Electronic Supplementary Information for

One-Pot Synthesis of Core-Shell-like Pt_3Co Nanoparticle Electrocatalyst with Pt-enriched Surface for Oxygen Reduction Reaction in Fuel Cells

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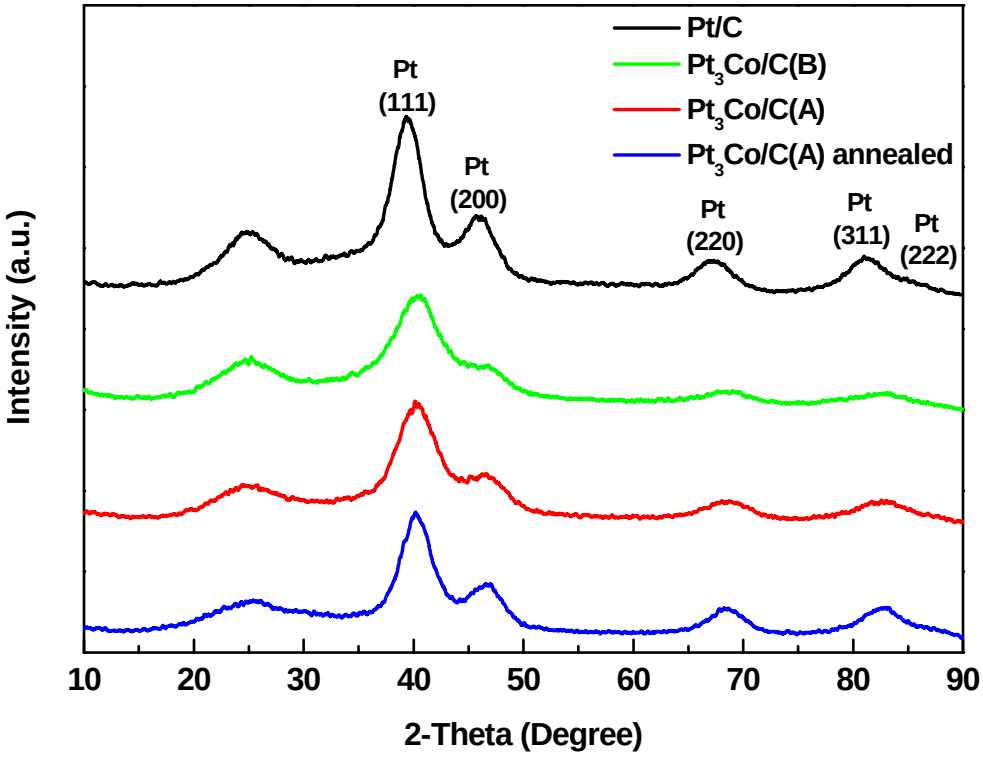

Fig. S1 XRD patterns of commercial Pt/C and Pt_3Co prepared by different methods.

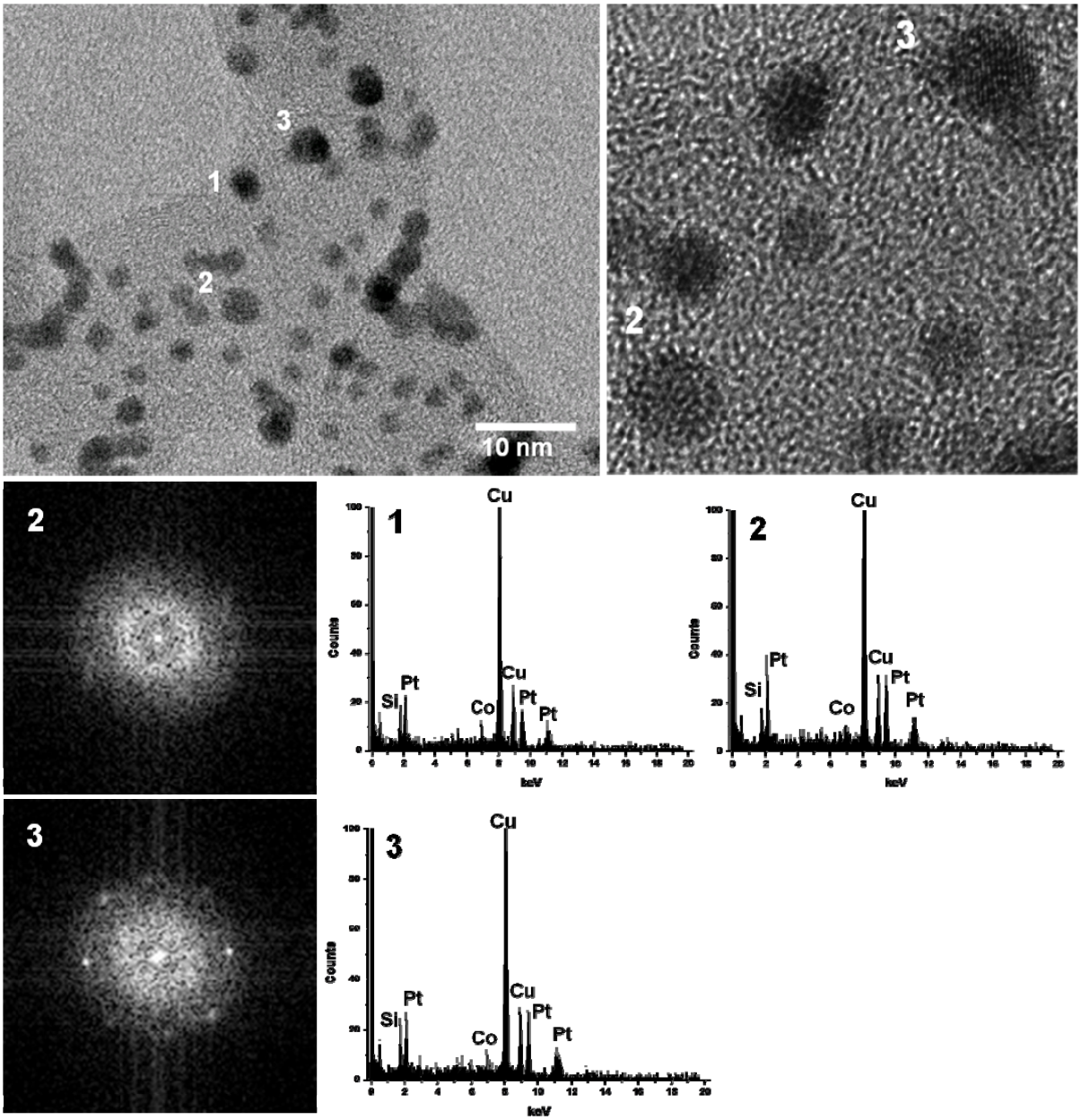

Fig. S2 TEM analyses of Pt_3Co(A) nanoparticles. Three NPs marked with numbers were analyzed for the compositions. The numbers in the EDX spectra, the HR-TEM image, and the ED patterns correspond to the numbers marked on the NPs in the upper left image. Regardless of the size (compare 1 to 2 and 3) and the degree of darkness in appearance (compare 2 to 1 and 3), all of the NPs show both Co and Pt in their EDX spectra (The Si and Cu peaks are from the system.). NPs 2 and 3 were further analyzed for their orientations by taking high resolution images. These were selected because they are of the same size but of different darkness. The FFT image of NP 3 shows sharp diffraction maxima indicating that it has a low index face oriented to the viewing direction. The FFT image of NP 2 shows no diffraction maxima indicating that it has a high index face oriented to the viewing direction. **We can, therefore, conclude that all of the NPs are composed of Co and Pt, and that the different darkness in appearance is due to the different orientations (diffraction effect) of the NPs not due to different compositions (mass effect).** TEM specimen was prepared by dropping the suspension onto a holely SiO_x film covering a TEM Cu grid. EDX analyses were conducted using ~1 nm probe under STEM mode in JEOL 2100F TEM.

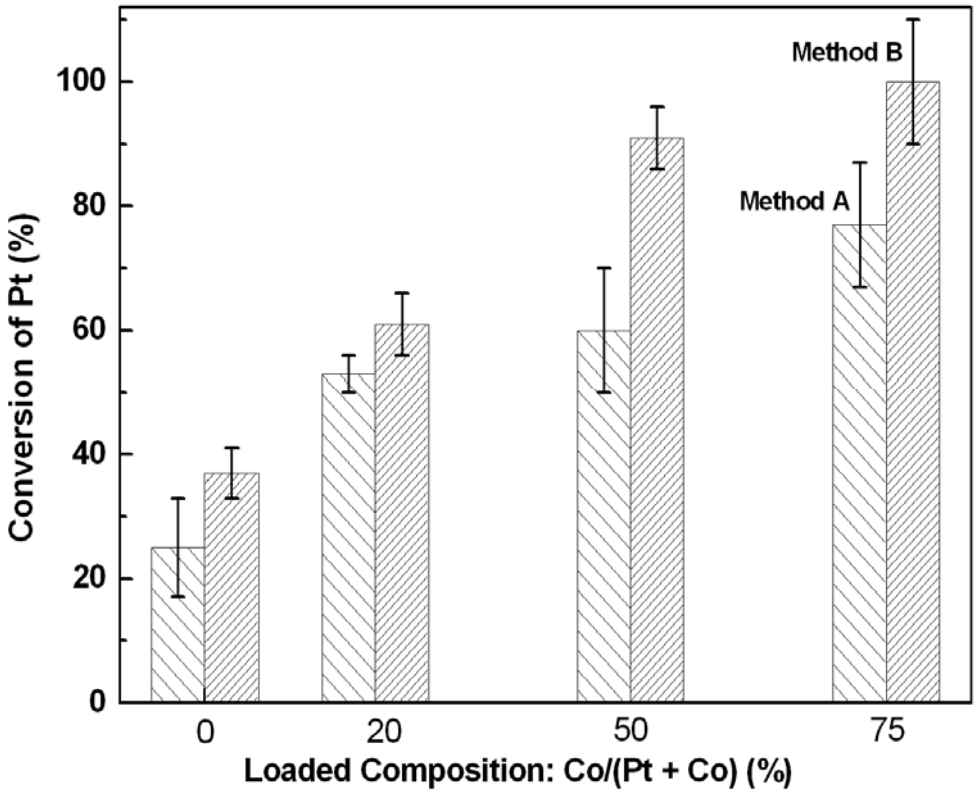

Fig. S3 Conversion efficiency of $Pt(acac)_2$ into Pt in the Pt_xCo NPs in the two methods as a function of the Co-content. The conversion efficiencies in this plot are calculated by using the equation below:

$$\text{CE of Pt (\%)} = \frac{\text{A}}{\left(\frac{B}{B+C+D}\right)}$$

A: Weight % of Pt analyzed by SEM/EDX

B: Theoretical mass of Pt converted from $Pt(acac)_2$

C: Theoretical mass of Co converted from $Co(acac)_2$

D: Mass of the carbon support

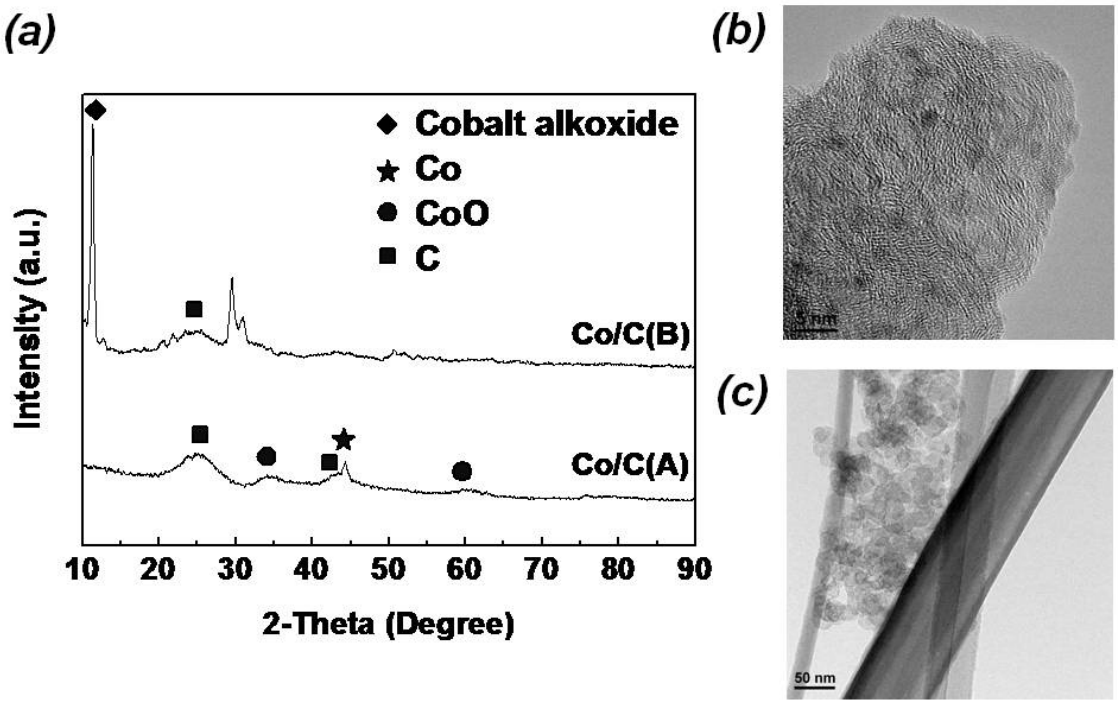

Fig. S4 Analysis data on the products of the reactions with $Co(acac)_2$ only by methods A and B: (a) XRD patterns and TEM images of the products by (b) method A and (c) method B.

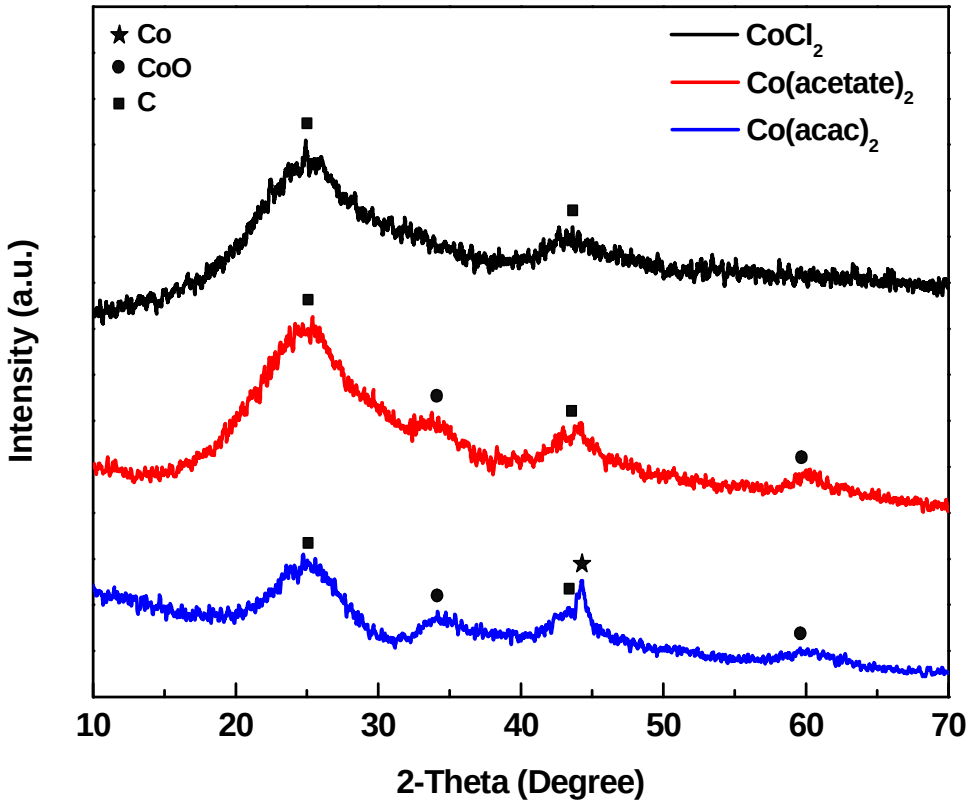

Fig. S5 XRD patterns of products synthesized with different cobalt precursors by method **A**. The peak positions are from the JCPDS Card no. 87-0642, no. 15-0806, and no 75-0419.

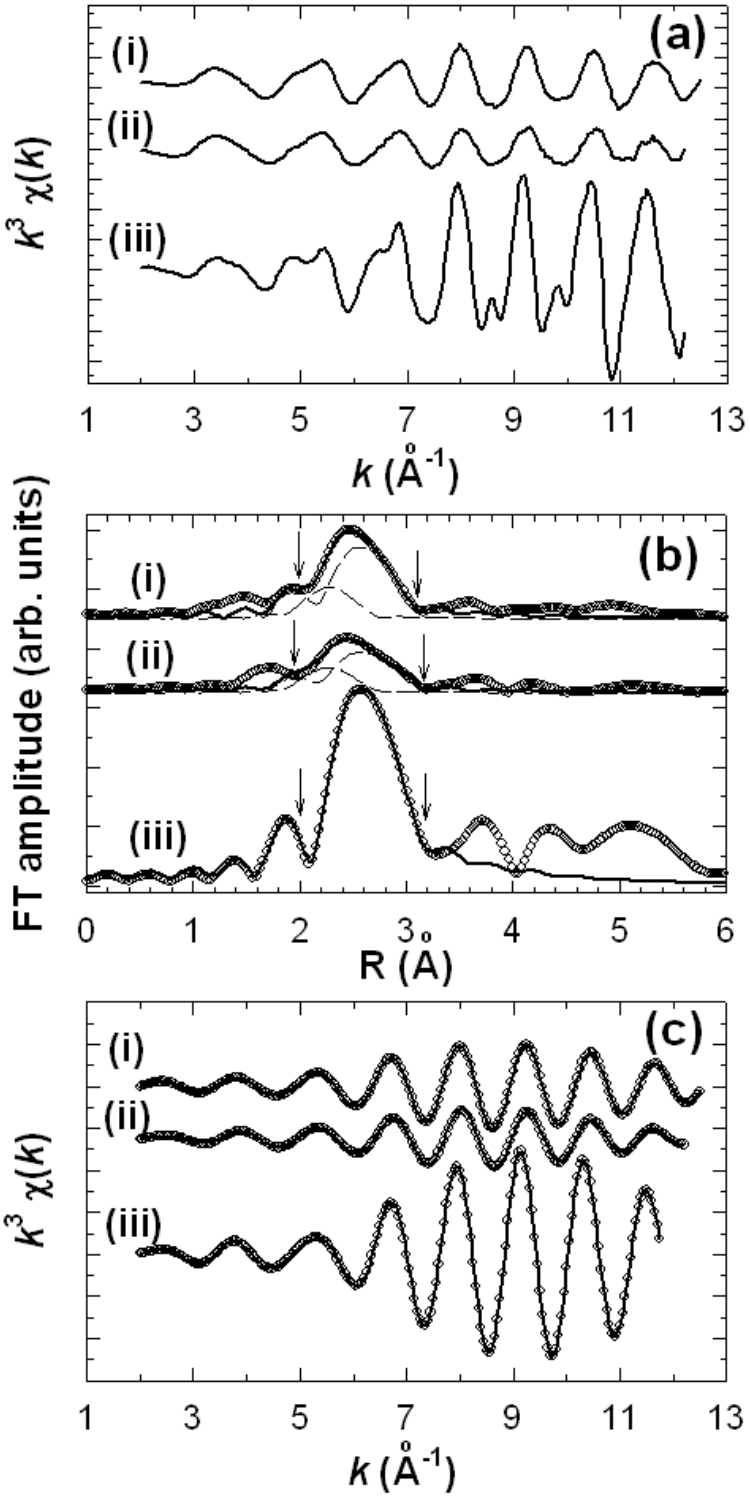

Fig. S6 (a) Experimental k^3-weighted, (b) Fourier-transformed, and (c) Fourier-filtered EXAFS spectra for the Pt L_{III}-edge data of (i) Pt_3Co(B), (ii) Pt_3Co(A), and (iii) the reference Pt metal. In the panels of (b) and (c), the solid lines and empty circles represent the best-fitted and experimental data, respectively. The ranges over which the Fourier filtering was made are shown by the arrows. In the data (i) and (ii) of the panel (b), the dashed lines represent the FT peaks corresponding to the (Pt-Co) and (Pt-Pt) shells.

Table S1. Results of curve fitting analyses on the Pt L_{III}-edge EXAFS spectra of Pt_3Co samples and Pt metal.

Sample	Bond	*CN*	*R* (Å)	σ^2 (10^{-3} × Å^2)
Pt_3Co(A)	(Pt–Co)	0.9	2.66	5.87
	(Pt–Pt)	3.7	2.77	7.24
Pt_3Co(B)	(Pt–Co)	1.1	2.67	5.92
	(Pt–Pt)	5.5	2.75	6.63
Pt metal	(Pt–Pt)	12.0	2.76	4.44

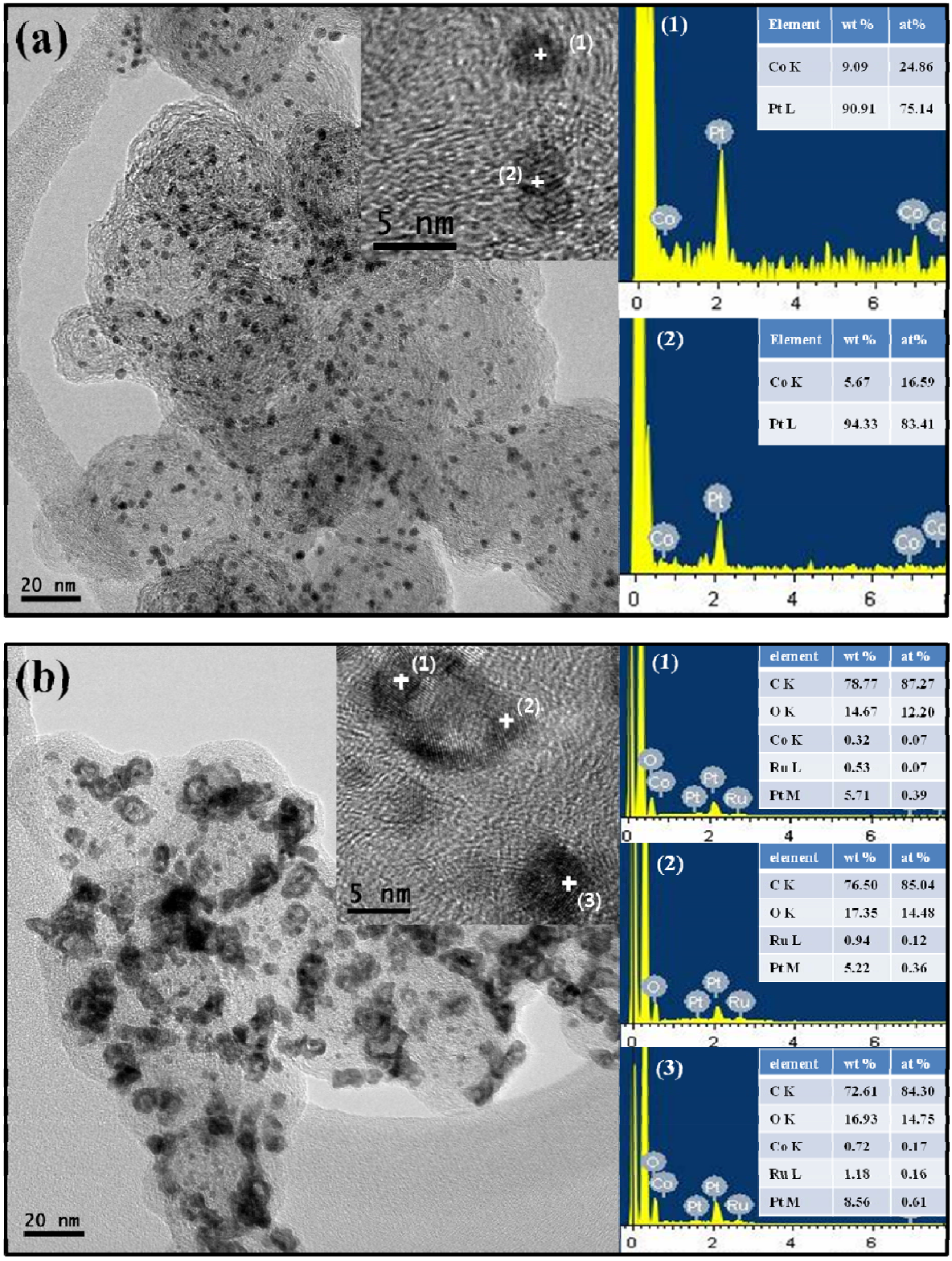

Fig. S7 TEM and EDX analysis results of Ru replaced (a) Pt_3Co(A) and (b) Pt_3Co(B). The insets are high magnification images. The (+) marked points were analyzed with EDX whose compositions are shown in the right hand side. In Pt_3Co(A) sample, there is no Ru detected. EDX analyses were conducted using ~1 nm probe under STEM mode in JEOL 2100F TEM.

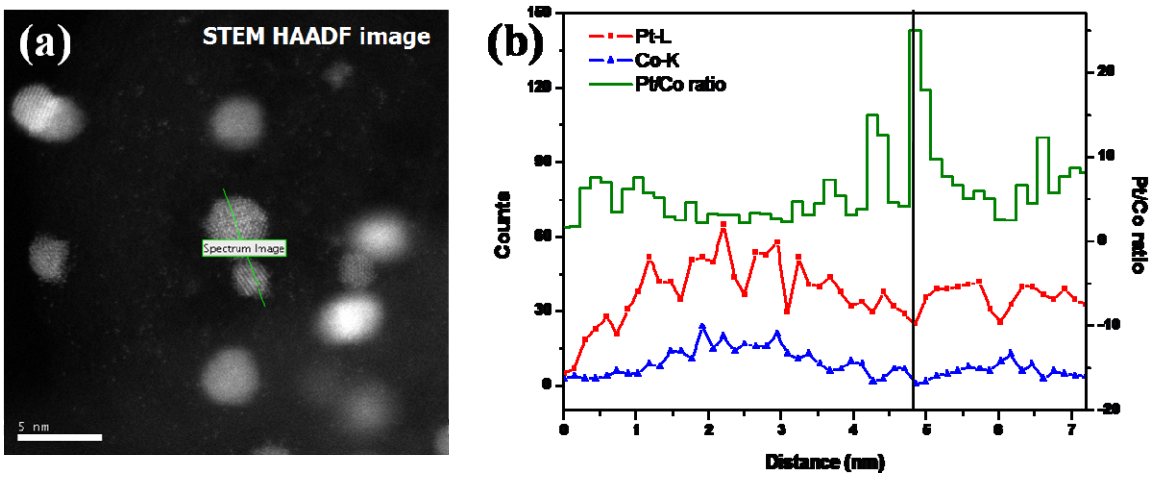

Fig. S8 (a) STEM image and (b) EDX analysis results of Pt_3Co(A). The Cs-corrected STEM was employed to perform the high spatial resolution EDX analysis of nanoparticles. EDX analysis was conducted using a ~0.13 nm probe under STEM mode in JEOL ARM200F Cs-corrected TEM. EDX line profiles of elements Pt and Co were acquired across the two adjecnt nanoparticles as shown in STEM high angle annular dark field (HAADF) image (a). The vertical line at distance ~ 4.8 nm is a guide to divide the data for the large (in the left-hand side) and the small nanoparticles (in the right-hand side) of the two nanoparticles scanned. The plot of Pt/Co ratio (green line) is subject to some artifact due to the low counts. Nevertheless, the plot clearly demonstrates Pt-rich shells of both of the nanoparticles.