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Supplementary information

Nanoengineering a library of metallic nanostructures using a single microfluidic reactor

Víctor Sebastián[a,#] and Klavs F. Jensen[a]

a. Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA. email: kfjensen@mit.edu.

Department of Chemical Engineering, Aragon Institute of Nanoscience (INA), University of Zaragoza, Campus Rio Ebro, 50018 Zaragoza, Spain and Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), 28029 Madrid, Spain.

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Experimental details

Reagents: Potasium bromide (KBr, Aldrich); dipotassium tetrachloroplatinate(II) (K_2PdCl_4,Aldrich); platinum (II) acetylacetonate (Pt(acac)2, Adrich); sodium tetracholoropalladate (Na_2PdCl_4, Aldrich); Silver nitrate ($AgNO_3$, Aldrich); Nickel Chloride (II) ($NiCl_2.6H_2O$, Aldrich); CobaltChloride (II) ($CoCl_2.6H_2O$, Aldrich); Ruthenium Chloride (III) ($RuCl_3.3H_2O$, Aldrich), Ascorbic Acid (AA, Aldrich); sodium borohydride($NaBH_4$, Aldrich); polyvinylpyrrolidone (PVP, MW = 55000, Aldrich); tetradecyltrimethylammonium bromide (TTAB, Aldrich); Ethylene glycol (EG, Aldrich); N,N-dimethylformamide (DMF, Omnisolv EMD); oleic acid (OLA, Sigma Aldrich), oleylamine (OAm, Across Organics). All chemical were of analytical grade and were used without further purification.

Synthesis setup: The reactants were introduced in the microfluidc reactor by three separated inlets, oxidant, reductant and a spare inlet that could blocked when no additional reagents were required. The reagents were introduced in the mixing zone by means of two high pressure syringe pumps (ISCO 100 DM), insuring good control of the flow rates and residence time. The mixing zone for laminar and segmented flow contacting (Figure S1) was maintained at room temperature by circulation of cold water. The product stream exited the microreactor through the cold zone, quenching the nanoparticles growth. A back-pressure regulator (Jasco, Model BP-1580) maintained a set pressure inside the reactor while enabling samples to be collected in a continuous mode without depressurizing the system.

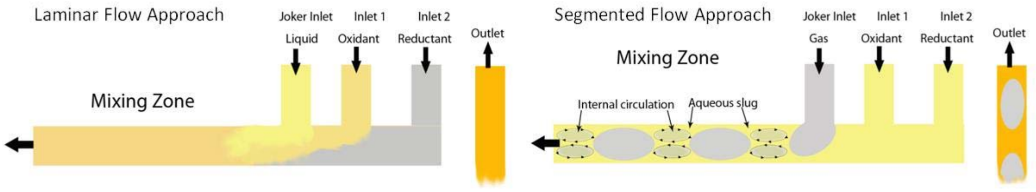


Figure S1- Schematic of the laminar and gas segmented approached used in this work

The microfluidic channels and ports were etched into silicon wafers by a deep reactive ion etch (DRIE). The silicon surface was then oxidized to silica and anodically bonded to a Pyrex wafer to cap the channels, providing a glass surface compatible with reagents used.[1] The reactor was designed to have a reaction volume of 100 μl. The nanostructures were analyzed by transmission electron microscopy (TEM, JEOL Model 200CX , HRTEM JEOL 2010 and STEM JEOl 2011F). The UV-Vis spectra was measured using an Agilent 8453 UV-Visible spectrophotometer.

Synthesis of nanomaterials

Synthesis of Pt NPs: Dipotassium tetrachloroplatinate(II) and TTAB were mixed together with Milli-Q water (oxidant flow). Sodium borohydride was dissolved in water in an ice bath (reductant fow).The oxidant flow was contained an aqueous solution of 1.0mM K_2PtCl_4 on metal basis and 100 mM TTAB. The reducing flow was composed of 30 mM $NaBH_4$. A constant molar ratio of TTAB / (Pt precursor / reducing agent of 100/1/30 was maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge by using a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions. Water was replaced with a mixture of water/ethanol (84/16 v/v) to study the effect of ethanol in nanoparticle synthesis. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of Pd NPs: Sodium tetracholoropalladate and TTAB were mixed together with Milli-Q water (oxidant flow). Sodium borohydride was dissolved in water in an ice bath (reductant fow).The oxidant flow was contained an aqueous solution of 1.0mM Na_2PdCl_4 on metal basis and 100 mM TTAB. The reducing flow was composed of 30 mM $NaBH_4$. A constant molar ratio of TTAB / Pd precursor / reducing agent of 100/1/30 was maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge controlled by a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions. A constant back pressure of 2 MPa was used for all the reaction

Ethylene glycol was used as reducing agent in the polyol process. The reductant/oxidant flow ratio, residence time and synthesis temperature were varied between 1-2.4 v/v, 10-120 s and 120-200ºC, respectively. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of Au NPs: The oxidant flow (O) composition was constituted by a 1-5 mM aqueous solution of chloroauric acid and a 20-100 mM solution of TTABr, maintaining in all experiments the molar ratio TTABr / HAuCl4= 1/20. The reducing flow (R) was composed of a 38.8-194 mM solution of sodium borohydride (Aldrich). The oxidant/reductant flow ratio of 10 was maintained constant for all experimental conditions. Air was injected through a mass flow controller to create slugs during the segmented flow approach, using equal flows of the aqueous and gas phases. The residence time was tuned from 5 to 300 s by varying the gas/liquid flow rate; the synthesis temperature was varied between room temperature and 150ºC. A constant back pressure of 0.8 MPa was used for all the reaction

Synthesis of AuPd NPs: The oxidant flow (O) composition consisted of 0.5-2.5 mM aqueous solution of chloroauric acid, 0.5-2.5 mM sodium tetrachloropalladate and a 20-100 mM solution of TTABr. In all experiments, the molar ratio was TTABr/ Metal= 1/ 20; palladium and gold precursors were mixed in a molar ratio 1 to1. The reducing flow (R) was a 38.8-194 mM solution of sodium borohydride (Aldrich). The oxidant/reductant flow ratio of 10 was maintained constant for all experimental conditions. Air was injected through a mass flow controller to create slugs during the segmented flow approach, using equal volumetric flows of the aqueous and gas phases. The residence time was tuned from 5 to 300 s by varying the gas/liquid flow rate; the synthesis temperature was varied between room temperature and 150ºC. A constant back pressure of 0.8 MPa was used for all the reaction.

Synthesis of Pt-Pd core-shell NPs: Dipotassium tetrachloroplatinate(II), sodium tetrachloropalladate and TTAB were mixed separately with Milli-Q water (oxidant flow1 and oxidant flow 2). Sodium borohydride was dissolved in water cooled by an ice bath (reductant flow). The oxidant flow 1 and oxidant flow 2 were combined with an aqueous solution of 100 mM TTAB, 0.5mM K_2PtCl_4, and 0.5mM Na_2PdCl_4. The reducing flow was composed of 30 mM $NaBH_4$. A constant molar ratio of TTAB / metal precursor / reducing agent of 100/1/30 were maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge by using a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions, but core-shell nanostructures were only obtained at 5 s. To modify the shell thickness, platinum and palladium precursor molar ratio (Pt/Pd) was tuned by the oxidant flow 1 and oxidant flow 2 control from 0.3-3. A constant back pressure of 2 MPa was used for all the reaction

Synthesis of Pd nanoparticles decorated with Pt NPs: Dipotassium tetrachloroplatinate(II), sodium tetrachloropalladate and TTAB were mixed together with Milli-Q water (oxidant flow). Sodium borohydride was dissolved in water in an ice bath (reductant flow). Ethanol was injected in the jocker inlet. The oxidant flow contained an aqueous solution of 0.5mM K_2PtCl_4, 0.5mM Na_2PdCl_4 on metal basis and 100 mM TTAB. The reducing flow was composed of 30 mM $NaBH_4$. A constant molar ratio of TTAB / metal precursor / reducing agent of 100/1/30 was maintained throughout the experiment. The aqueous solution/ethanol flow ratio was varied between 2.5 and 15, with the best results were obtained at the ratio of 5. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge by using a feedback controller. The residence time inside the reactor was varied between 5 – 100 s by changing the flow rates of the feed solutions. Platinum and palladium precursor molar ratios (Pt/Pd) were tuned from 0.3-3 to modify the density of Pt nanoparticles deposited in the Pd nanoparticles. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of PtPd nanocubes: Dipotassium tetrachloroplatinate(II), sodium tetrachloropalladate, potasium bromide were mixed together with Milli-Q water (oxidant flow). PVP was dissolved in ethylene glycol in a EG/PVP-monomer molar ratio equal to 170 (reductant flow). The oxidant flow was contained an aqueous solution of 10 mM K_2PtCl_4, 25 mM Na_2PdCl_4 on metal basis. The molar ratio KBr to Na_2PdCl_4+ K_2PtCl_4 was kept constant in the value of 35. An air stream was introduced in the jocker inlet to generate the gas-liquid segmented flow. The reducing/oxidant flow ratios were modified in the range of 0.3 to 4. The gas/liquid flow ratio was kept constant at 1. A constant back pressure of 0.8 MPa was used for all the reaction. The nanostructures collected were washed with acetone to remove the EG and the excess PVP.

Synthesis of PtPd nanodendrites: Dipotassium tetrachloroplatinate(II), sodium tetrachloropalladate and TTAB were mixed together with Milli-Q water (oxidant flow). An aqueous solution of 30 mM Ascorbic Acid was prepared (reductant fow).The oxidant flow was contained an aqueous solution of 0.5mM K_2PtCl_4, 0.5mM Na_2PdCl_4 on metal basis and 100 mM TTAB. A constant molar ratio of TTAB / metal precursor / reducing agent of 100/1/30 was maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge controlled by a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of AgPd Janus-like particles: Sodium tetrachloropalladate and silver nitrate were separately dissolved in ethylene glycol (oxidant flow 1 and oxidant flow 2). The EG/ Na_2PdCl_4 and EG/$AgNO_3$ molar ratios were kept constant at 7.1. PVP was dissolved in ethylene glycol in a EG/PVP-monomer molar ratio equal to 20 (reductant flow). The oxidant flow 1 oxidant flow 2 were injected in equal ratio. The synthesis temperature was varied from 100ºC to 230ºC. The reducing/oxidant flow ratios were modified from 0.3 to 4, with AgPd Janus-like particles observed at a ratio of 2 , 130ºC and 100s residence time. A constant back pressure of 2 MPa was used for all the reaction. The nanostructures collected were washed with acetone to remove the EG and the excess PVP.

Synthesis of AgPd core-shell particles: Sodium tetrachloropalladate and silver nitrate were separately dissolved in ethylene glycol (oxidant flow 1 and oxidant flow 2). The EG/ Na_2PdCl_4 and EG/$AgNO_3$ molar ratios were 1200 and 120. PVP was dissolved in ethylene glycol in a EG/PVP-monomer molar ratio equal to 170 (reductant flow). The oxidant flow 1 and oxidant flow 2 were injected in equal ratio. The reducing/oxidant flow ratios were kept constant at 2. The synthesis temperature was varied from 100ºC to 230ºC , with AgPd core shell particles produced at a residence time of 120 s and temperatures between 160ºC and 180 ºC. A constant back pressure of 2 MPa was used for all the reaction. The nanostructures collected were washed with acetone to remove the EG and the excess PVP.

Synthesis of AgPd tadpole nanostructures: Sodium tetrachloropalladate and silver nitrate were separately dissolved in ethylene glycol (oxidant flow 1 and oxidant flow 2). The EG/ Na_2PdCl_4 and EG/$AgNO_3$ molar ratios were 1200 and 120. PVP was dissolved in ethylene glycol in a EG/PVP-monomer molar ratio equal to 170 (reductant flow). The oxidant flow 1 and oxidant flow 2 were injected in equal ratio. The reducing/oxidant flow ratios were kept constant at 2. The synthesis temperature was varied from 210ºC to 230ºC, obtaining AgPd tadpole at 210ºC and a residence time of 120 s. A rapid metal deposition occurred at temperatures higher than 210ºC, blocking the microchannel reactor. A constant back pressure of 2 MPa was used for all the reaction. The nanostructures collected were washed with acetone to remove the EG and the excess PVP.

Synthesis of Pt nanodendrites: Dipotassium tetrachloroplatinate(II)and TTAB were mixed together with Milli-Q water (oxidant flow). An aqueous solution of 30 mM Ascorbic Acid was prepared (reductant flow).The oxidant flow contained an aqueous solution of 1mM K_2PtCl_4on metal basis and 100 mM TTAB. A constant molar ratio of TTAB / Pt precursor / reducing agent of 100/1/30 was maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge controlled by a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of PtNi nanodendrites: Dipotassium tetrachloroplatinate(II), nickel chloride (II) and TTAB were mixed together with Milli-Q water (oxidant flow). An aqueous solution of 30 mM Ascorbic Acid was prepared (reductant fow).The oxidant flow contained an aqueous solution of 0.5mM K_2PtCl_4, 0.5mM $NiCl_2$ on metal basis and 100 mM TTAB. A constant molar ratio of TTAB / metal precursor / reducing agent of

100/1/30 was maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge controlled by a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of PtCo nanodendrites: Dipotassium tetrachloroplatinate(II), cobalt chloride (II) and TTAB were mixed together with Milli-Q water (oxidant flow). An aqueous solution of 30 mM Ascorbic Acid was prepared (reductant flow).The oxidant flow contained an aqueous solution of 0.5mM K_2PtCl_4, 0.5mM $CoCl_2$ on metal basis and 100 mM TTAB. A constant molar ratio of TTAB / metal precursor / reducing agent of 100/1/30 was maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge controlled by a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of PtRu nanodendrites: Dipotassium tetrachloroplatinate(II), Ruthenium chloride (III) and TTAB were mixed together with Milli-Q water (oxidant flow). An aqueous solution of 30 mM Ascorbic Acid was prepared (reductant flow).The oxidant flow was contained an aqueous solution of 0.5mM K_2PtCl_4, 0.5mM $RuCl_3$ on metal basis and 100 mM TTAB. A constant molar ratio of TTAB / metal precursor / reducing agent of 100/1/30 was maintained throughout the experiment. The temperature of the reactor was varied between 100 – 200ºC with a heating cartridge controlled by a feedback controller. The residence time inside the reactor was varied between 5 – 60 s by changing the flow rates of the feed solutions. A constant back pressure of 2 MPa was used for all the reaction.

Synthesis of Pd nanorods: Sodium tetrachloropalladate and potasium bromide were mixed together with Milli-Q water (oxidant flow). PVP was dissolved in ethylene glycol in a EG/PVP-monomer molar ratio equal to 175 (reductant flow). The oxidant flow was contained an aqueous solution 40 mM Na_2PdCl_4 on metal basis. The molar ratio KBr to Na_2PdCl_4 was kept constant at 35. An air stream was introduced in the spare inlet to generate the gas-liquid segmented flow. The reducing/oxidant flow ratios were modified in the range of 0.25 to 1.8. The gas/liquid flow ratio was tuned in the range 0.8-3.5 v/v. A constant back pressure of 0.8 MPa was used for all the reaction. The nanostructures collected were washed with acetone to remove the EG and the excess PVP.

Synthesis of Pd nanodumbbells: A solution of the as-made Pd nanorods, purified with acetone and dispersed in water, was injected in the microfluidic reactor. A second current composed of a 0.2 mM Na_2PdCl_4 solution was injected, varying the Pd nanorods/palladium precursor flow ration between 5-0.5 v/v. The residence time was tuned between 20-600 s. The microfluidic reactor was immersed in an ultrasonic bath, maintaining the temperature at 25ºC.

Synthesis of PdAu nanodumbbells: A solution of the as-made Pd nanorods, purified with acetone and dispersed in water, was injected in the microfluidic reactor. A second current composed of a 0.2 mM $HAuCl_4$ solution was injected, varying the Pd nanorods/gold precursor flow ration between 5-0.5 v/v. The residence time was tuned between 20-600 s. The microfluidic reactor was immersed in an ultrasonic bath, maintaining the temperature at 25ºC.

Synthesis of Pd nanosheets: Sodium tetrachloropalladate and potasium bromide were mixed together with Milli-Q water (oxidant flow 1). PVP and TTAB were dissolved in DMF in a DMF/PVP-monomer and DMF/TTAB molar ratio equal to 100 and 240, respectively (oxidant flow 2). The oxidant flow 1 contained an aqueous solution 75 mM Na_2PdCl_4 on metal basis. The molar ratio KBr to Na_2PdCl_4 was varied between 2-15. A Carbon monoxide stream (reductant flow) was introduced in the spare inlet to generate the gas-liquid segmented flow. The reducing/oxidant flow ratios was kept constant at 1. A constant back pressure of 0.8 MPa was used for all the reaction. The reaction temperature was varied between room temperature and 170ºC. A residence time of 150 s was maintained during the experiment. The nanostructures collected were washed with acetone to remove the EG and the excess PVP.

Synthesis of PdAu nanostars: A solution of the as-made Pd nanosheets, purified with acetone and dispersed in water, was injected in the microfluidic reactor. A second current composed of a 0.2 mM $HAuCl_4$ solution was injected, varying the Pd nanosheets/gold precursor flow ration between 5-0.5 v/v. The residence time was tuned between 20-600 s. The microfluidic reactor was immersed in an ultrasonic bath, maintaining the temperature at 25ºC.

Synthesis of Pt nanocubes

A liquid stream (L1) composed of OAm and Pt(acac)2 was mixed in the MFR with a liquid stream (L2) composed of OLA and OAm in different volumetric flow ratios L2/L1= 0.5-4. The molar ratio OAm /Pt in L1 was modified (100–600) in order to modify the OLA/Pt ratios during the screening program. The liquid stream L1 and L2 were mixed with a carbon monoxide stream (CO/liquid volumetric flow ratio = 1), generating gas/liquid segmented flow of 40 µl/min. The pressure inside the reactor was maintained at 120 psi and the residence time was 150 s. Procedure was as follows: A solution composed of 5ml of OAm and 20 mg of Pt(acac)2 was filled in a 5 ml glass syringe (L1 stream). 4 ml of OAm and 1 ml of OLA was also filled in a 5 ml glass syringe (L2 stream). L1 and L2 was injected in the MFR at a flow rate of 10 µl/min, obtaining a OLA/Pt and OAm/OLA molar ratios of 62.3 and 8.6 respectively. The liquid stream was segmented by CO at a flow rate of 20 µl/min.

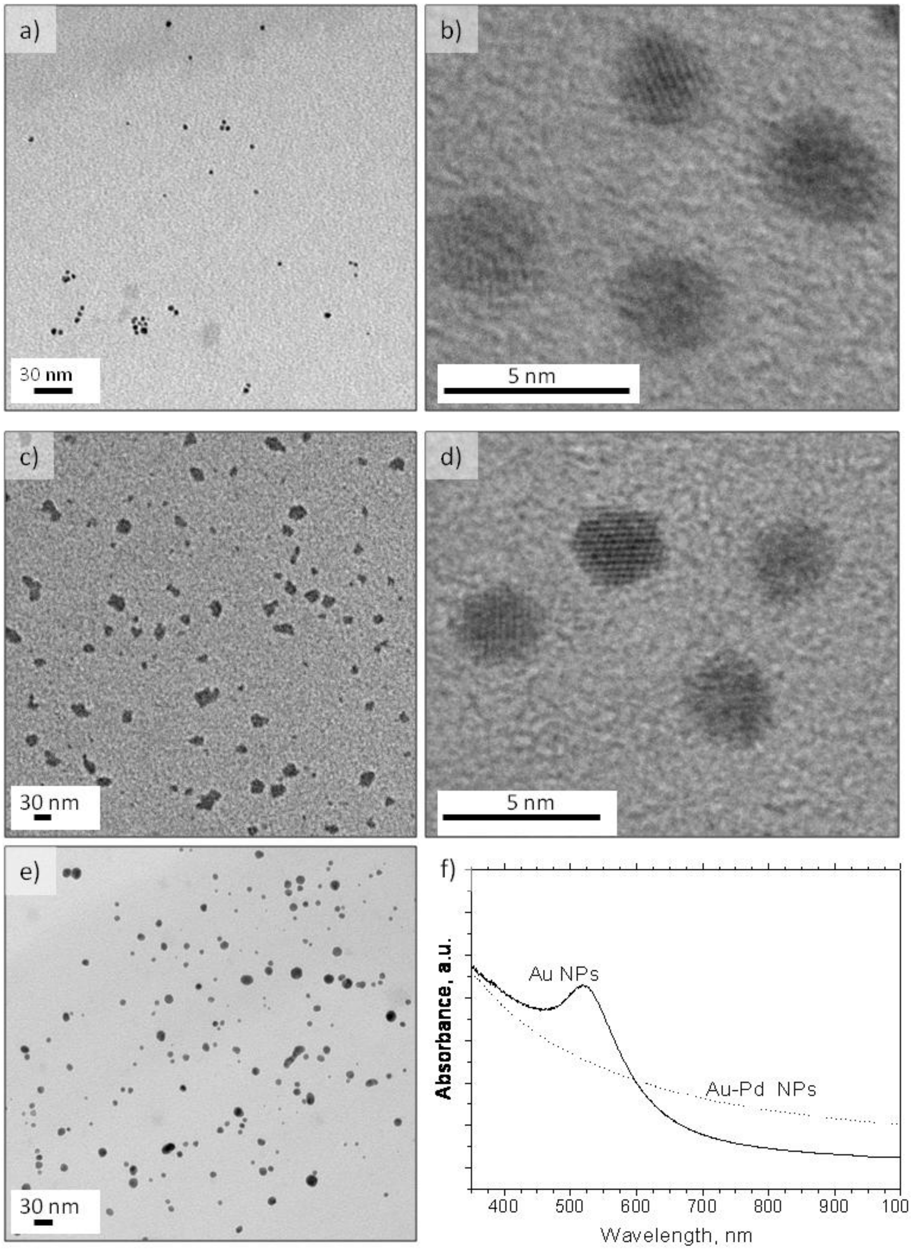


Figure S2.- TEM images: a) Pt NPs obtained at 125ºC and a residence time of 20s, using $NaBH_4$ as reducing agent; b) HRTEM image of Pt NPs obtained at 125ºC-20 s; c) Pd agglomerates obtained at 120ºC-30s, using $NaBH_4$ as reducing agent; d) HRTEM images of Pd NPs obtained with polyol method at 150ºC-60s;e) Au NPs obtained at 100ºC-10s in laminar flow; f) UV-VIS spectra of the Au and AuPd NPs obtained using the segmented flow approach,100ºC-10 s.

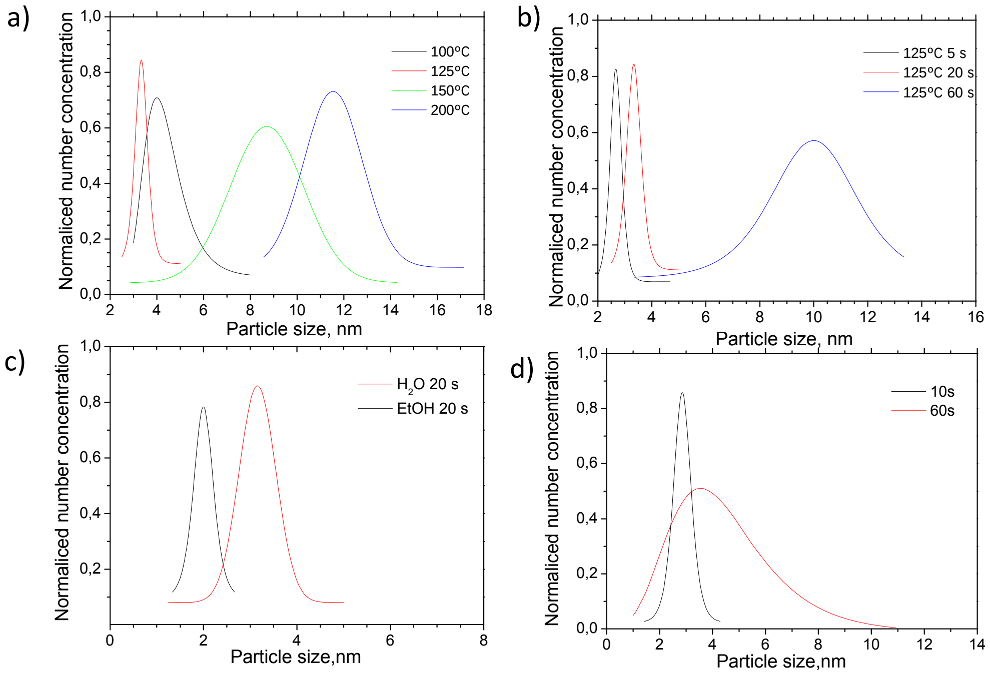


Figure S3.- Particle size distribution diagrams from: Pt NPs collected in laminar flow with water as solvent a) Effect of synthesis temperature (residence time =20 s), b) Effect of residence time(synthesis temperature =125ºC) and c) effect of solvent, water and ethanol (synthesis temperature = 125ºC); Au NPs collected in a segmented flow at 100ºC d) Effect of residence time.

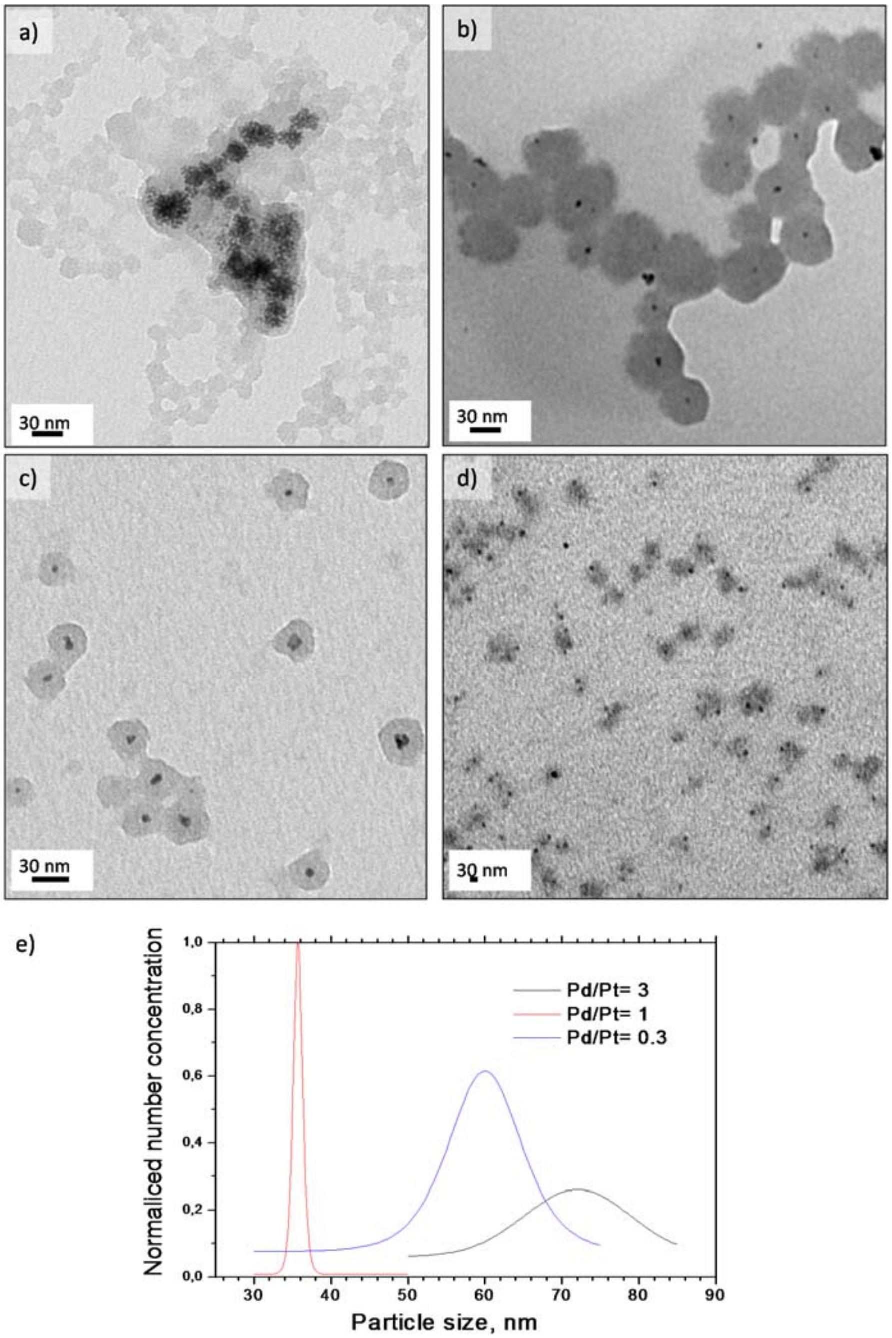


Figure S4- a) TEM image of Pt –Pd NPs obtained at 130ºC- 20 s. Pd/Pt molar ratio = 3; b) PtPd core-shell NPs obtained at 130ºC-5 s. Pd/Pt molar ratio = 3, c) PtPd core-shell Nps obtained at 130ºC-5 s. Pd/Pt molar ratio = 1; d) PtPd core-shell NPs obtained at 130ºC-5 s. Pd/Pt molar ratio = 0.3.e) Particle size distribution diagrams from Pt-Pd NPs core-shell NPs collected at different Pd/Pt ratios at 130ºC and 5 s.

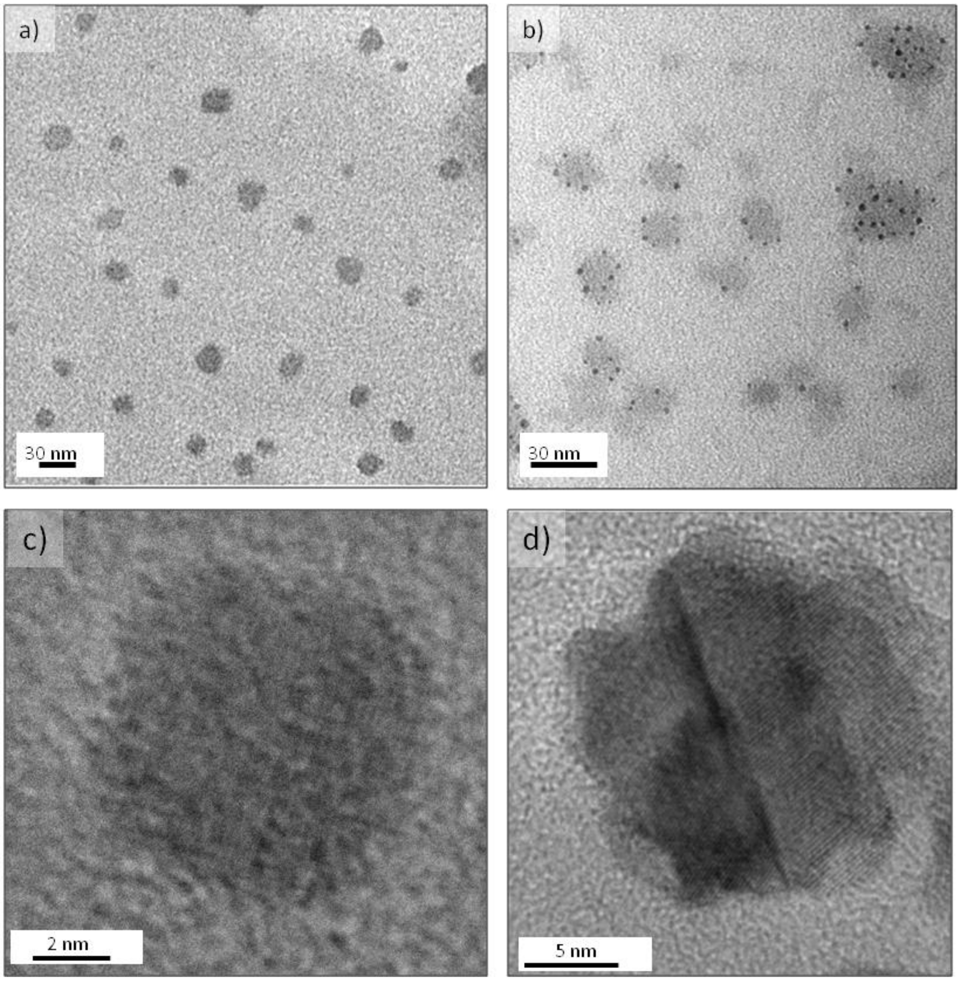
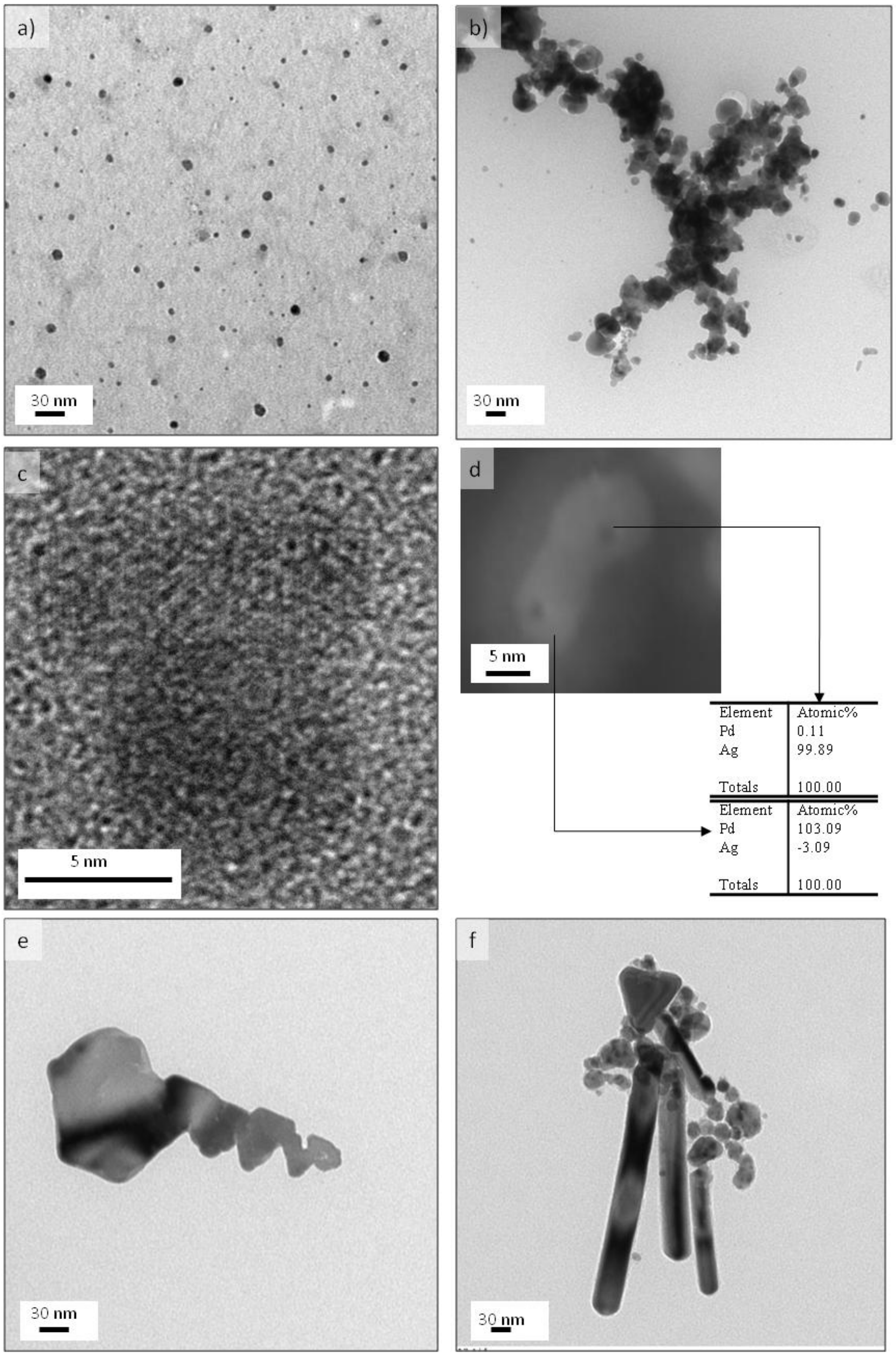


Figure S5 a)TEM image of Pd nanoparticles decorated with Pt, Tº= 100ºC- 40 s. The Pd/Pt molar ratio was equal to= 3; b) TEM image of Pd nanoparticles decorated with Pt, Tº= 100ºC- 40 s. The Pd/Pt molar ratio was equal to= 1.5; c) HRTEM image of PtPd nanocube obtained at 160ºC-120s, d) HRTEM of a PtPd nanodendrites obtained at 125ºC-20 s.



Element	Atomic%
Pd	0.11
Ag	99.89
Totals	100.00

Element	Atomic%
Pd	103.09
Ag	-3.09
Totals	100.00

Figure S6 a) TEM image of Pd and Ag NPs obtained at 100ºC-100s; b) TEM image of Ag-Pd agglomerates obtained at 120ºC-150 s; c) HRTEM of a PdAg Janus nanoparticle obtained at 130ºC-100s; d) STEM image and EDS analysis of a AgPd Janus nanoparticle obtained at 130ºC-100 s; e) PdAg nanokite particle obtained at 220ºC- 60 s, f) PdAg tadpole-like nanostructures obtained at 230ºC -120 s.

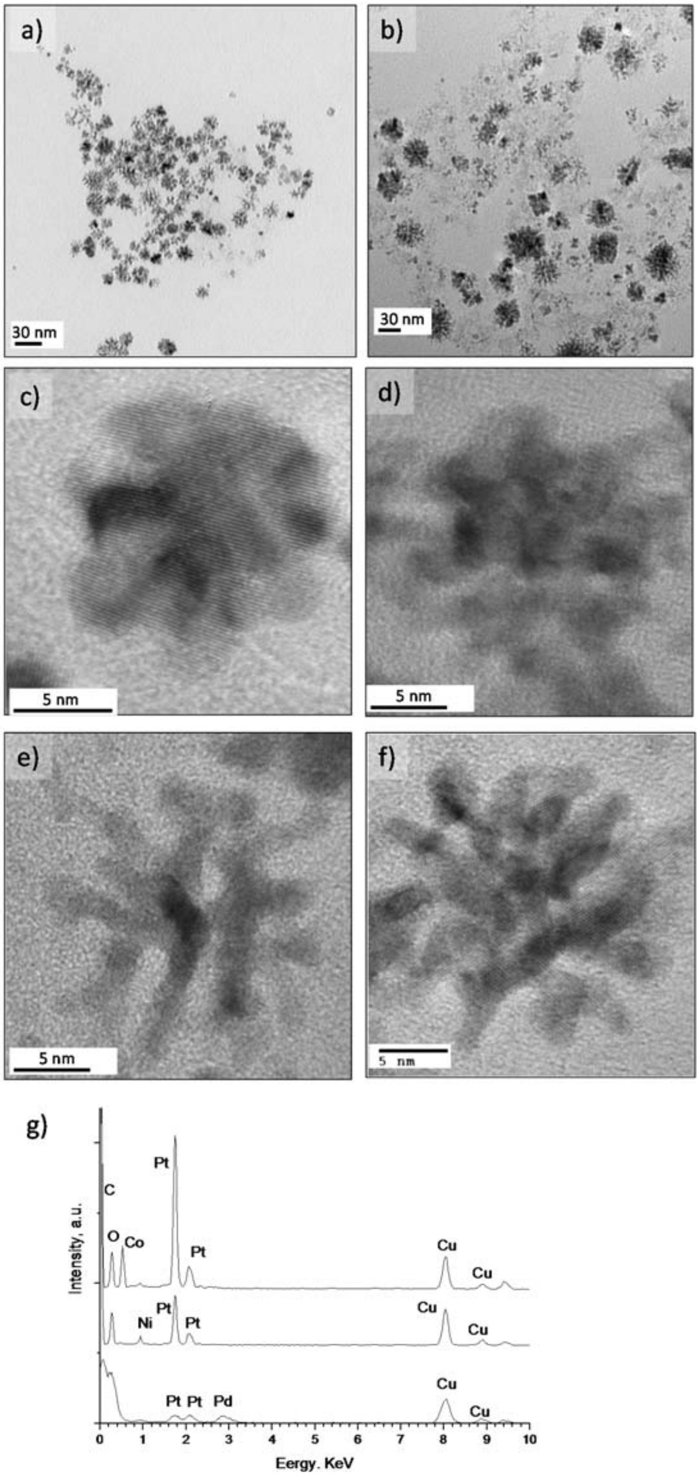


Figure S7 a) TEM images of PtCo nanostructured obtained using ascorbic acid as reducing agent at 150ºC-40s; b) TEM images of PtRu nanostructured obtained using ascorbic acid as reducing agent at 150ºC-20s; c)HRTEM image of a Pt nanodendrite obtained at 125ºC-20s; d) HRTEM image of a Pt-Co nanodendrite obtained at 135ºC-20s, e) HRTEM image of a Pt-Ru nanodendrite obtained at 125ºC-15s PtRu, f) HRTEM image of a Pt-Ni nanodendrite obtained at 135ºC-20s.g) EDS spectra of PtPd, PtNi nad PtCo NDs.

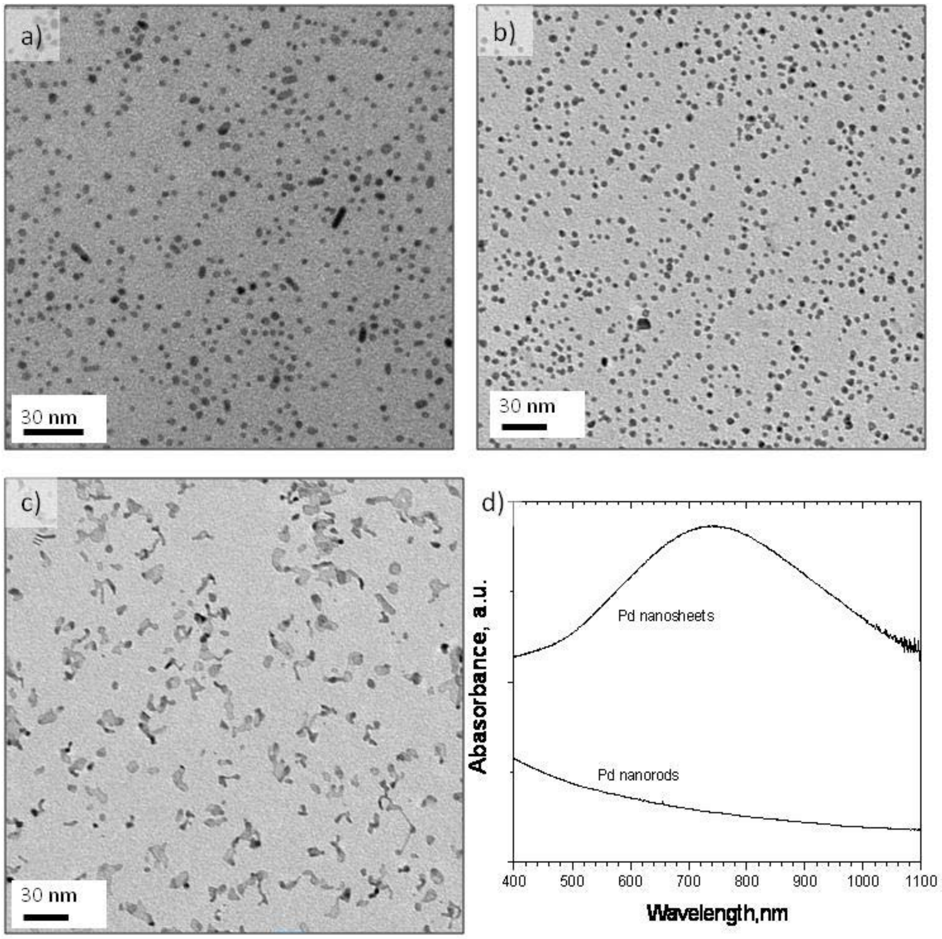


Figure S8 a) TEM image of Pd nanoparticles obtained at 165ºC-120s without air segmented flow. b) TEM image of Pd nanoparticles obtained at 150ºC-150 s without CO segmented flow, c) Pd nanostructures obtained in Co segmented flow at 170ºC - 150s d) UV-VIS spectra of Pd nanorods and Pd nanosheets obtained at 165ºC-120 s and 100ºC-150 s, respectively.

References

1. S. Marre, A. Adamo, S. Basak, C. Aymonier and K. F. Jensen, *Industrial & Engineering Chemistry Research*, 2010, **49**, 11310-11320.