

# Electronic Supplementary Information (ESI)

## Beyond Gold: Rediscovering Tetrakis-(Hydroxymethyl)-Phosphonium Chloride (THPC) as an Effective Agent for the Synthesis of Ultra-Small Noble Metal Nanoparticles and Pt-containing Nanoalloys

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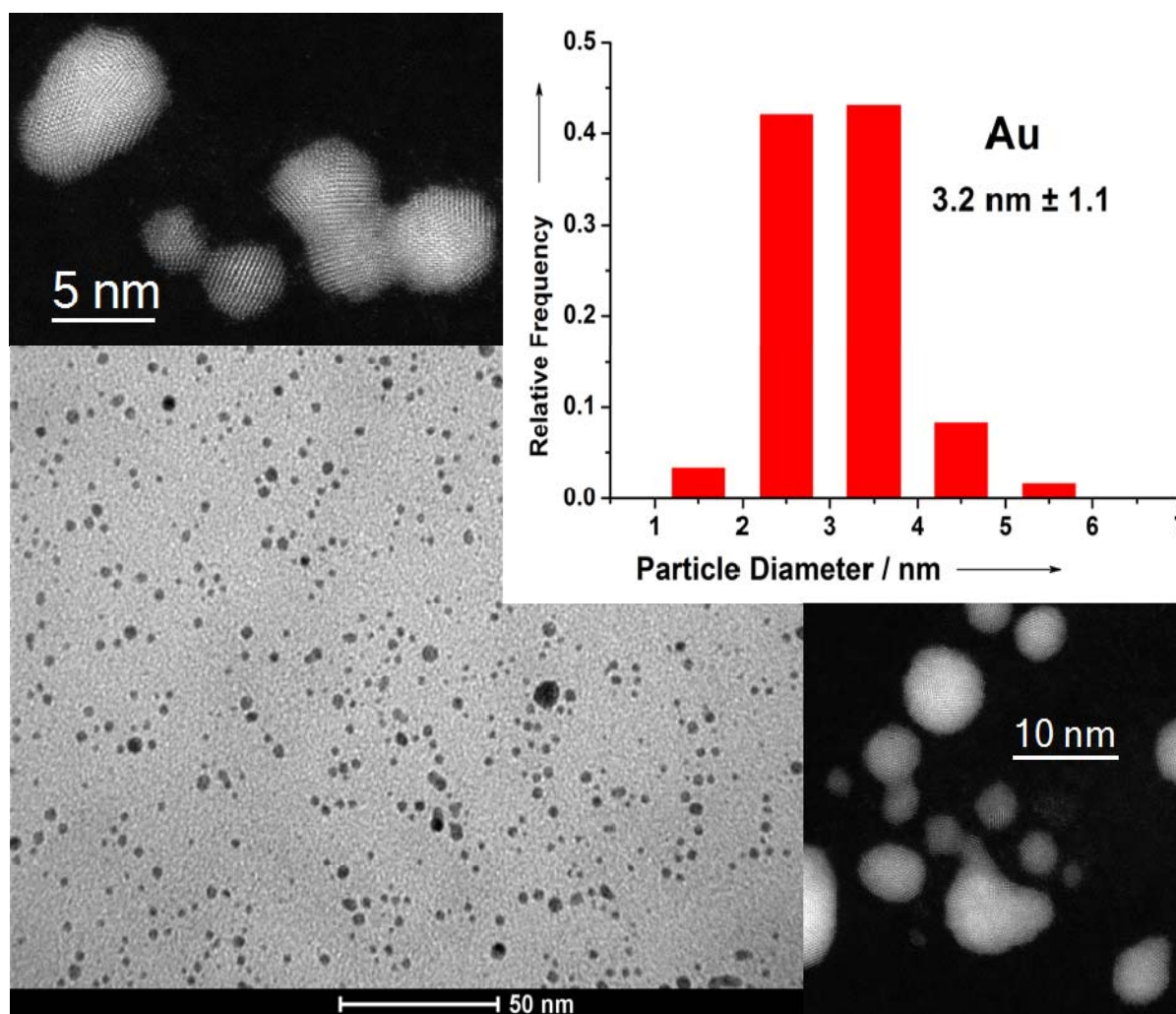
## SECTION S1: EXPERIMENTAL PROCEDURES

### Nanomaterials preparation: molar ratios

Catalyst, ligand and metal precursors molar ratios						
NaOH/THPC	THPC/ Au,Pt,Pd,Ru	Pt/Pd	Pt/Ru	Pt/Rh	Pt/Au	Pt/Pd/Rh
25	3.5	1	1	1	1	1/1/1

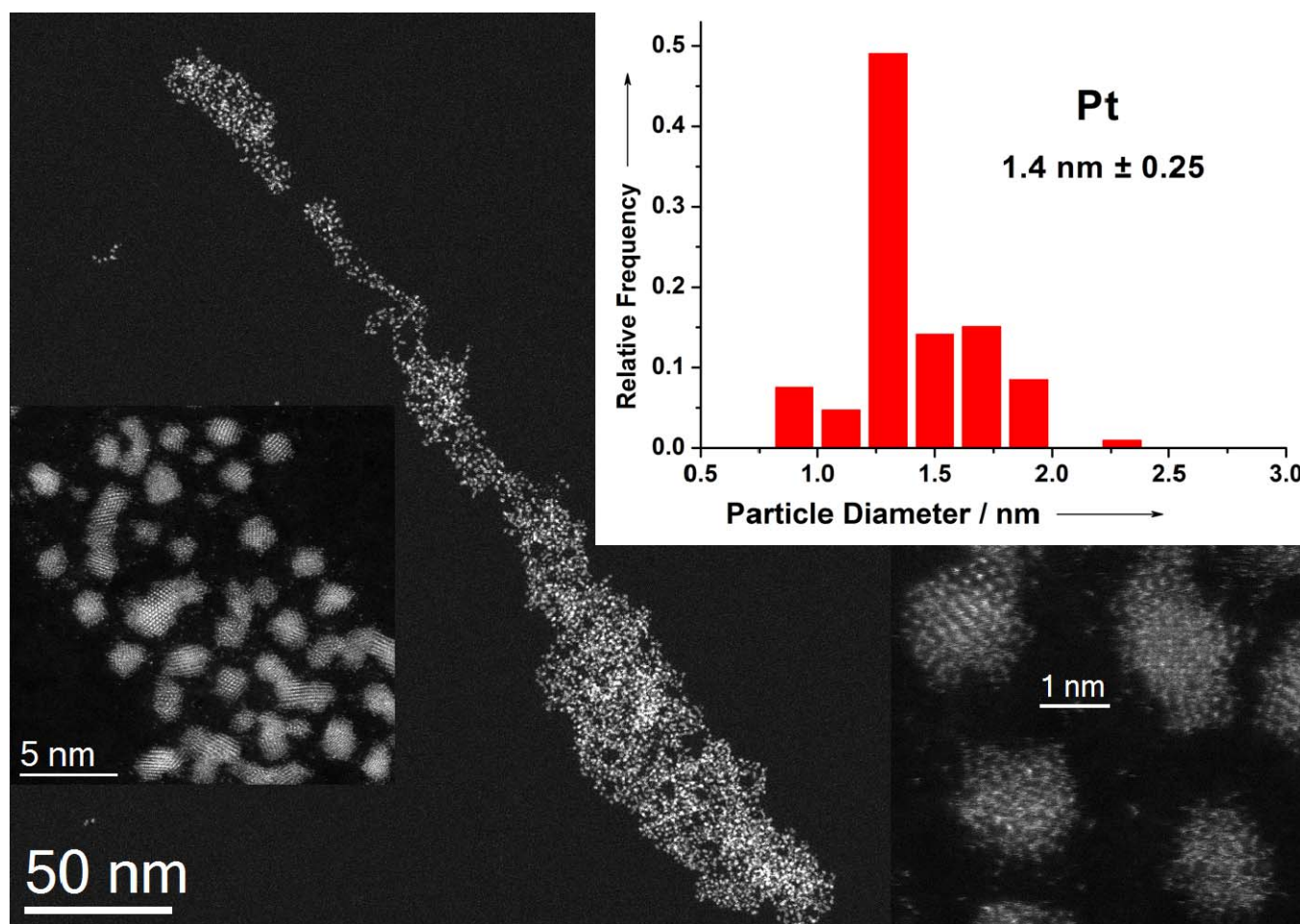
## SECTION S2: CHARACTERIZATION OF MONOMETALLIC NANOPARTICLES

### Gold Nanoparticles



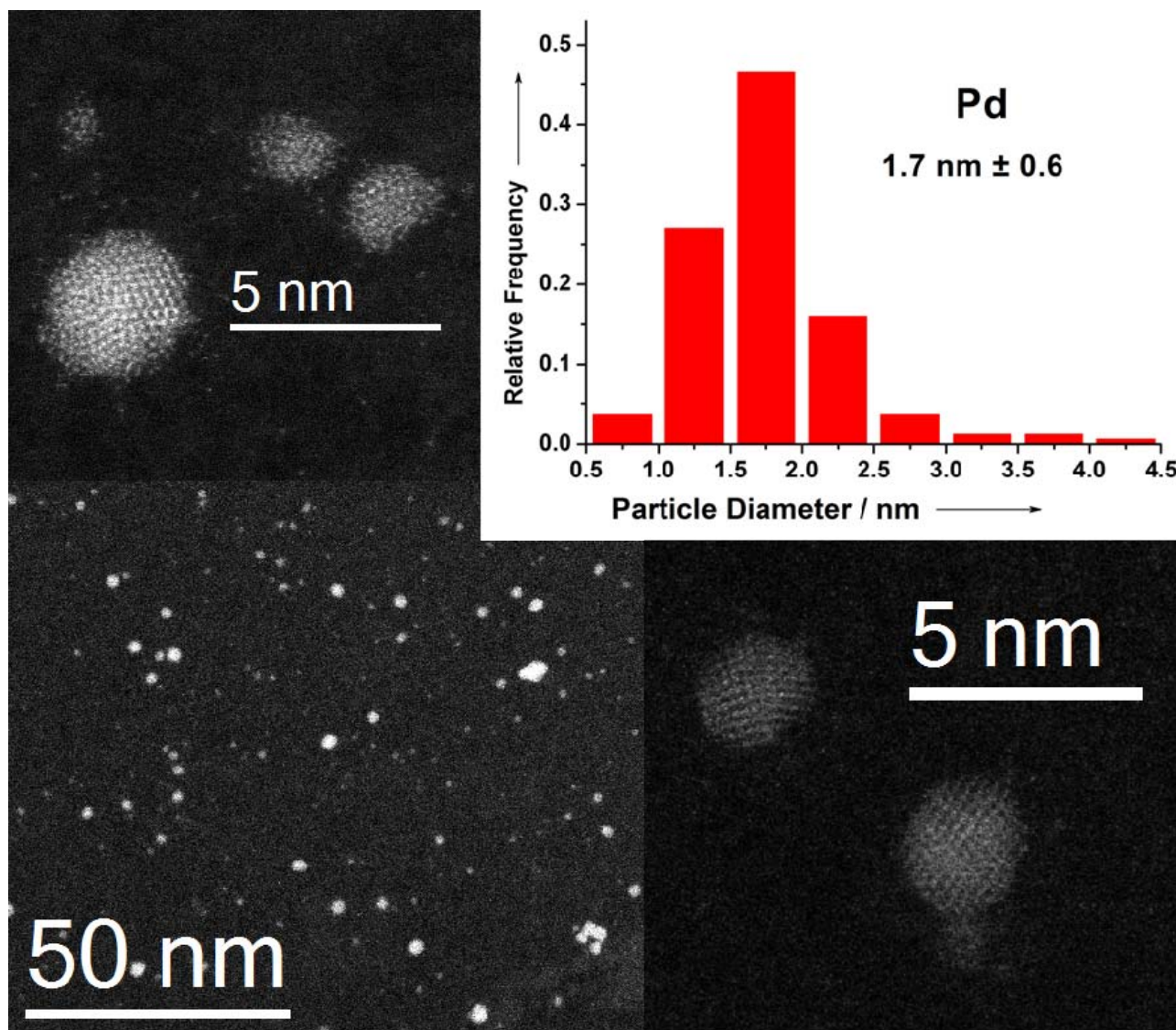
**Figure S1:** Representative HAADF-STEM and TEM images of gold nanoparticles synthesized with THPC. Corresponding particle size distribution for 174 nanoparticles ( $D_{av}$ :  $3.2 \pm 1.1$  nm).

## Platinum Nanoparticles



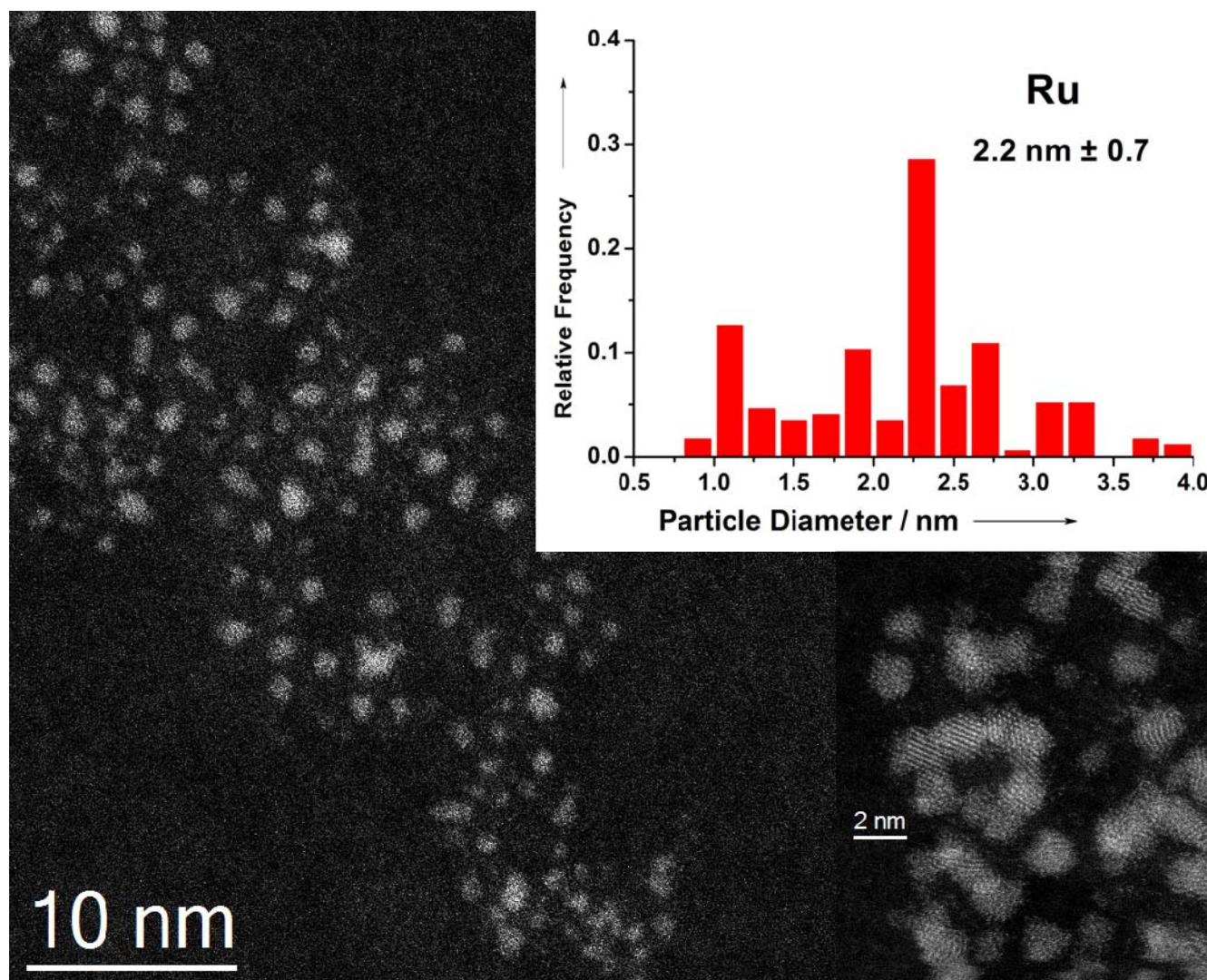
**Figure S2:** Representative HAADF-STEM images of platinum nanoparticles synthesized with THPC. Corresponding particle size distribution for 104 nanoparticles ( $D_{av}$ :  $1.4 \pm 0.3$  nm).

## Palladium Nanoparticles



**Figure S3:** Representative HAADF-STEM images of palladium nanoparticles synthesized with THPC. Corresponding particle size distribution for 162 nanoparticles ( $D_{av}$ :  $1.7 \pm 0.6$  nm).

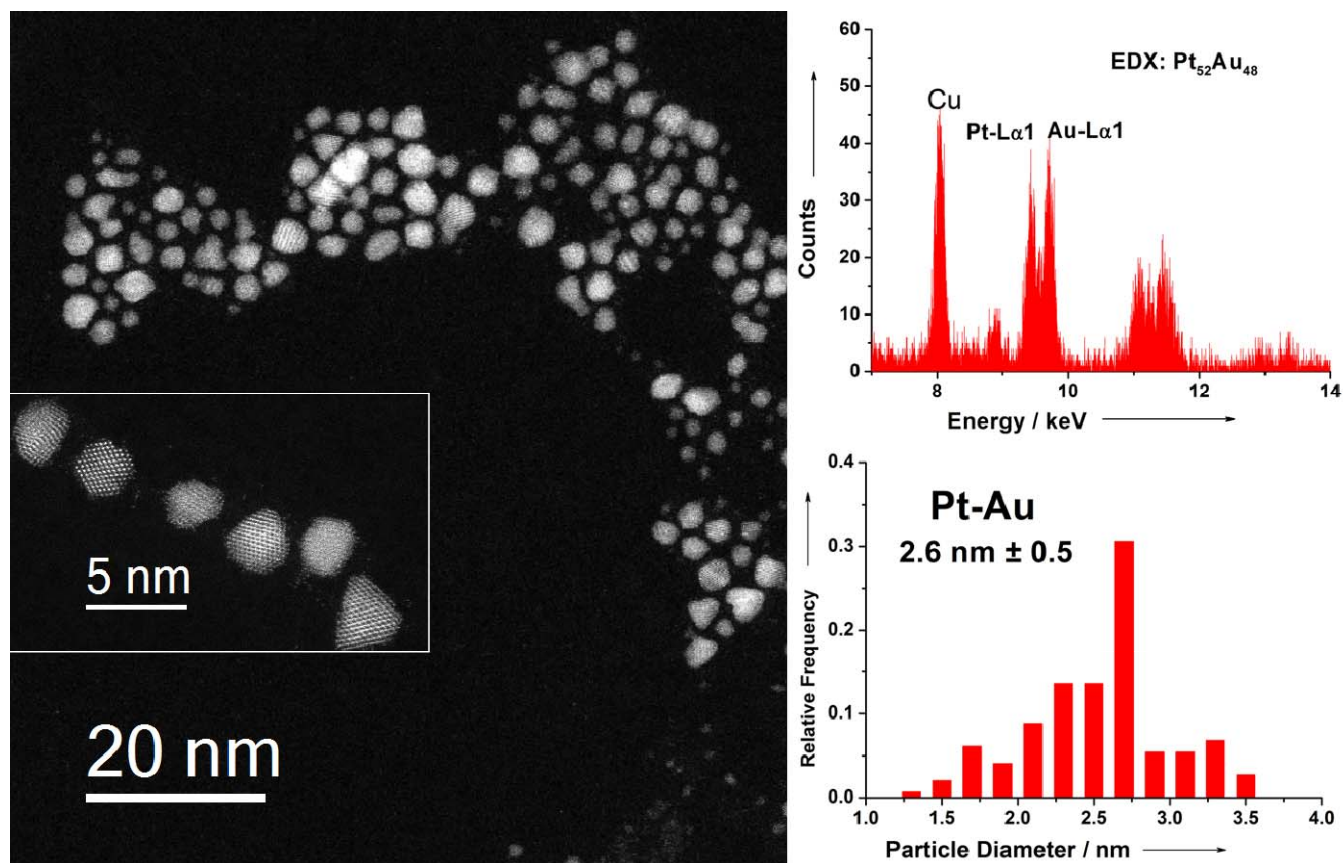
## Ruthenium Nanoparticles



**Figure S4:** Representative HAADF-STEM images of ruthenium nanoparticles synthesized with THPC. Corresponding particle size distribution for 178 nanoparticles ( $D_{av}$ :  $2.2 \pm 0.7$  nm).

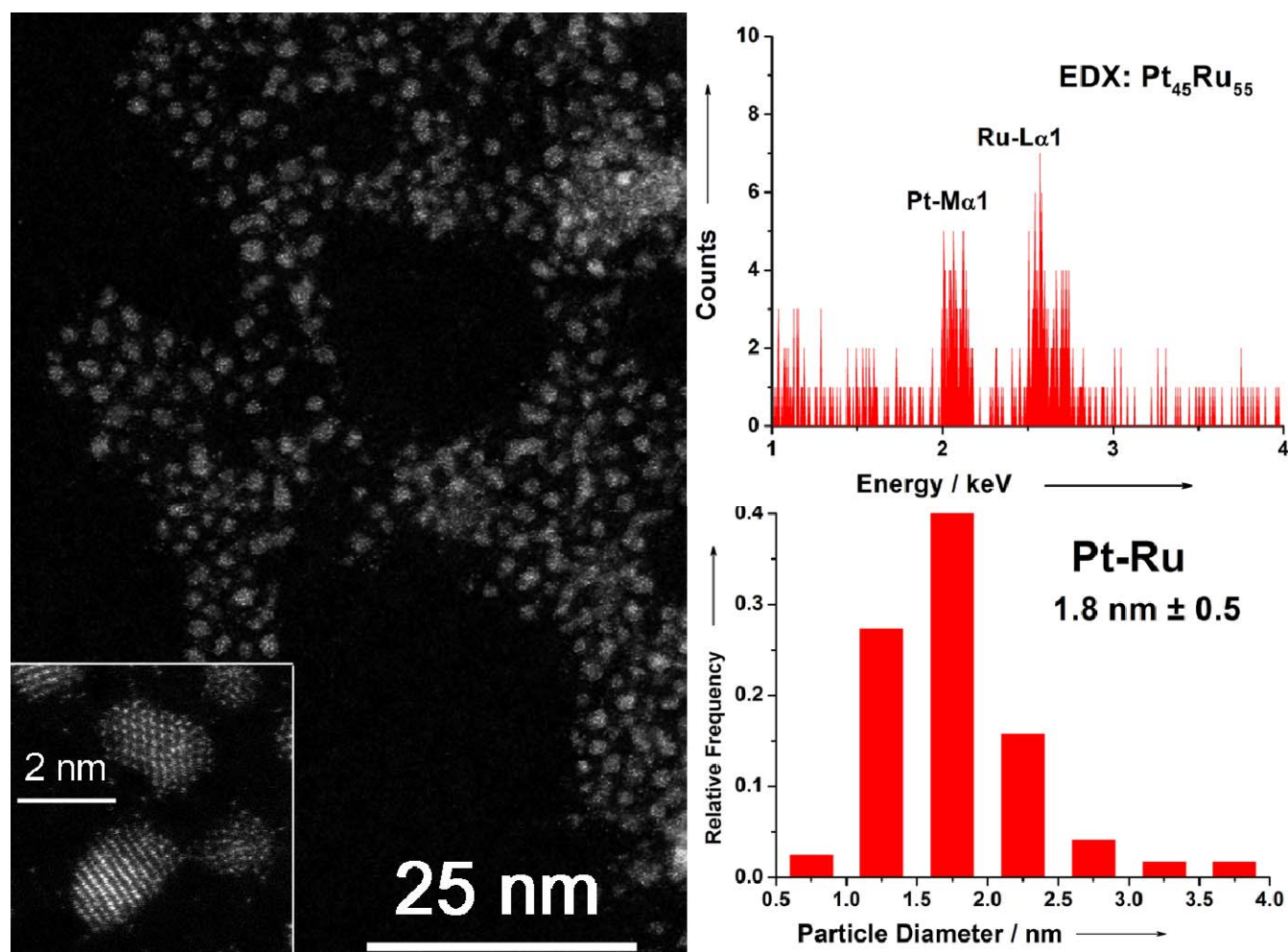
## SECTION S3: CHARACTERIZATION OF BIMETALLIC NANOPARTICLES

### Pt-Au Bimetallic Nanoparticles



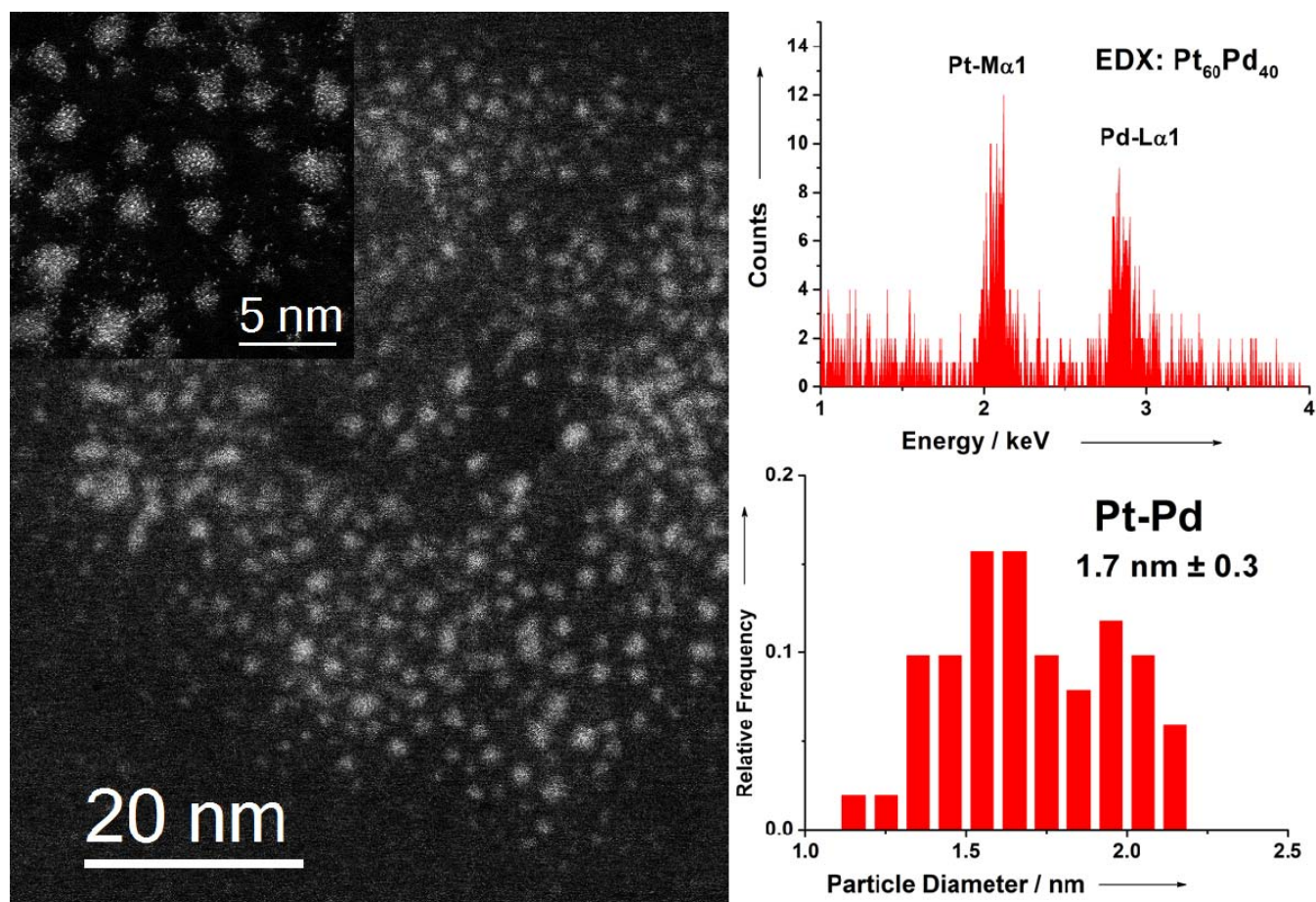
**Figure S5:** Representative HAADF-STEM images and EDX spectrum of Pt-Au bimetallic nanoparticles synthesized with THPC; Corresponding particle size distribution for 212 nanoparticles ( $D_{av}$ : 2.6  $\pm$  0.5 nm); (Average composition: Pt<sub>45</sub>Au<sub>55</sub>).

## Pt-Ru Bimetallic Nanoparticles



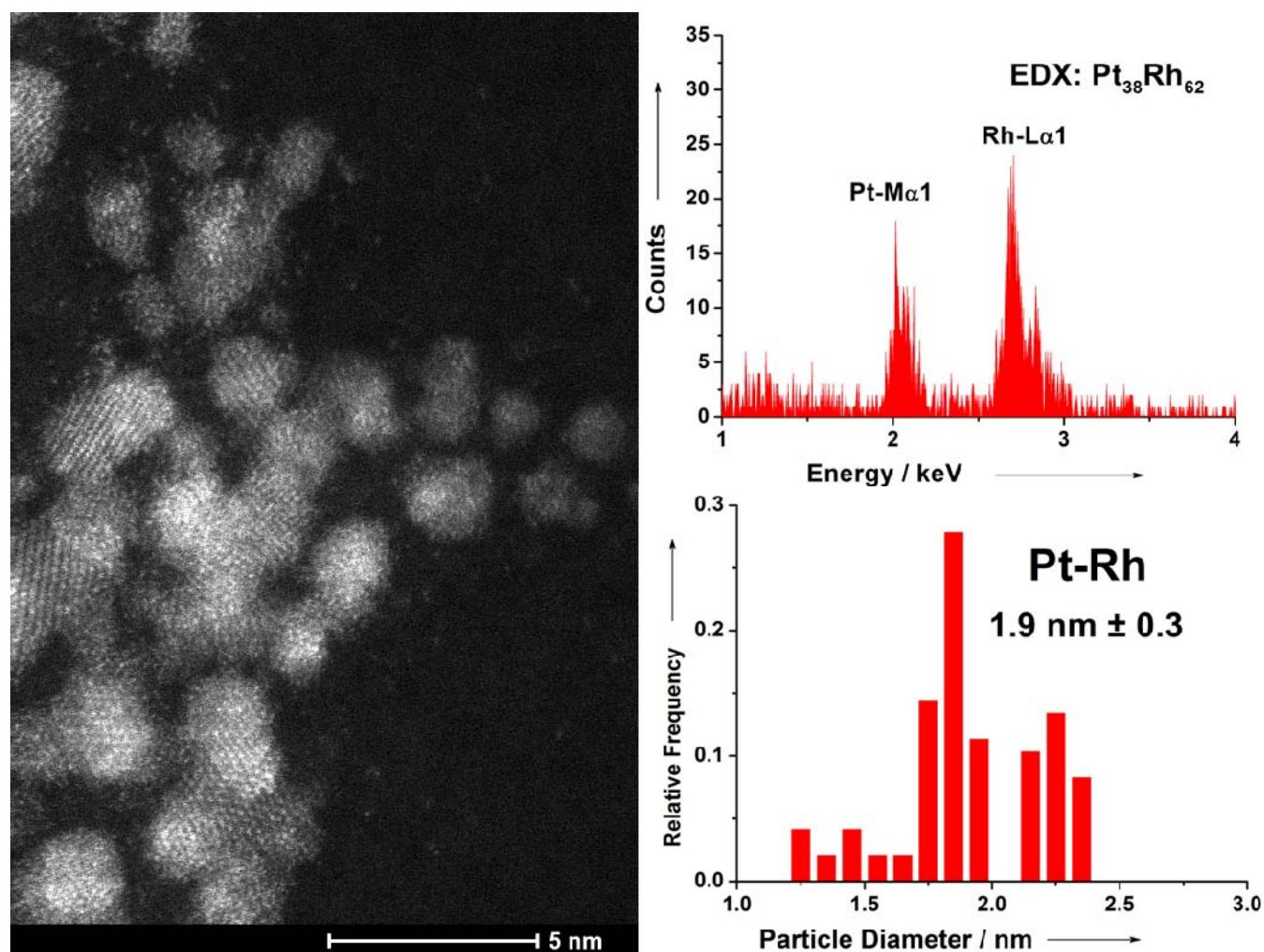
**Figure S6:** Representative HAADF-STEM images and EDX spectrum of Pt-Ru bimetallic nanoparticles synthesized with THPC; Corresponding particle size distribution for 125 nanoparticles ( $D_{av}$ : 1.8  $\pm$  0.5 nm); (Average composition: Pt<sub>40</sub>Ru<sub>60</sub>).

## Pt-Pd Bimetallic Nanoparticles



**Figure S7:** Representative HAADF-STEM images and EDX spectrum of Pt-Pd bimetallic nanoparticles synthesized with THPC; Corresponding particle size distribution for 104 nanoparticles ( $D_{av}$ :  $1.7 \pm 0.3$  nm); (Average composition: Pt<sub>60</sub>Pd<sub>40</sub>).

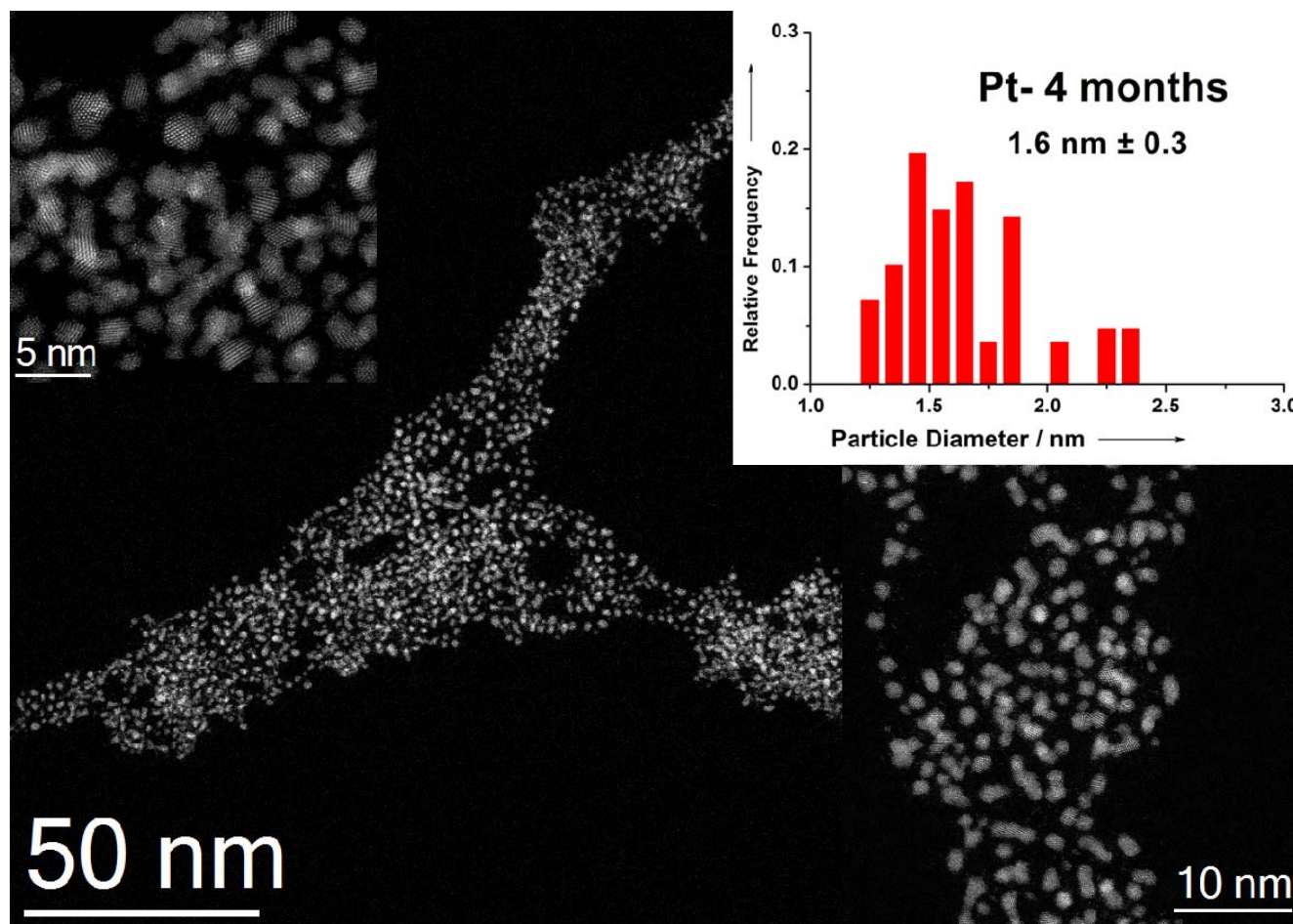
## Pt-Rh Bimetallic Nanoparticles



**Figure S8:** Representative HAADF-STEM images and EDX spectrum of Pt-Rh bimetallic nanoparticles synthesized with THPC; Corresponding particle size distribution for 93 nanoparticles ( $D_{av}$ :  $1.9 \pm 0.3$  nm); (Average composition: Pt<sub>40</sub>Rh<sub>60</sub>).

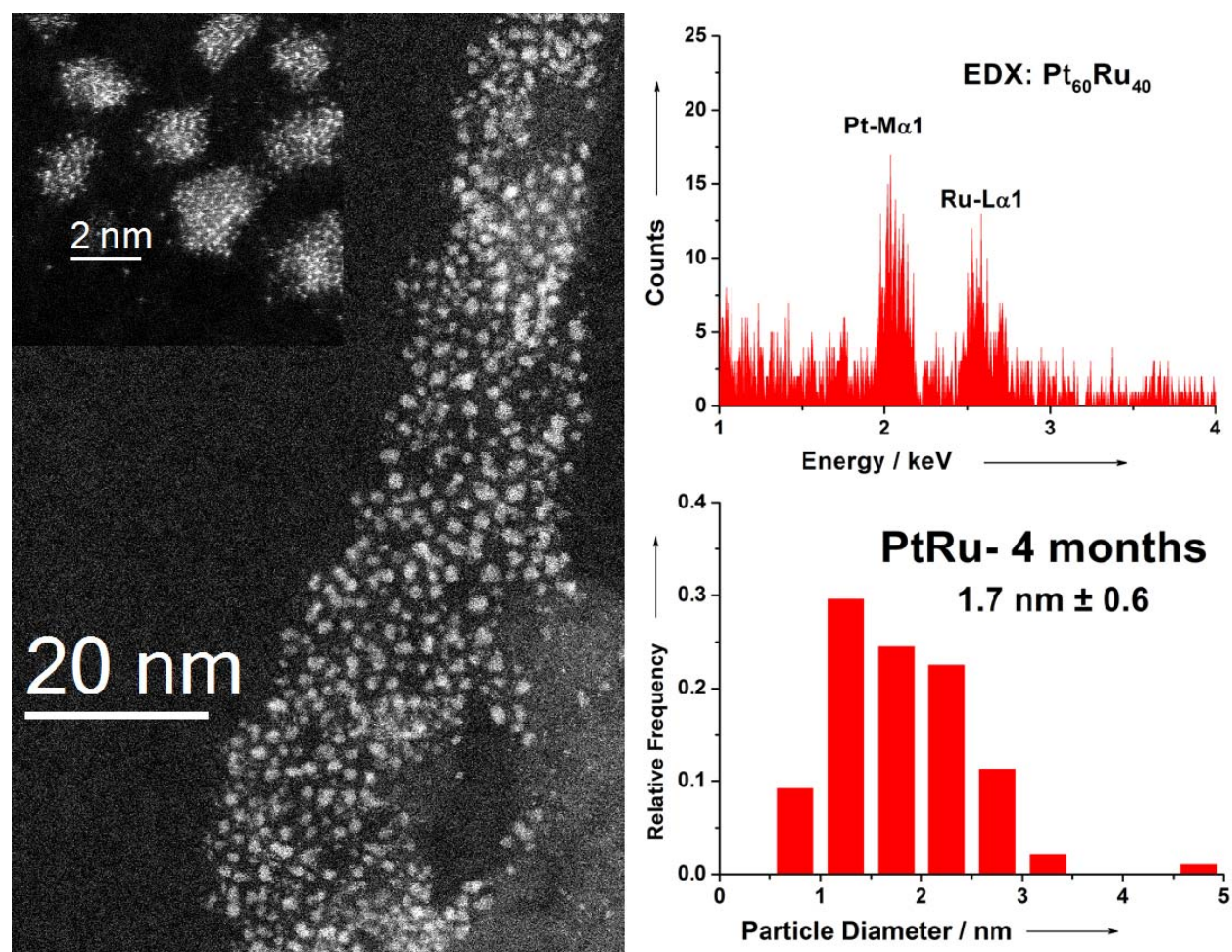
## SECTION S4: CHARACTERIZATION OF DIFFERENT AGED NANOPARTICLES

### Pt Monometallic Nanoparticles (Aged 4 months)



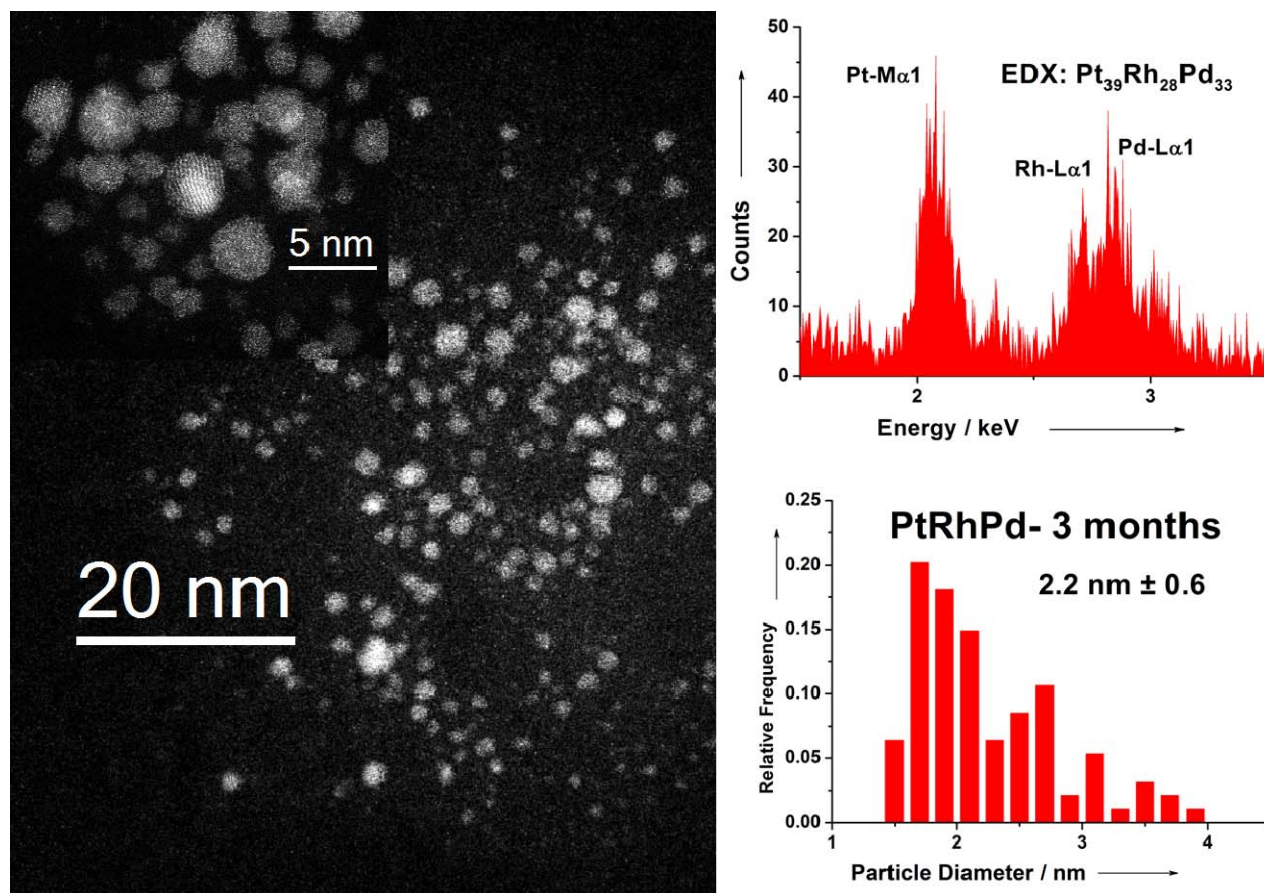
**Figure S9:** Representative HAADF-STEM images of Pt nanoparticles after 4 months of aging; Corresponding particle size distribution for 167 nanoparticles ( $D_{av}$ :  $1.6 \pm 0.3$  nm).

### Pt-Ru Bimetallic Nanoparticles (Aged 4 months)



**Figure S10:** Representative HAADF-STEM images and EDX spectrum of Pt-Ru nanoparticles after 4 months of aging; Corresponding particle size distribution for 105 nanoparticles ( $D_{av}$ :  $1.7 \pm 0.6$  nm); (Average composition: Pt<sub>55</sub>Ru<sub>45</sub>).

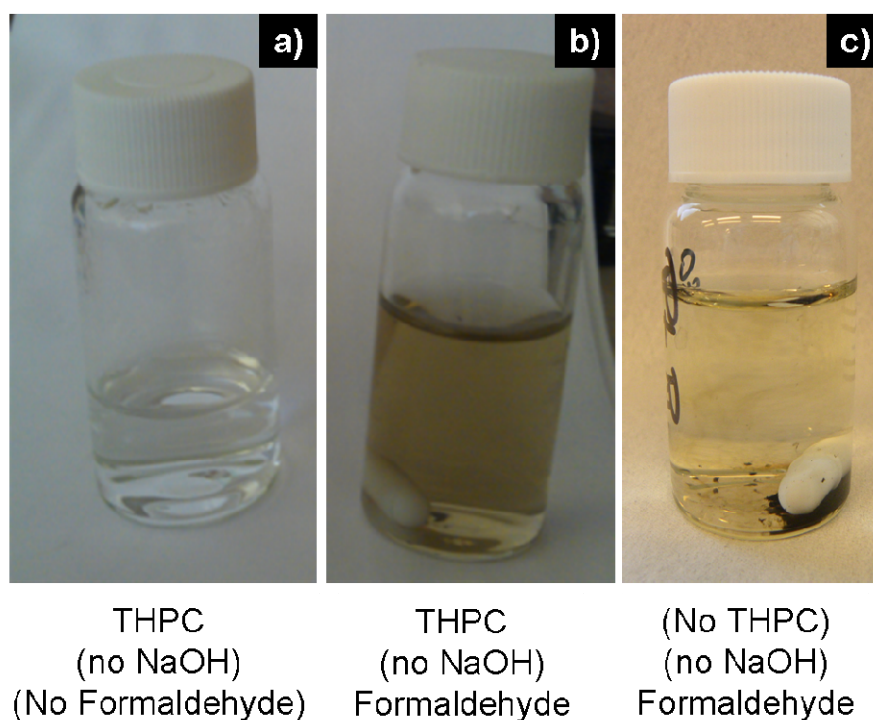
## Pt-Rh-Pd Trimetallic Nanoparticles (Aged 3 months)



**Figure S11:** Representative HAADF-STEM images and EDX spectrum of Pt-Rh-Pd trimetallic nanoparticles after 3 months of aging; Corresponding particle size distribution for 96 nanoparticles ( $D_{av}$ :  $2.2 \pm 0.6$  nm); (Average composition: Pt<sub>42</sub>Rh<sub>29</sub>Pd<sub>29</sub>).

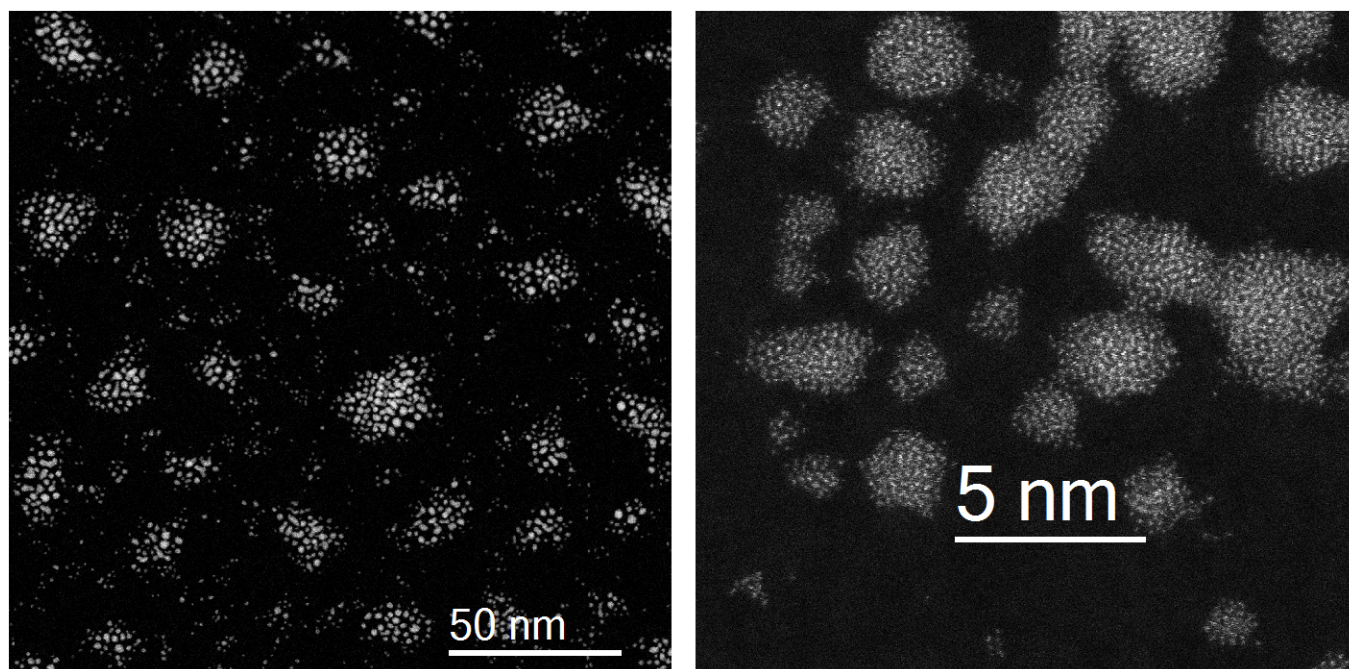
## SECTION S5: CONTROL EXPERIMENTS TO EVALUATE THE ROLE OF THPC

The present control experiments have a three-fold objective: i) evaluation of the role of THPC in the absence of basic conditions; ii) evaluation of the addition of formaldehyde as reducing agent; iii) evaluation of the role of THPC as stabilizer agent in the presence of added formaldehyde. In a first vial, 100  $\mu\text{L}$  of  $\text{HPtClO}_4$  8 wt. % solution was added to 3 mL of distilled water in a glass vial under magnetic stirring. Meanwhile, 333  $\mu\text{L}$  of a 65 mM THPC was added, but no NaOH was subsequently added in order to test the influence of alkaline media in the activation of the reducing power of THPC. After 4 days of stirring no evidence of nanoparticle formation and darkening of the solution could be observed (Figure S12a). In a second vial, the same sequence of reagents was added but after several minutes, a 12 mL formaldehyde solution (calculated from the stoichiometric decomposition of THPC in an alkaline media, assuming a single mol of formaldehyde formed) was injected in a continuous mode at a flow rate of 3  $\mu\text{L}/\text{min}$ . The reaction vial was capped with a septum to prevent any formaldehyde evaporation. The reaction mixture was kept at room temperature for 4 days, wrapping an aluminium foil to preserve the reaction mixture from photothermal decomposition and the formation of Pt nanoparticles was detected by visual inspection of the vial (see Figure S12b) and the STEM analysis of the colloidal solution (Figure S13). Furthermore, the stabilizing role of THPC could be corroborated with a third experiment where all the sequence of reactants was identical to vial-2 except for the absence of the phosphine compound. In this case, the Pt nanoparticles were formed due to the reducing power of formaldehyde but without the presence of THPC, interparticle sintering could not be prevented and big agglomerates were formed after 1-2 days of reaction (Figure S12c).



**Figure S12:** Digital micrographs of vials corresponding to different control experiments for the synthesis of Pt NPs:

- a) Pt salt precursor and THPC without NaOH or formaldehyde;
- b) Pt salt precursor reduced in the presence of formaldehyde with THPC as stabilizer (without NaOH);
- c) Pt NPs reduced in the presence of formaldehyde showing tendency to aggregation and precipitation in the absence of THPC.



**Figure S13:** STEM images corresponding to the Pt NPs formed with formaldehyde and THPC (Control experiment b).