Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Leveling the Playing Ground: Screening for Synergistic Effects in Coalesced Bimetallic Nanoparticles

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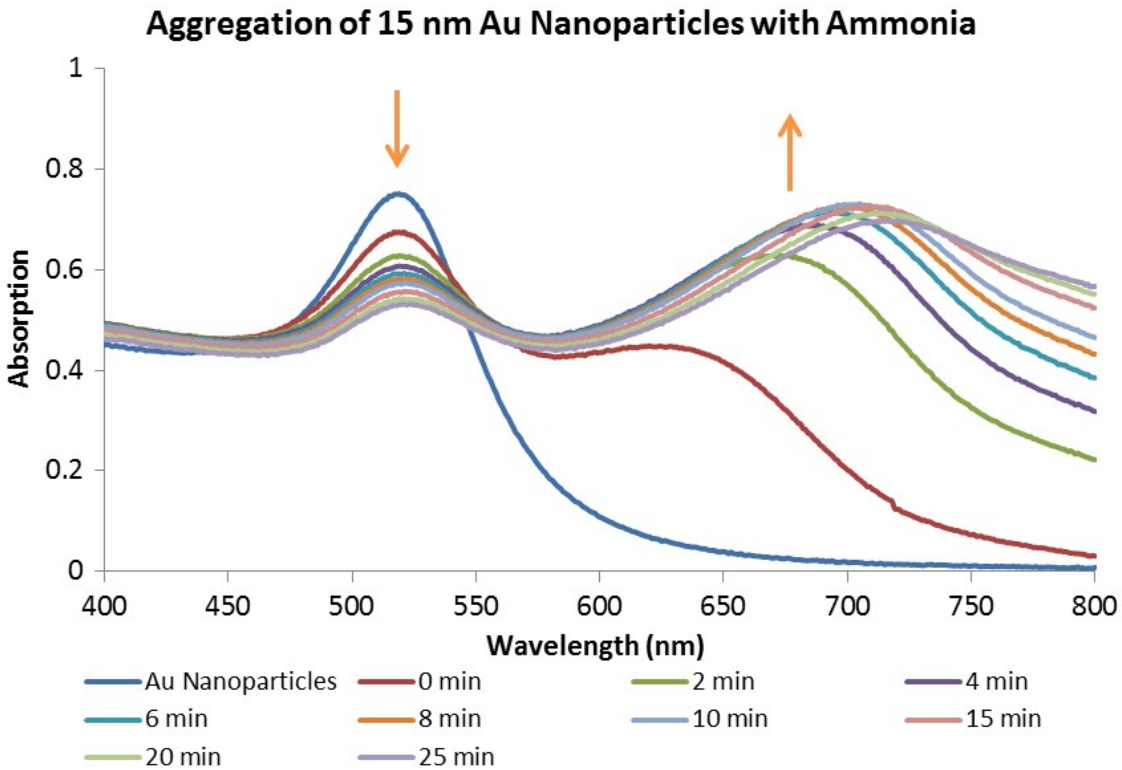


Figure S1. Kinetics UV-vis spectra showing the change in absorption of 15 nm Au nanoparticles caused by the addition of ammonia (final concentration: 360 mM). The decrease in absorption of 520 nm peak and the increase in absorption and redshift of the 650-700 nm peaks were caused by the aggregation of Au nanoparticles.

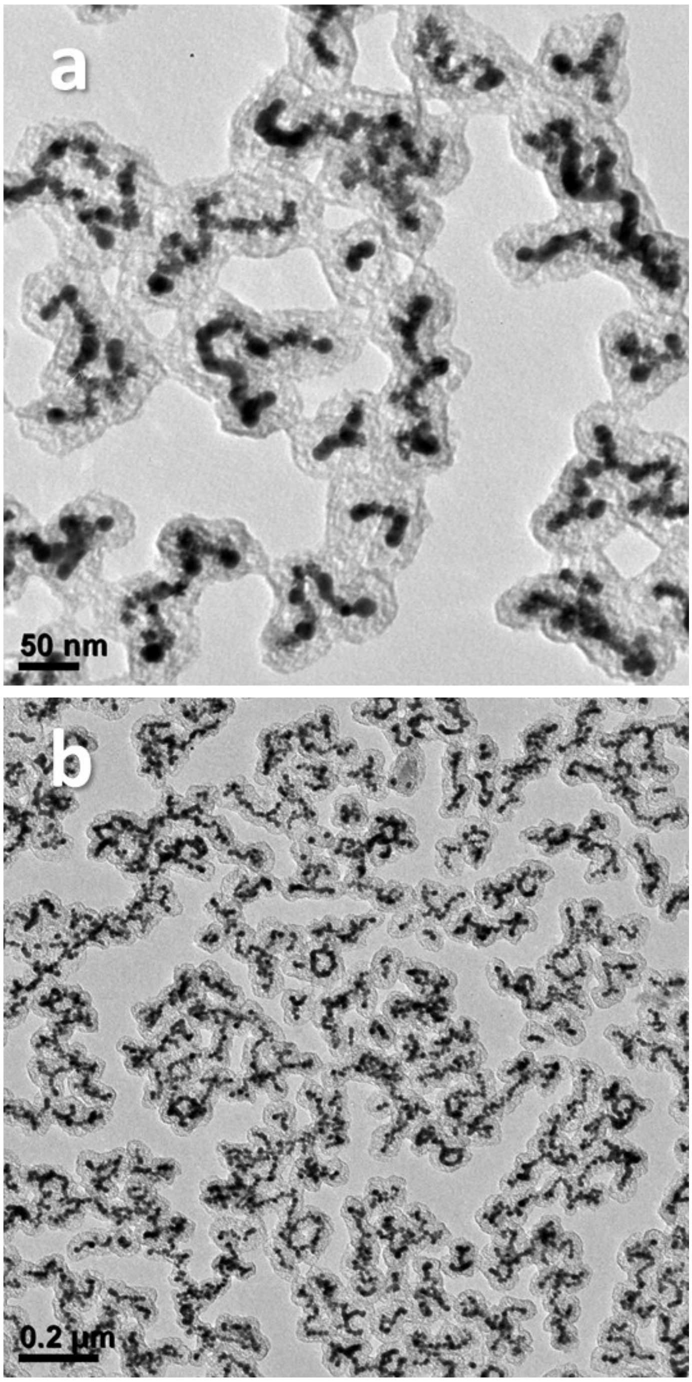


Figure S2. TEM images of Au-Pt bimetallic samples prepared with 15-20 nm nanoparticles: (a) zoom in, and (b) zoom out.

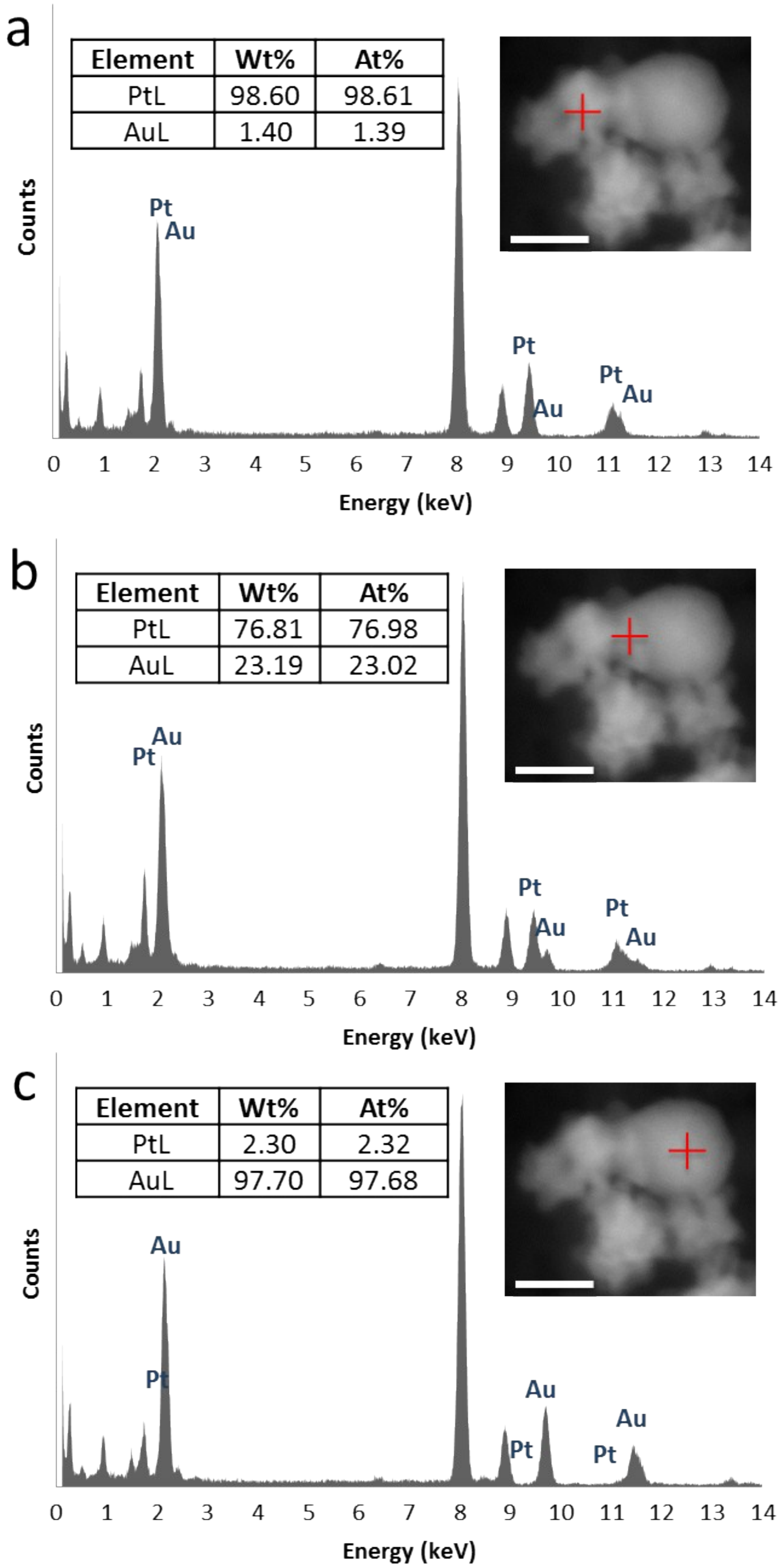


Figure S3. EDS point scans of 3 different regions showing metal composition: (a) Pt; (b) Au-Pt; and (c) Au. Insert scale bars are 10 nm.

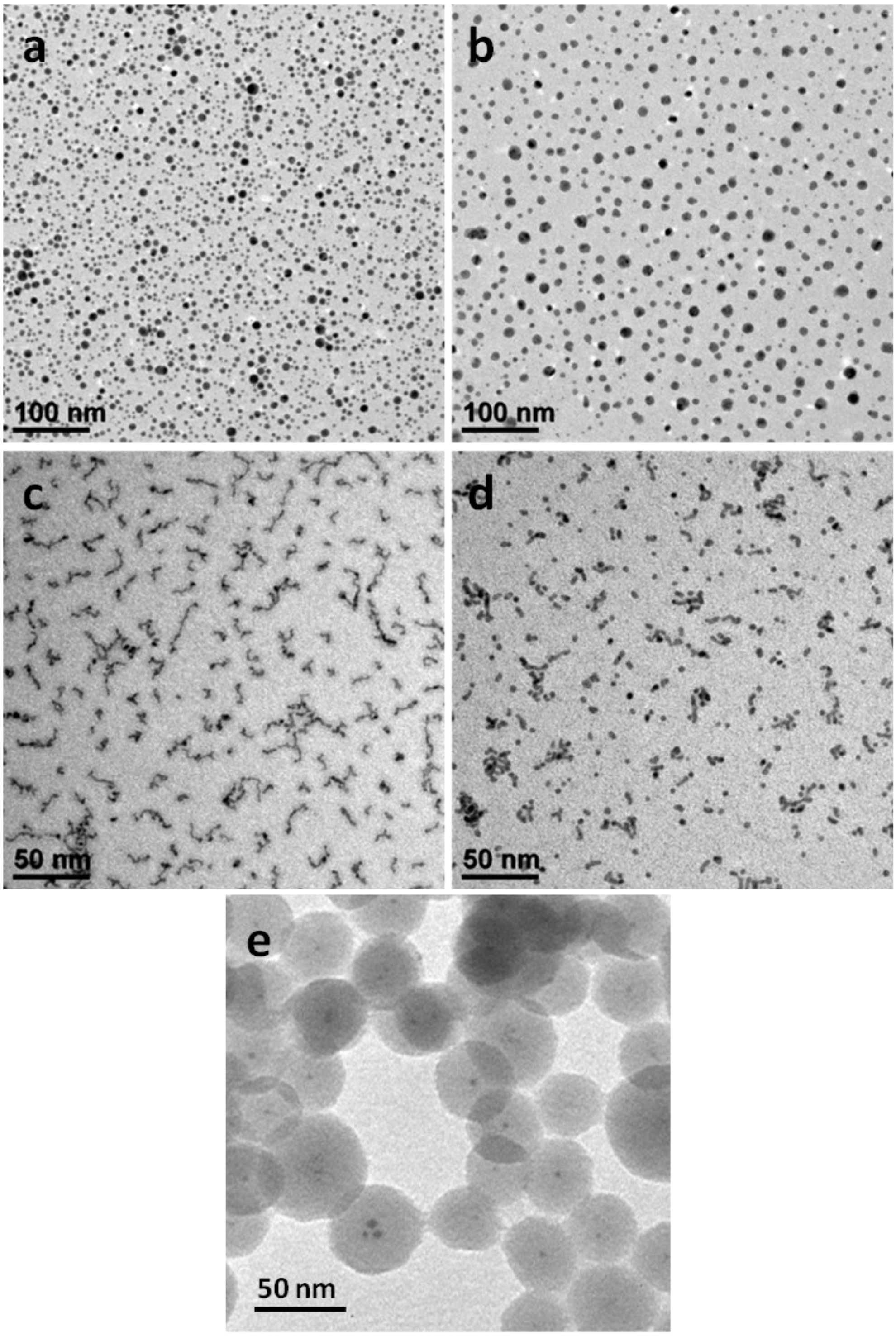


Figure S4. TEM images of nanoparticle stock solution of 5 nm small nanoparticles: (a) Au, (b) Ag, (c) Pt, (d) Pd, and (e) To investigate the aggregation state of the 5 nm Pt nanoparticles, they were coated by silica shells using the reverse emulsion method, giving core-shell nanostructures. The results showed that most of the nanoparticles were not aggregated, suggesting that the slight aggregation observed in c was due to the drying process during TEM sample preparation.

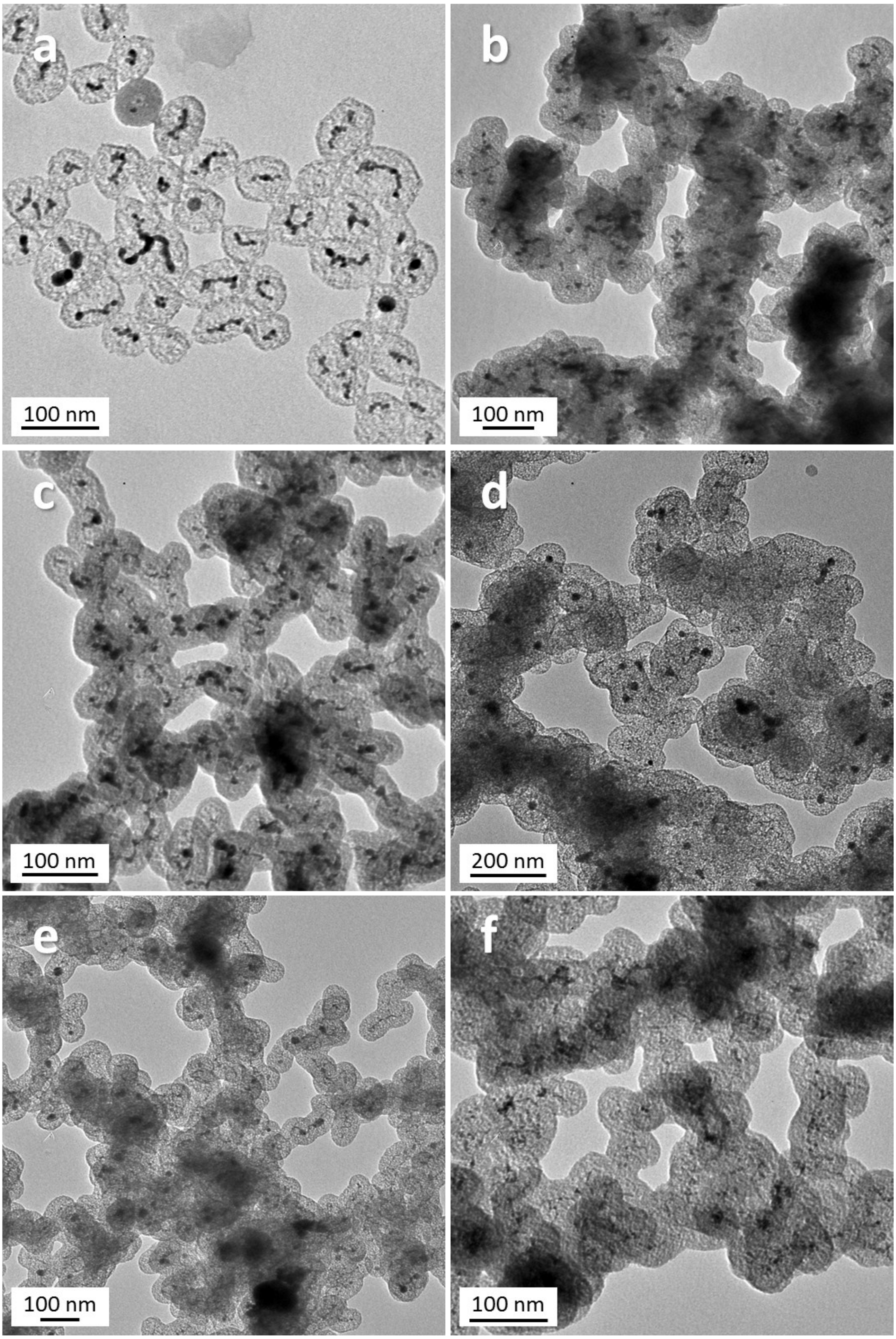


Figure S5. TEM images of bimetallic samples formed with different combinations: (a) Au-Ag; (b) Au-Pd, (c) Au-Pt, (d) Ag-Pd, (e) Ag-Pt, and (f) Pt-Pd.

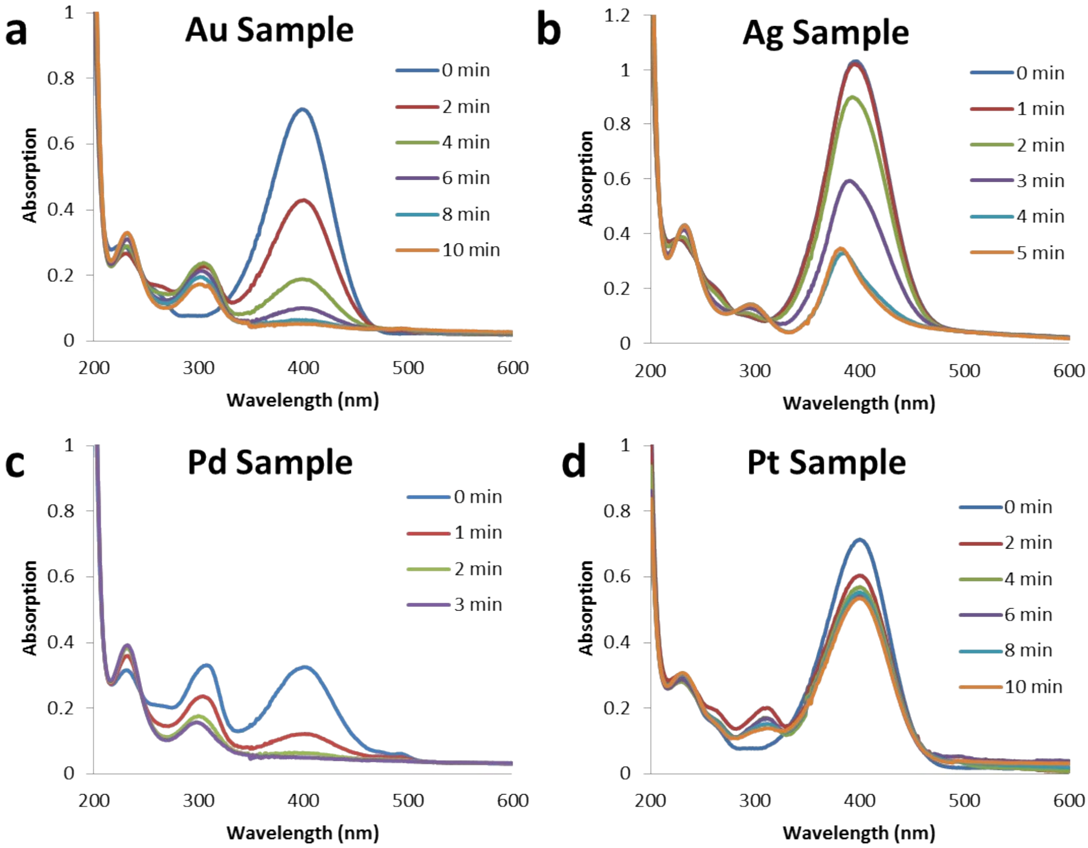


Figure S6. Kinetic UV-Vis spectra of reduction of 4-nitrophenol using mono-metallic samples: (a) Au, (b) Ag, (c) Pd, and (d) Pt.

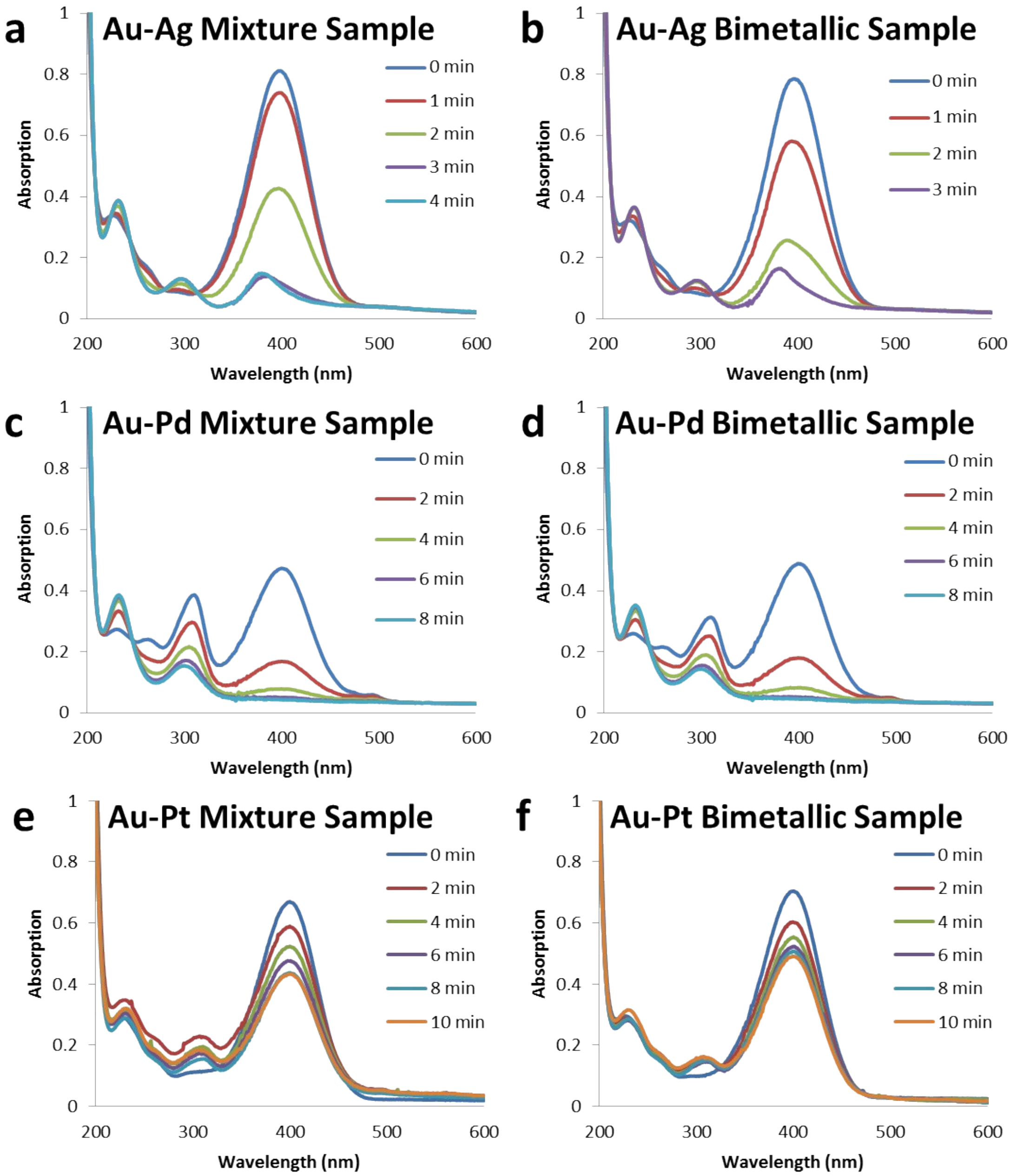


Figure S7. Kinetic UV-Vis spectra of reduction of 4-nitrophenol using mixture and bimetallic samples: (a, b) Au-Ag, (c, d) Au-Pd, and (e, f) Au-Pt.

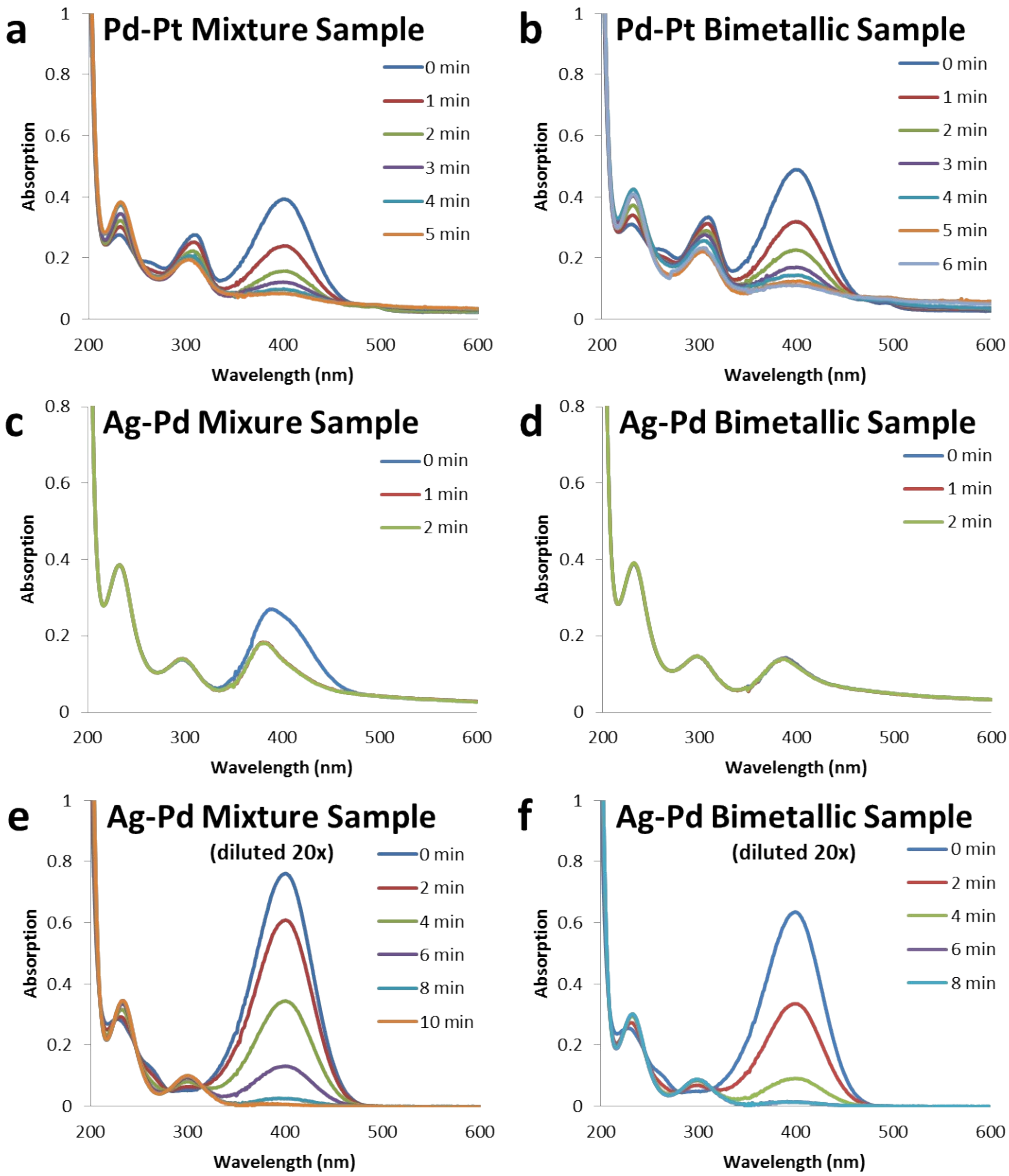


Figure S8. Kinetic UV-Vis spectra of reduction of 4-nitrophenol using mixture and bimetallic samples: (a, b) Pd-Pt, (c, d) Ag-Pd, and (e, f) Ag-Pd (diluted 20 times).

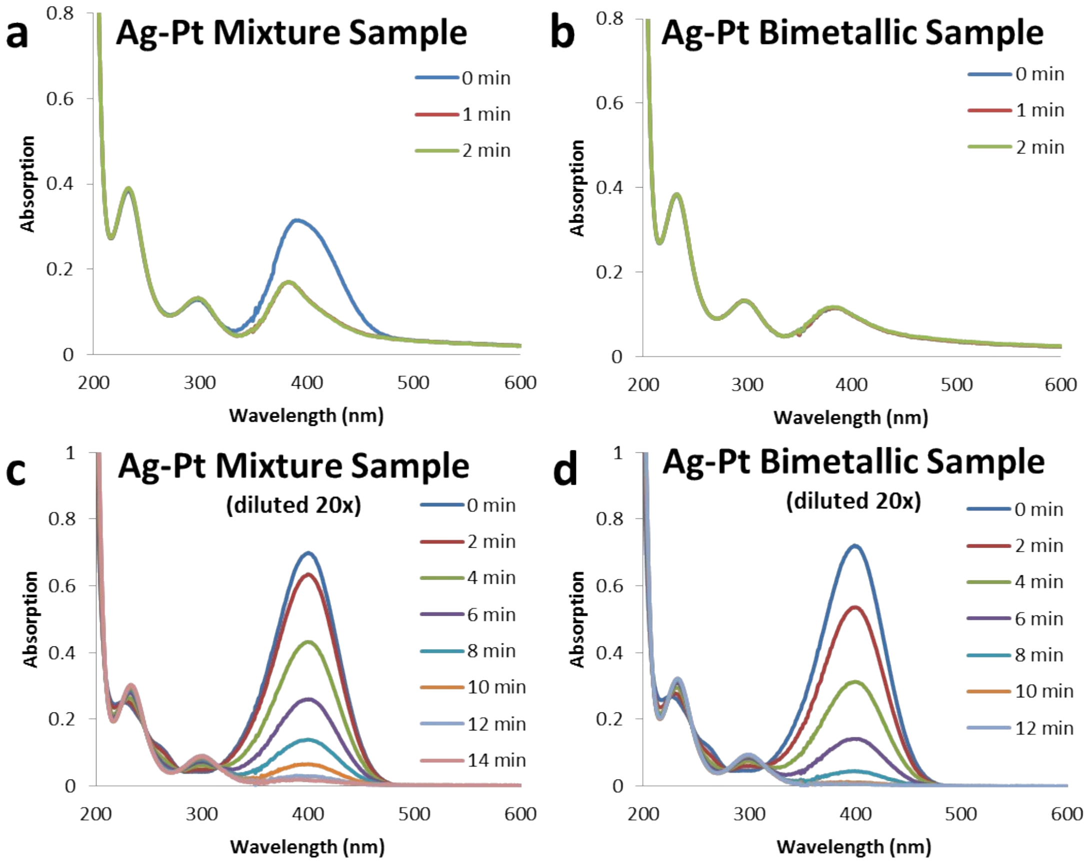


Figure S9. Kinetic UV-Vis spectra of reduction of 4-nitrophenol using mixture and bimetallic samples: (a, b) Ag-Pt, and (c, d) Ag-Pt (diluted 20 times).

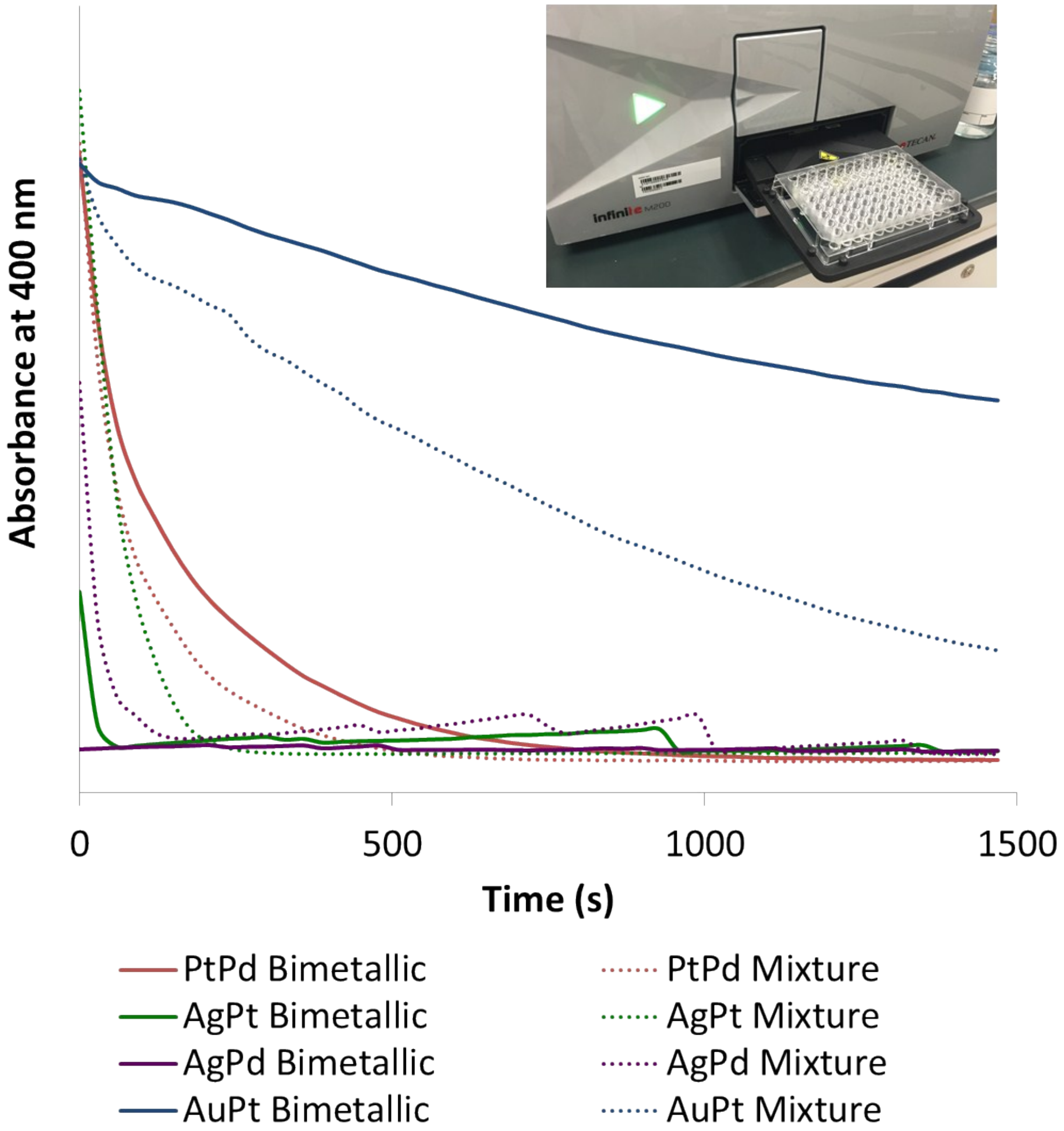
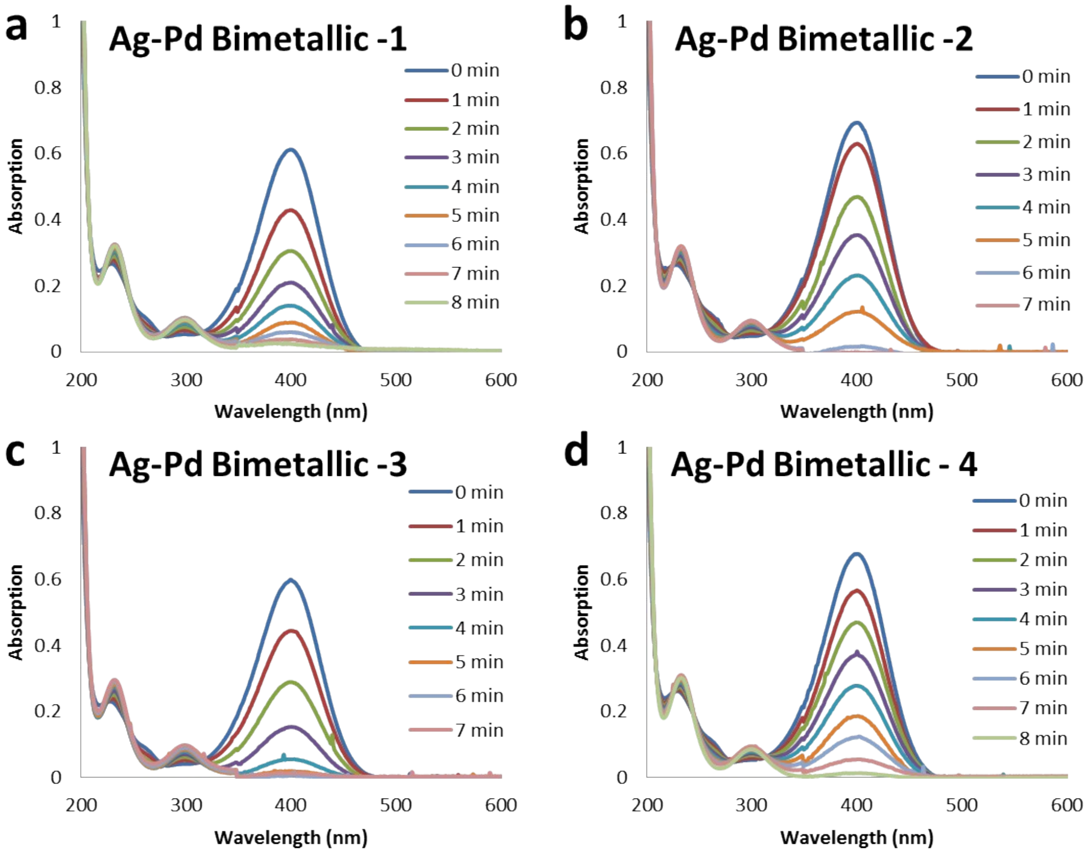
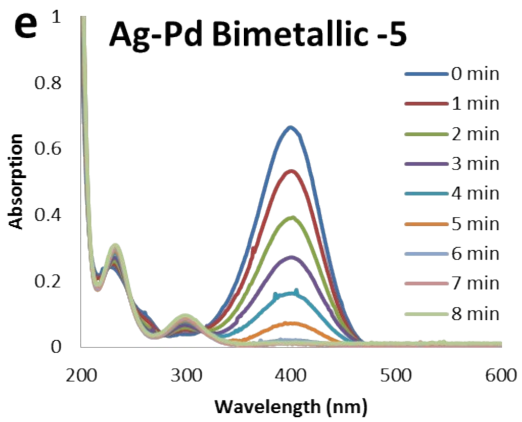


Figure S10. UV-Vis absorption trace at 400 nm for 4 combinations of samples during catalysis (insert: the 96-well microwell plate used in multi-plate reader).





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Sample	Reaction Time (s)	TOF (s^{-1})
AgPd-1	480	30.5×10^{-3}
AgPd-2	420	34.9×10^{-3}
AgPd-3	420	34.9×10^{-3}
AgPd-4	480	30.5×10^{-3}
AgPd-5	480	30.5×10^{-3}
Average TOF		$(32 \pm 2) \times 10^{-3}$

Concentration of catalyst and reactant are 1.46×10^{-9} M and 2.14×10^{-8} M, respectively.

Figure S11. (a-e) Kinetic UV-Vis spectra recorded during the catalytic reduction of 4-nitrophenol with 5 different batches of Ag-Pd bimetallic samples. (f) Tabulation of turnover frequency for the 5 samples in a-e.

Calculations

Enhancement Factor

Total number of moles of metal atoms during nanoparticle synthesis

$$number\ of\ moles\ of\ metal\ atoms = number\ of\ moles\ of\ metal\ salt = 250\ \mu L \times 50\ mM = 1.25 \times 10^{-5}\ mol$$

Number of moles of metal atoms in a typical silica encapsulation (1 mL of each type of nanoparticle used; total metal nanoparticle synthesis volume = 52.2 mL)

$$number\ of\ moles\ of\ metal\ atoms\ used\ during\ silica\ encapsulation$$

$$= 1.25 \times 10^{-5}\ mol \div 52.2\ mL \times 2\ mL = 4.79 \times 10^{-7}\ mol$$

Etching silica encapsulated nanoparticles to form yolk-shell structures (1mL of silica encapsulation solution used, then concentrated to 100 µL)

$$number\ of\ moles\ of\ metal\ atoms\ after\ yolkshell\ structure\ formation$$

$$= 4.79 \times 10^{-7}\ mol \div 1.642\ mL = 2.92 \times 10^{-7} mol\ in\ 100\ \mu L\ solution$$

Number of moles of each type of metal atoms used in each catalytic reaction (10 µL of concentrated solution)

$$number\ of\ moles\ of\ metal\ atoms\ used\ for\ each\ catalytic\ reaction = 2.92 \times 10^{-7} \times \frac{10}{100} = 2.92 \times 10^{-8}\ mol$$

Number of moles of 4-nitrophenol in each catalytic reaction

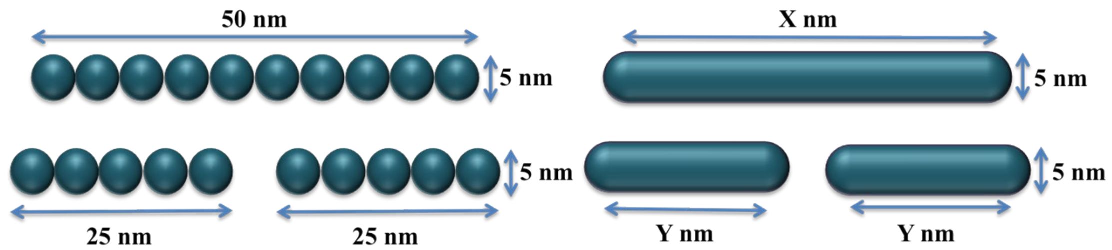
$$number\ of\ moles\ of\ 4-nitrophenol = 15\ mM\ \times 100\ \mu L \times \frac{10}{700} = 2.14 \times 10^{-8}\ mol$$

Turnover Frequency (TOF) = number of mole of product/(number of mole of catalyst × time)

Monometallic Catalyst	Mole of Reactant	Mole of Catalyst	Reaction Time	TOF (s^{-1})
Au	2.14 x10^{-8}	2.92 x 10^{-8}	600	1.22x10^{-3}
Ag	2.14 x10^{-8}	2.92 x 10^{-8}	300	2.44x10^{-3}
Pt	2.14 x10^{-8}	2.92 x 10^{-8}	-	-
Pd	2.14 x10^{-8}	2.92 x 10^{-8}	180	5.94x10^{-3}

Metal Combination	Mole of Reactant	Mole of Catalyst	TOF Mixture (s^{-1})	TOF Bimetallic (s^{-1})	Enhancement Factor (EF)
AuAg	2.14 x10^{-8}	2.92 x 10^{-8}	3.05×10^{-3}	4.07×10^{-3}	1.33
AuPd	2.14 x10^{-8}	2.92 x 10^{-8}	1.53×10^{-3}	1.53×10^{-3}	1
AuPt	2.14 x10^{-8}	2.92 x 10^{-8}	-	-	-
AgPd	2.14 x10^{-8}	1.46 x 10^{-9}	24.4×10^{-3}	30.5×10^{-3}	1.25
AgPt	2.14 x10^{-8}	1.46 x 10^{-9}	17.4×10^{-3}	20.4×10^{-3}	1.17
PdPt	2.14 x10^{-8}	2.92 x 10^{-8}	2.44×10^{-3}	2.04×10^{-3}	0.83

Surface Area Calculation



Total volume of nanoparticles (5 nm)

$$volume\ of\ each\ \ nanoparticle = \frac{4}{3}\pi r^3$$

$$total\ volume\ of\ 10\ nanoparticles = 10 \times \frac{4}{3}\pi r^3$$

$$total\ volume\ of\ 5\ nanoparticles = 5 \times \frac{4}{3}\pi r^3$$

Surface area of nanowire formed from the coalescence of 10 nanoparticles

$$Volume\ of\ nanowire = \frac{4}{3}\pi r^3 + \pi r^2 X$$

$$10 \times \frac{4}{3}\pi r^3 = \frac{4}{3}\pi r^3 + \pi r^2 X$$

$$10 \times \frac{4}{3}\pi r(2.5)^3 = \frac{4}{3}\pi(2.5)^3 + \pi(2.5)^2X$$

$$X = 30\ nm$$

$$Surface\ area = 4\pi r^2 + 2\pi rX = 4\pi(2.5)^2 + 2\pi(2.5)(30) = 550\ nm^2$$

Surface area of two nanowire formed from the coalescence of 5 nanoparticles each

$$Volume\ of\ nanowire = \frac{4}{3}\pi r^3 + \pi r^2Y$$

$$5 \times \frac{4}{3}\pi(2.5)^3 = \frac{4}{3}\pi(2.5)^3 + \pi(2.5)^2Y$$

$$Y = 13.3\ nm$$

$$Surface\ area = 2\left[4\pi r^2 + 2\pi rY\right] = 2\left[4\pi(2.5)^2 + 2\pi(2.5)(13.3)\right] = 575\ nm^2$$

% Surface area difference between a nanowire formed by coalescence of 10 nanoparticles and two nanowires formed by coalescence of 5 nanoparticles each

$$\%\ Difference = \frac{575 - 550}{575} \times 100\% = 4.3\%$$

__Number of nanoparticles in our encapsulation system__

Mass of two metal = 4.79×10^{-7} mol × 196.96657 mol/g = 9.4347×10^{-5} g

Total volume of Au metal = mass ÷ density

= $(9.4347 \times 10^{-5}/2) \div 19.3\ g/cm^3 = 2.4442 \times 10^{-6}\ cm^3$

Volume of one 5 nm nanoparticle = $4/3 \times \pi \times (2.5)^3 = 65.5\ nm^3$

Number of nanoparticles for Au metal = $2.4442 \times 10^{-6} \div 65.5 \times 10^{-20} = 3.73 \times 10^{12}$ particles