Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Understanding alloy structure and composition in sinter-resistant AgPd@SiO$_2$ encapsulated catalysts and their effect on catalytic properties

SourikMondal,[a] Thattarathody Rajesh,[a] Basab B Dhar,[b] Markus Snellman,[c] JunjieLi,[c] Francis Leonard Deepak,*[,c] R. Nandini Devi,*[,a]

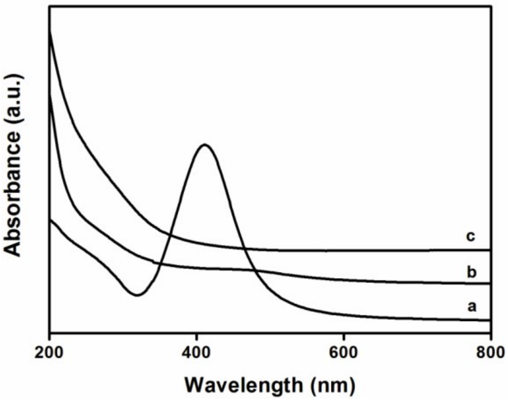
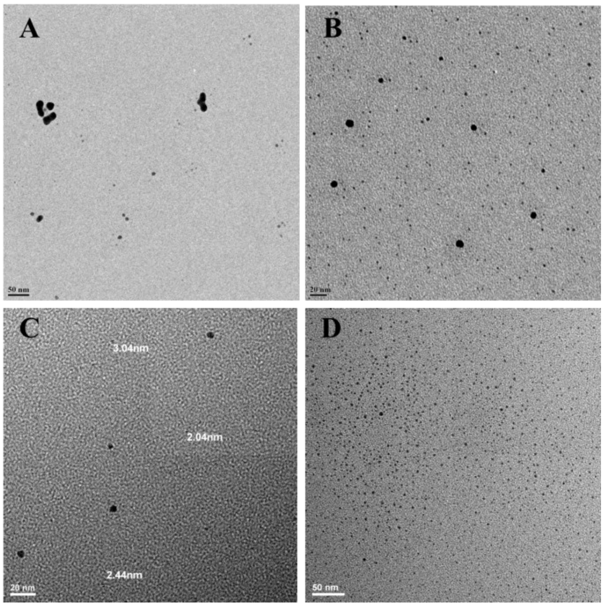


Fig.S1: UV-vis absorption spectra of silver nanoparticles having (a) Ag:thiol-1:0.12 (b-AgNPs) (b) Ag:thiol-1:2 (m-AgNPs) (c) Ag:thiol-1:4 (s-AgNPs)



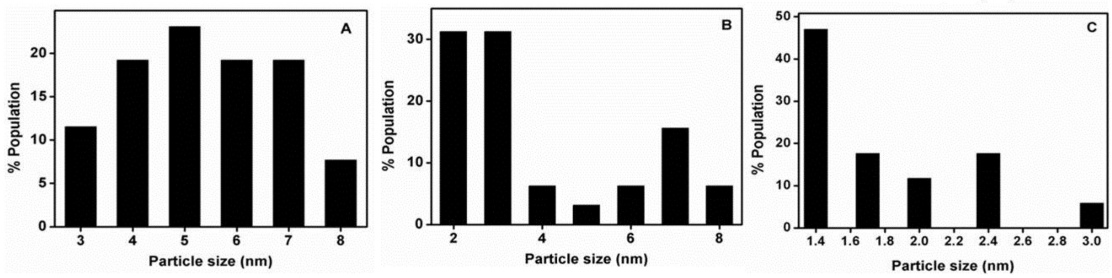


Fig. S2: (Top) HRTEM images of (A) Ag:thiol-1:0.12 (b-AgNPs) (B) Ag:thiol-1:2 (m-AgNPs) (C) Ag:thiol-1:4 (s-AgNPs) (D) Pdnanoclusters. We observed agglomeration of particles in Ag nanoclusters under electron beam. Hence big particles are avoided in calculating the histogram. This is in accordance with the UV result which does not show any Plasmon resonance peaks. (Bottom) Histograms of (A) Ag:thiol-1:0.12 (b-AgNPs) (B) Ag:thiol-1:2 (m-AgNPs) (C) Ag:thiol-1:4 (s-AgNPs).

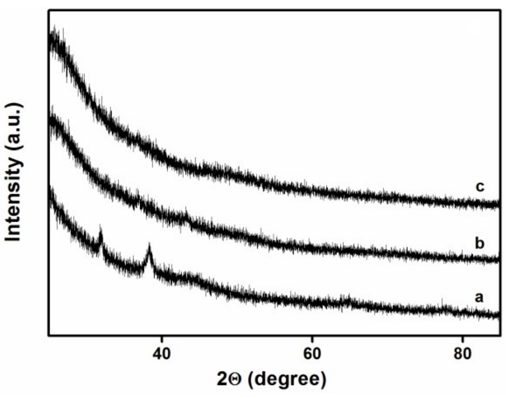


Fig.S3: Powder XRD patterns of (a) b-AgNPs (b) m-AgNPs (c) s-AgNPs.

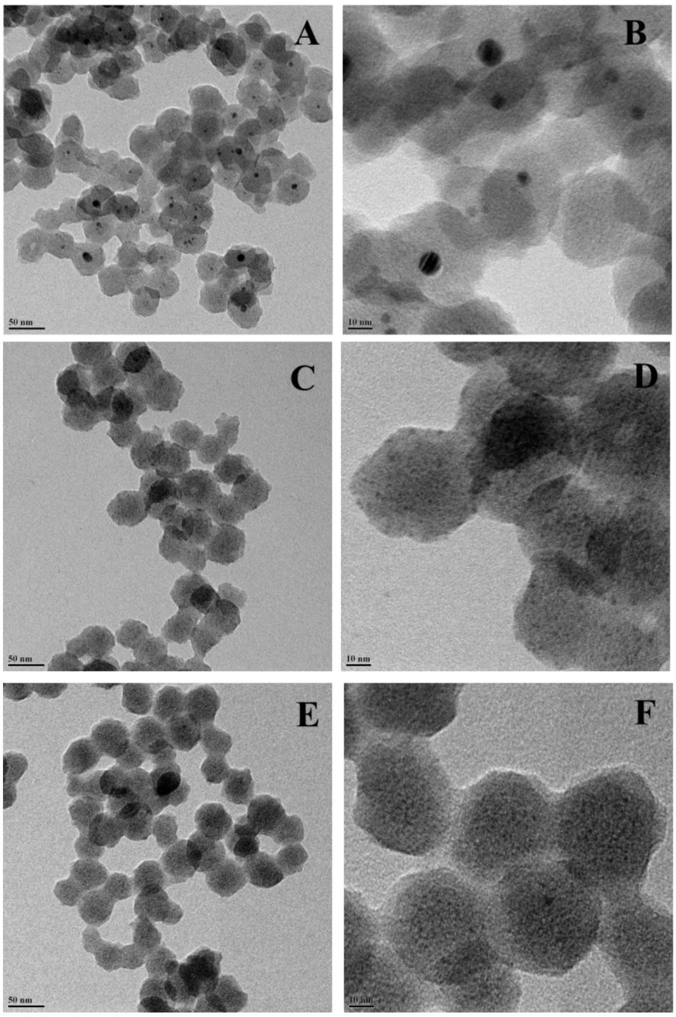


Fig. S4: TEM images of the as synthesised samples of b-AgPd(A,B), m-AgPd(C,D),s-AgPd(E,F). Scale bars: 50 nm(A,C,E), 10 nm(B,D,F)

Table S5. EDAX data of the as-synthesised as well as calcined and reduced samples.

Catalysts	Ag:Pdwt % ratio from EDAX	
	Initial composition added	Final Ag-Pd@SiO_2
s-AgPd	1:1	1.5:1
m-AgPd	1:1	1.6:1
b-AgPd	1:1	1.7:1

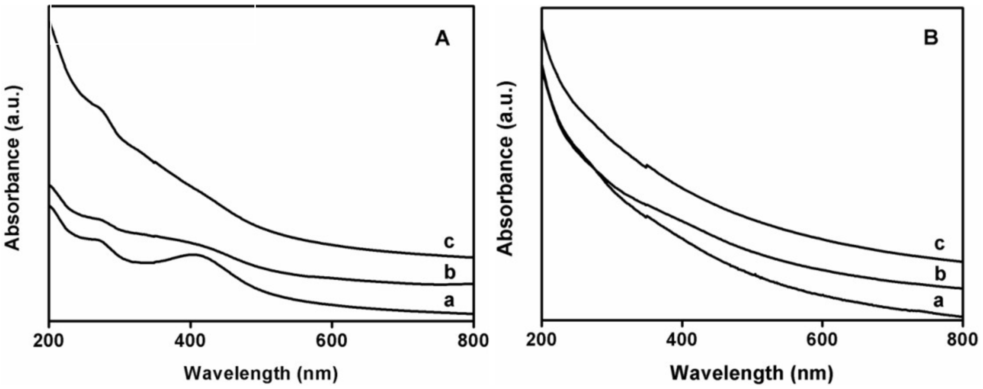


Fig.S6: UV-Vis spectra of as synthesised (A) b-AgPd, m-AgPd, s-AgPd (a-c) and calcined and reduced at 400 ^{o}C (B) b-AgPd, m- AgPd , s-AgPd (a-c)

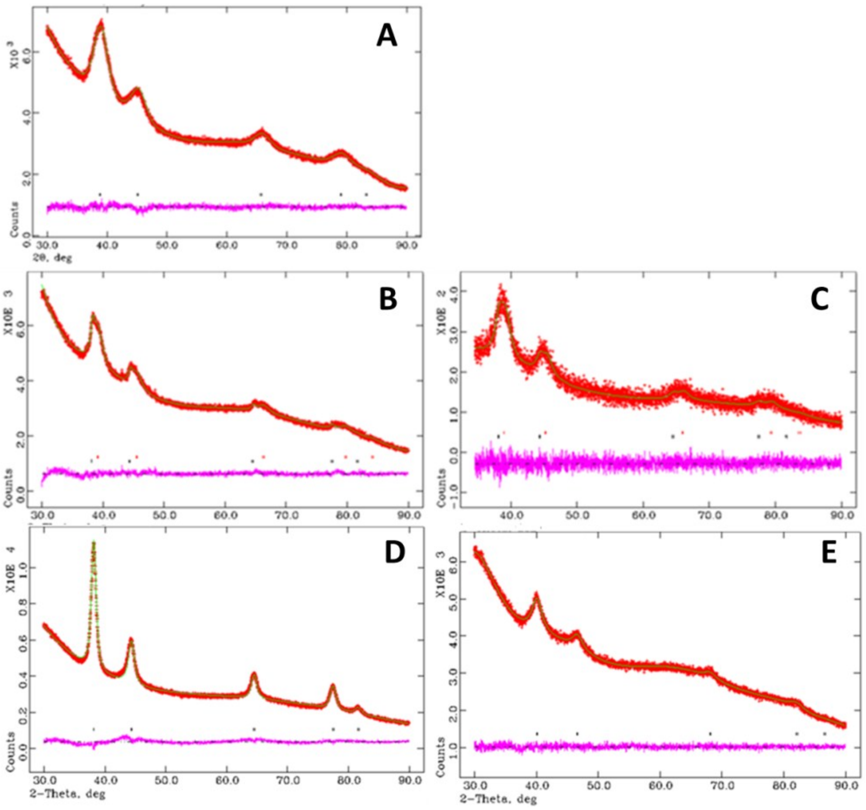


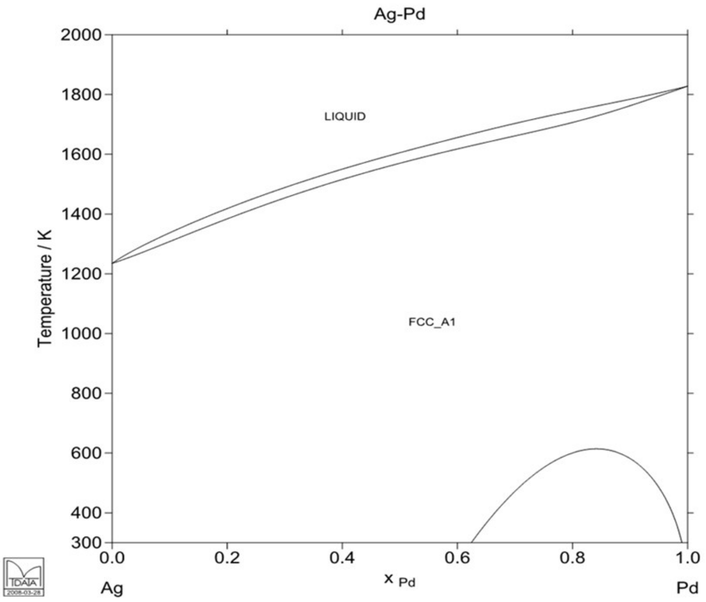
Fig.S7: Rietveld refinement plots of(A) s-AgPd (B) m-AgPd (C) b-AgPd (D) Ag (E) Pd

Crystal Structure analysis

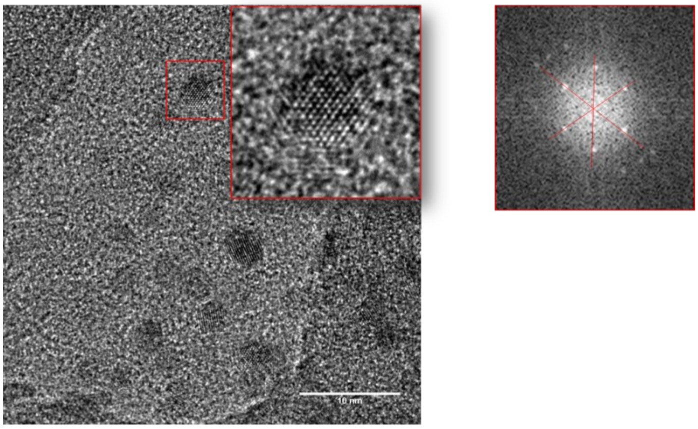
- Both Ag and Pd have the FCC unit cell – we can expect a mixture to have FCC aswell
- Using diffraction pattern and selection rules, we can calculate the lattice constant
- Using Vegard's law, we can approximate amount of each element in a crystal

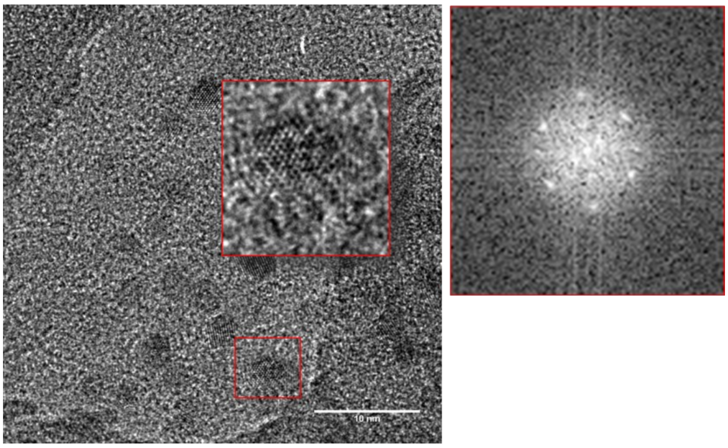
$$a_{\mathrm{A}_{(1-x)}\mathrm{B}_x} = (1-x)a_{\mathrm{A}} + xa_{\mathrm{B}}$$

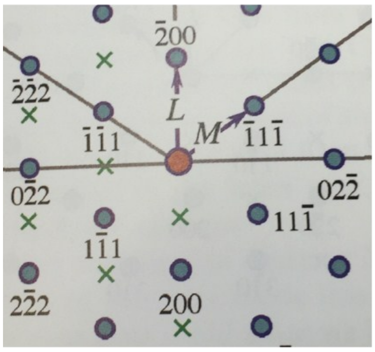
Lattice constant of Silver: 4,079 Å
Lattice constant of Palladium: 3,859 Å



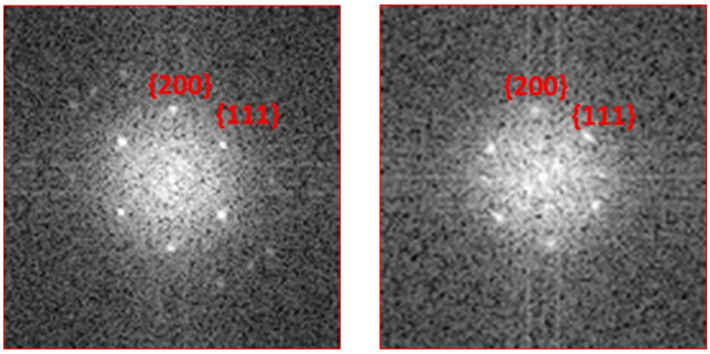
s-AgPd





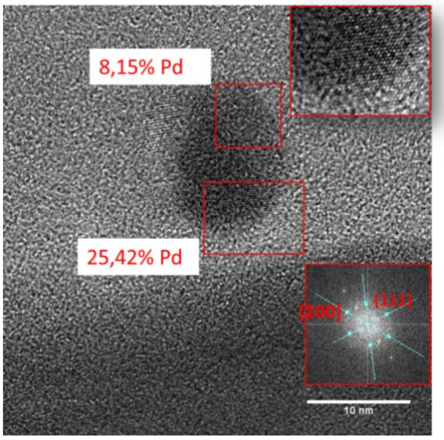


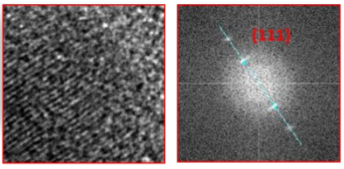
[011] FCC Direction

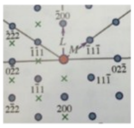


- Results:
  - Lattice constant from first DP = 3.911 Å ± 0.113 Å
  - Lattice constant from second DP = 3.948 Å ± 0.065 Å
  - $(a_{Ag} = 4.079\text{ Å}\ a_{Pd} = 3.859\text{ Å})$
  - Amount of Pd in first particle: 76.28%
  - Amount of Pd in second particle: 59.7% ± 28.93% (units)

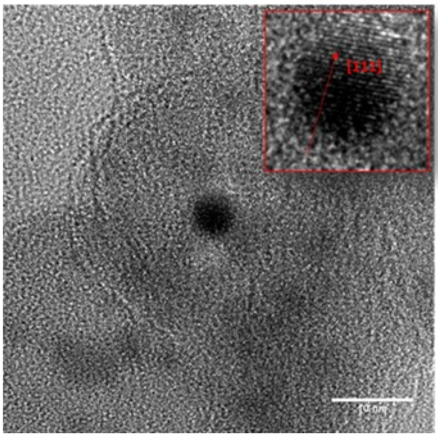
m-AgPd

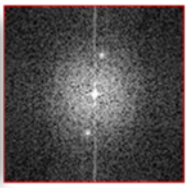




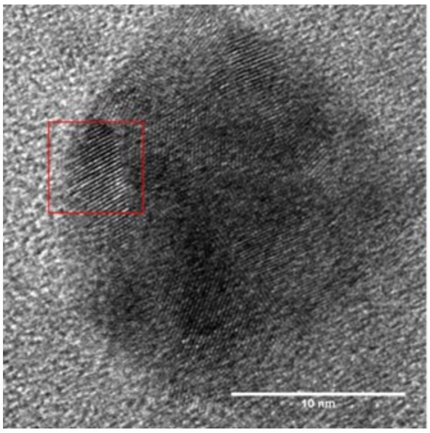


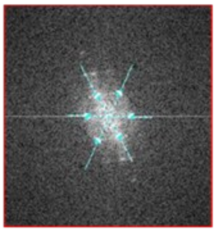
Lattice constants are 4,023 Å and 4,061 Å respectively, ($a_{\mathrm{Ag}} = 4{,}079$ Å and $a_{\mathrm{Pd}} = 3{,}859$ Å)





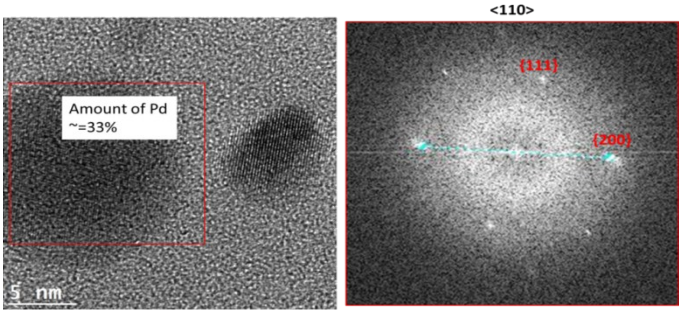
Lattice constants calculated to 3,986 Å => composition calculated to 42,27% Pd
($a_{\mathrm{Ag}} = 4{,}079$ Å and $a_{\mathrm{Pd}} = 3{,}859$ Å)

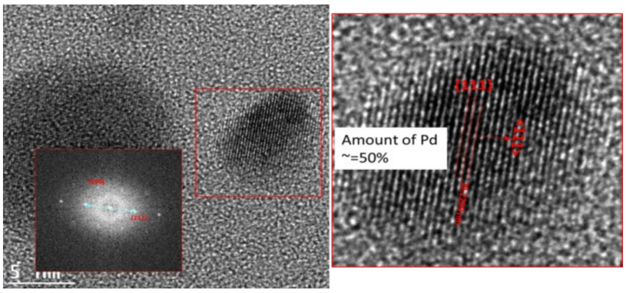




Lattice constants calculated to 3,9292 Å => composition calculated to 68,11% Pd
($a_{\mathrm{Ag}} = 4{,}079$ Å and $a_{\mathrm{Pd}} = 3{,}859$ Å)

b-AgPd


Amount of Pd
~=33%
5 nm
<110>
{111}
{200}


5 nm
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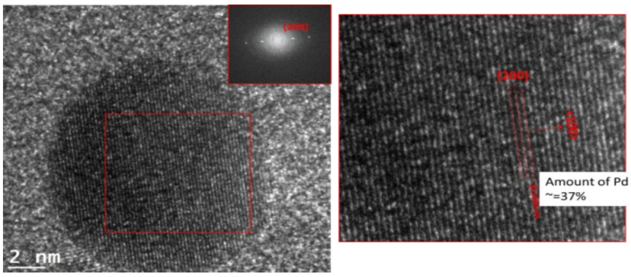
Amount of Pd
~=50%


2 nm
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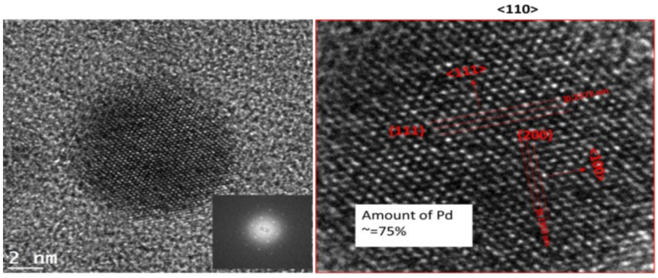
Amount of Pd
~=37%


2 nm
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Amount of Pd
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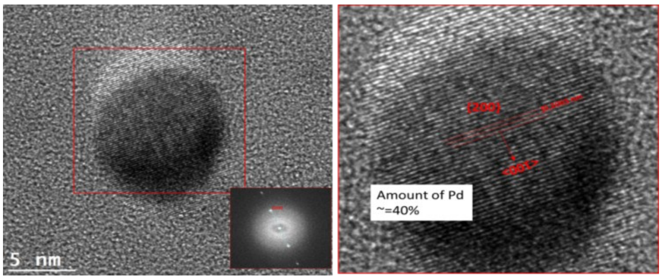
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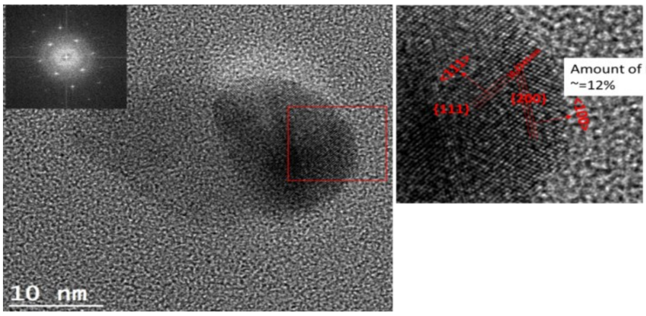
Amount of Pd
~=40%


10 nm
<111>
{111}
{200}
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Amount of Pd
~=12%

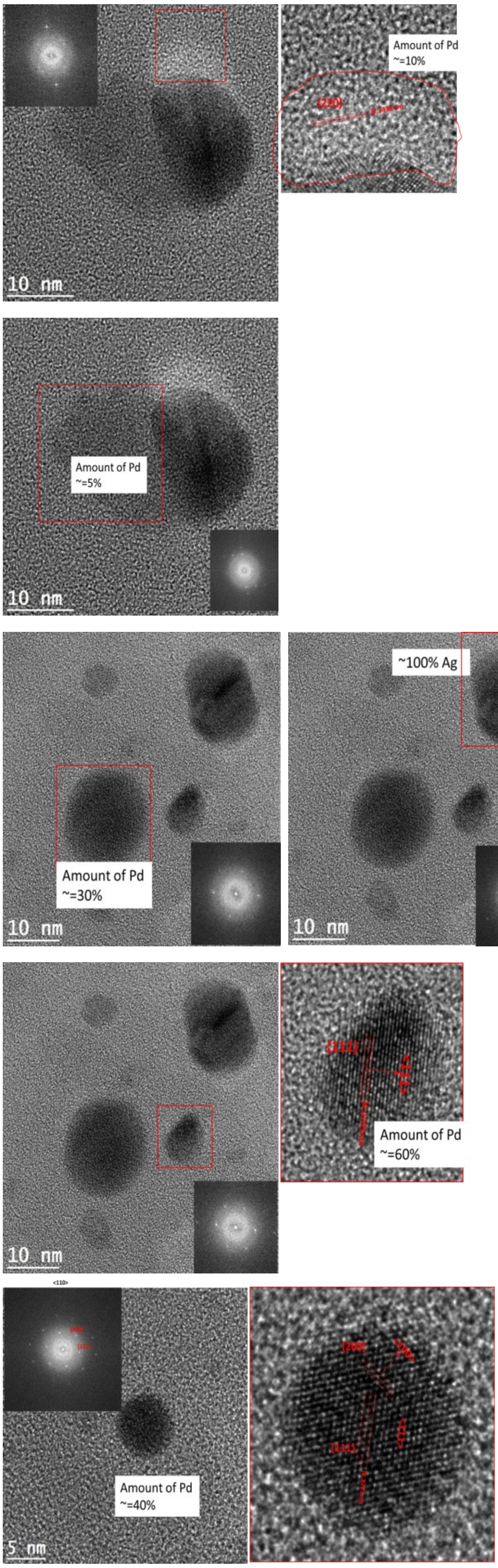


Fig.S8: Lattice fringe analysis of s-AgPd, m-AgPd and b-AgPdby HRTEM and vegard's law

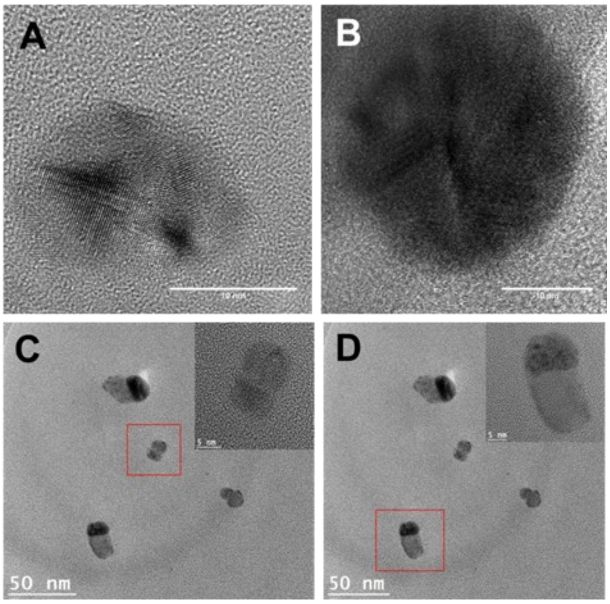
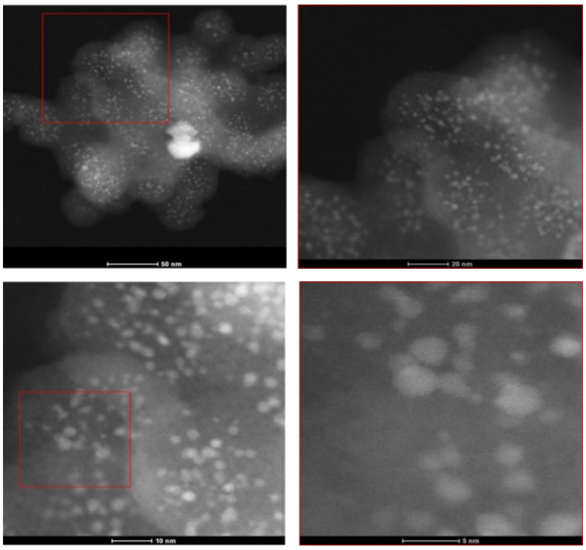
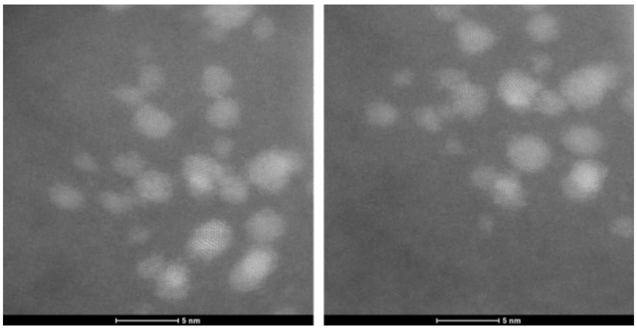


Fig.S9: HRTEM images showing twinned and interfacial particles of m-AgPd (A,B) and b-AgPd (C,D)

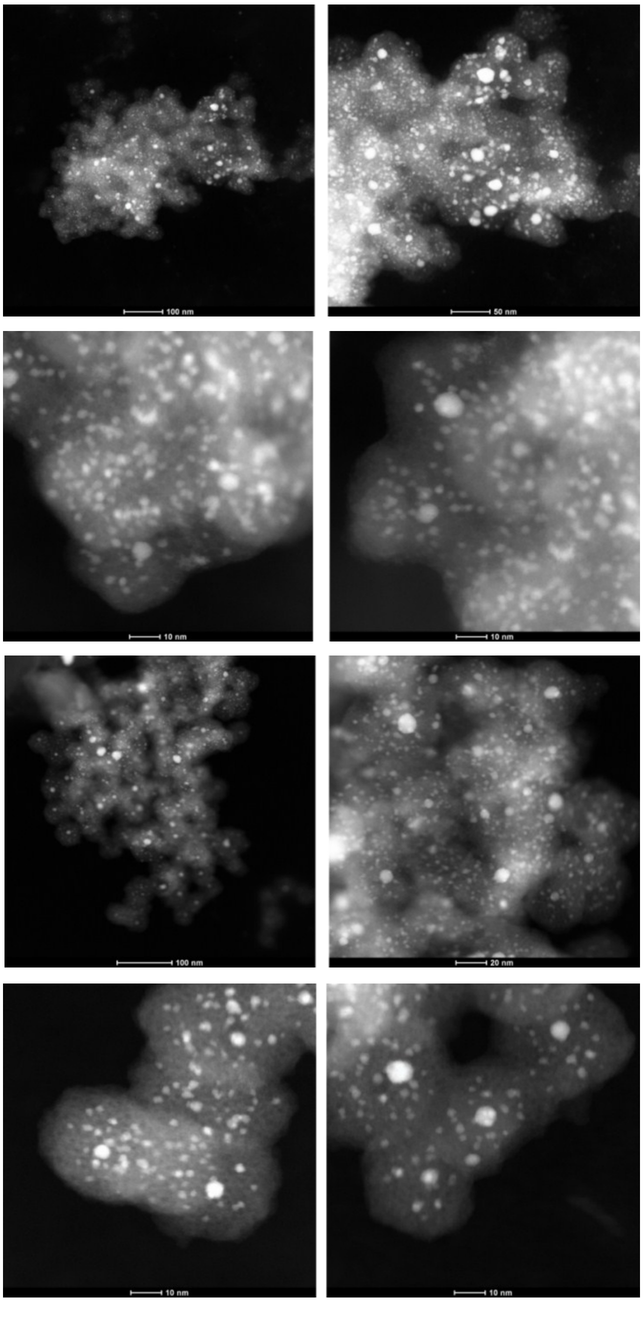
HAADF-STEM imaging

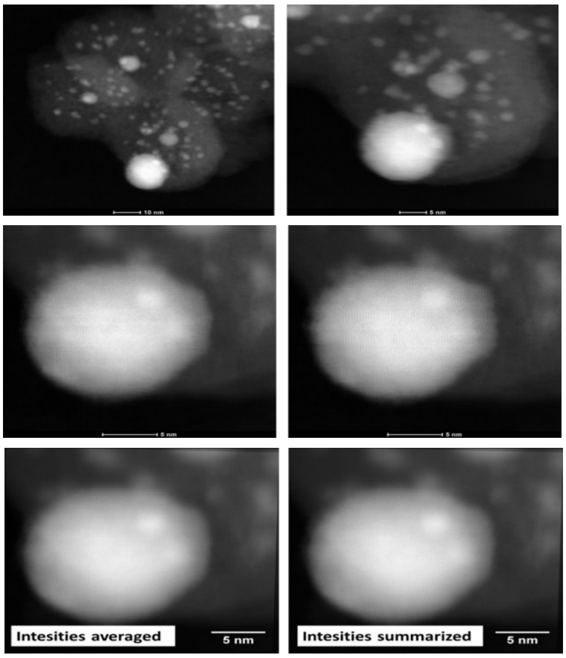
s-AgPd





m-AgPd





b-AgPd

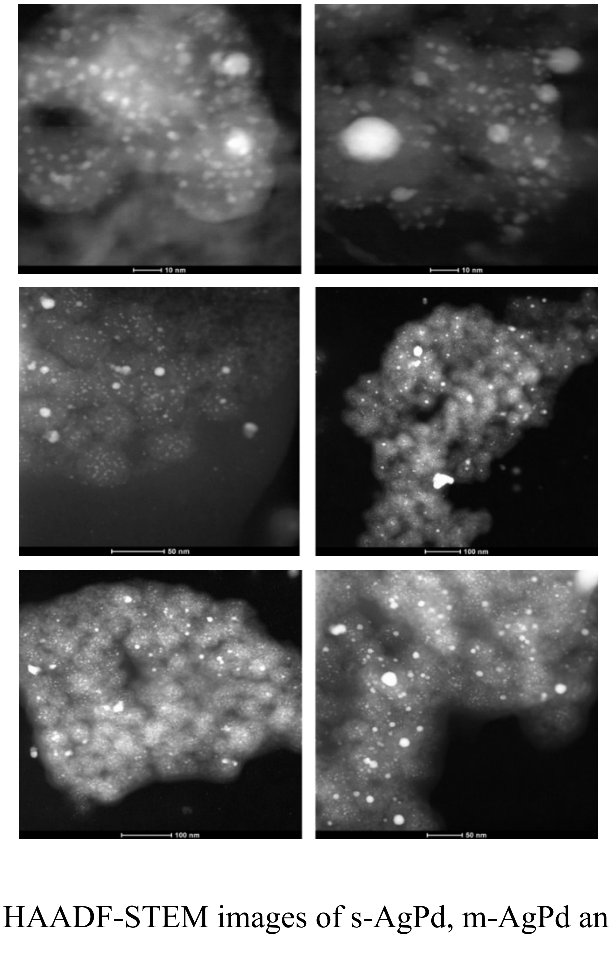
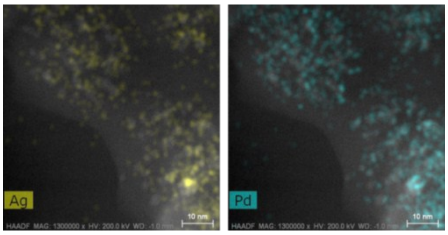
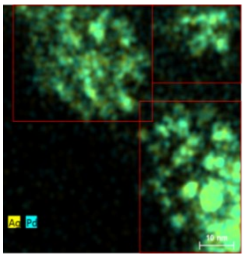


Fig.S10: HAADF-STEM images of s-AgPd, m-AgPd and b-AgPd

HAADF-STEM elemental mapping

s-AgPd



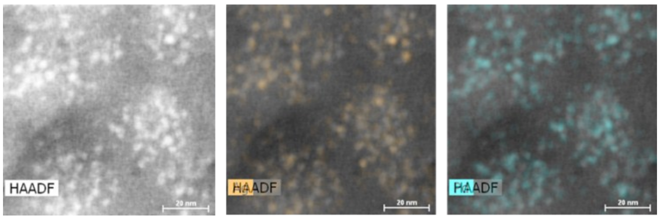


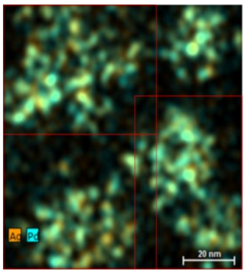
Silver: 48,41 atomic %
Palladium: 51,59 atomic %

Silver: 47,95 atomic %
Palladium: 52,05 atomic %

Silver: 43,05 atomic %
Palladium: 56,95 atomic %

Silver: 48,37% atomic %
Palladium: 51,63 atomic %





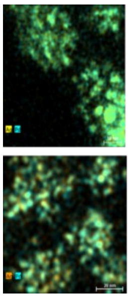
Silver: 54,68 atomic %
Palladium: 45,32 atomic %

Silver: 53,53 atomic %
Palladium: 46,47 atomic %

Silver: 56,40 atomic %
Palladium: 43,60 atomic %

Silver: 49,29% atomic %
Palladium: 50,71 atomic %

Silver: 51,54% atomic %
Palladium: 48,46 atomic %

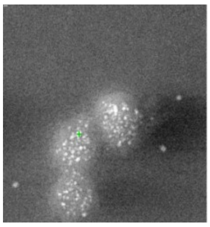


Average composition from both maps:

Silver: 49,96 atomic %
Palladium: 50,04 atomic %

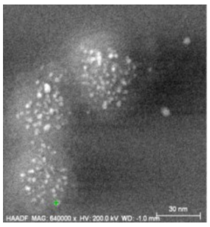
Theoretical composition:

Silver: 66 atomic %
Palladium: 34 atomic %



Quantification L-lines:

Silver: 47,67 atomic %
Palladium: 52,33 atomic %



Quantification L-lines:

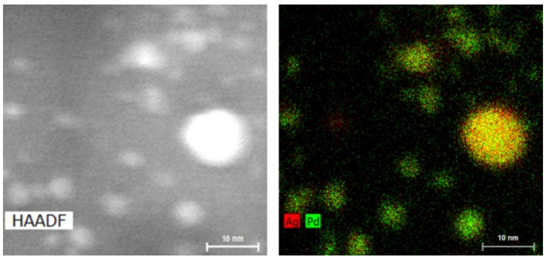
Silver: 69,63 atomic %
Palladium: 30,37 atomic %

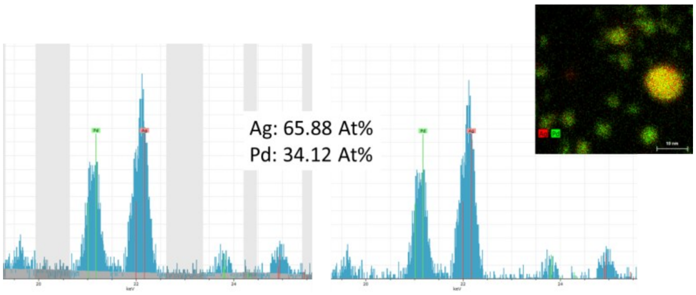
- Composition differs significantly from Ag66Pd34, it is closer to Ag50Pd50

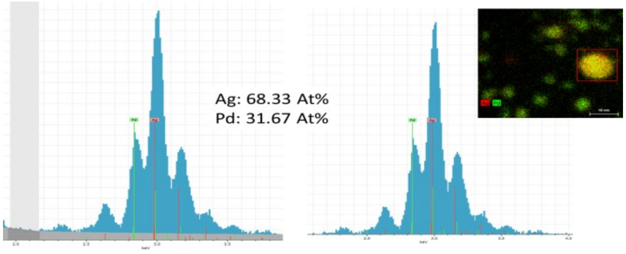
- Second point however gave a result close to the hypothesized values

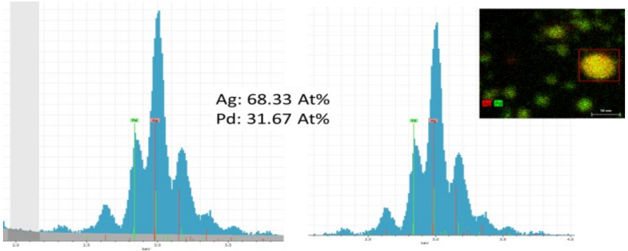
- Maps indicate particles of pure Ag or Pd

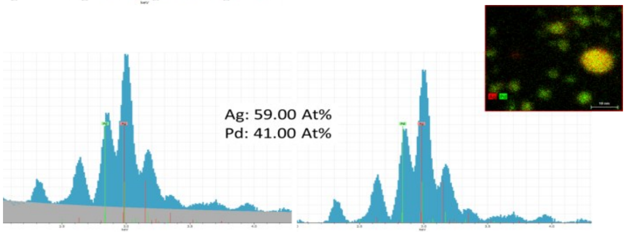
m-AgPd

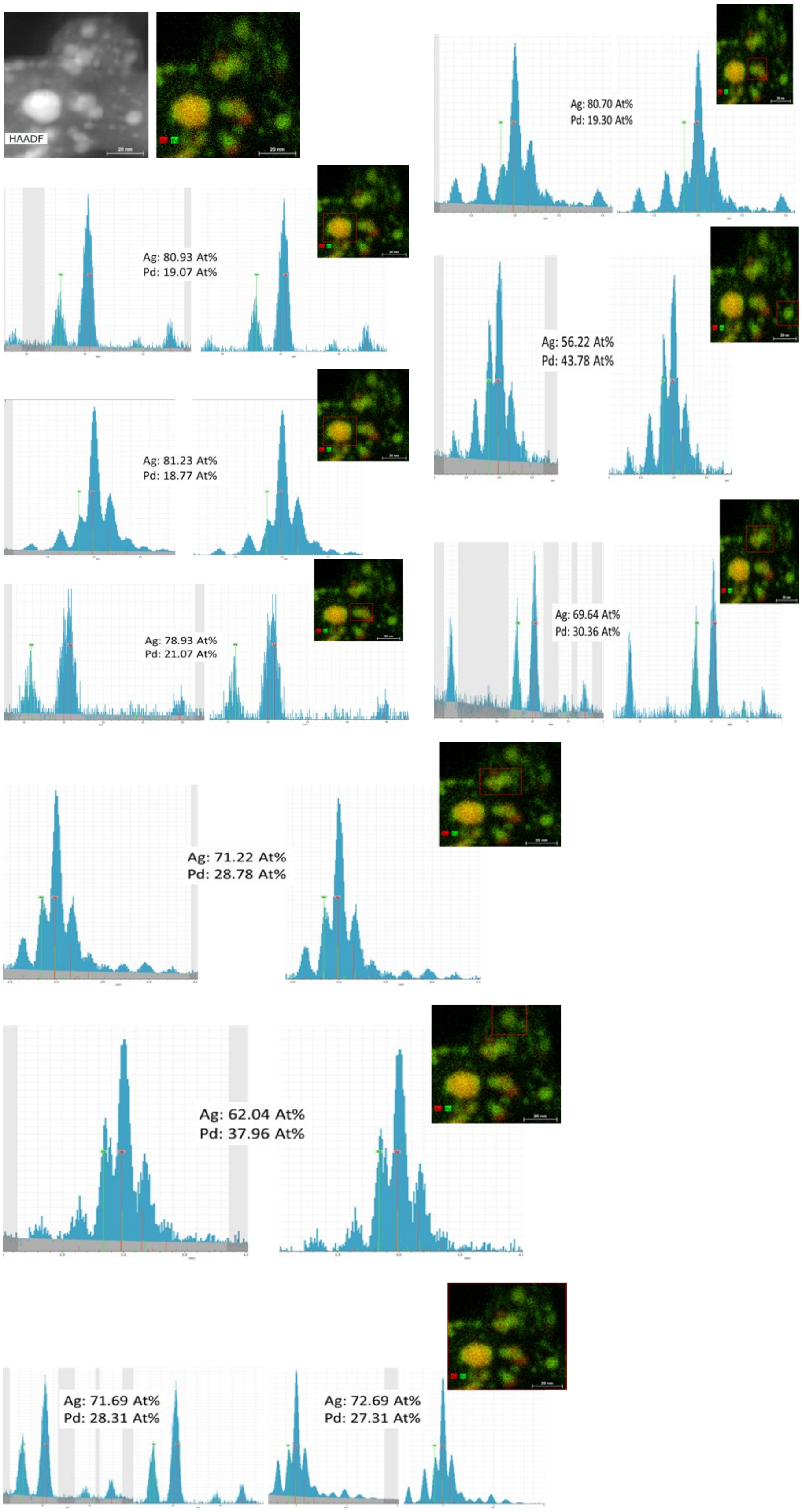

HAADF
10 nm
Ag
Pd
10 nm

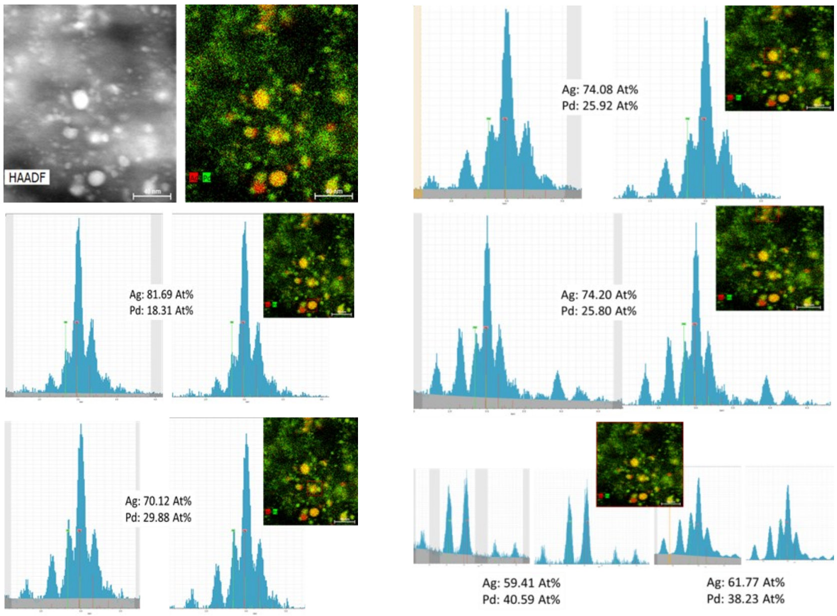

Ag: 65.88 At%
Pd: 34.12 At%

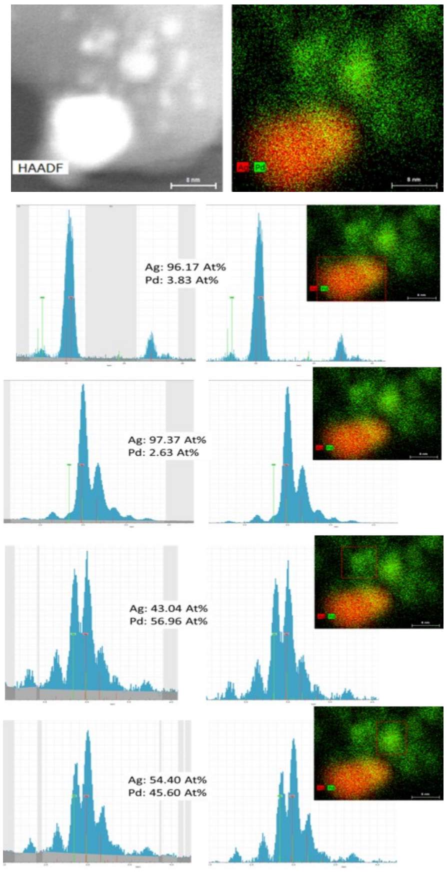

Ag: 68.33 At%
Pd: 31.67 At%

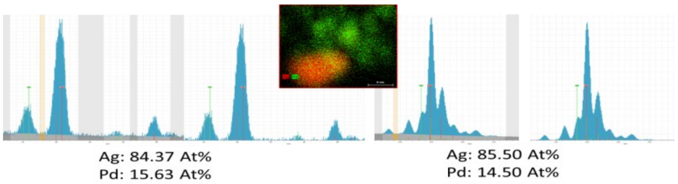

Ag: 68.33 At%
Pd: 31.67 At%


Ag: 59.00 At%
Pd: 41.00 At%


HAADF
20 nm
20 nm
Ag: 80.70 At%
Pd: 19.30 At%
Ag: 80.93 At%
Pd: 19.07 At%
Ag: 56.22 At%
Pd: 43.78 At%
Ag: 81.23 At%
Pd: 18.77 At%
Ag: 78.93 At%
Pd: 21.07 At%
Ag: 69.64 At%
Pd: 30.36 At%
Ag: 71.22 At%
Pd: 28.78 At%
Ag: 62.04 At%
Pd: 37.96 At%
Ag: 71.69 At%
Pd: 28.31 At%
Ag: 72.69 At%
Pd: 27.31 At%
20 nm







- Total average K-lines:
  - Ag = 69,97 At%
  - Pd = 32,03 At%
- Total average L-lines:
  - Ag = 69,74 At%
  - Pd = 30,26 At%
- Total average all lines:
  - Ag = 68,855 At%
  - Pd = 31,145 At%

- Theoretical compo:
  - Ag48Pd52 and Ag phase

b-AgPd

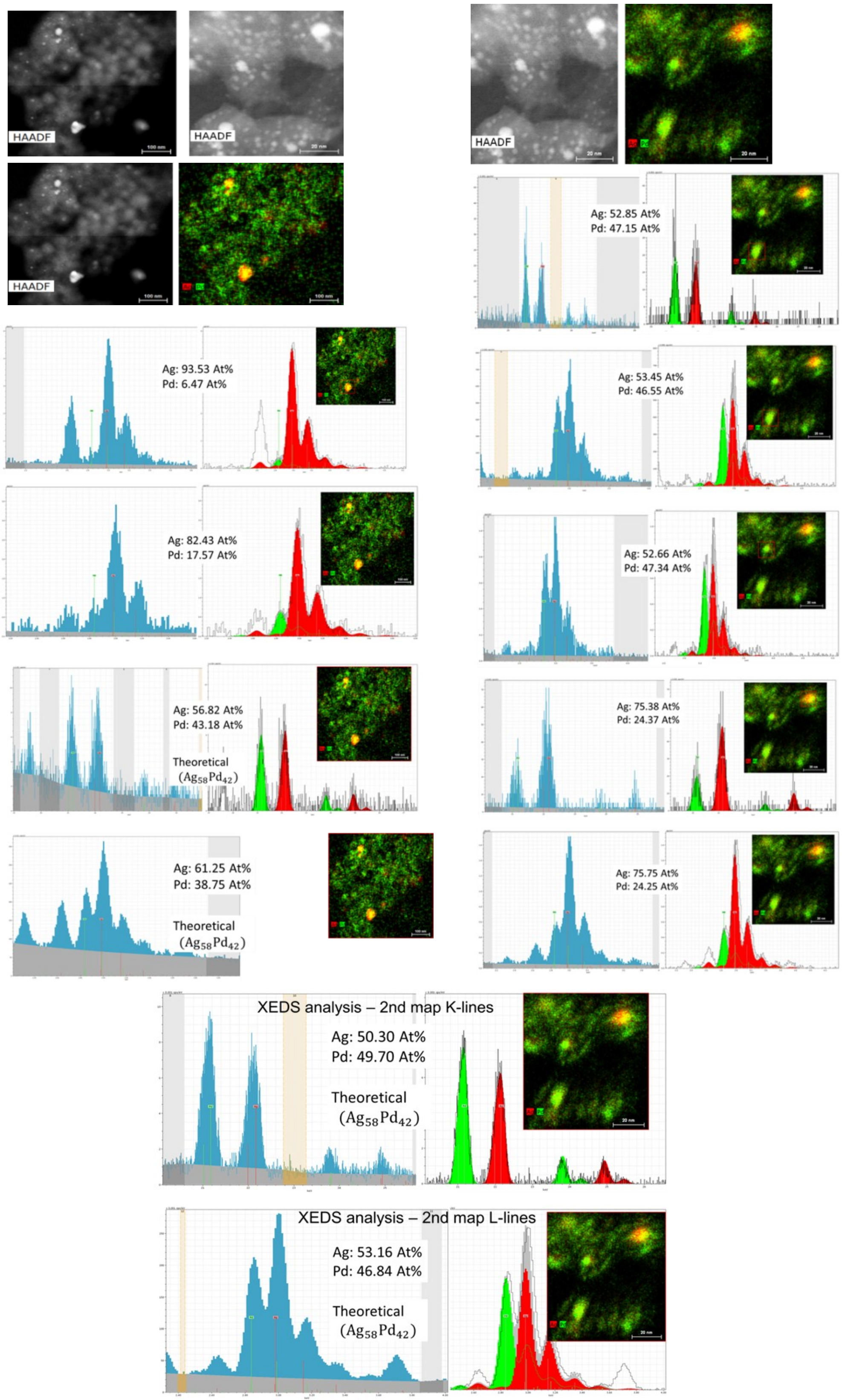


Fig.S11: HAADF-STEM elemental mapping of s-AgPd, m-AgPd and b-AgPd

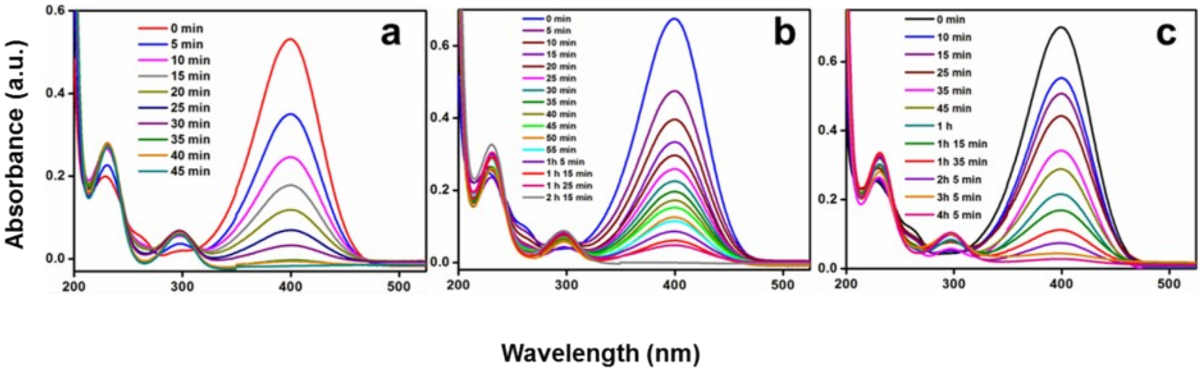


Fig.S12: Time dependent UV-Vis spectra of the reaction mixture with (a) s-AgPd (b) m-AgPd (c) b-AgPd

Table S13: The rates of the reaction with respect to the alloy composition and the available literature survey of the catalysts for PNP reduction

Sample	Rate constants (min^{-1})	Amount of catalyst used(mg)	Acivity ($min^{-1}g^{-1}$)	Alloy composition
s-AgPd	0.0751	0.025	3004	Ag50Pd50
m-AgPd	0.0387	0.025	1548	Ag69Pd31
b-AgPd	0.0209	0.035	597	Ag64Pd36
Ag	0.025	0.0325	769	-
Pd	0.035	0.0375	933	-

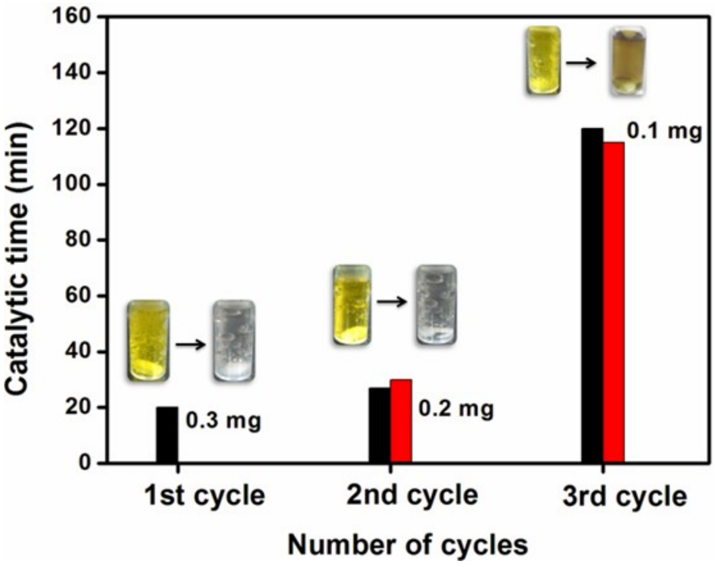


Fig.S14: Recyclability studies of s-AgPd. Used catalyst is indicated by Black bars and freshly added catalyst is indicated by Red bars.

The study showed that in the initial run, the catalyst amount taken is 0.3 mg and the time taken for full decolourisation is 20 min. Then the catalyst was recovered by centrifuge but the amount which could be recovered was 0.2 mg. In this run, time taken was ~25 min. This discrepancy could be attributed to the reduction in amount of catalyst which could be recovered since the same amount of fresh catalyst also took 25 min for full decolourisation. Further reduction of recovered catalyst amount to 0.1

mg in the third cycle affected the catalytic activity drastically but showed comparable data with fresh catalyst. Hence we can conclude that the catalyst does not undergo any degradation during the reaction and can be recycled.