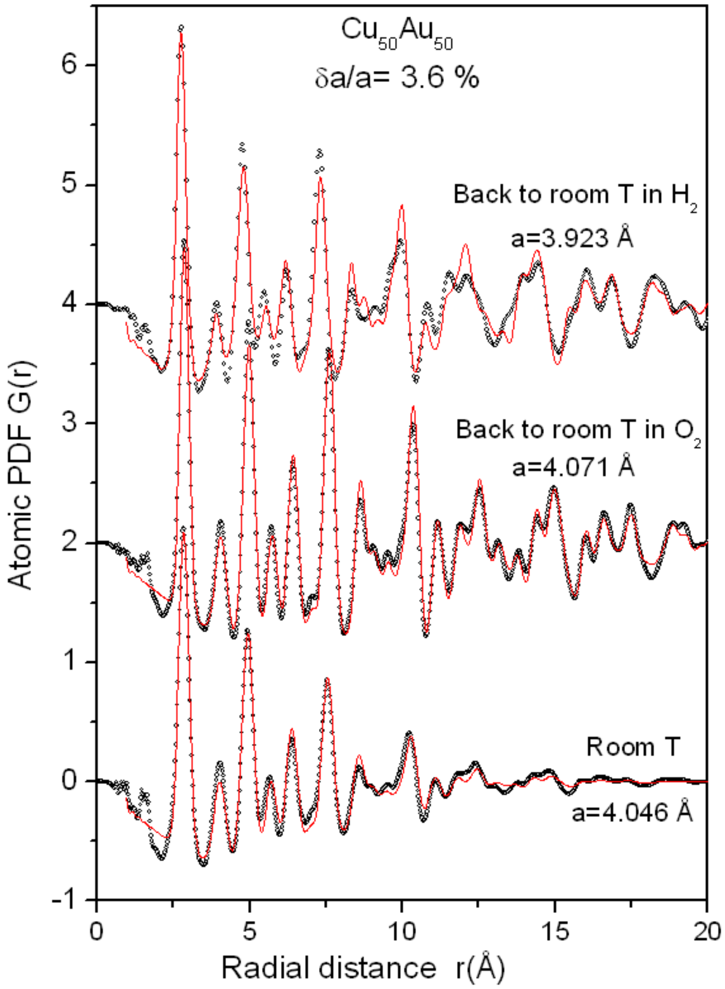


Figure S10. Experimental (symbols) and model (solid line) atomic PDFs for as obtained carbon supported $Cu_{50}Au_{50}$ NPs and NPs that have thermally treated in O_2 (240 ^oC) and H_2 (400 ^oC) atmospheres and then cooled down to room T (a). The refined fcc-lattice parameters are given by each data set.

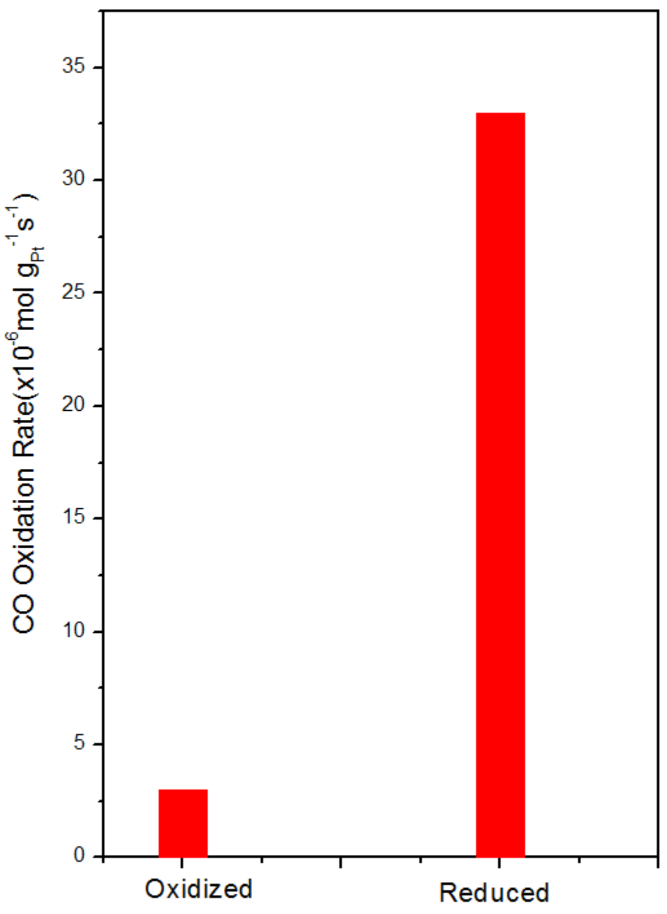


Figure S11. Comparison of CO conversion rates (at 60 ^{o}C) for $Pt_{25}Ni_{16}Co_{59}$ NPs treated in oxidizing and reducing atmospheres. The CO conversion was measured by taking samples from the reaction gas mixture consisting of CO, O_2 and N_2 with a volume ratio of 0.5:10:89.5.

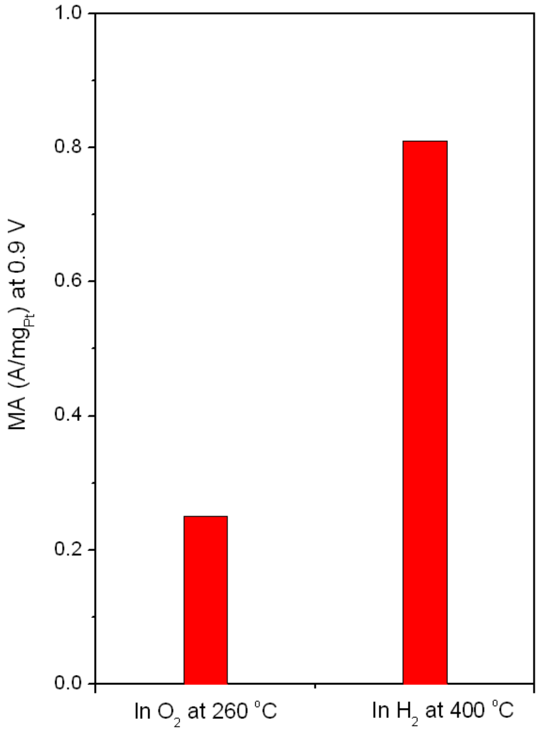


Figure S12. Catalytic mass activity (MA) of $Pt_{25}Ni_{16}Co_{59}$ NPs treated in oxidizing and reducing atmospheres as described in the text. The mass activity data for electrocatalytic oxygen reduction reaction were obtained by rotating disk electrode measurements in an 0.1 M $HClO_4$ electrolyte saturated with O_2. The catalyst was inked on a glassy carbon disk (geometric area: 0.196 cm^2). A typical ink of the catalyst was prepared by suspending 1.0 mg of the catalyst in 1 mL of water with diluted (5% vol.) Nafion (5 wt %, Aldrich). The measured kinetic current at 0.9 V (vs RHE) and total Pt inked on the catalyst on the electrode were used to calculate the mass activity (mA per mg of Pt).

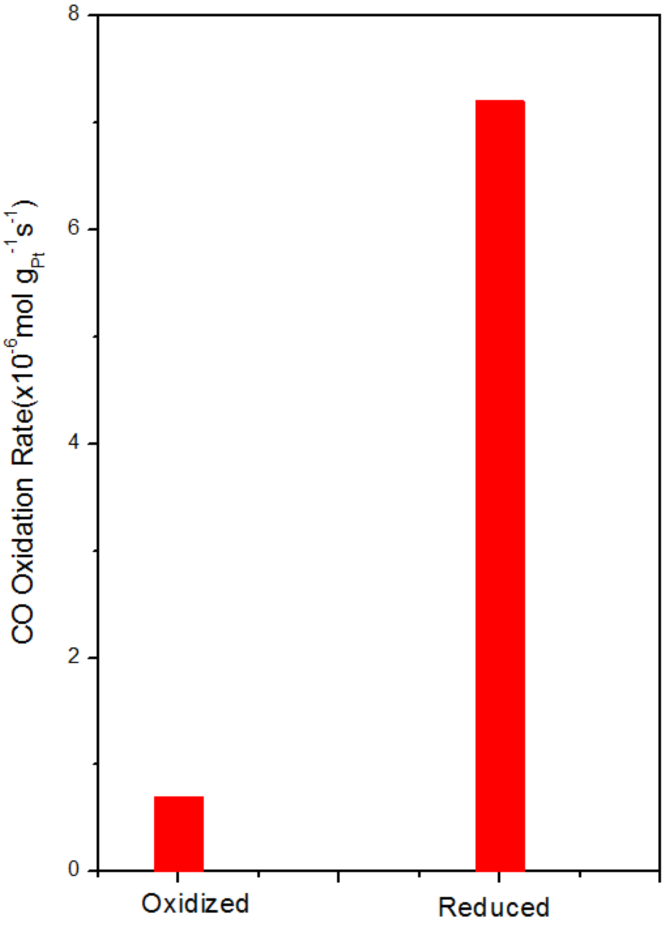


Figure S13. Comparison of Pt mass specific CO oxidation rates of $Pt_{45}Co_{55}$ NPs treated in oxidizing and reducing atmosphere. Reaction temperature: 60° C.

Table S1. First coordination numbers, CN, distances, R_{ij} [Å] and Debye-Waller (D-W) factors [10^{-3} Å^2] for selected atomic pairs in PtNiCo/C ternary NP alloys treated in oxidizing (O_2) and reducing (H_2) atmosphere as obtained by *ex situ* XAFS experiments conducted at Pt L_3 and TM** K edges.

O_2 atmosphere				H_2 atmosphere			
Atomic pair	CN	R_{ij} [Å]	D-W	Atomic pair	CN	R_{ij}[Å]	D-W
Pt-Pt	8±0.6	2.74***	5.7	Pt-Pt	7±0.6	2.66***	5.9
Pt-O	1.1±0.4	1.99	2.7	Pt-O*	0.2±0.5	1.97	2.7
Ni-O	4.7±0.6	2.04	4.7	Ni-O*	1.5±0.5	2.04	4.3
Co-O	2.8±0.6	1.92	5.9	Co-O*	1.1±0.5	1.92	5.4
TM-TM**	8.0±1.0	2.63***	6.1	TM-TM**	6.7±1.0	2.55***	6.3

*The residual oxygenated species in the H_2 treated samples are due to the exposure of the NP to ambient conditions during the *ex situ* XAFS experiments.
** TM=Co, Ni
*** - Note the relative change in the first neighbor Pt-Pt and TM-TM distances with changing the reactive gas atmosphere is about 3 % in line with the findings of the XRD/atomic PDF studies (see the text of the paper)

Table S2. First coordination numbers, CN, distances, R_{ij} [Å] and Debye-Waller (D-W) factors [10^{-3} Å^2] for Pt involving atomic pairs in PtCo/C binary NP alloys treated in oxidizing (O_2) and reducing (H_2) atmosphere as obtained by *ex situ* XAFS experiments conducted at Pt L_3 edge.

O_2 atmosphere				H_2 atmosphere*			
Atomic pair	CN	R_{ij} [Å]	D-W	Atomic pair	CN	R_{ij}[Å]	D-W
Pt-Pt	6±1	2.73**		Pt-Pt	6.7±0.6	2.69**	
Pt-O	2.0±0.4	1.99		Pt-O*	0.4±0.3	1.99	

* The residual oxygenated species in the H_2 treated sample are due to the exposure of the NP to ambient conditions during the *ex situ* XAFS experiments.
** - Note the relative change in the first neighbor Pt-Pt distances with changing the reactive gas atmosphere is about 1.5 % in line with the findings of the XRD/atomic PDF analysis (see the text of the paper)

Table S3. Structure types and corresponding lattice parameters of selected bulk NM (Pt) and TM (Co, Ni) metals and oxides.

Metal/Oxide type	Structure type	Lattice parameter [Å]
Pt	fcc/cubic	3.924
Co	hcp/hexagonal	a=2.50 and c=4.07
Co	fcc/cubic	3.54
Ni	fcc/cubic	3.52
PtO	tetragonal	a=3.07 and c=5.34
PtO_2	hexagonal	a=3.11 and c=4.34
CoO	cubic	4.26
Co_2O_3	hexagonal	a=4.64 and c=5.75
Co_3O_4	cubic	8.065
NiO	cubic	4.19