Supporting Information

Seed-mediated synthesis of bimetallic ruthenium-platinum nanoparticles efficient in cinnamaldehyde selective hydrogenation

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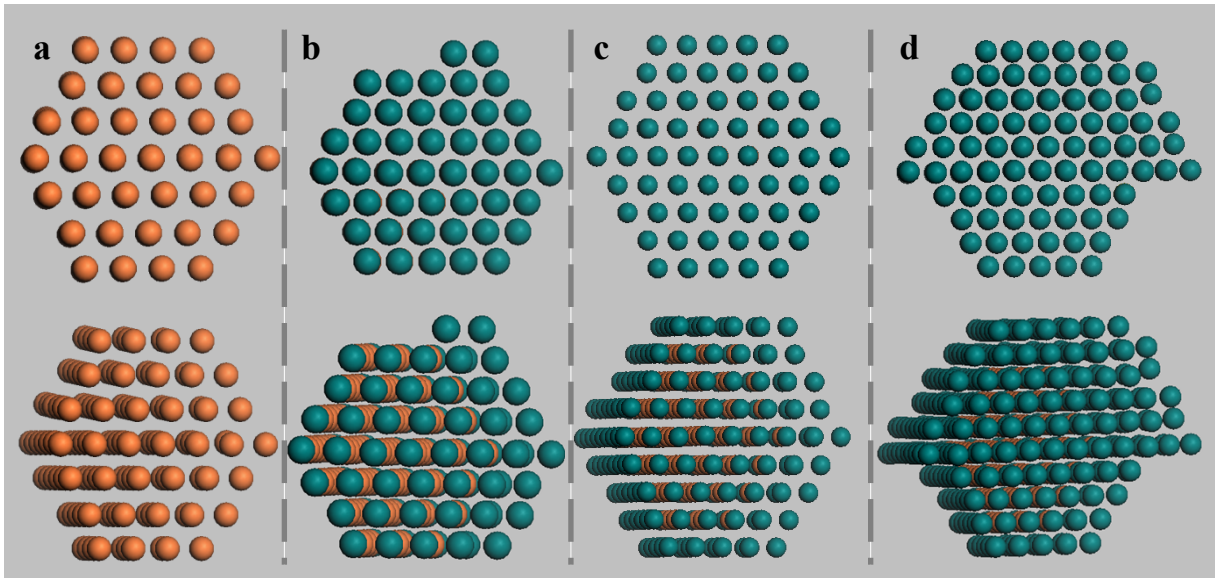
SI.1 Models of bimetallic nanoparticles

The models have been constructed using Accelrys Materials Studio for materials modelling and simulation software.

RuPt nanoparticles.



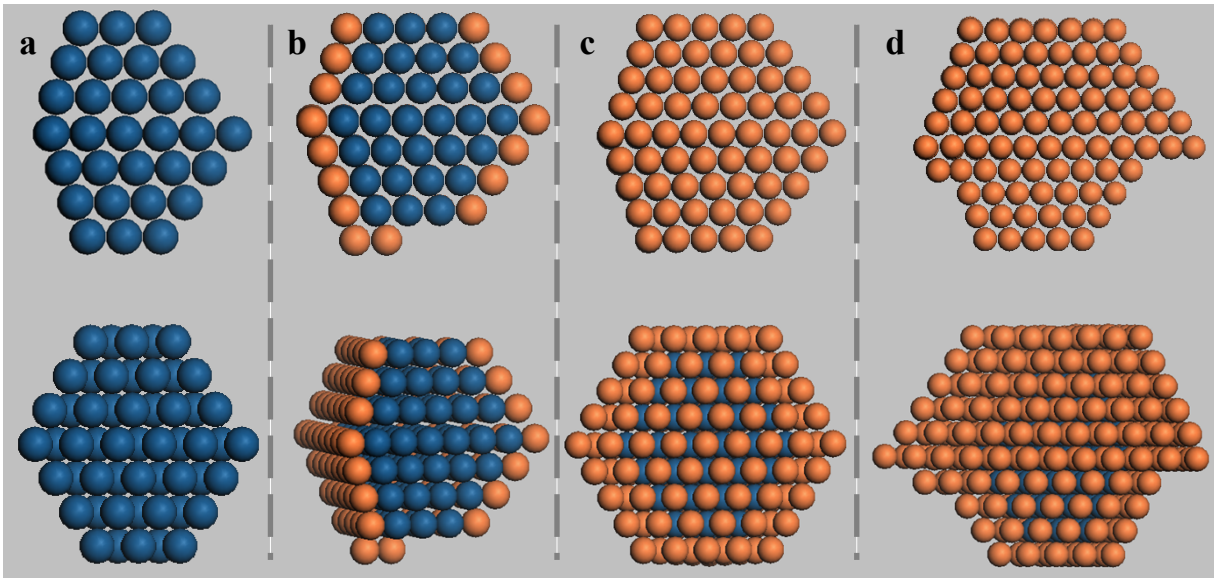
a) Nanoparticle model of monometallic Ru (001) nanoparticles (top along Y axis view and bottom with angles). Model containing 83 atoms (Empirical radius of ruthenium was used in the cluster model, 1.30×2×6=1.56 nm).

b) Nanoparticle model of partial covered core-shell **Ru1Pt1** nanoparticles (top along Y axis view and bottom with angles). Ru:Pt = 1:1= 83 Ru atoms : 83 Pt atoms; 162 atoms are needed to form a monolayer, *i. e.* just half monolayer is formed. (Particle diameter: 1.56+0.54=2.10 nm).

c) Nanoparticle model of partial covered core-shell **Ru1Pt2** nanoparticles (top along Y axis view and bottom with angles). Ru:Pt = 1:2 = 83 Ru atoms: 166 Pt atoms; 162 atoms are needed to form a monolayer, *i. e.* a Pt monolayer is formed with 4 shell atoms left. (Particle diameter: 1.56+0.54=2.10 nm).

d) Nanoparticle model of partial covered core-shell **Ru1Pt4** nanoparticles (top along Y axis view and bottom with angles). Ru:Pt = 1:4= 83 Ru atoms : 332 Pt atoms; 162 atoms are needed to form the first layer and 252 for the second layer, *i. e.* a Pt monolayer is formed with 170 shell atoms left which partially cover the first monolayer. (Particle diameter: 1.56+0.54=2.10 nm).

PtRu nanoparticles.



a) Nanoparticle model of monometallic Pt (111) nanoparticles (top along Y axis view and bottom with angles). Model containing 83 atoms (Empirical radius of platinum was used in the cluster model, 1.35×2×6=1.62 nm).

b) Nanoparticle model of partial covered core-shell **Pt1Ru1** nanoparticles (top along Y axis view and bottom with angles). Pt:Ru = 1:1= 83 Pt atoms : 83 Ru atoms; 162 atoms are needed to form a monolayer, *i. e*. just half monolayer is formed. (Particle diameter: 1.62+0.52=2.14 nm).

c) Nanoparticle model of partial covered core-shell **Pt1Ru2** nanoparticles (top along Y axis view and bottom with angles). Pt:Ru = 1:2= 83 Pt atoms : 166 Ru atoms; 162 atoms are needed to form a monolayer, *i. e*. a Ru monolayer is formed with 4 shell atoms left. (Particle diameter: 1.62+0.52=2.14 nm).

d) Nanoparticle model of partial covered core-shell **Pt1Ru4** nanoparticles (top along Y axis view and bottom with angles). Pt:Ru = 1:4= 83 Pt atoms : 332 Ru atoms; 162 atoms are needed to form the first layer and 252 for the second layer, *i. e*. a Ru monolayer is formed with 170 shell atoms left which partially cover the first monolayer. (Particle diameter: 1.62+0.52=2.14 nm).

SI.2 TEM images of Pt/PPP nanoparticles

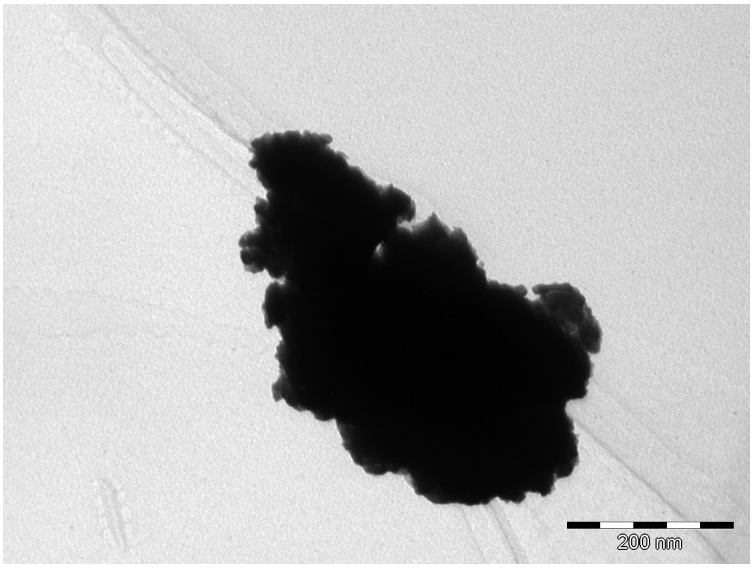


Figure 1. TEM micrographs of **Pt/PPP** particles.

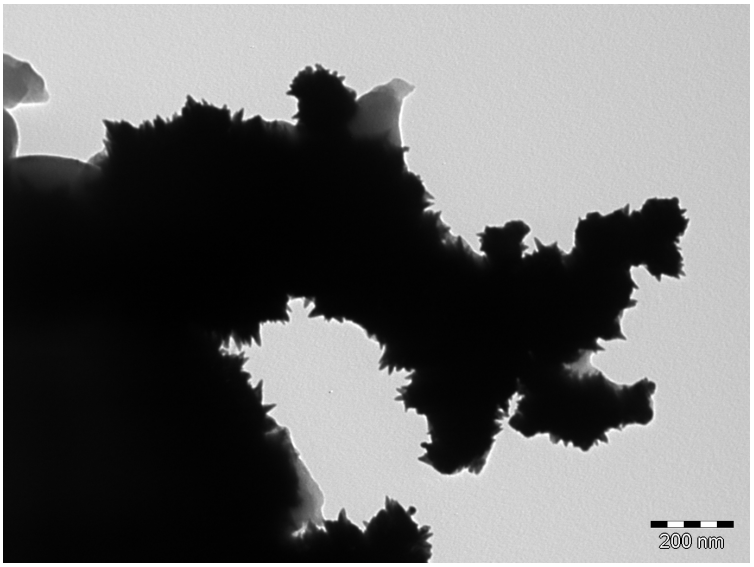


Figure 2. TEM micrographs of **Pt/PPP** particles.

SI.3 HRTEM and EDX analyses

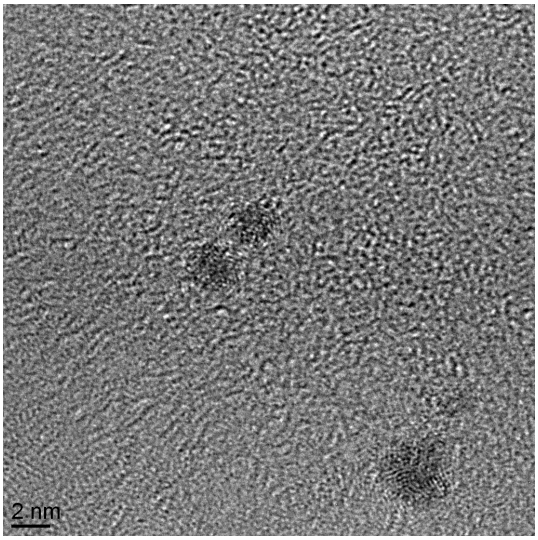


Figure 3. HRTEM image of **Ru1Pt1** nanoparticles.

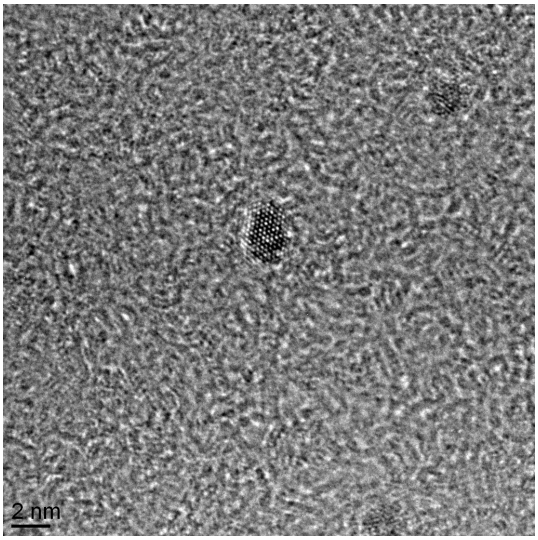


Figure 4. HRTEM image of **Ru1Pt2** nanoparticles.

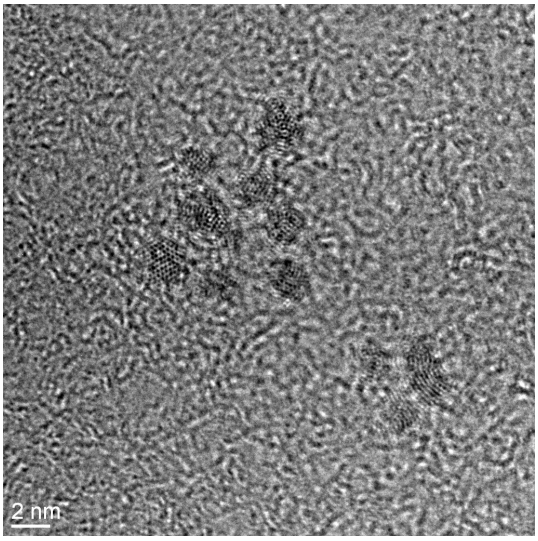


Figure 5. HRTEM image of **Ru1Pt4** nanoparticles.

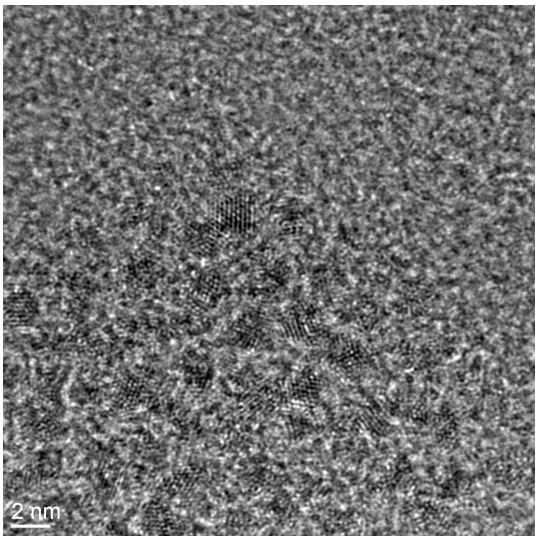


Figure 6. HRTEM image of **Pt1Ru1** nanoparticles.

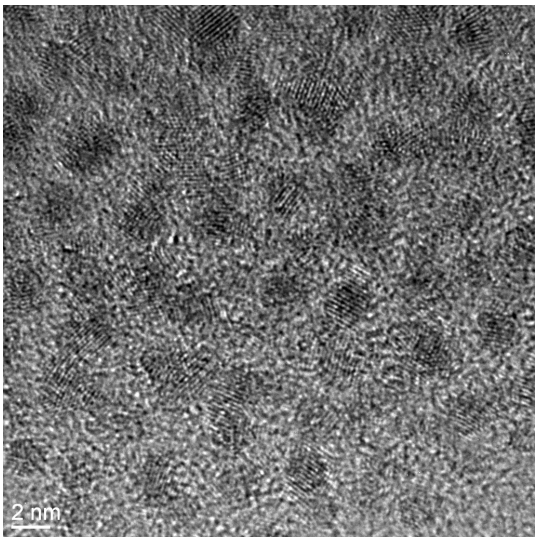


Figure 7. HRTEM image of **Pt1Ru2** nanoparticles.

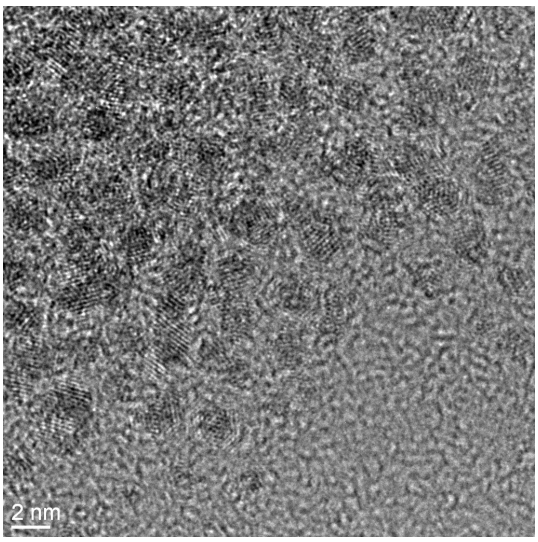


Figure 8. HRTEM image of **Pt1Ru4** nanoparticles.

EDX analyses

Table 1. EDX analyses and metal content by ICP.

NP sample	%Ru (%w by EDX)	%Pt (%w by EDX)	%Ru (%w by ICP)	%Pt (%w by ICP)
Ru1Pt1	38.76	61.24	23.1	37.1
Ru1Pt2	18.15	81.85	15.9	31.1
Ru1Pt4	12.12	87.88	8.6	75.3
Pt1Ru1	49.4	50.6	19.7	24.8
Pt1Ru2	66.86	33.14	35.5	19.5
Pt1Ru4	81.15	18.85	56.7	3.4

SI.4 Catalysis with a Pt/CO-Ru/PPP NPs mixture

Catalytic experiments with a mixture of platinum (**Pt/CO**) and ruthenium (**Ru/PPP**) monometallic nanoparticles were performed in order to be compared to the **PtRu** bimetallic systems. For **RuPt** series these experiments were not realized since **Pt/PPP** NPs size is too big to be compared to the respective bimetallic systems.
An equivalent amount of **Pt/CO** and **Ru/PPP** NPs to the **Pt1Ru1** NPs (1mg of **Ru/PPP** and 1mg of **Pt/CO**) and **Pt1Ru2** NPs (2mg of **Ru/PPP** and 1mg of **Pt/CO**) was introduced on the autoclave and the reaction was carried out as indicated in the experimental part (the equivalent **Pt1Ru4** system was not carried out as the **Pt/CO** required mass was to small to be correctly weighed)

Table 2. Cinnamaldehyde hydrogenation with a mixture of monometallic nanoparticles **Ru/PPP and Pt/CO**.

Entry	Catalysts	Time [h]	Conv. [%]	TON	TOF [h^{-1}]	HCAL [%]	HCOL [%]	COL [%]	Acetal [%]
1	**1 Pt/CO +**	2	43	443	221	91	9	0	0
2	**1 Ru/PPP**	4	45	456	114	84	12	0	3
3		6	54	554	92	76	8	10	5
4		22	74	761	34	64	13	17	6
5	**1 Pt/CO +**	2	42	235	117	93	7	0	0
6	**2 Ru/PPP**	4	56	311	78	78	7	14	0
7		6	58	319	53	70	12	18	0
8		22	78	430	19	55	21	23	0

Reaction conditions: cinnamaldehyde (7.5 mmol), isopropanol (50 mL), P_{H2}=20 bar, T=70°C. Yields were determined by GC analysis using nonane (3.7 mmol) as an internal standard. n. d.: not detected.

SI.5 TEM analyses after CAL hydrogenation

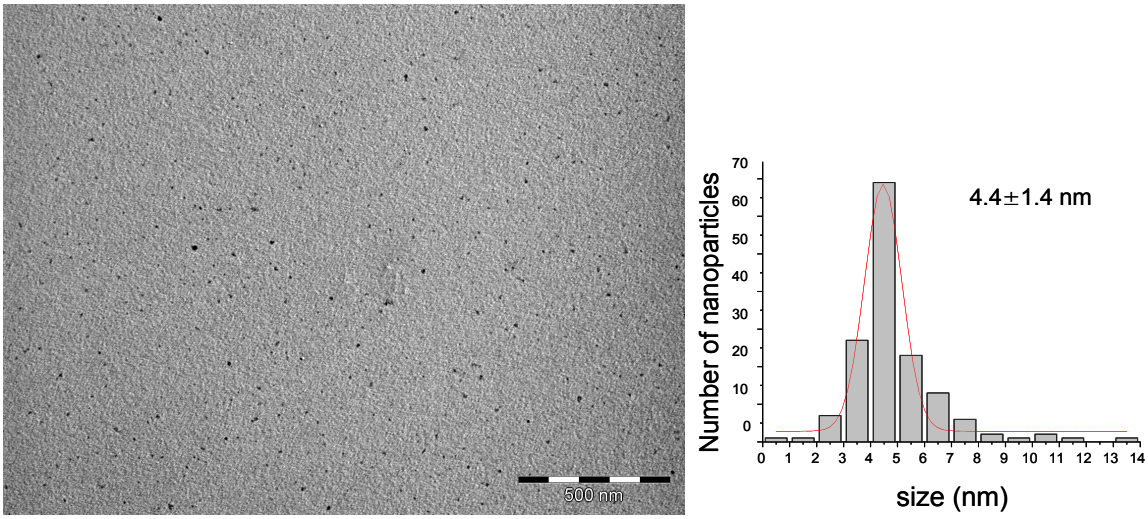


Figure 10. TEM image with the corresponding size histogram of **Ru1Pt1** nanoparticles after CAL hydrogenation.

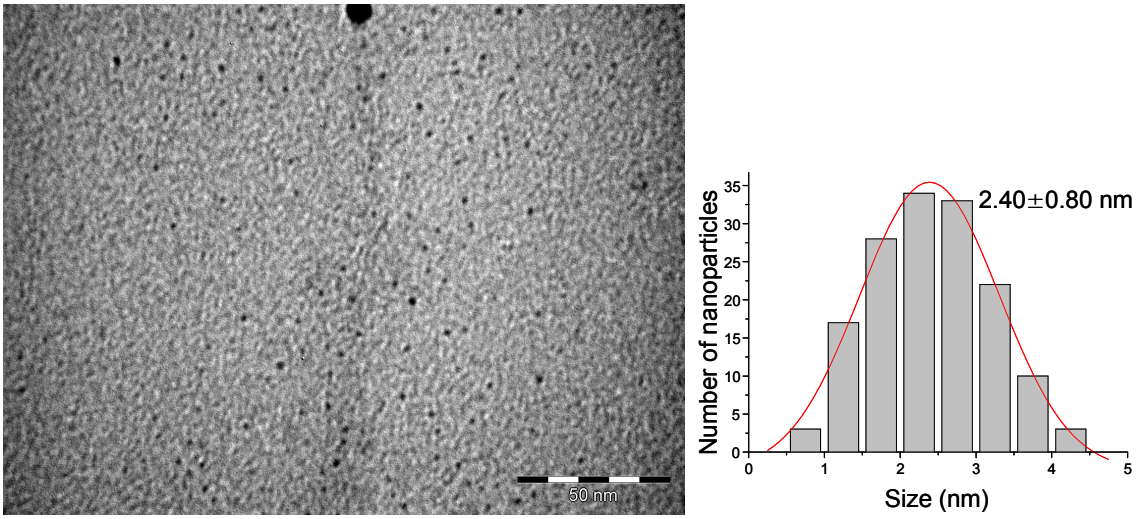


Figure 11. TEM image with the corresponding size histogram of **Ru1Pt2** nanoparticles after CAL hydrogenation.

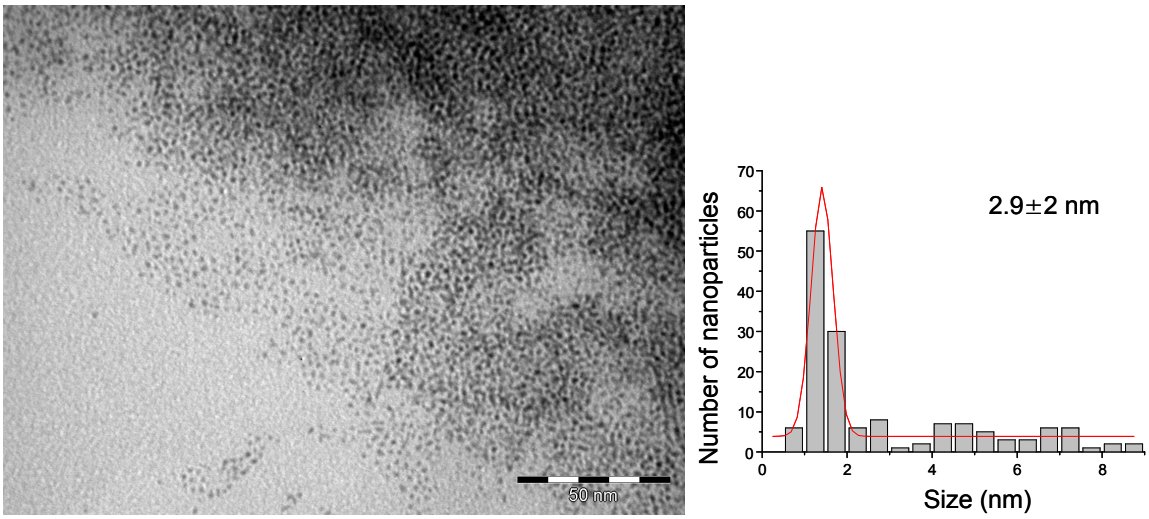


Figure 12. TEM image with the corresponding size histogram of **Ru1Pt4** nanoparticles after CAL hydrogenation.

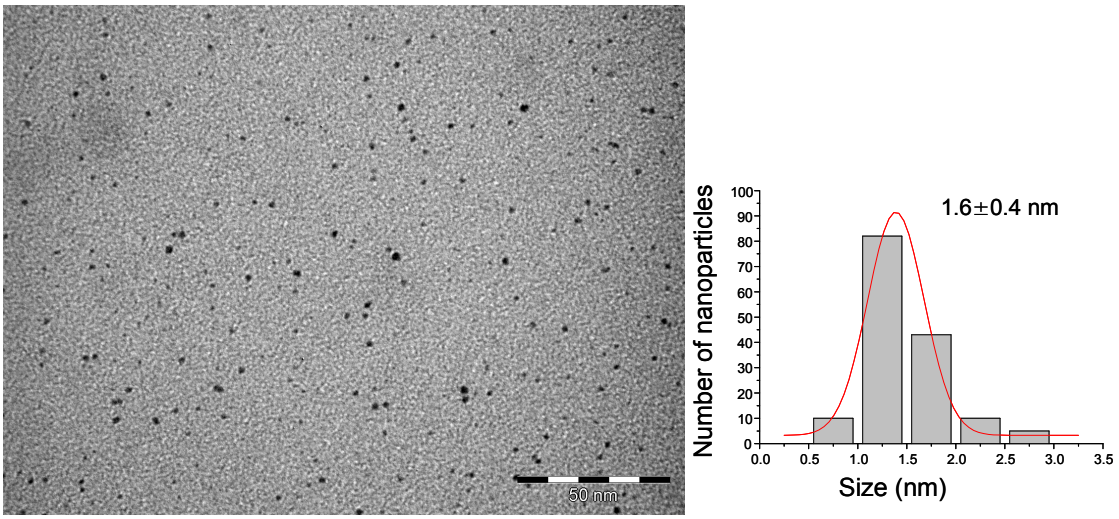


Figure 13. TEM image with the corresponding size histogram of **Pt@Ru** nanoparticles after CAL hydrogenation.

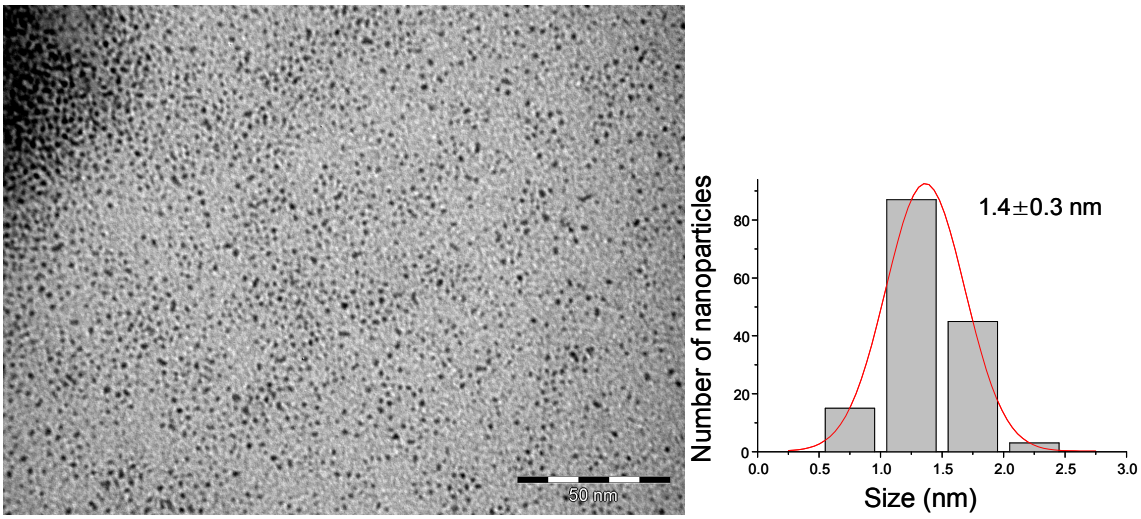


Figure 14. TEM image with the corresponding size histogram of **Pt1Ru1** nanoparticles after CAL hydrogenation.

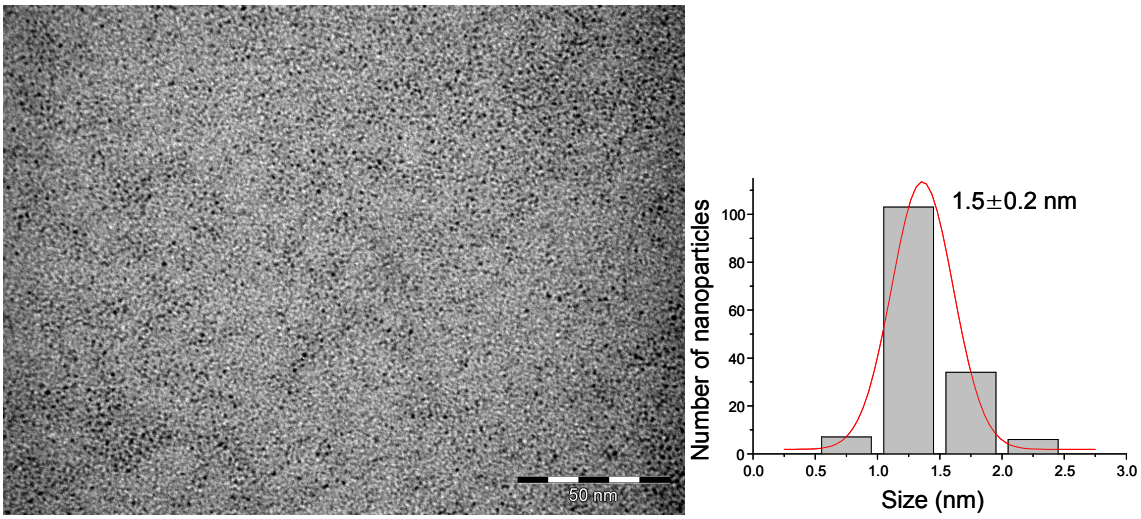


Figure 15. TEM image with the corresponding size histogram of **Pt1Ru2** nanoparticles after CAL hydrogenation.

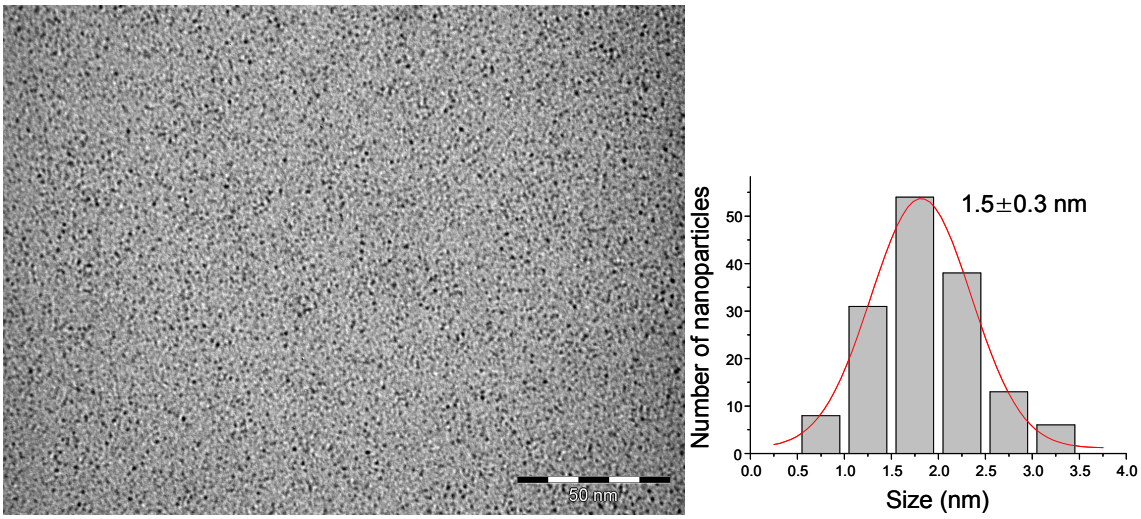


Figure 16. TEM image with the corresponding size histogram of **Pt1Ru4** nanoparticles after CAL hydrogenation.

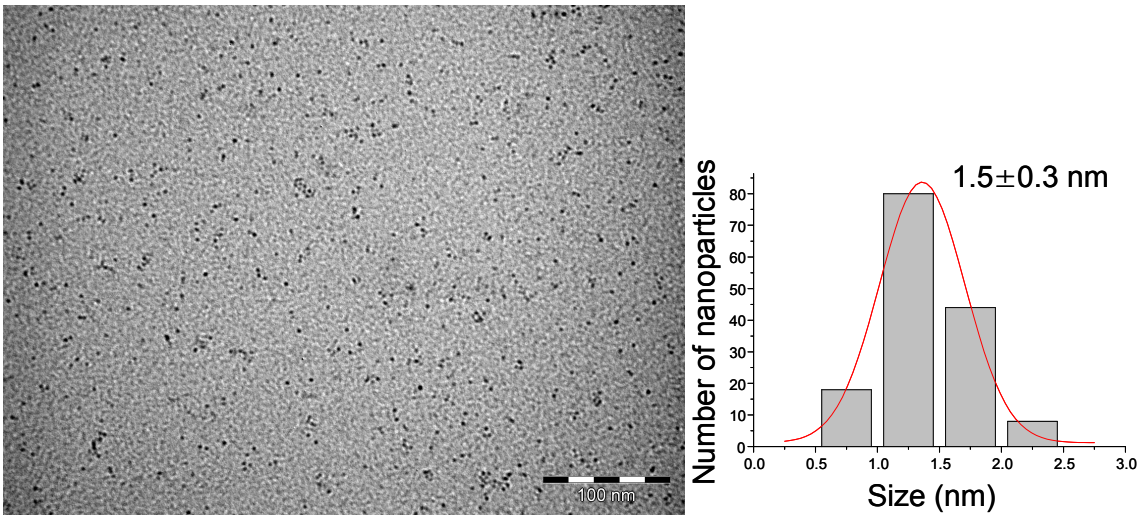


Figure 17. TEM image with the corresponding size histogram of **Ru/PPP** nanoparticles after CAL hydrogenation.

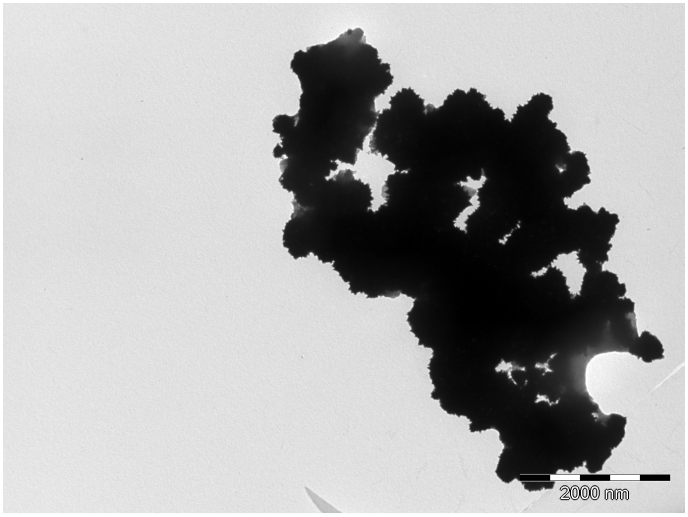


Figure 18. TEM image of **Pt/PPP** particles after CAL hydrogenation.

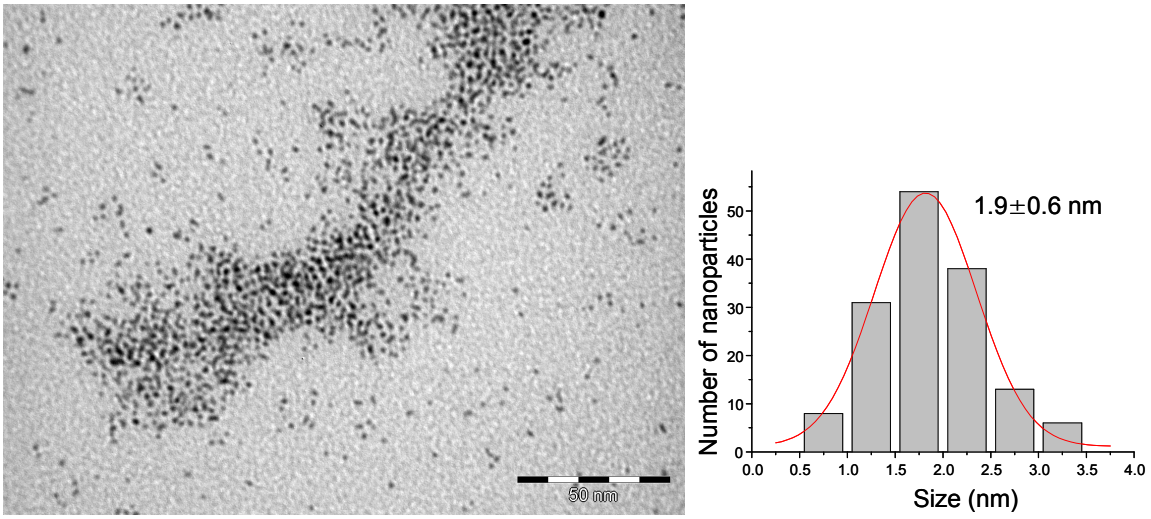


Figure 19. TEM image with the corresponding size histogram of **Pt/CO** nanoparticles.

SI.6 IR analyses

We performed the IR spectra of **PtRu** nanoparticles before CO adsorption (Figure 9 SI). Interestingly, they show a CO band coming from the first step of the synthesis, at 1922 cm^{-1} for **Pt1Ru1**, 1918 cm^{-1} for **Pt1Ru2**, and 1899 cm^{-1} for **Pt1Ru4**. The wavenumber decreased when increasing the ruthenium content. We observed that the CO band resulting from the first step of the NP synthesis is shifted of *ca*. 70 cm^{-1} with respect to the CO band observed when CO is reacted after the synthesis of the NPs, this change on the wave number can be due to: 1) low CO covering on the surface after synthesis *i. e.* decrease of the band frequency, 2) that CO coming from the **Pt/CO** particles occupies different metal sites than the incoming CO and/or 3) this difference could also result from different chemical environments depending on the ligand coordination. In that sense **Pt/CO** nanoparticles showed the same CO band frequency (2020 cm^{-1}) as synthesized or after CO exposure as they do not have any other ligand on the surface and they have not undergone a second step synthesis decreasing the CO covering on the surface.

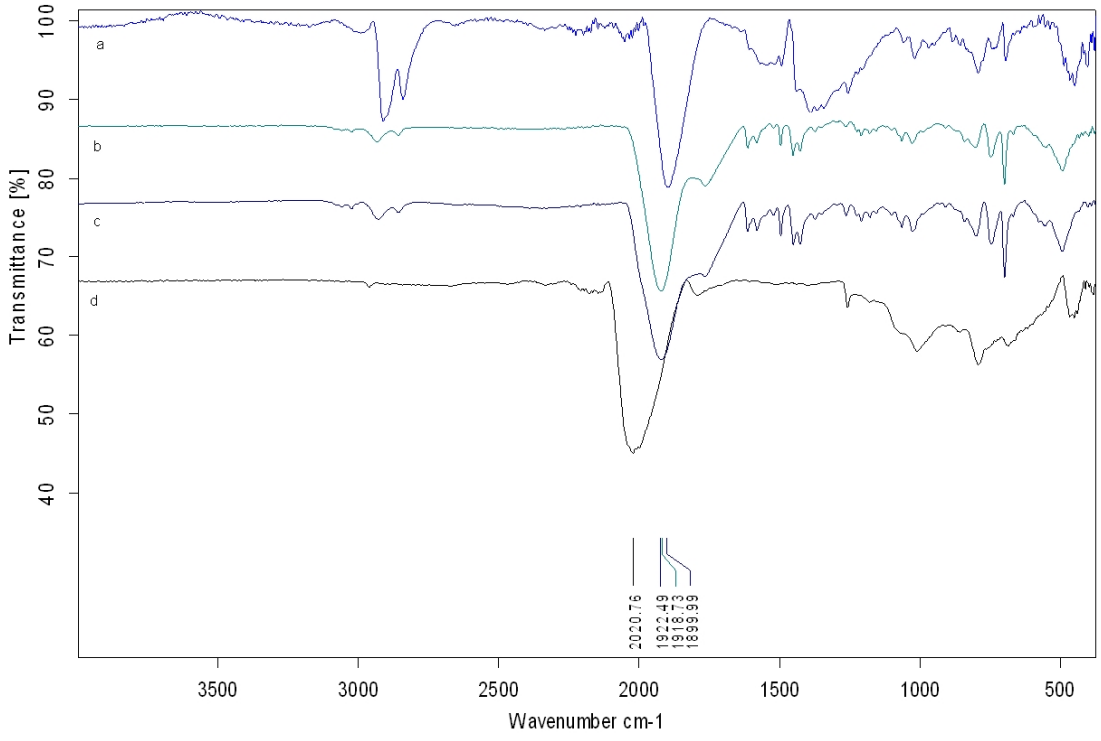


Figure 9. ATR-IR spectra for **PtRu** nanoparticles: a) **Pt1Ru4** (1899 cm^{-1}), b) **Pt1Ru2** (1918 cm^{-1}), c) **Pt1Ru1** (1922 cm^{-1}), and d) **Pt/CO** (2018 cm^{-1}).