

Supporting information

Insight into the formation mechanism of PtCu alloy nanoparticles

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Table S1 List of solvents and reagents used

Name	Purity	CAS #	Company	Catalogue #
Platinum(II) acetylacetonate	98%	15170-57-7	Strem Chemicals	78-1400
Copper(II) sulfate	98%	7758-98-7	Strem Chemicals	93-2957
Polyvinylpyrrolidone ($M_w \sim 55,000$ Da)		9003-39-8	Sigma Aldrich	856568
Ethylene glycol	99%	107-21-1	Alfa Aesar	A11591
Copper(II) acetylacetonate	98%	13395-16-9	Strem Chemicals	93-2968
Copper(II) acetate	97%	142-71-2	Strem Chemicals	93-2988
Chloroplatinic acid hexahydrate	99.9%	18497-13-7	Strem Chemicals	78-0200
Acetone (CP grade)	99.5%	67-64-1	Bio-lab LTD	010302
Hexanes (CP grade)	95%	110-54-3	Bio-lab LTD	083002
Ethanol (CP grade)	96%	64-17-5	Bio-lab LTD	052102
Chloroform (stab. amylene, CP grade)	99%	67-66-3	Bio-lab LTD	030802

Web page of Strem Chemicals: <http://www.strem.com/catalog/>

Web page of Sigma Aldrich: <http://www.sigmaaldrich.com>

Web page of Alfa Aesar: <http://www.alfa.com/en/go160w.pgm?srchtyp=product>

Web page of Bio-lab LTD: <http://www.biolab-chemicals.com>

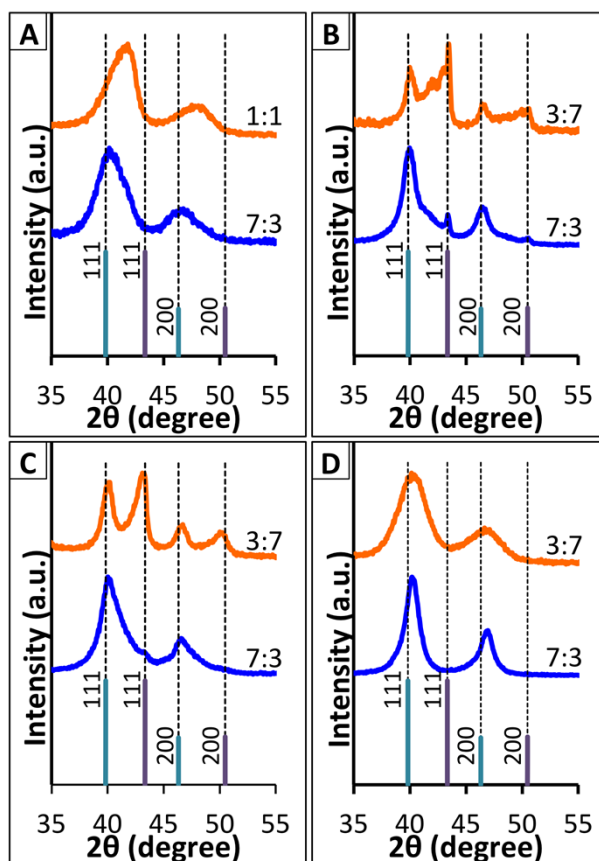


Fig. S1 The effect of the metal precursors. XRD of NPs prepared with: (A) Pt(acac)₂ and CuSO₄. (B) Pt(acac)₂ and Cu(acac)₂. (C) Pt(acac)₂ and Cu(ac)₂. (D) H₂PtCl₆ and Cu(acac)₂. The initial molar ratios are indicated next to the patterns. Blue vertical lines represent the fcc-Pt phase and purple vertical lines represent the fcc-Cu phase.

Two different molar ratios (7:3 and 1:1) of Pt(acac)₂ and CuSO₄ precursors were reacted at 197 °C. The XRD analysis of the formed alloy is presented in Fig. S1A. The initial Pt:Cu ratio of 7:3, gives uniform peaks positioned between the Pt and Cu diffraction lines at 40.35° and 46.6°. The lattice constant corresponding to the (111) peak position is 3.87 Å. The composition of the alloy as calculated by using Vegard's law is 84:16 Pt:Cu.

When the lower Pt:Cu initial ratio (1:1) was used, the diffraction peaks still appeared between the Pt and Cu diffraction lines (41.8° and 47.95°). However, the peak was not uniform, but rather tilted. This suggests that more than one alloy was formed, with different compositions. The TEM images obtained from these syntheses are presented in Fig. S2.

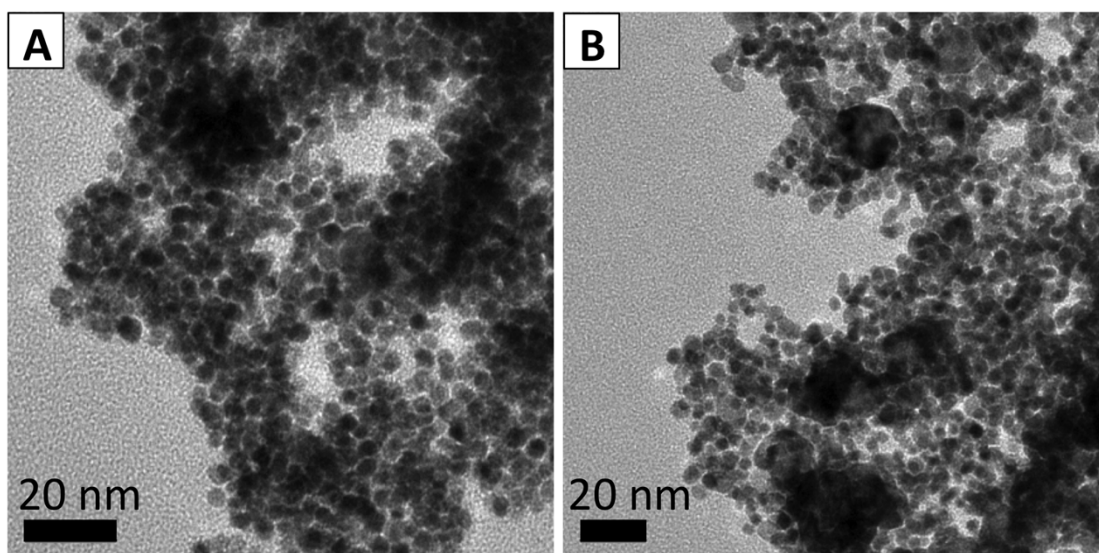


Fig. S2 TEM images of PtCu NPs prepared with $\text{Pt}(\text{acac})_2$ and CuSO_4 at different initial Pt:Cu molar ratios: (A) 7:3. (B) 1:1.

Fig. S1B shows $\text{Pt}(\text{acac})_2$ and $\text{Cu}(\text{acac})_2$ at 7:3 and 3:7 molar ratios after a reaction at 197 °C. For both ratios a uniform alloy wasn't formed. In both XRD patterns there are several peaks positioned between the Pt and Cu diffraction lines. For the 7:3 initial ratio, one Pt-rich alloy peak is present next to the Pt diffraction line and one Cu peak is positioned on the Cu diffraction line. An alloy with intermediate composition between the Pt-rich alloy and the Cu was also formed, as indicated by the shoulder next to the Pt-rich peak, at higher 2θ values. The 3:7 initial ratio results in an XRD pattern with multiple peaks positioned between the Pt and Cu diffraction lines. The most pronounced peaks are of Pt-rich alloy positioned next to the Pt diffraction line, and a strong Cu peak. Between these two peaks, there are several low-intensity peaks, indicating several different PtCu alloys with various compositions. The TEM images the products (Fig. S3) show non-uniform shape and size distribution. In both samples, small spherical particles, as well as large faceted particles were formed. At the lower Pt:Cu ratio (3:7), large particles (>50nm) can also be observed. These results are consistent with the multiple peaks in the XRD.

Fig. S3 TEM images of PtCu NPs prepared with $\text{Pt}(\text{acac})_2$ and $\text{Cu}(\text{acac})_2$ at different initial Pt:Cu molar ratios: (A) 7:3. (B) 3:7.

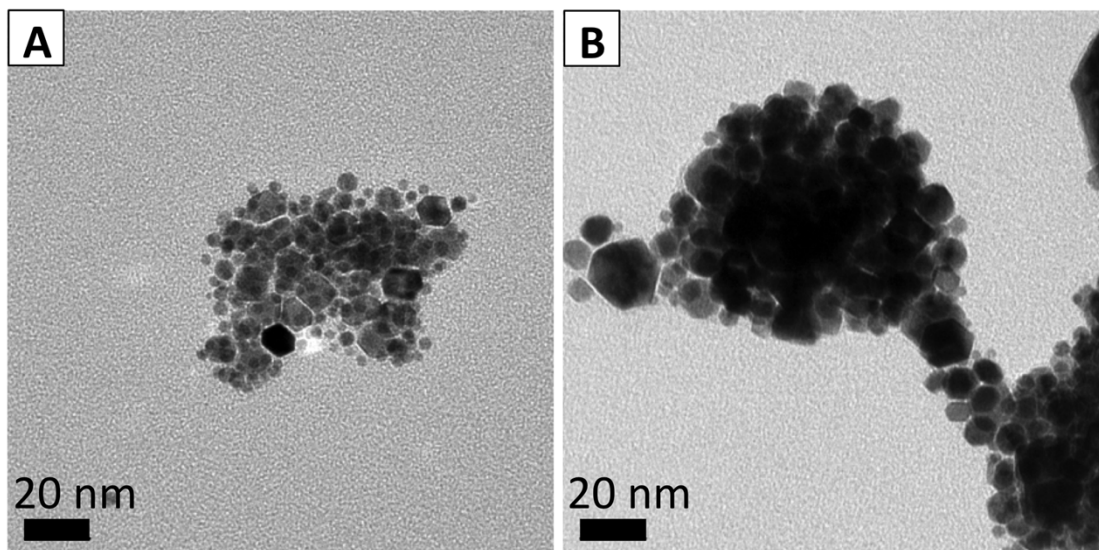


Fig. S1C shows the XRD analysis of a synthesis using $\text{Pt}(\text{acac})_2$ and $\text{Cu}(\text{ac})_2$ precursors at 197 °C. When the 7:3 Pt:Cu initial ratio was used, one pronounced non-uniform peak appeared next to the Pt diffraction line, indicating the formation of Pt-rich alloys. In addition, a Cu peak at low intensity is also observed. However, when 3:7 Pt:Cu initial ratio was used, two non uniform peaks were formed. One is positioned next to the Pt diffraction line, indicating the formation of Pt-rich alloys. The second is positioned next to the Cu diffraction line, indicating the formation of Cu-rich alloys. In the TEM results (Fig. S4), non-uniform NPs are seen for both ratios. Small and large (>50 nm) NPs are present in both samples. The TEM images support the XRD analysis, in which non-uniform compositions are present. Furthermore, there is a difference in the NP shape between the syntheses. At 7:3 Pt:Cu ratio the NPs are spherical and faceted, while at 3:7 Pt:Cu ratio there is a mixture of faceted and concave NPs.

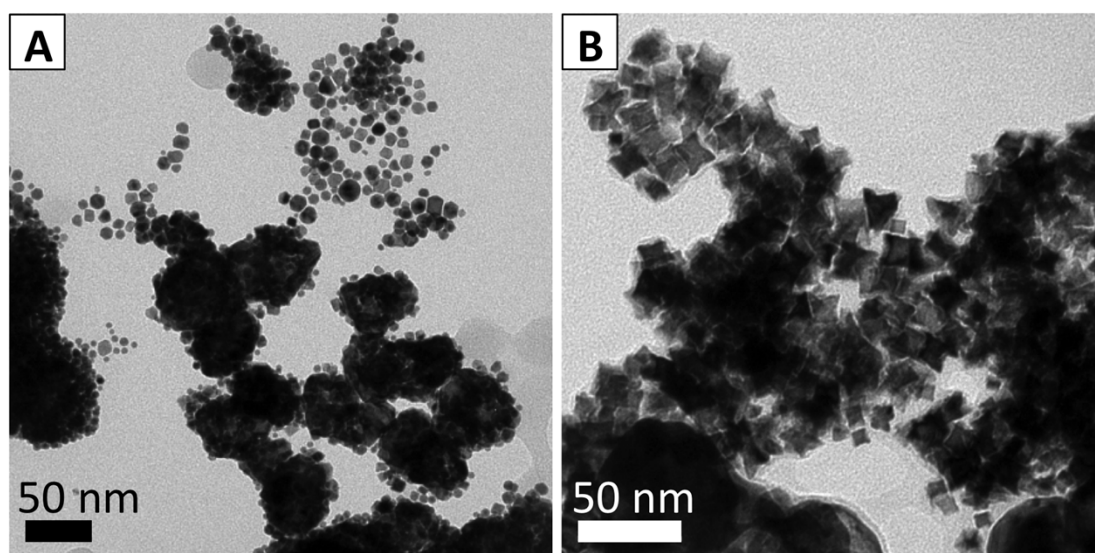


Fig. S4 TEM images of PtCu NPs prepared with $\text{Pt}(\text{acac})_2$ and $\text{Cu}(\text{ac})_2$ at different initial Pt:Cu molar ratios: (A) 7:3. (B) 3:7.

A 197 °C reaction of H_2PtCl_6 and $\text{Cu}(\text{acac})_2$ precursors at 3:7 and 7:3 initial molar ratios, resulted in uniform XRD peaks (Fig. S1D). For both ratios, the peaks are positioned between the Pt and Cu diffraction lines, indicating the formation of one uniform alloy. When 7:3 Pt:Cu initial ratio was used, the (111) and (200) peaks are positioned at 40.15° and 46.85° , respectively. Using Bragg's law gives a lattice constant of $d_{111}=3.89 \text{ \AA}$, which corresponds to 90:10 (Pt:Cu). When 3:7 Pt:Cu initial ratio is used, the (111) and (200) peaks appear at 40.2° and 46.65° , respectively. These peaks are practically at the same position, meaning that the alloy's composition did not change due to the precursor ratio variation. The TEM images of both samples (Fig. S5) present non-uniform shape and at 7:3 (Pt:Cu) initial ratio, also non-uniform size.

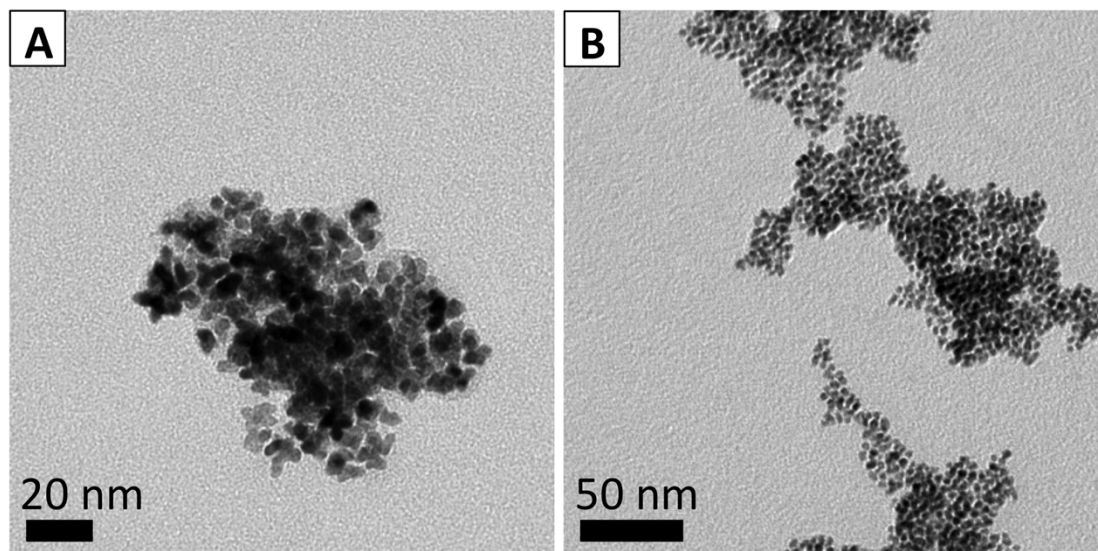


Fig. S5 TEM images of PtCu NPs prepared with H_2PtCl_6 and $\text{Cu}(\text{acac})_2$ at different initial Pt:Cu molar ratios: (A) 7:3. (B) 3:7.

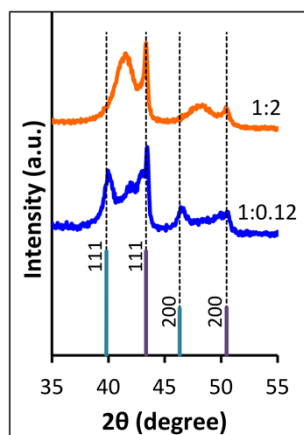


Fig. S6 Studying the effect of PVP concentration at 197 °C. XRD of NPs prepared with 3:7 initial molar ratios of $\text{Pt}(\text{acac})_3$ and $\text{Cu}(\text{acac})_2$. The $[\text{M}]:[\text{PVP}]$ ratios are indicated next to the patterns.

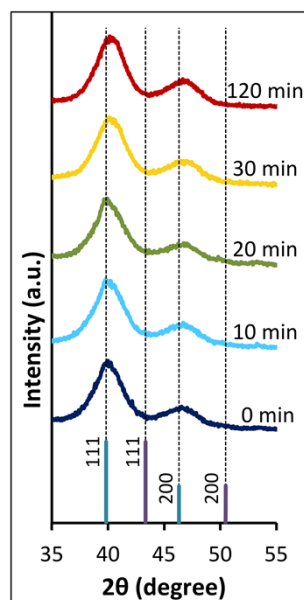


Fig. S7 Studying the evolution in time of PtCu NPs. XRD of NPs prepared with 3:7 initial molar ratio of H_2PtCl_6 and $\text{Cu}(\text{acac})_2$ at 180 °C. Termination times are indicated next to the patterns.

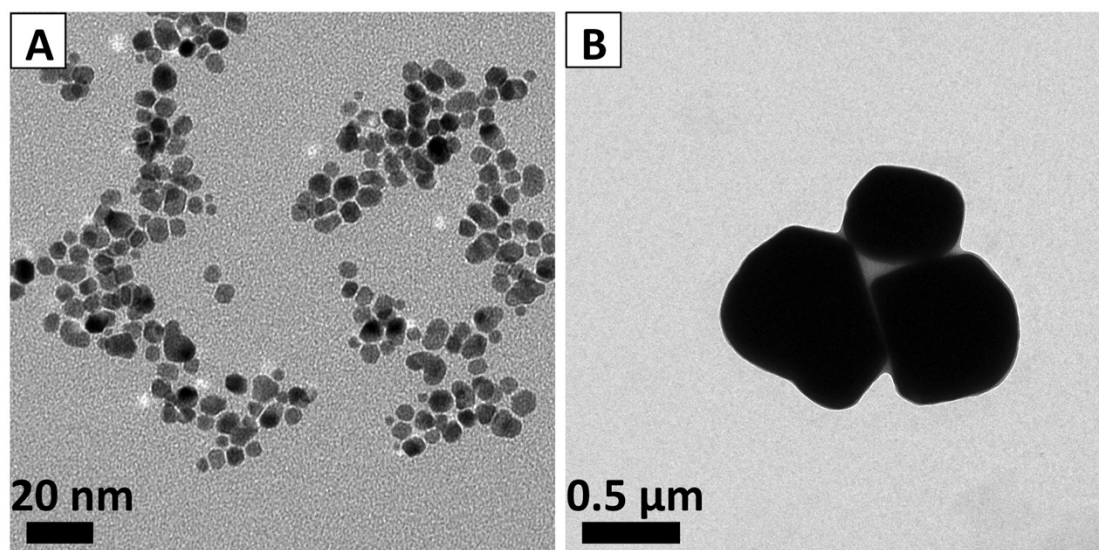


Fig. S8 TEM images of pure metallic NPs. (A) Pt NPs prepared using $\text{Pt}(\text{acac})_3$ (B) Cu NPs prepared using $\text{Cu}(\text{acac})_2$.

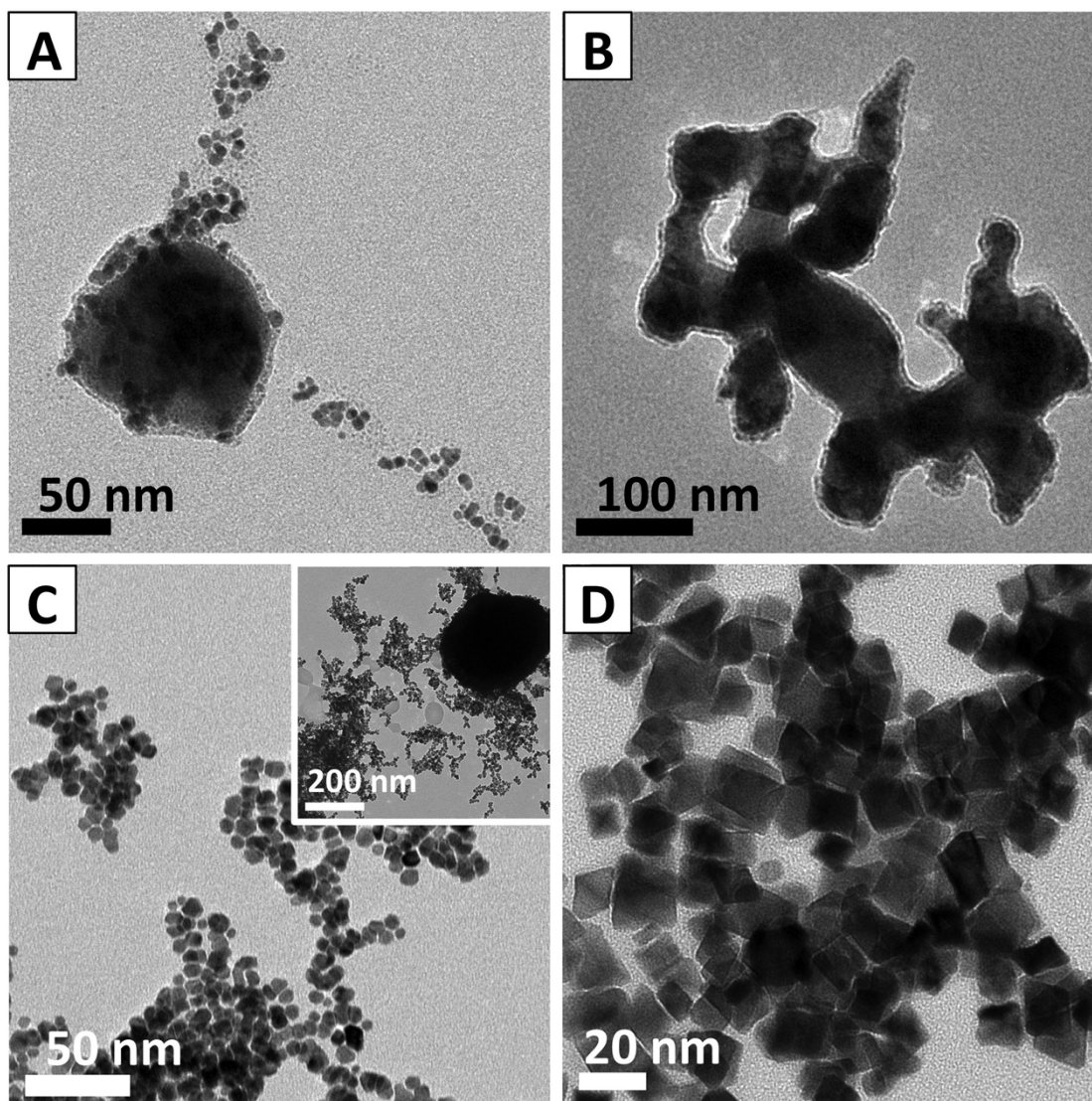


Fig. S9 TEM image of the products obtained for reactions in which $\text{Pt}(\text{acac})_3$ and $\text{Cu}(\text{acac})_2$ were added at different stages. (A) Pt and Cu NPs were formed separately and then heated together at 180 °C. (B) Pt NPs were formed first, and $\text{Cu}(\text{acac})_2$ was added to the washed particles. Cu NPs were formed first and $\text{Pt}(\text{acac})_3$ was added to (C) washed Cu NPs. Inset: low-magnification showing also a Cu NP. (D) unwashed Cu NPs.