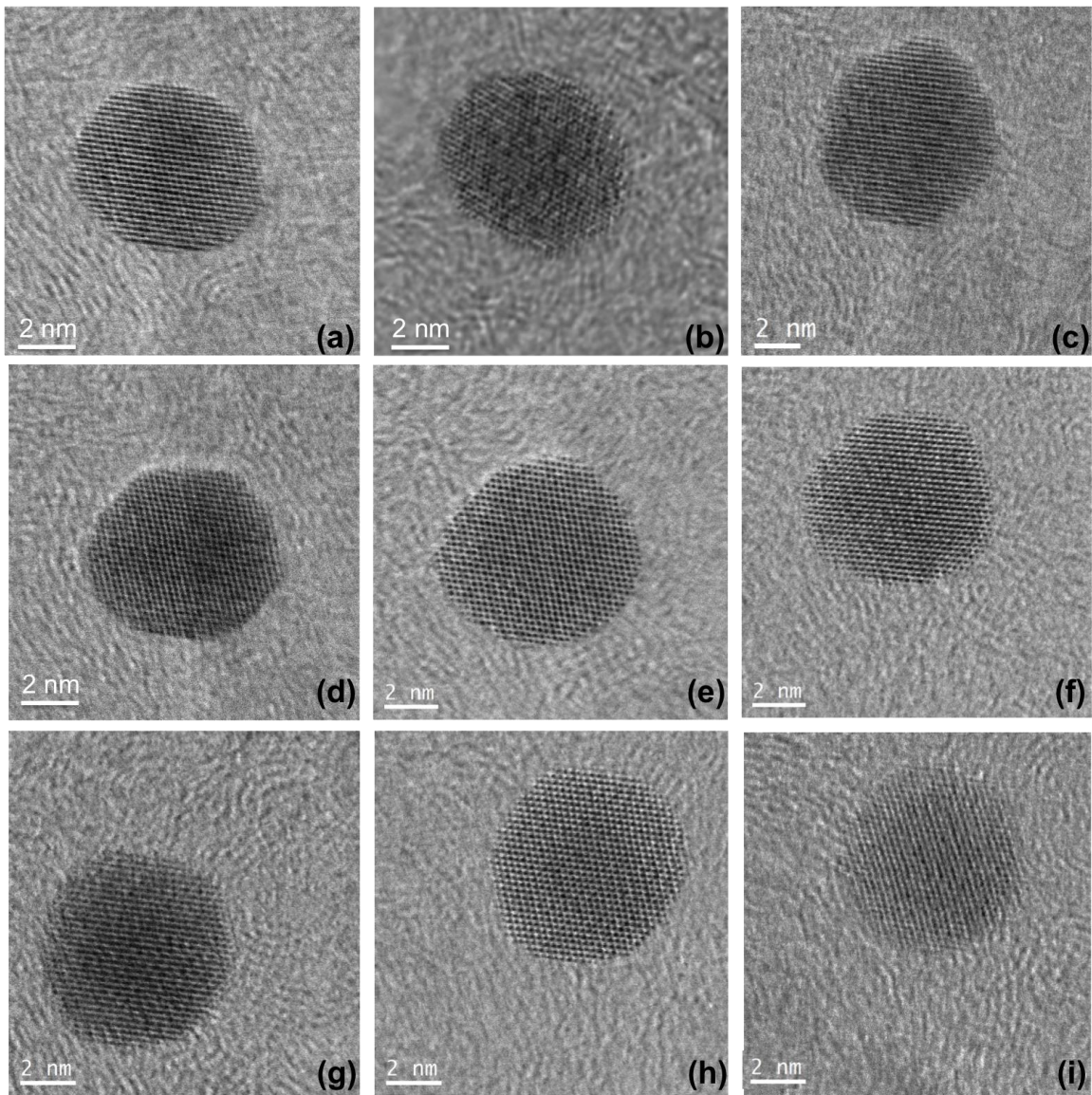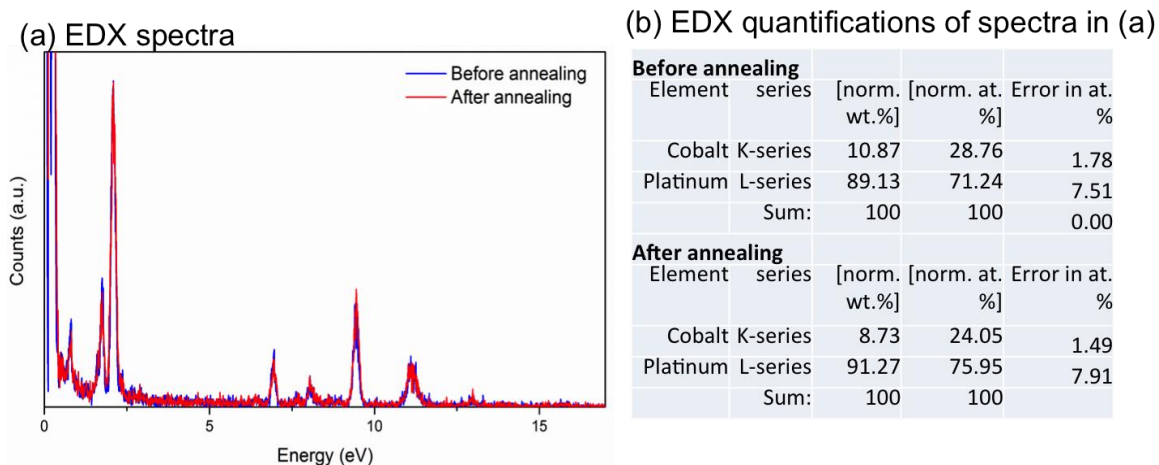Supplementary Figure 1. (a)-(d) HAADF images of pristine Pt_3Co NPs show excellent size homogeneity and monodispersivity on supporting carbon.
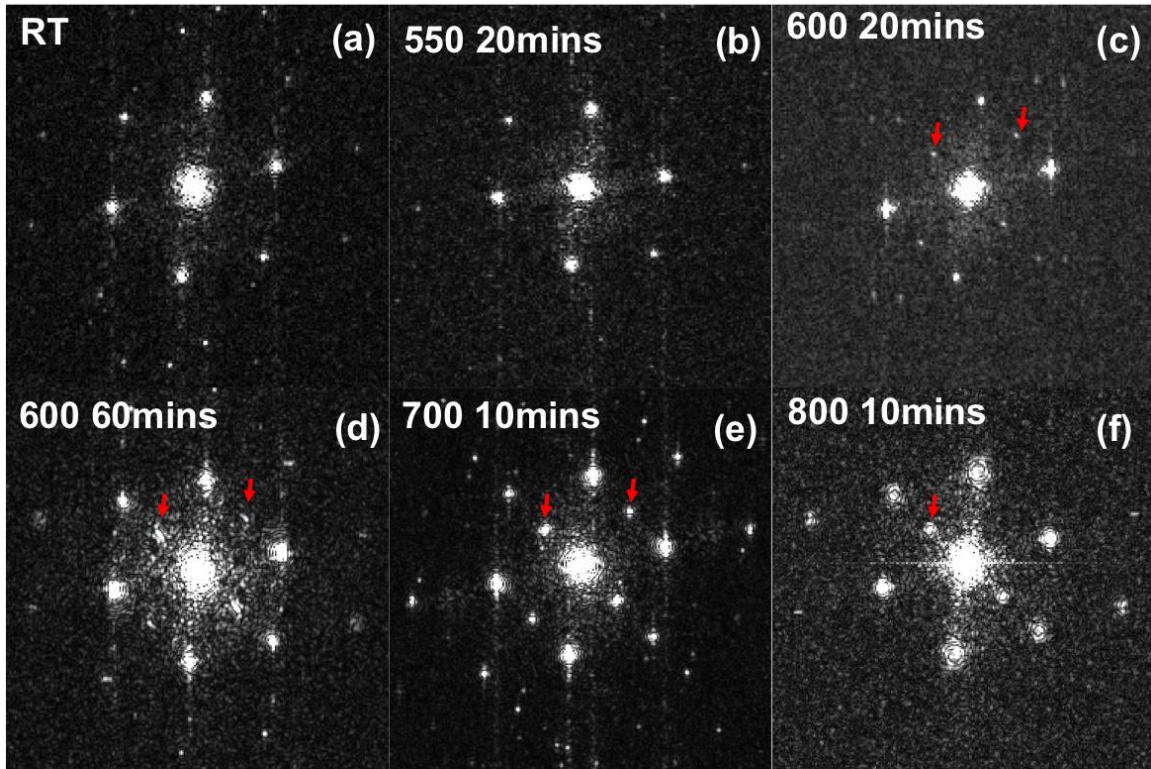
Supplementary Figure 2. Atomic-resolution bright-field (BF) STEM images of the single Pt_3Co NP that were acquired simultaneously with the HAADF-STEM images in Fig. 2.

(a) EDX spectra

Before annealing
After annealing

Counts (a.u.)

Energy (eV)

(b) EDX quantifications of spectra in (a)

Before annealing

Element	series	[norm. wt.%]	[norm. at. %]	Error in at. %
Cobalt	K-series	10.87	28.76	1.78
Platinum	L-series	89.13	71.24	7.51
	Sum:	100	100	0.00

After annealing

| Element	series	[norm. wt.%]	[norm. at. %]	Error in at. %
Cobalt	K-series	8.73	24.05	1.49
Platinum	L-series	91.27	75.95	7.91
	Sum:	100	100	

Supplementary Figure 3. Energy-dispersive X-ray spectra of the NP in Fig. 2 pre- and post-annealing. Both spectra were acquired at RT; the post-annealing spectrum was acquired after the particle was quenched from 800°C to RT. Both the spectra (a) and the corresponding elemental quantification (b) show no detectable chemical loss on the NP.

RT   350°C   550°C
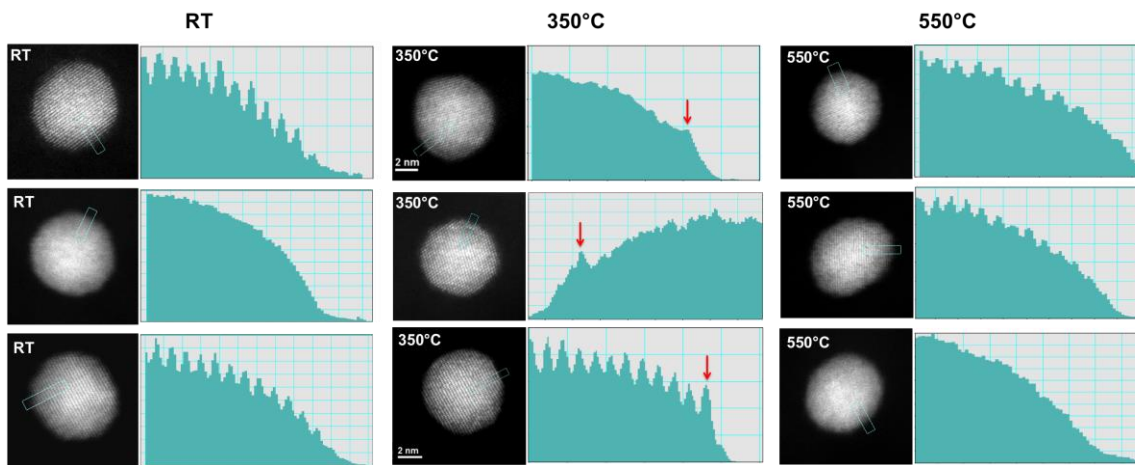
Supplementary Figure 4. Additional representative Pt$_3$Co NPs showed the same segregation behavior at different annealing temperatures as exhibited by the particle in Figs. 2 and 3. The enhanced contrast at the surface region was observed on the 350°C annealed particles, as marked by arrows on the profiles.

Supplementary Figure 5. Fast Fourier transforms computed from selected high-resolution images in Fig. 2. The representative ordering periodicities ½{001} and ½{011} are indicated by arrows.
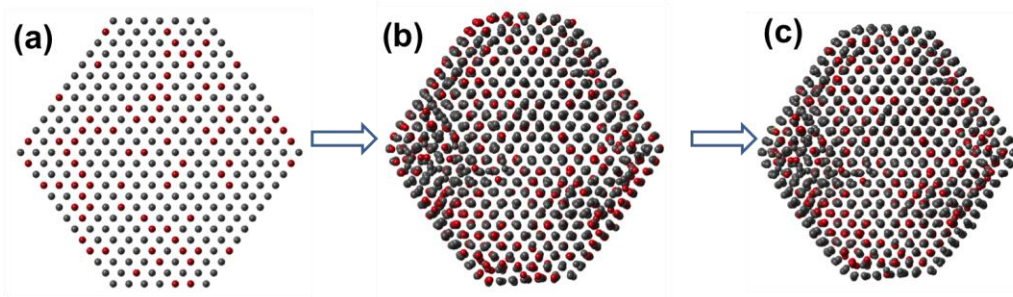
Supplementary Figure 6. calculated structural models of Pt$_3$Co NPs for multi-slice STEM image simulations: randomly alloyed NP in a cubo-octahedron shape (a); after structural relaxation (b); and with Pt segregation (c).
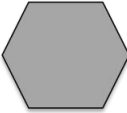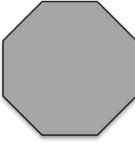
a

b
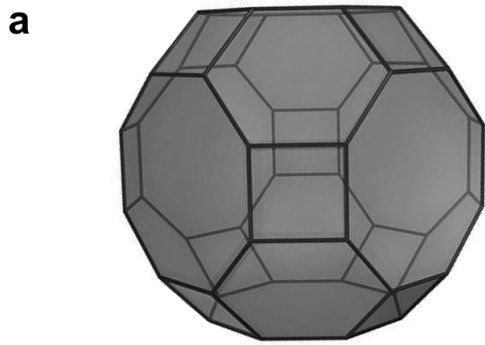
3-D model of truncated cubooctahedron
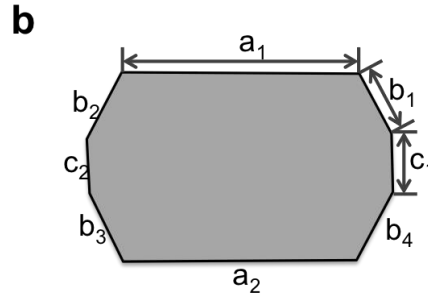
2-D projection at [110], and the edges for the calculation were labeled.

c

12X 110

$$S_{(110)} = 4(xy + yz + xz) \quad \ldots\ldots\ldots\ldots\ (1)$$

8X 111

$$S_{(111)} = 8 \times 3 \times \frac{\sqrt{3}}{2} y^2 \quad \ldots\ldots\ldots\ldots\ (2)$$

6X 100

$$S_{(100)} = 3[(1 + 2\sqrt{2})(a^2 + c^2) + ab + ac] \quad \ldots\ldots\ldots\ldots\ (3)$$

$$x = \frac{a}{(1 + \sqrt{2})} \quad \ldots\ldots\ldots\ldots\ (4)$$

$$y = b \quad \ldots\ldots\ldots\ldots\ (5)$$

$$z = \frac{c}{(1 + \sqrt{2})} \quad \ldots\ldots\ldots\ldots\ (6)$$

Supplementary Figure 7. Schematic of facets and calculation equations that are used for estimating enclosing facet area of the NP. The 3D schematic model of truncated cubooctahedron (a) and its 2-D projection at [110] direction (b); the lengths of a_i, b_i, and c_i (i=1,2,3…) are measured from STEM images for facet evaluations. A truncated cubo-octahedron contains 8X{111}, 6X{100} and 12X{110} facets (c). x, y, and z are

the side lengths of the (100) facets, and a, b, and c are the averages from the

measured a_i, b_i, and c_i values respectively. The area of surface facets are calculated

using equation (1)-(3), and the mathematic relationship between x, y, z and a, b, c

are shown in equation (4)-(6).

Supplementary Table 1. Microscopy parameters for image simulation

Voltage (kV)	Convergent angle	C1	A1	A2	B2	C3	A3	A4
200	30 mrad	700 pm	2.22 nm	35.5 nm	30.4 nm	100.1 nm	264.7 nm	8.1 um