

Crystallinity-induced shape evolution of Pt-Ag nanosheets from branched nanocrystals

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Experimental Details

Regents: Pt(acac)₂, AgNO₃, HAuCl₄·xH₂O, PdCl₂, RhCl₃·xH₂O, Cu(acac)₂, Co(acac)₂, poly(vinylpyrrolidone) (PVP; Mw 8000), were purchased from Alfa Aesar Co.Ltd, and Ni(NO₃)₂, KI, tris (hydroxymethyl) aminomethane, HCHO solution (37 wt%), formamide, and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals were analytical grade and used as received without any purification for the Synthesis of Pt-Ag Nanosheets and Pt-Ag-Cu Tetrapods.

Synthesis of Pt-Ag nanosheets: Nanosheets synthesis were carried out by two-step method. In the first step a mixture of 50 mg tris (hydroxymethyl) aminomethane and 200 mg PVP was dissolved in 2 mL HCHO solution and transferred to Teflon-lined stainless steel autoclave which was heated at 200°C for 3 hours. After that the autoclave was cooled down at room temperature. We washed the gel with acetone. After washing we centrifuged the gel like material then dried at 70°C. In the second step a homogeneous solution of 0.01mmol Pt(acac)₂, 0.01mmol AgNO₃, 0.06 g KI and 0.03 g ascorbic acid was prepared in 2 ml formamide solvent and pour into 12 ml Teflon-lined stainless steel autoclave along with gel which was prepared in the first step, and kept the autoclave in oven at 130°C for 3 h. Final product was obtained after washing by using acetone.

Synthesis of Pt-Ag-Cu tetrapods: The synthesis procedure and experimental conditions for Pt-Ag-Cu tetrapods were same as the nanosheets, except that, we added Cu(acac)₂ precursor in the second step for tetrapods.

Characterization:

Transmission electron Microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) were recorded on a HITACHI H-7700 TEM with an accelerating voltage of 100 kV, and FEI Tecnai G2 F20 S-Twin high-resolution TEM equipped with energy dispersive spectrometer (EDS) analyses at 200 Kv. The samples for HRTEM analysis were prepared by dropping ethanol dispersion of samples onto 300-mesh molybdenum grids.

X-ray diffraction (XRD): XRD patterns were measured with a Bruker D8-advance X-ray powder diffractometer operated at 40 KV voltage and instrument run at a scan rate of 0.02 deg / s in the angle range of 5° to 90° and the wave length of the incident radiation was $\lambda = 1.5418 \text{ \AA}$.

X-ray photoelectron spectroscopy (XPS): XPS measurements were conducted on a scanning X-ray microprobe (Quantera SXM, ULVAC-PHI. INC) operated at 250 kV, 55 eV with monochromated Al K α radiation.

ICP-MS: Elemental analysis of the samples was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, Thermo Fisher).

Electrochemical Tests: Cyclic voltammetry (CV) measurements were carried out using a CHI650D electrochemical analyzer (CHI Instrument, USA) at 298 K in a three electrode electrochemical cell in which Pt wire was used as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a glassy carbon (GC) electrode as the working electrode. The potentials were given with respect to SCE. The GC electrode was prepared by polishing with Al₂O₃ paste, and dried after washing with ethanol and deionized water, before use. The catalysts ink was prepared by mixing a weighed amount of carbon black with Pt-Ag nanosheets, Pt-Ag-Cu tetrapods and Nafion (Alfa Aesar, 0.5 wt%, 1.5 μL) in water and sonicated for 1 h to

obtain a homogeneous solution. The resultant Solution was loaded gradually on the GC electrode by using a micro syringe with the same loading of 8 μL and dried in the air for some time. Catalysts concentration was determined by ICP-OES. Electrolyte was prepared by bubbling N_2 in a solution prepared from analytical grade reagents (0.5 M H_2SO_4 and 0.25 M HCOOH) and deionized water. CV measurements were performed under N_2 at room temperature, and potential was scanned from -0.2 to 1.0 V (vs. saturated calomel electrode, SCE) at a sweep rate of 50 mVs^{-1} . The electrochemical surface area (ECSA) of each sample was estimated by CV measurements carried out in freshly prepared nitrogen-saturated 0.5 M H_2SO_4 solution, and the potential was scanned from -0.24 to 0.1V (vs. SCE) at a sweep rate of 50 mV s^{-1} .

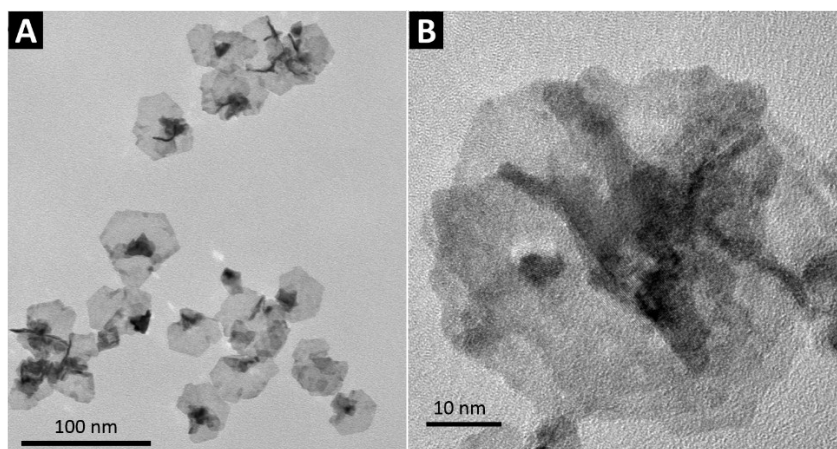


Figure S1 (A) TEM and (B) HRTEM image of Pt-Ag nanosheet at 130°C for 3h.

Analyses of the nanosheets using TEM (fig S1.A) and HRTEM (fig S1.B). As nanosheets were formed through the shape transformation of Pt-Ag nanocrystals, and at 5 min reaction time Pt-Ag alloy transferred into multipods (Tripods, Y-shaped and tetrapods), and further into nanosheets at 3 hour reaction time. The dark areas (fig S1 A, B) are the overlapped nanosheets formed during phase transformation.

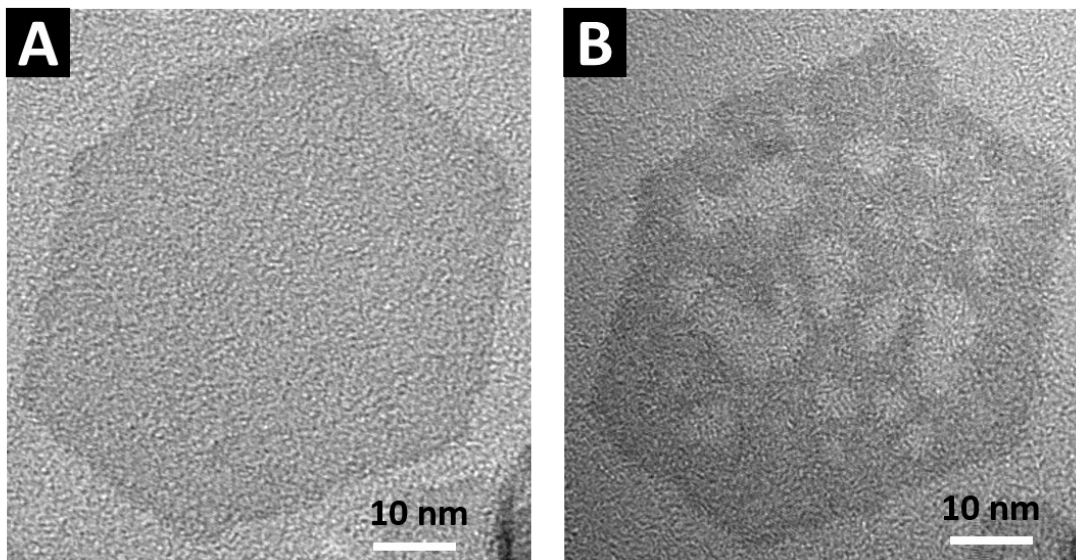


Figure S2 (A). HRTEM images of ultrathin hexagonal Pt-Ag nanosheets taken at low electron-beam intensity and (B) Taken at strong electron radiations.

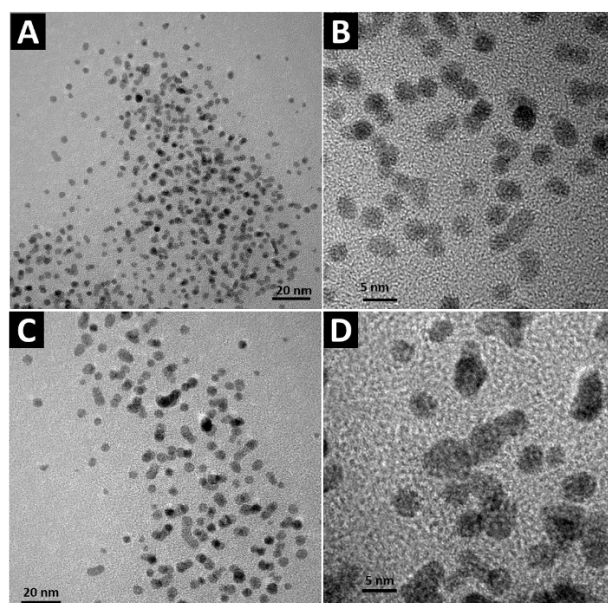


Figure S3. TEM and HRTEM image of (A, B) Pt-Ag and (C, D) Pt-Ag-Cu nanostructures at 130 °C for 2 min.

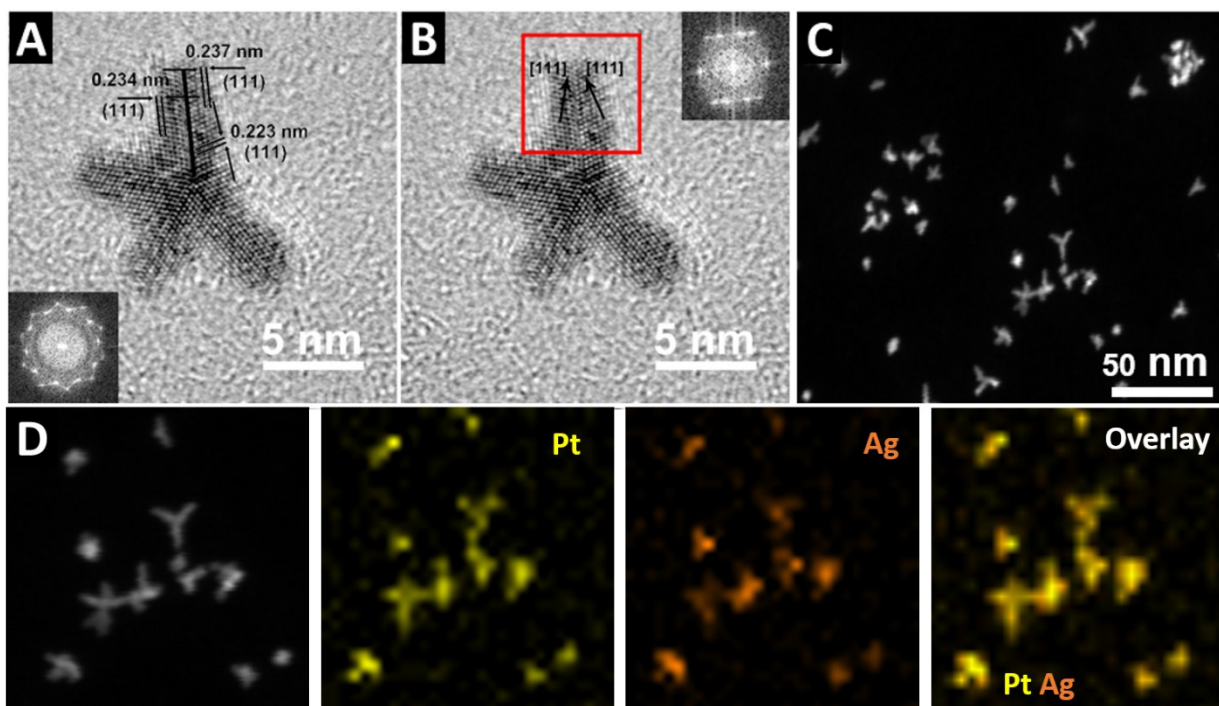


Figure S4. HRTEM images of Pt-Ag nanocrystals synthesized at 130 °C for 5 min, (A) Pt-Ag; inset show twin FFT pattern of whole branched structure; (B) Pt-Ag ; inset show twin FFT pattern of one arm of the branched structure; (C) Pt-Ag; HADF image and (D) Corresponding element maps of Pt-Ag.

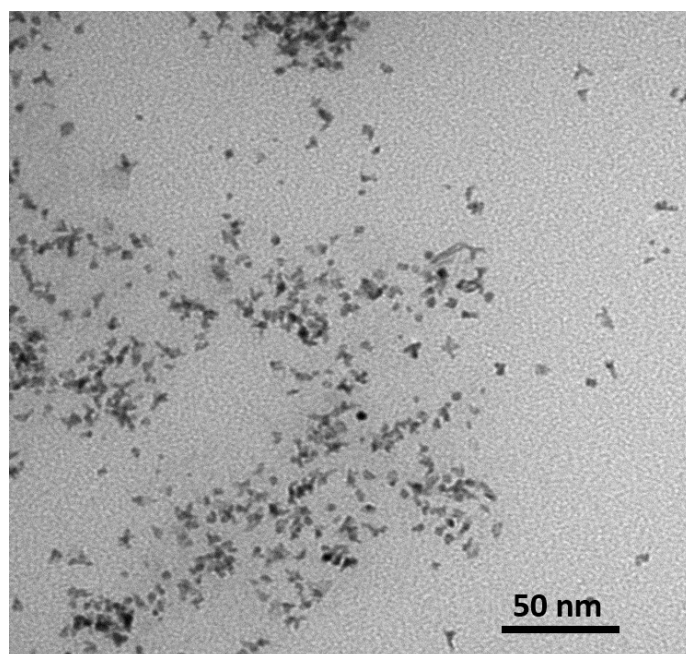


Figure S5. TEM image of the Pt-Ag nanocrystals prepared under the standard experimental Condition for 15 minutes reaction time.

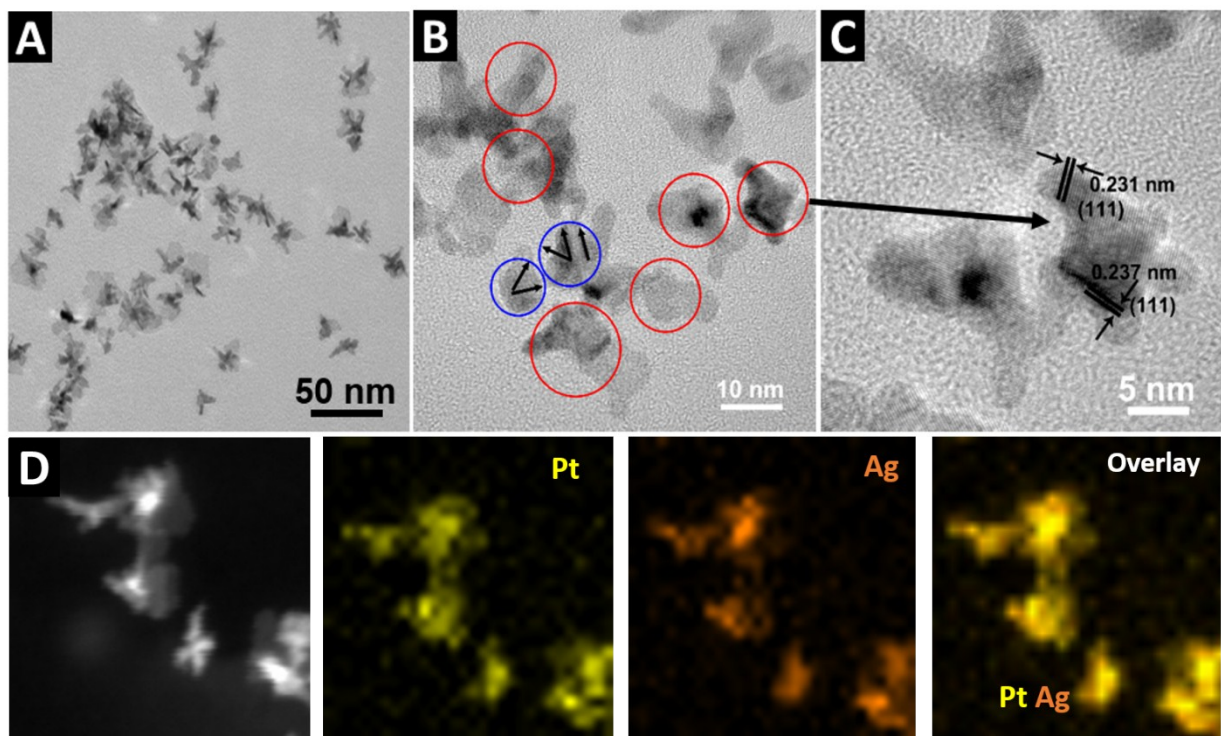


Figure S6. (A) TEM (B,C) HRTEM images and (D) Corresponding element maps of Pt-Ag nanocrystals synthesized at 130 °C for 30 min.

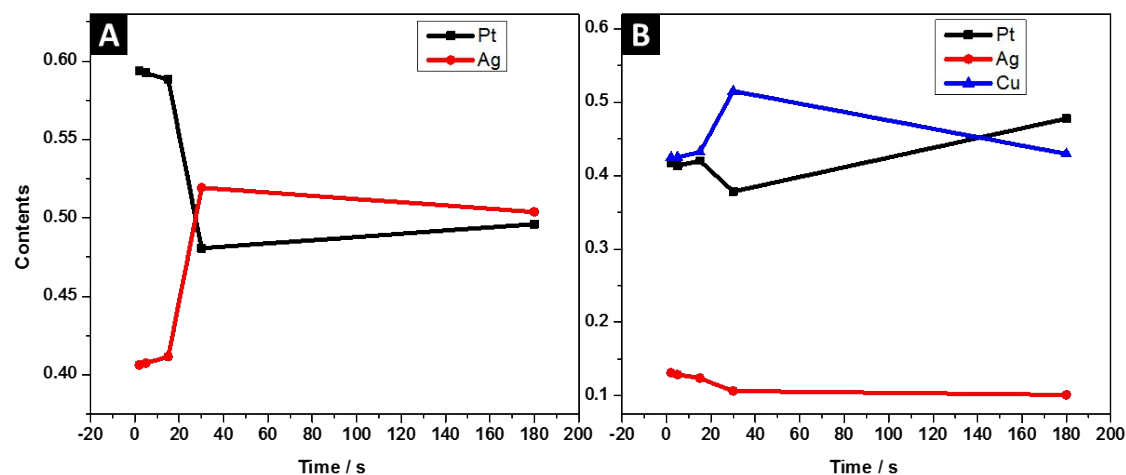


Figure S7. ICP-MS results of Pt-Ag nanosheets and Pt-Ag-Cu tetrapods.

Time dependent reduction trend of two and three metals (Pt, Ag and Pt, Ag, Cu) shows that as the reaction time prolonged, the contents of silver (red line) increased in two metal alloy due to oxidative etching (Figure S7 A) but remain constant in three metal alloy due to the incorporation of Cu^{2+} (Figure S7 B). Secondly we can see that copper (blue line in figure S4 B) plays a very important role in three metal alloy, by changing the crystallinity to form the tetrapods.

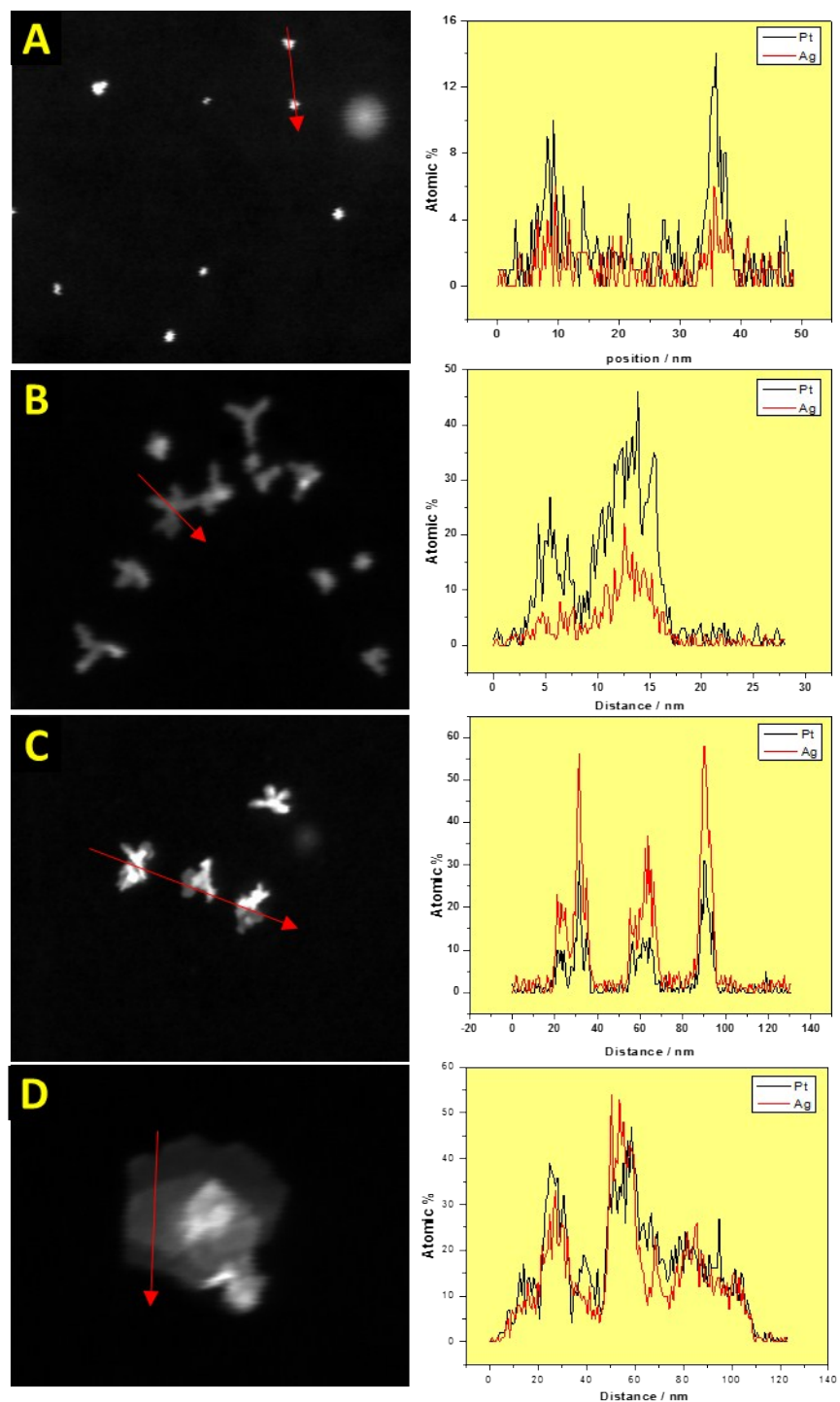


Figure S8. Time dependent morphology evolution with line scanning profiles of the Pt-Ag nanostructures 2 min; (B) 5 min; (C) 30 min; (D) 180 min; at standard reaction conditions.

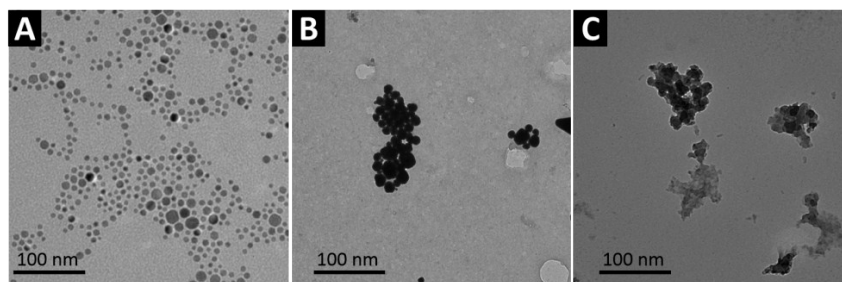


Figure S9. TEM images of nanostructures prepared with different noble metals (A) Rh-Ag, (B) Pd-Ag, (C) Au-Ag at 130 °C for 3 h.

Replacement of Pt with other noble metal precursors (Rh, Pd and Au) were resulted small nanoparticles (fig S9. A, B, C) at standard reaction conditions.

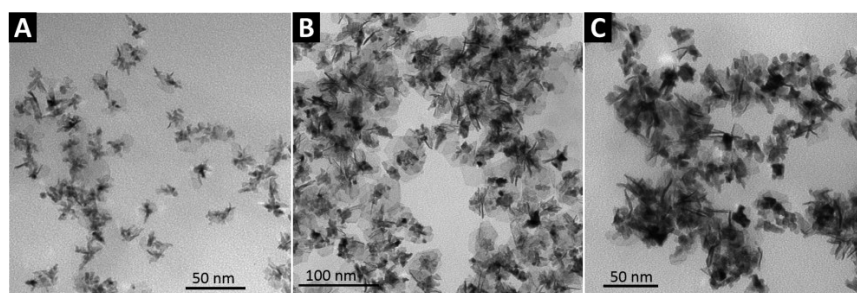


Figure S10. TEM images of Pt-Ag nanocrystals synthesized at different Temperature (A) 100°C, (B) 150°C, (C) 180°C for 3 h.

We analyses Pt-Ag alloy at different temperature and observed that nanosheets can not be formed at low temperature (fig.S10 A) but aggregated at high temperature (fig.S10 B, C).

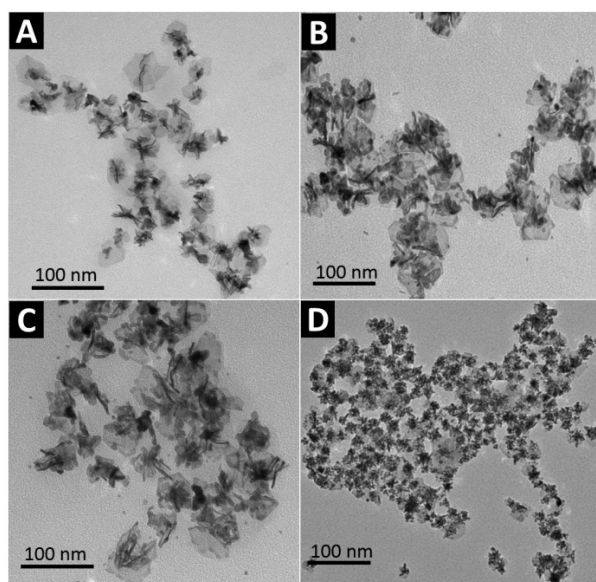


Figure S11. TEM images of nanostructures prepared with different molar ratios of Pt(acac)₂ / AgNO₃ (A) 0.005:0.01, (B) 0.02:0.01, (C) 0.01:0.005, (D) 0.01:0.02 at 130 °C for 3 h.

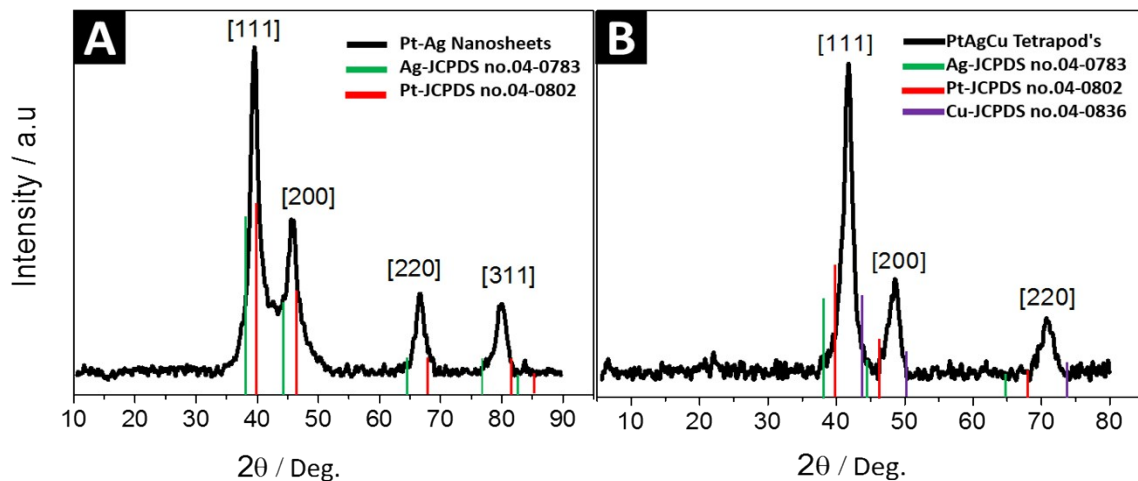


Figure S12. XRD pattern of the obtained Pt-Ag and Pt-Ag-Cu alloy produced from 3-hr Reactions.

Figure S6 Shows an X-ray powder diffraction (XRD) patterns of Pt-Ag and Pt-Ag-Cu alloys synthesized at 130 C for 3 hours. From the diffraction peaks, Pt-Ag and Pt-Ag-Cu alloy can be identified as fcc structures. Figure S12.A shows the XRD patterns of the Pt-Ag bimetallic nanosheets with information for pure Pt (Pt-JCPDS no.04-0802) and Ag (Ag-JCPDS no.04-0783) references. Pt-Ag nanosheets exhibited diffraction peaks of (111), (200), (220) and (311), respectively. Meanwhile, Pt-Ag nanosheets peaks were observed between pure Pt and Ag diffraction peaks, suggesting the formation of alloy. Figure S12.B shows XRD pattern of Pt-Ag-Cu alloy branched structure, No diffraction peaks for single-component Ag, Cu and Pt were observed in XRD patterns, and all the peaks shift to higher angle than that of Pt-Ag alloy and pure Pt (JCPDS no.04-0802), which is indication of uniform Pt-Ag-Cu alloy formation. Shifting of peaks towards the higher angle than Pt-Ag alloy was due to the incorporation of the Cu.¹

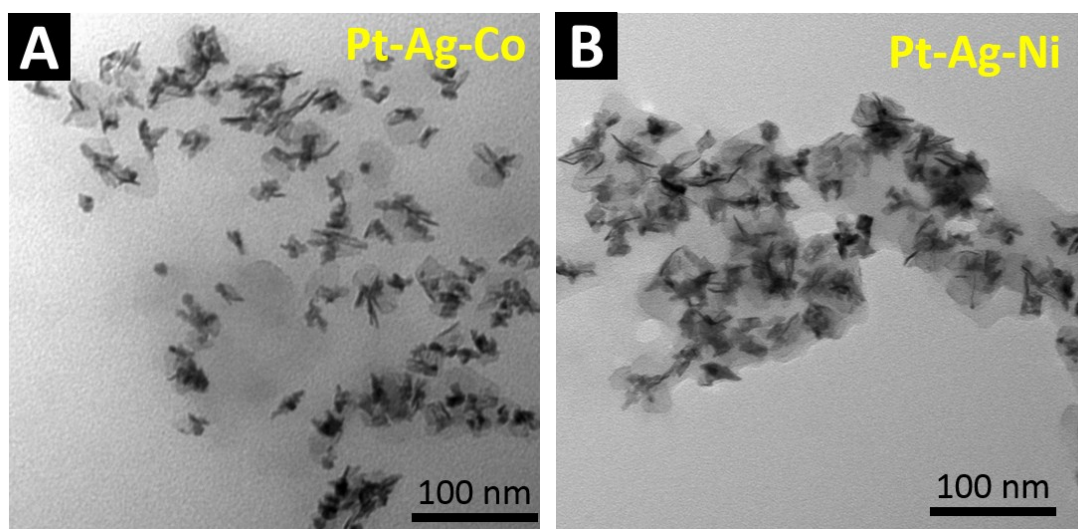


Figure S13. TEM images of the products that were prepared using the standard procedure, by adding $\text{Co}(\text{acac})_2$ (figure A) and $\{\text{Ni}(\text{NO}_3)_2\}$ figure B with Pt and Ag in the same molar amount as the $\text{Cu}(\text{acac})_2$.

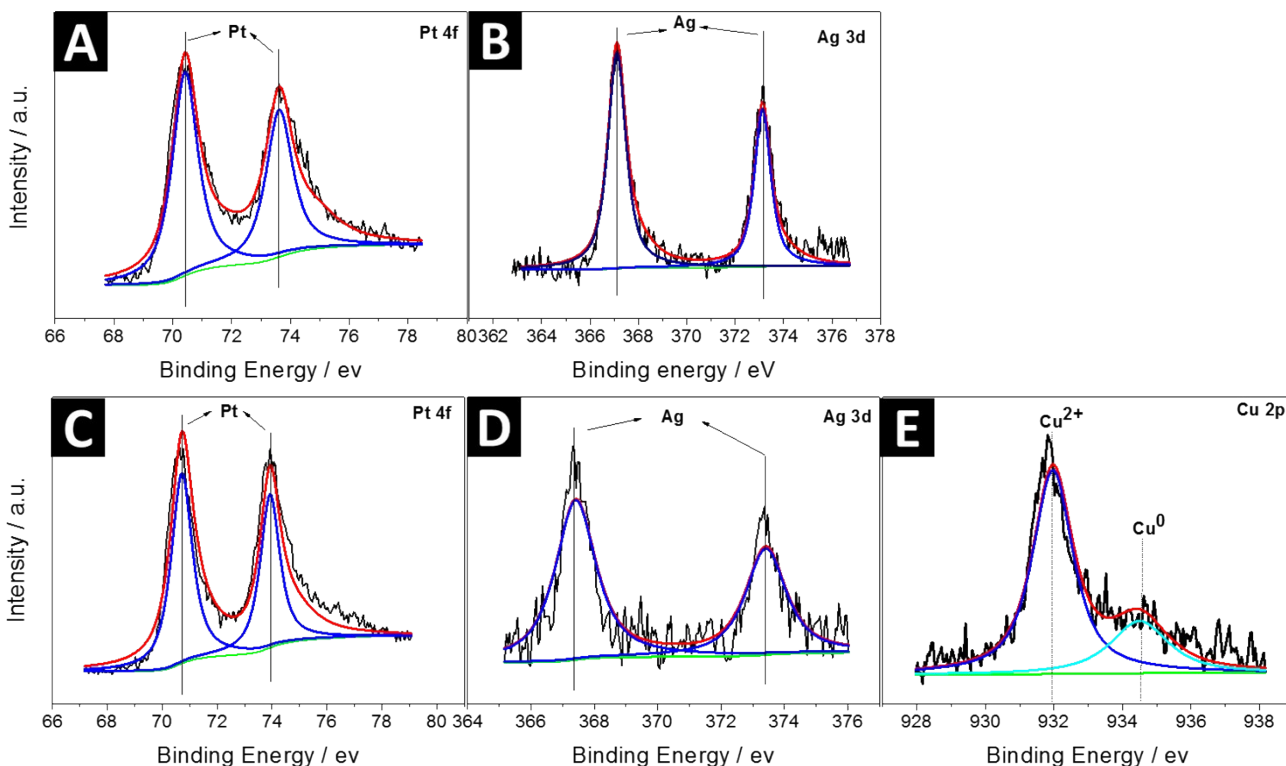


Figure S14. X-ray photoelectron spectroscopy (XPS) of Pt-Ag nanosheets and Pt-Ag-Cu tetrapods.

XPS was used to examine the surface composition and valence state of the nanosheets (A,B) and tetrapod's (C,D,E). For nanosheets, XPS spectrum of Pt 4f displays two peaks at 70.36 eV and 73.50 eV with a spin-orbit separation of 3.14 eV (figure .A), and XPS spectrum of Ag 3d (figure .B) shows two peaks with spin orbit separation of 6.01 at 367.09 and 373.1 respectively. XPS spectra of the tetrapod's shown in the (C) Pt 4f, (D) Ag 3d and (E) Cu 2p regions. Compared to the values of Pt-Ag nanosheets the binding energies of Pt 4f, Ag 3d, and Cu 2p in the Pt-Ag-Cu exhibited a slight shift of energy, respectively. For example, the binding energy of Pt $4f_{7/2}$ in tetrapods exhibited a positive shift of 0.39 eV compared with that in Pt-Ag nanosheets, and for Ag $3d_{5/2}$ in tetrapods also a positive shift of 0.16 eV. In contrast, the binding energy of Cu $2p_{3/2}$ in tetrapods was 0.85 eV lower than the standard value for Cu^0 state. Thus, the obvious shift of binding energies in Pt-Ag-Cu alloy indicates that the electron density increases (charge transfer from Cu).

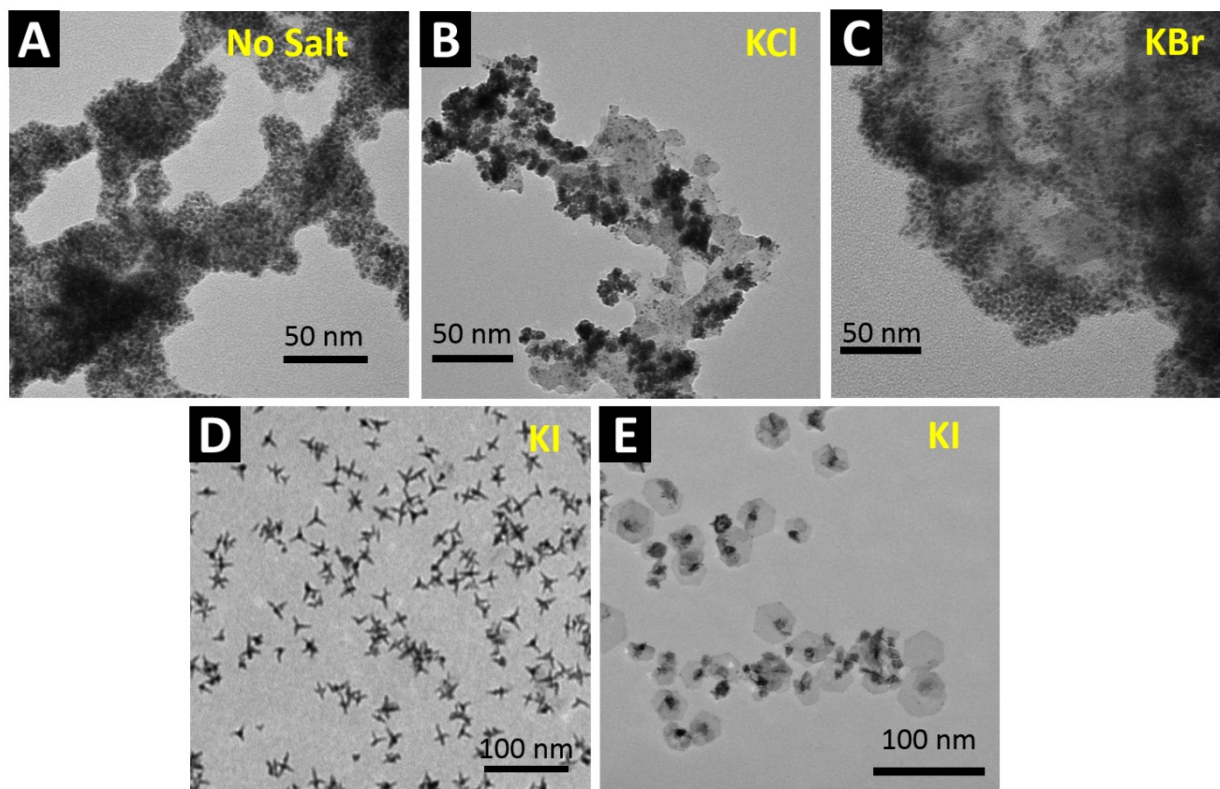


Figure S15. TEM images of the products with and without Halogens.

TEM images of the products collected after three hour reactions time where different halide anions were used (B) KCl, (C) KBr and (D-E) KI, where all the other reaction conditions were same. There was no morphology formation without salt (A), as well with KCl and KBr salts. However the formation of nanosheets and tetrapods occurred when we use KI.

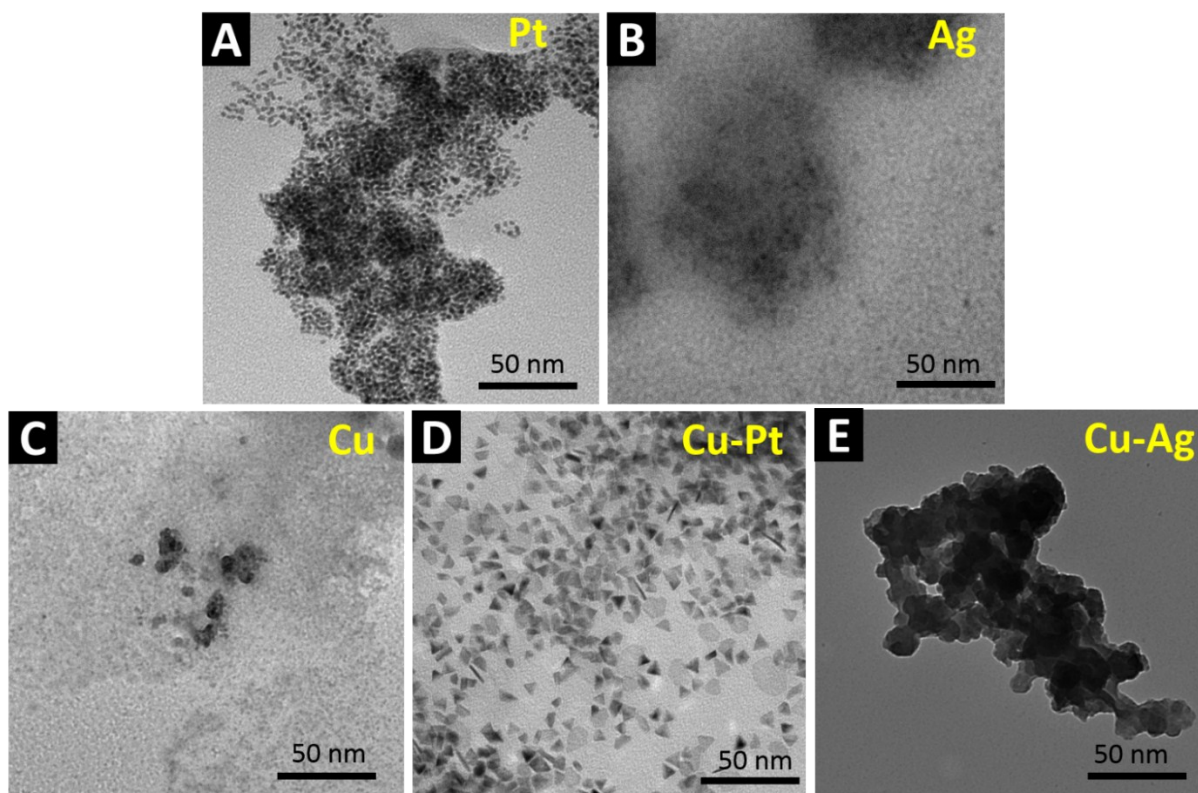


Figure S16. TEM images of the products synthesized under the standard experimental condition in the absence of (A,D) AgNO_3 , (B,C) $\text{Pt}(\text{acac})_2$, (C) AgNO_3 and $\text{Pt}(\text{acac})_2$.

Firstly, we conducted the experiment with individual metals precursor. TEM images (A) Pt, (B) Ag and (C) Cu, result indicates that there is no morphology evolution through the direct reduction of $\text{Pt}(\text{acac})_2$, AgNO_3 and $\text{Cu}(\text{acac})_2$. Secondly, we conducted the experiment in the absence of Ag (D), we obtained ultrathin nanosheets and we already have been reported it.² Third in the absence of Pt, there was no morphology evolution between Ag and Cu (E). But, in the absence of Cu, Pt-Ag alloy form unstable branched structures as we discuss earlier, so we stabilize these branched structures by Cu UDP to obtain the well define branched structure of Pt-Ag-Cu alloy.

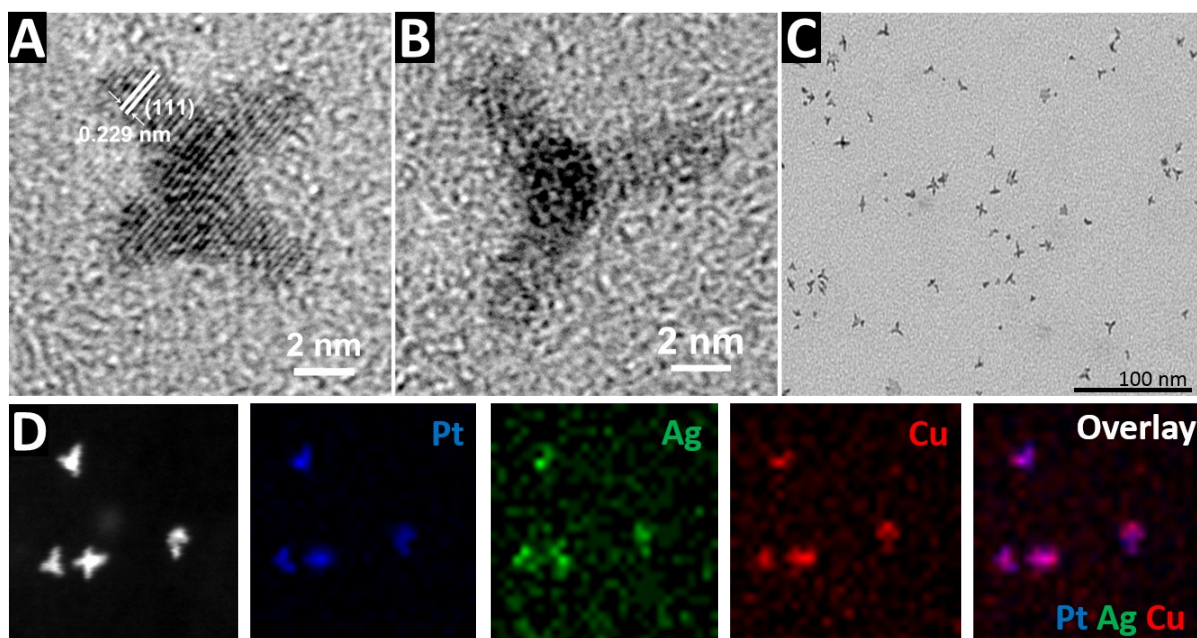


Figure S17. (A, B)HRTEM (C) TEM images and (D) Corresponding element maps of Pt-Ag-Cu; nanocrystals synthesized at 130 °C for 5 mint.

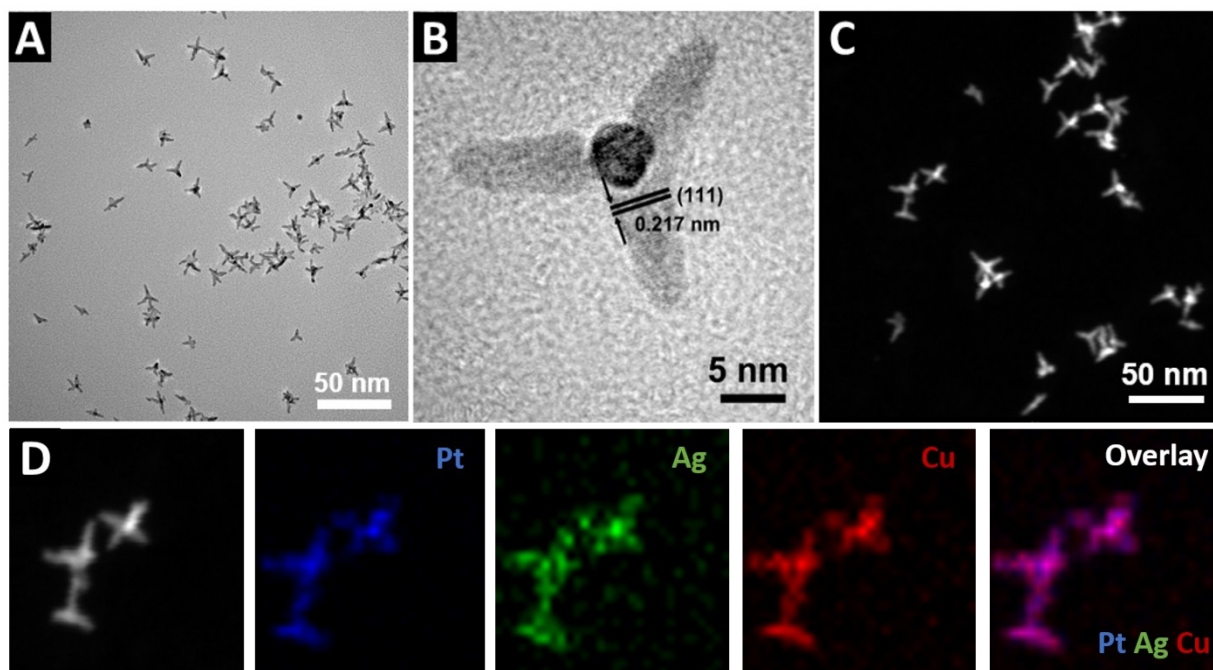


Figure S18. (A) TEM (B) HRTEM (C) HADAF images and (D) Corresponding element maps of Pt-Ag-Cu; nanocrystals synthesized at 130 °C for 30 mint.

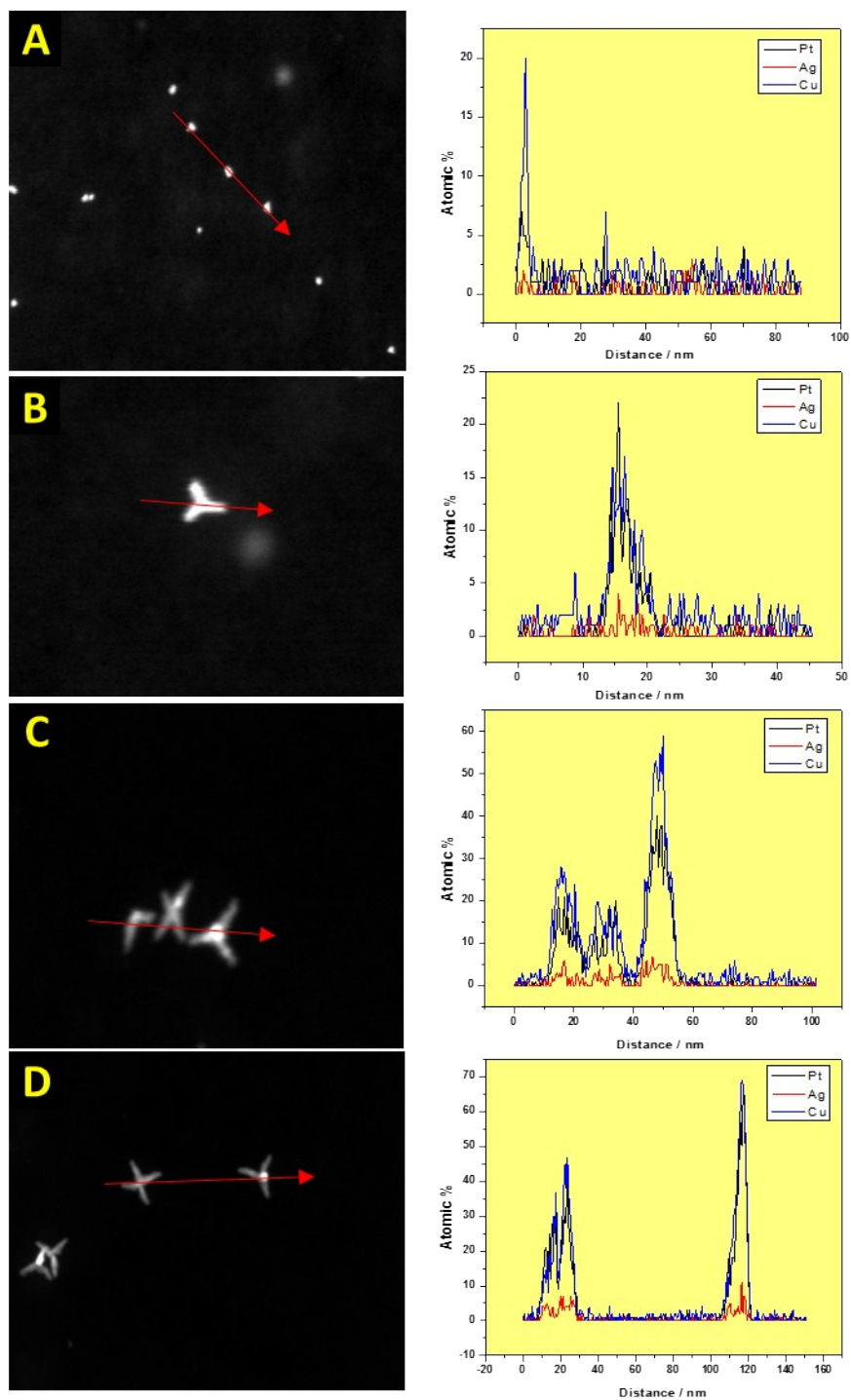


Figure S19. Time dependent morphology evolution with line scanning profiles of the Pt-Ag-Cu nanostructures 2 min; (B) 5 min; (C) 30 min; (D) 180 min; at standard reaction conditions.

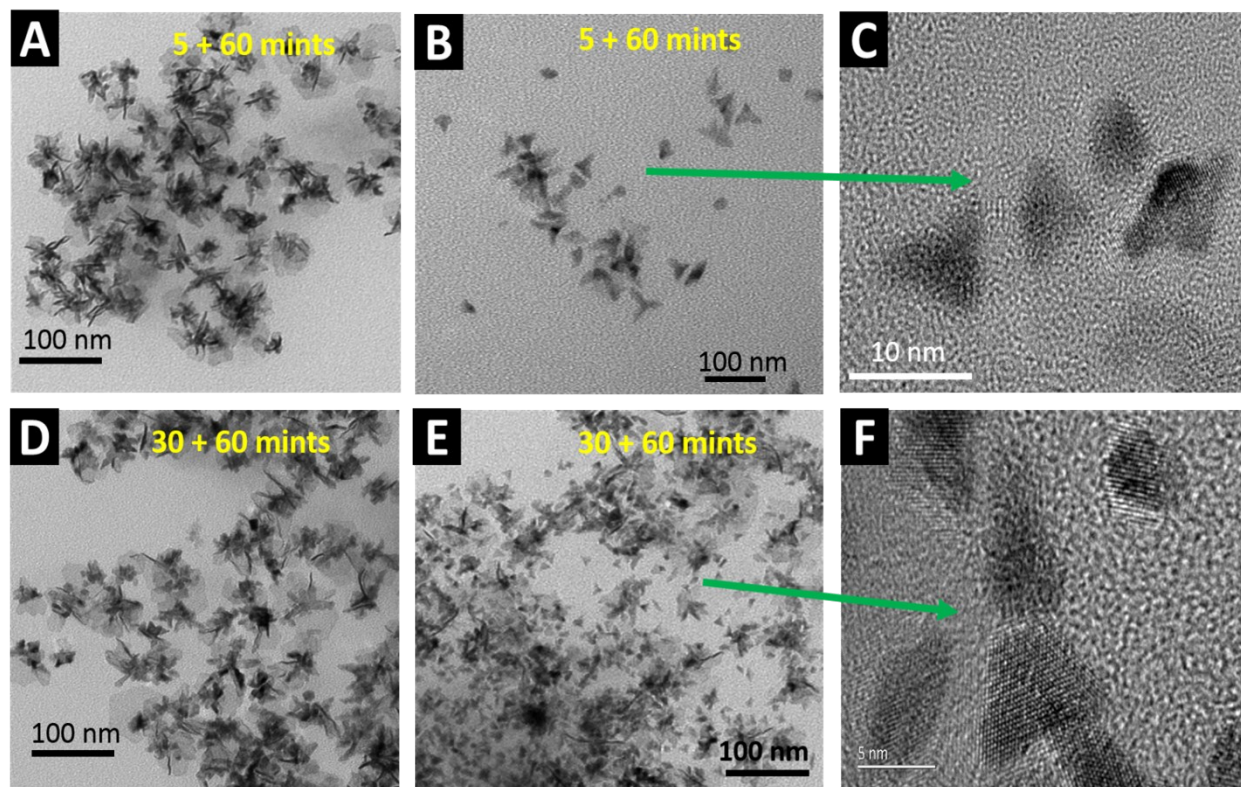


Figure S20. TEM images of the products before (A, D) and after (B,E) addition of the $\text{Cu}(\text{acac})_2$ at different reaction time and HRTEM images (C, F)after addition of copper.

First, we conducted the reactions in four autoclaves and obtained products of Pt-Ag alloy at different reaction time (2 autoclaves for 5 mints and remaining two for 30 mints). We cool down them at room temperature, then we add equal amounts of copper without washing just in two autoclaves (one of 5 mints and other of 30 mints) and again, run the reaction for one hour at standard experimental conditions. The autoclaves run without copper form the sheets like structures (TEM images A and D), but addition of the $\text{Cu}(\text{acac})_2$ indicates that crystallinity of the Pt-Ag alloy changes (twin to single crystalline) and weakness the chemisorption of CO. Further, we verify it by HRTEM (C, F).

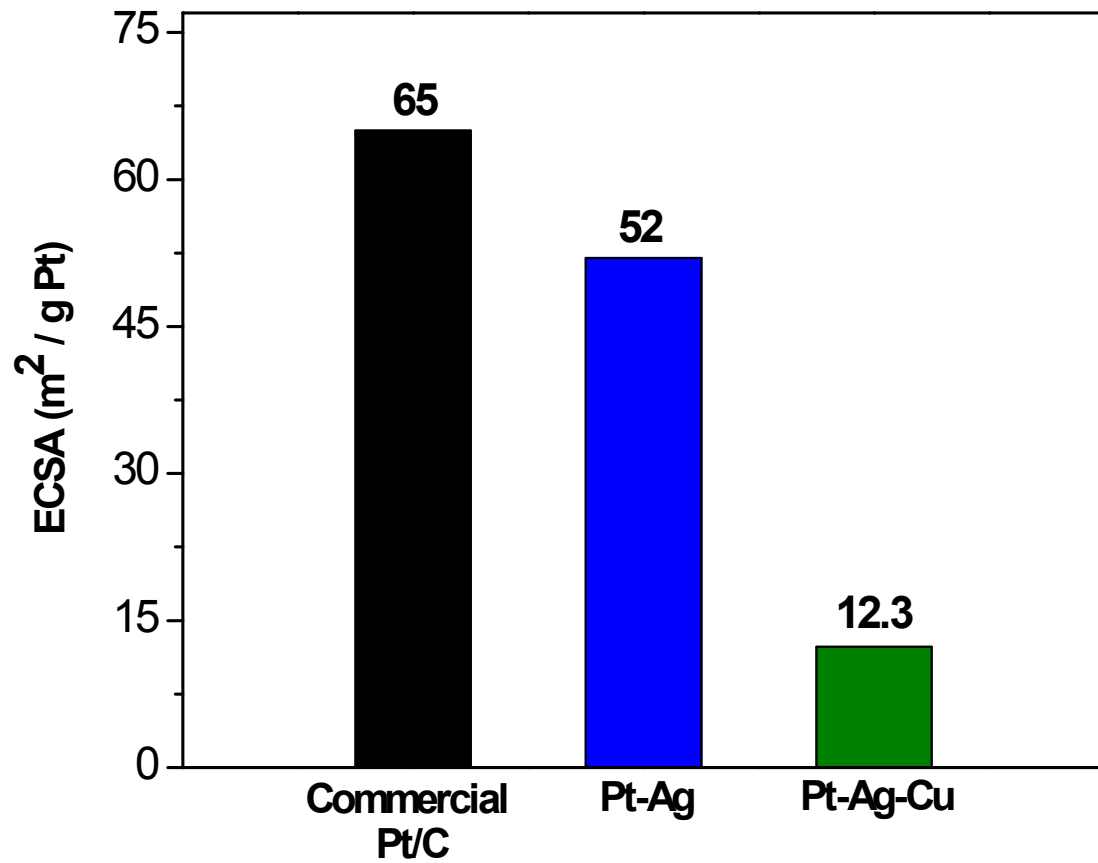


Figure S21. ECSA for commercial Pt/C, Pt-Ag nanosheets and Pt-Ag-Cu Tetrapods.

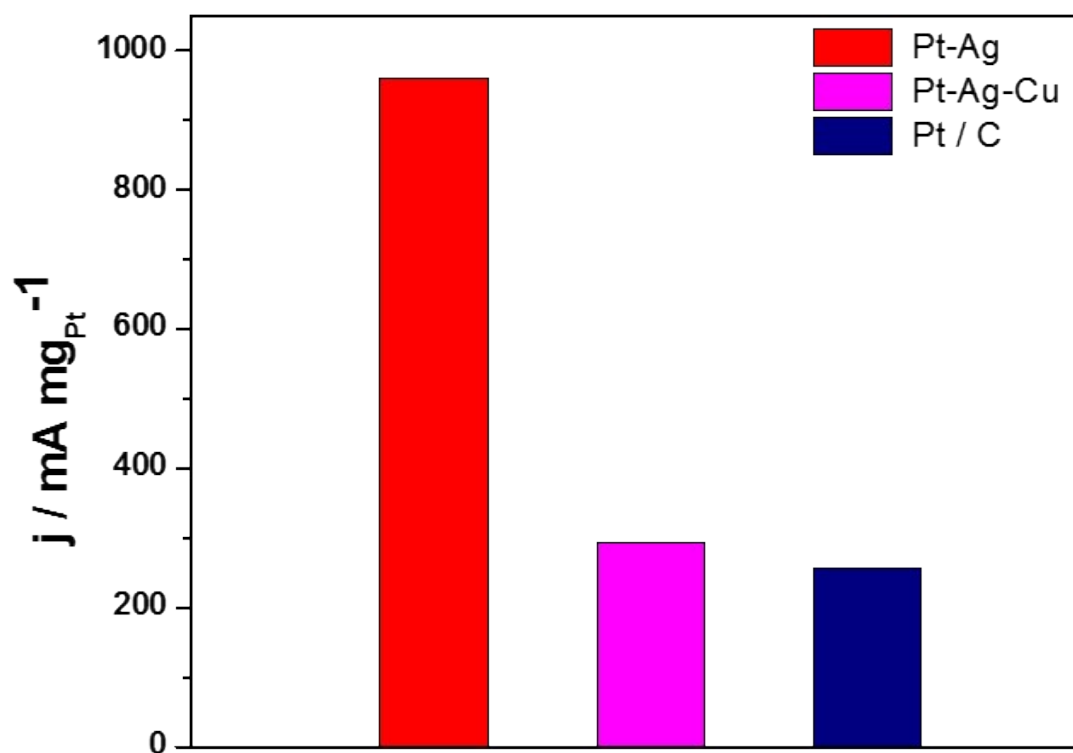


Figure S22. Mass activities of three kinds of catalysts are 961, 294 and 257 m²g⁻¹ for Pt-Ag, Pt-Ag-Cu and Commercial Pt.

- 1 Y. Zhou and D. Zhang, J. Power Sources, 2015, 278, 396-403.
- 2 F. Saleem, Z. Zhang, B. Xu, X. Xu, P. He and X. Wang, J. Am. Chem. Soc., 2013, 135, 18304-18307.