Rational synthesis of mono and bi-metallic nanoparticles for plasmonic catalysis

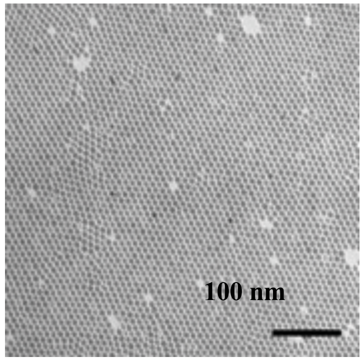
Alexa COURTY

Sorbonne University, Laboratory : From **Mo**lecule to **Na**no-object: **R**eactivity, **I**nteractions and **S**pectroscopies (MONARIS)

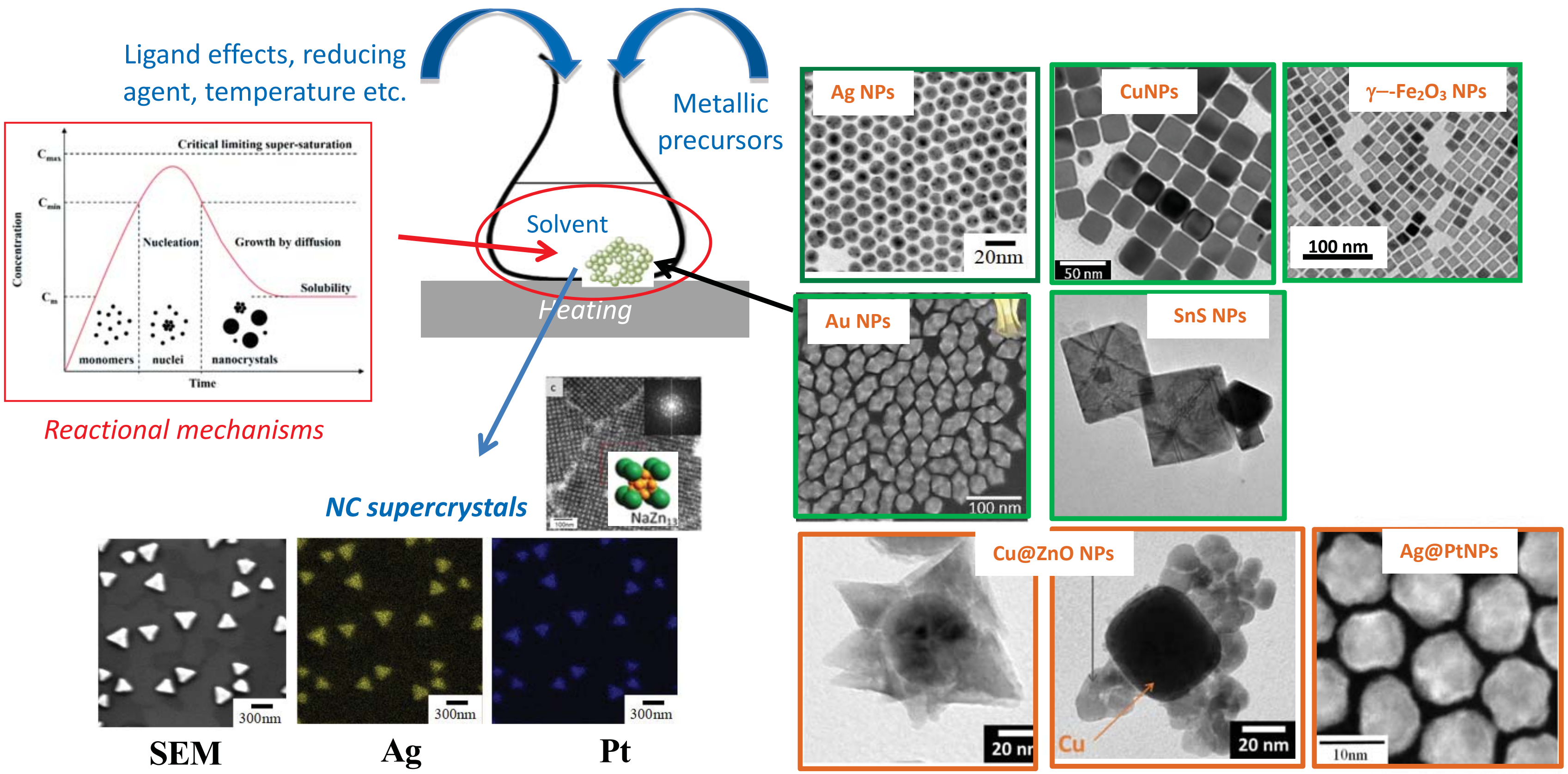
GDR Or-nano/ plasmoniqueActive , 25-27 octobre 2023

Nanomaterials and nanostructured materials:
Reactivity, Caracterisations and
Spectroscopies

NARCOS TEAM

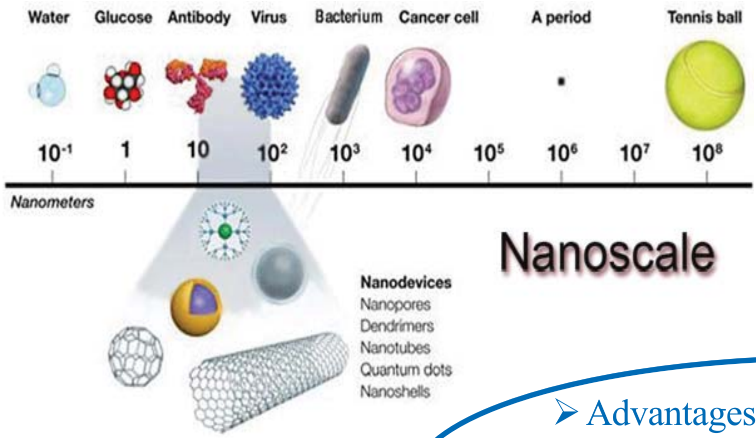


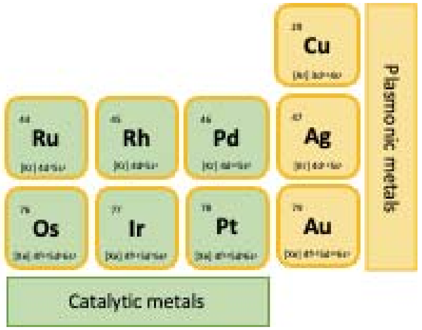
Rational synthesis of mono and multicomponent NCs

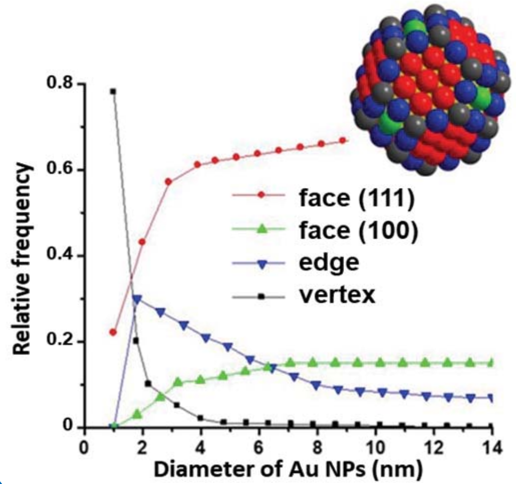


General introduction

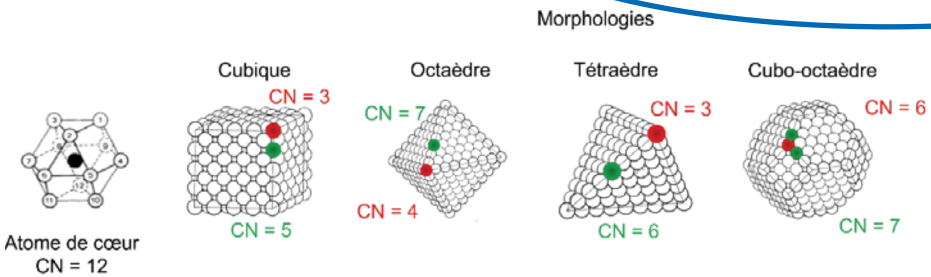
Nanomaterials as Nanocatalysts



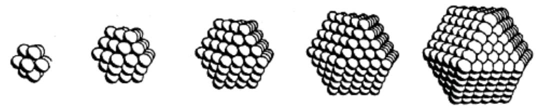




- ➢ Advantages of **nanomaterials**
  - High surface area per unit volume
  - High density of low coordination atoms
- ➢ **Efficient for catalysis**

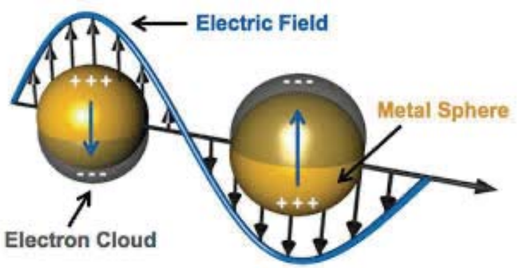


Full-Shell "Magic Number" Clusters

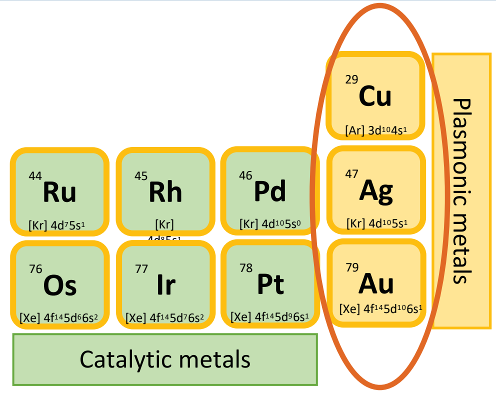


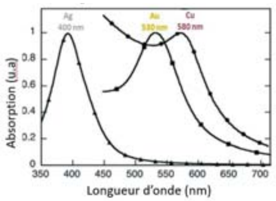
Number of shells	1	2	3	4	5
Number of atoms in cluster	M_{13}	M_{55}	M_{147}	M_{309}	M_{561}
Percentage surface atoms	92%	76%	63%	52%	45%

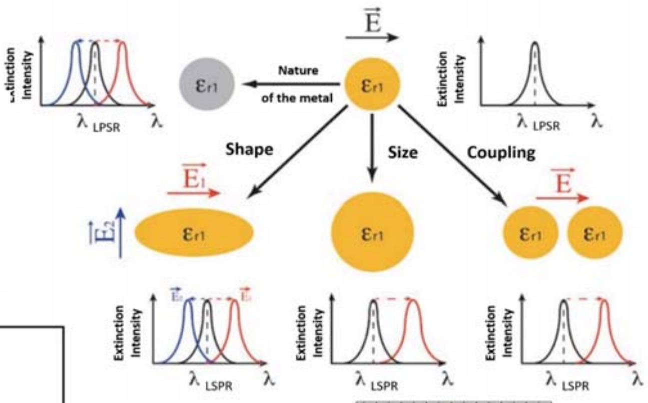
Nanocatalysts and plasmonic properties

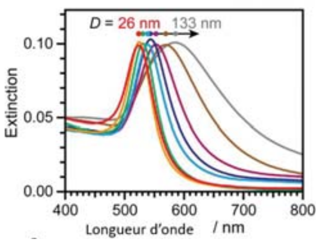


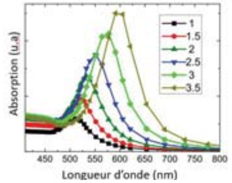
Localized Surface plasmon Resonance (LSPR) :
Collective oscillation of conduction electrons of metal nanoparticles (NPs) irradiated by an external electromagnetic field



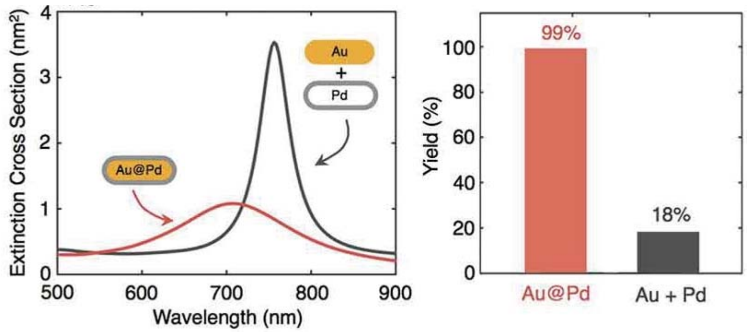








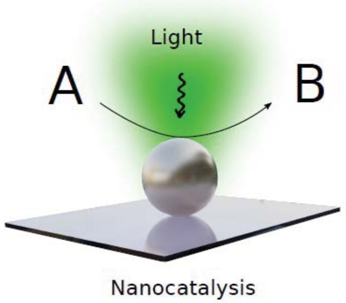
yield of the Suzuki coupling reaction between bromobenzene and m-tolylboronic acid under illumination

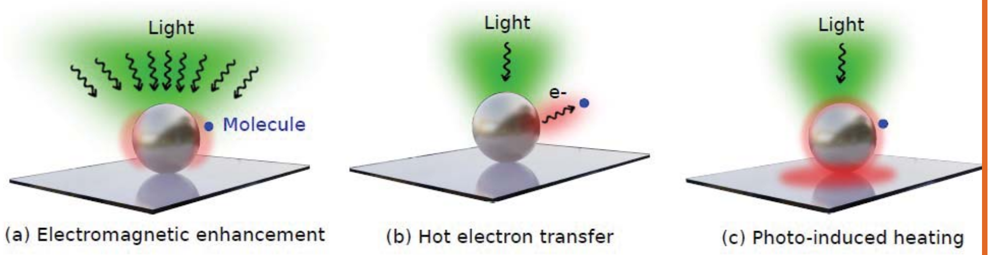


K. Sytwu et al , Advances in physics, 2019 n 4, 1619840

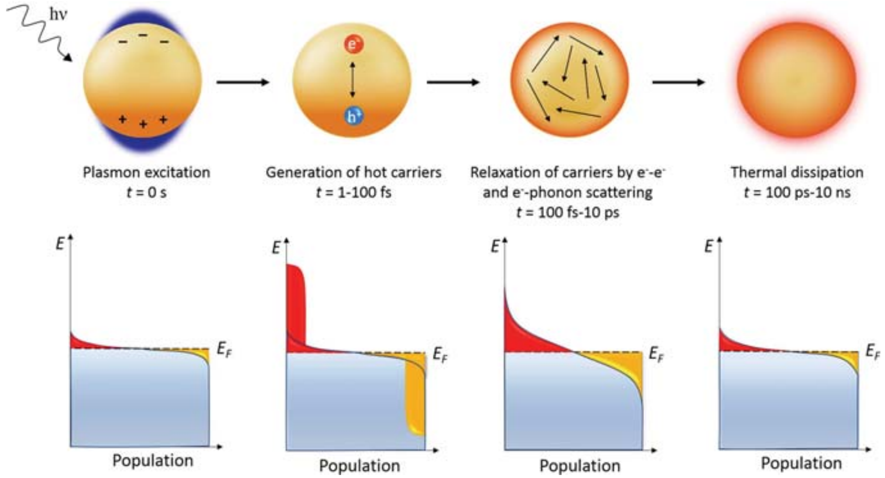
Nanocatalysts and plasmonic properties

❖ **Mechanisms in plasmonic catalysis**



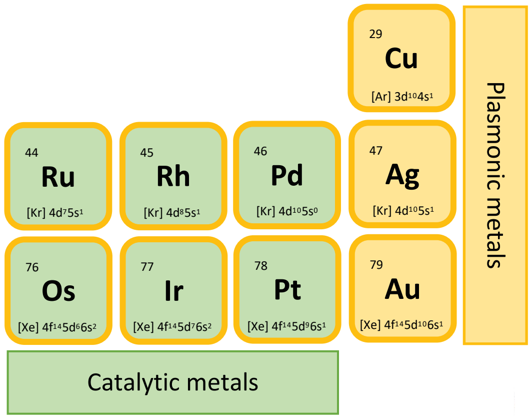


❖ **Time scale:**

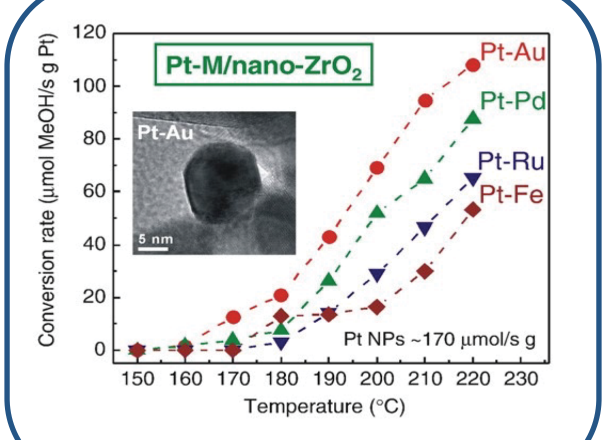


M. Ahlawat et al, COMMUNICATIONS MATERIALS | (2021) 2:114 | https://doi.org/10.1038/s43246-021-00220-4

Advantages of bi-component NPs

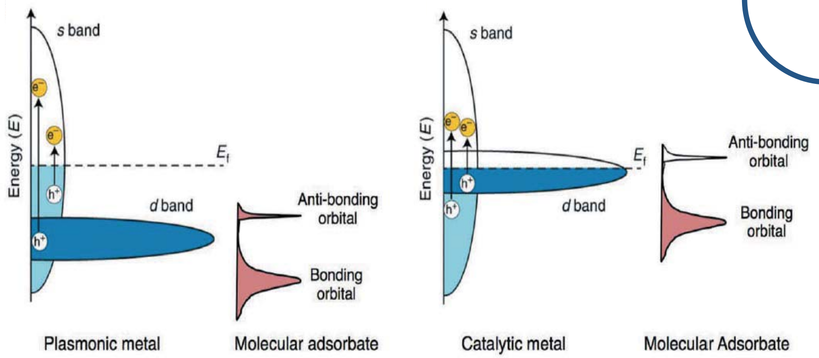


- Combine materials with different properties
- offer increased reaction rates and product selectivity in catalysis
- Stability
- Economic interest



Appl. Catal. A, 350, J.R. Croy et al., 2008

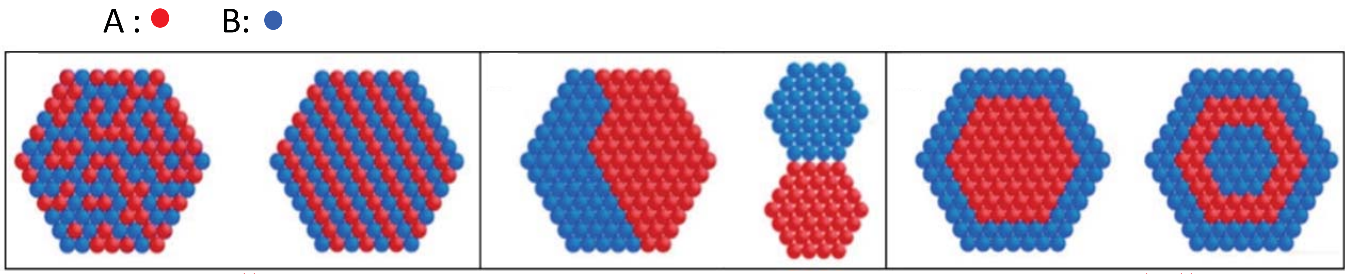
Plasmonic metals



Catalytic Metals

synergy

Structure of bi-component NPs



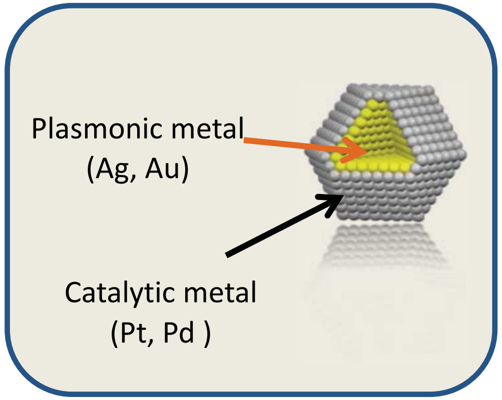
Alloys Janus Core-shell

➢ Parameters affecting miscibility:

- Bond dissociation energy (alloys favor for $E_{AB} > E_{AA}$ and E_{BB})
- Surface energies
- Relative atomic radius
- Electronic transfer from less to more electronegative elements
- Ligand adsorption

➢ Plasmonic core @catalytic shell NPs:

optical and electronic coupling with distinct interface between the two metal (synergetic effects)



Zaleska-Medynska, A.; Marchelek, M.; Diak, M.; Grabowska, E. Noble Metal-Based Bimetallic Nanoparticles: The Effect of the Structure on the Optical, Catalytic and Photocatalytic Properties. Adv. Colloid Interface Sci. 2016, 229, 80–107. https://doi.org/10.1016/j.cis.2015.12.008.

Synthesis process of Ag@Pt NPs

Synthetic approach of Ag@Pt NPs

➢ **Physical-chemical properties of Ag, Pt metals**

Metals	Crystal lattice	Lattice parameter (A)	Bulk cohesive energy	Reduction potentials (E^0)	Surface energy (Jm^{-2})	Atomic radius (pm)	Electro-negativity
Ag	fcc	4.09	284	0.80	~1.2	160	1.9
Pt	fcc	3.92	564	1.18	~2.6	139	2.2

Higher redox potential, cohesive energy and surface energy of Pt than of Ag

↓

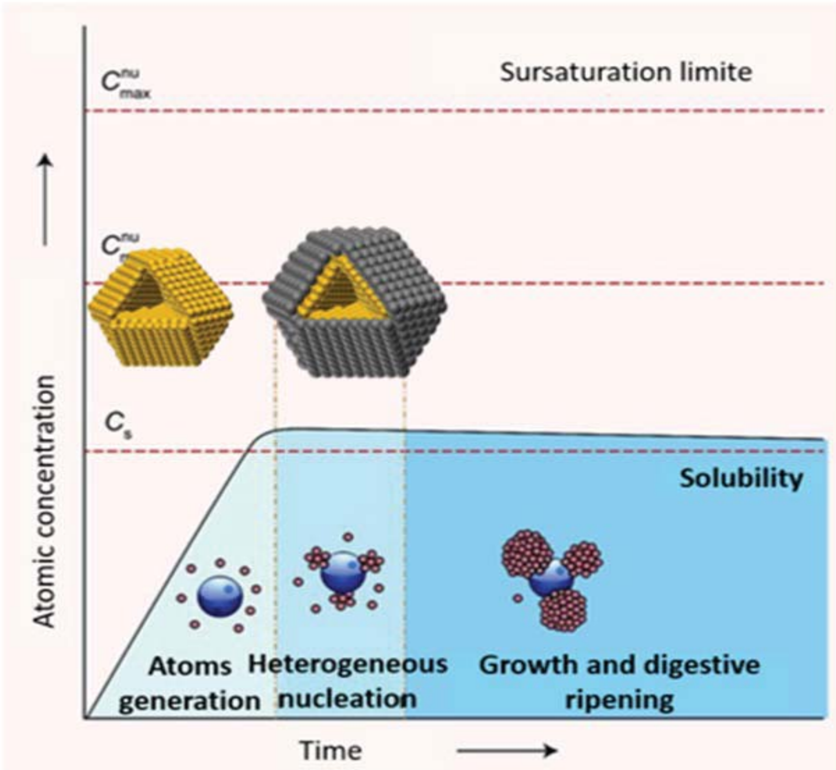
Pt@Ag NPs

↓

Seed mediated growth (two-steps process): to obtain Ag@Pt NPs and prevent the formation of Pt@Ag NPs

Synthetic approach of Ag@Pt NPs

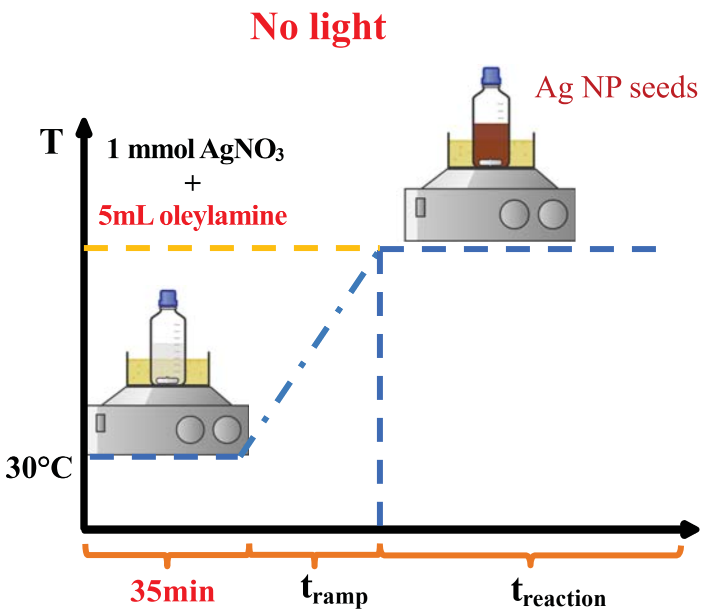
➤ **Seed mediated growth (two-steps) process**

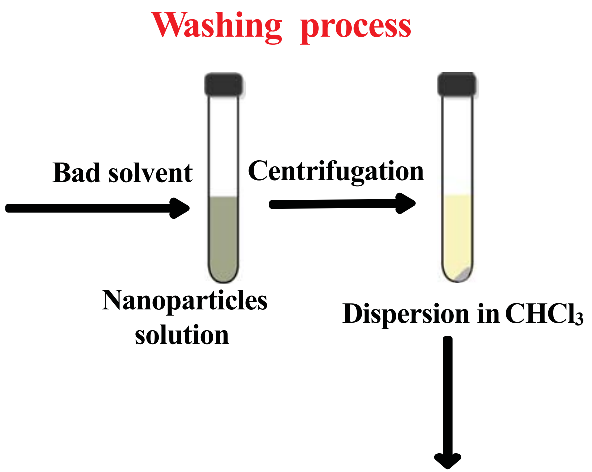


Y. Sun, Interfaced heterogeneous nanodimers, National Science Review 2(3) (2015) 329-348.

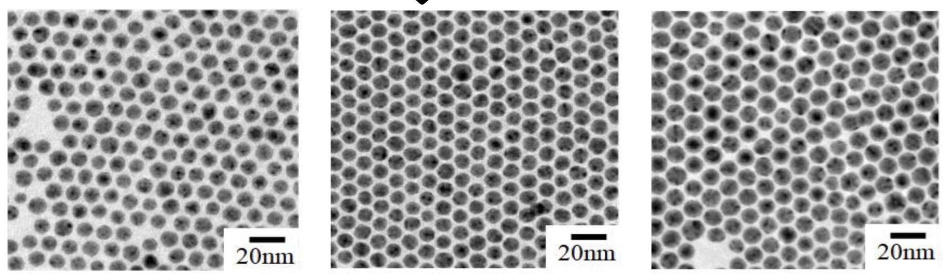
Synthetic approach of Ag@Pt NPs

➢ first step : synthesis of Ag NPs





Ramping rate: 450°C/h
$t_{reaction}$= 1h
T = 120°C, 140°C and 240°C



8.4±0.7 nm 10.5±0.9nm 13.3±1.3 nm

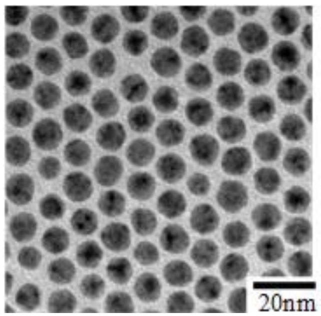
Y. Fanet al. Ag@Pt Core−Shell Nanoparticles for Plasmonic Catalysis, ACS Appl. Nano Mater., 6, 2, 1193–1202 (2023)

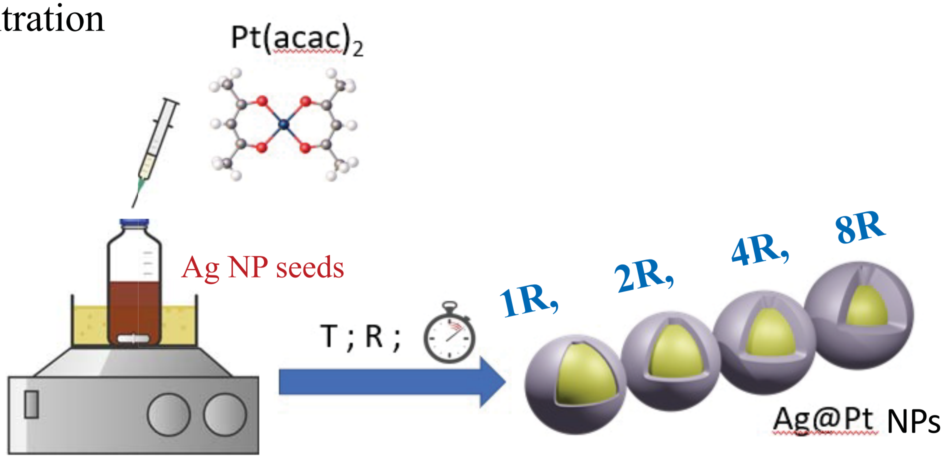
Synthetic approach of Ag@Pt NPs

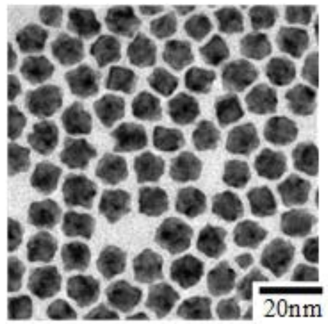
➢ second step: growth of Pt shell

- Fixed Ag seeds concentration at 0.105 µmolL^{-1}
- Changeable Pt concentration

1R=[Pt precursor]/ [Ag seeds]=6.7*10^{4}
1R= to obtain minimum Pt shell (one atomic layer) on the larger $Ag_{13.3nm}$ NP seeds



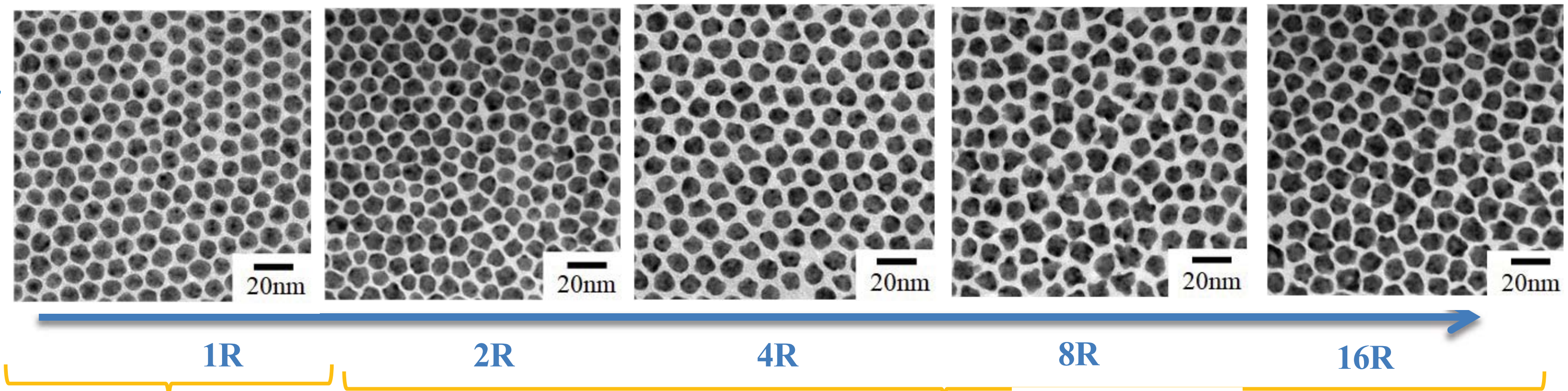




➢ A synthesis method able of depositing Pt with monolayer accuracy

Synthetic approach of Ag@Pt NPs: control of Pt content

$Ag_{8.4nm}$ seeds
T=200°C
$t_{reaction}$=1hour



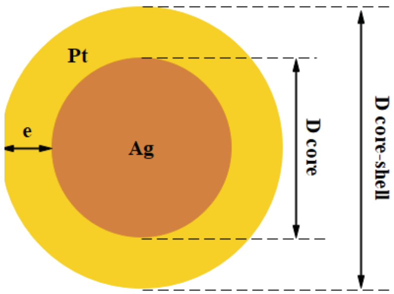
Growth mode of Pt layers

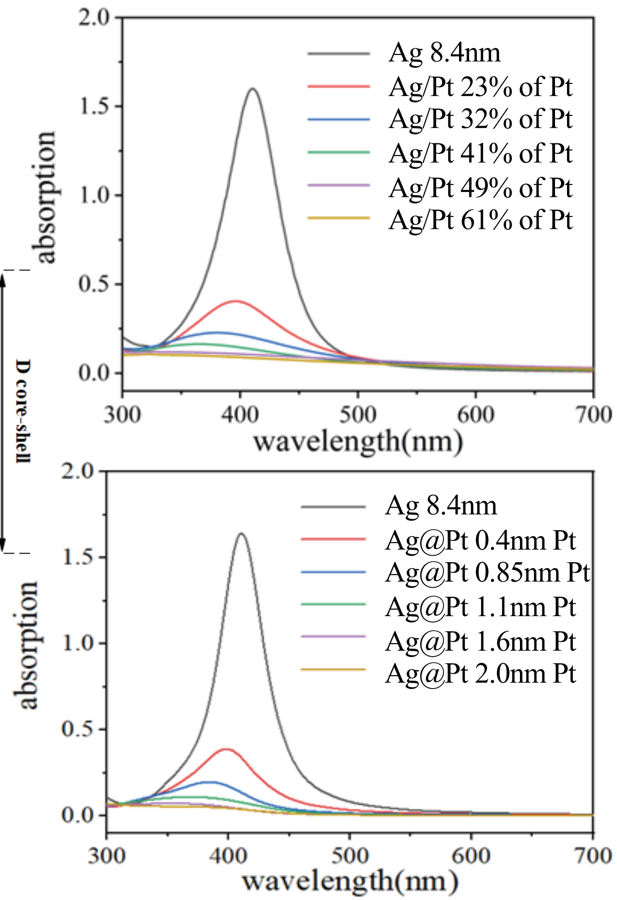
xR	1R	2R	4R	8R	16R
EDS (Pt%)	23	32	41	49	61
EDS (Ag%)	77	68	59	51	39

- **The Pt content in bimetallic NPs increases with [Pt precursor]/ [Ag seeds] concentration ratio**
- **The changes of morphologies and mean size increase highlight the formation of bimetallic Ag/Pt NPs**

Characterization of Ag@Pt Nanoparticles

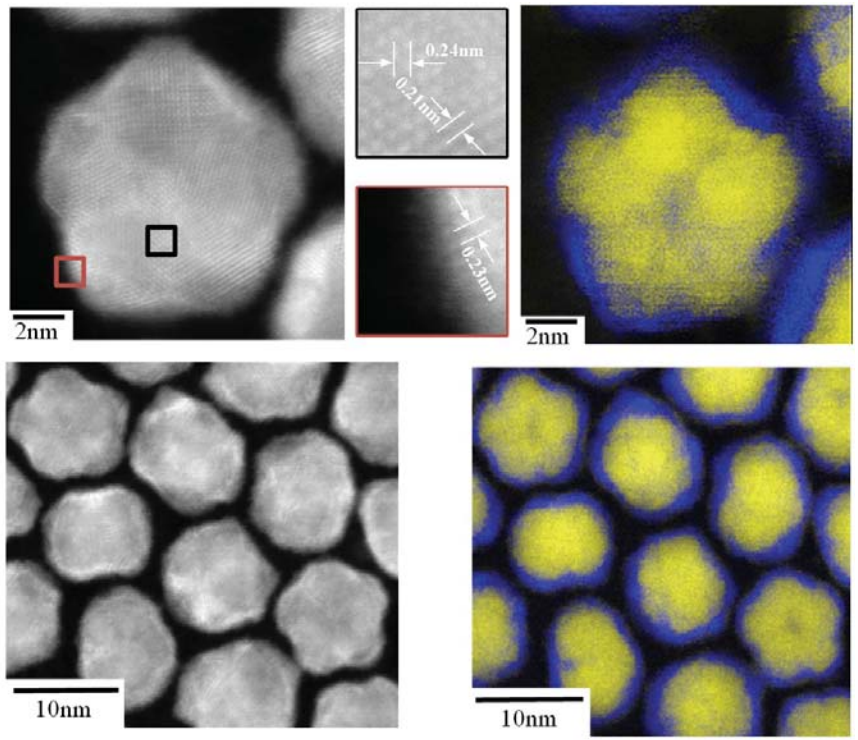
- **UV-visible experiments**





DDA calculation
for core-shell system

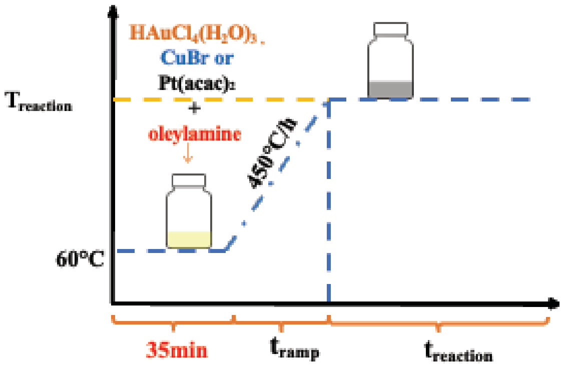
- **STEM HAADF images and EELS mapping**

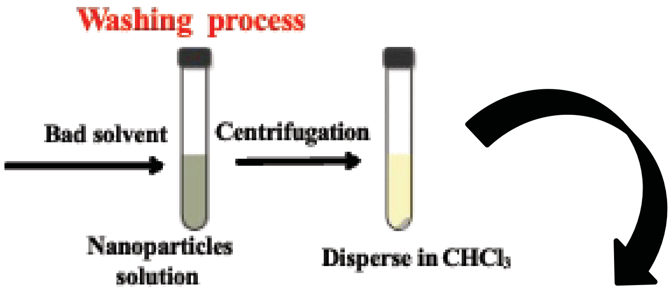


S. Lee et al. Nanotechnology 32(9) (2020) 095604.

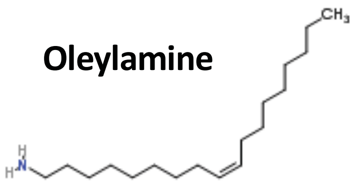
A versatile and robust synthesis method

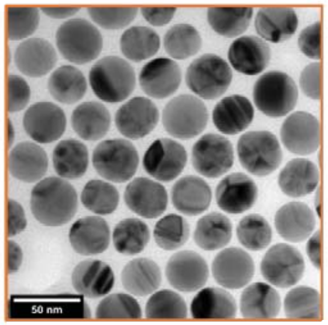
One component NPs





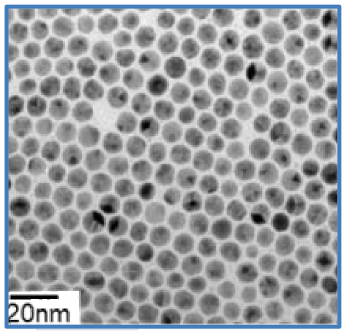
Oleylamine





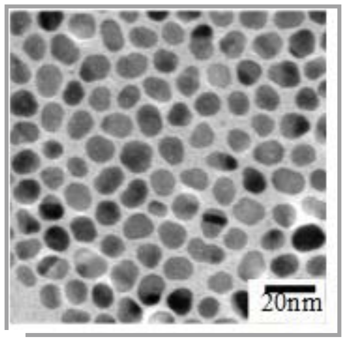
Cu NPs

$T_{reaction}$=280°C, $t_{reaction}$= 5 min
D=30 nm ± 0.3 nm



Au NPs

$T_{reaction}$=120°C, $t_{reaction}$= 30min
D=10.6±0.8 nm



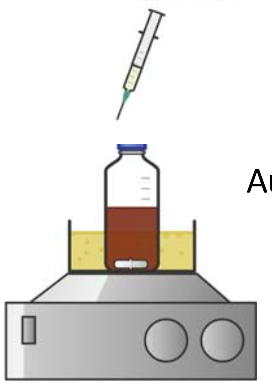
Pt NPs

$T_{reaction}$=240°C, $t_{reaction}$= 1h
D=9.7±1.6 nm

A versatile and robust synthesis method

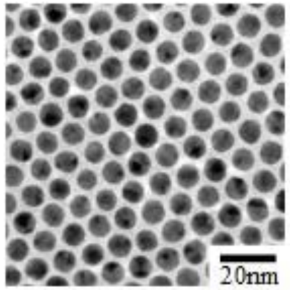
❖ Bi-component NPs

Pt/Pd(acac)$_2$

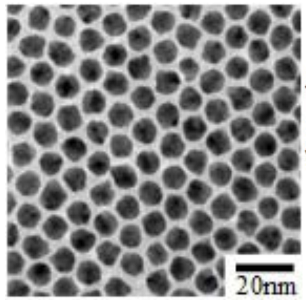


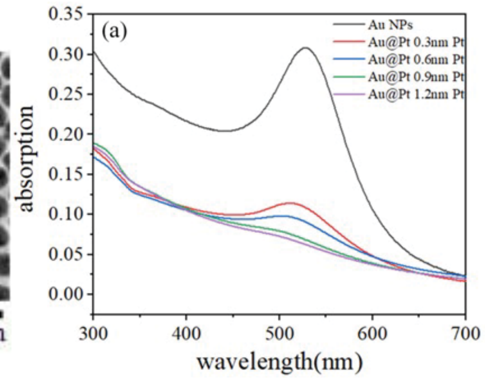
AuNPs/AgNPs

$Au_{10.5nm}@Pt_{0.5nm}$

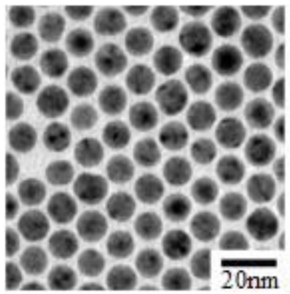


$Au_{10.5nm}@Pt_{1.0nm}$

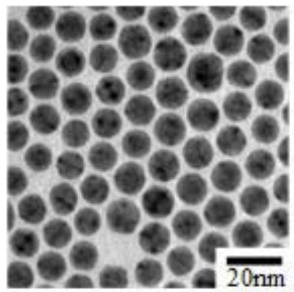


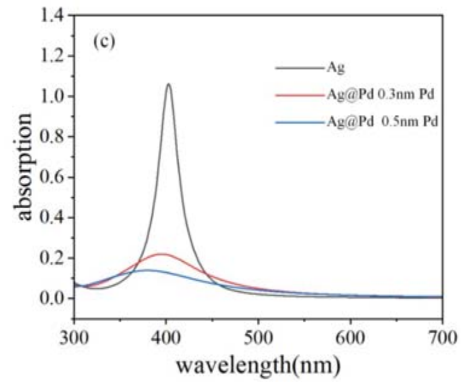


$Ag_{13.3nm}@Pd_{0.3nm}$



$Ag_{13.3nm}@Pd_{0.7nm}$

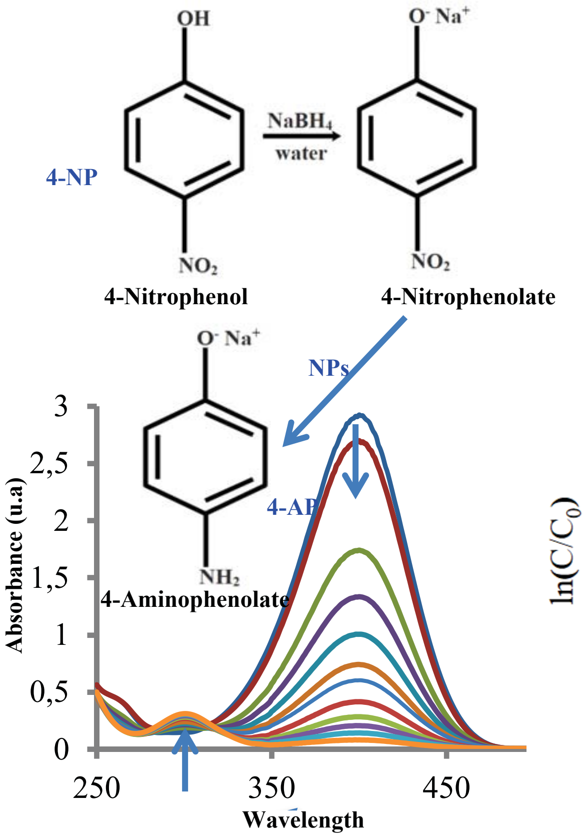


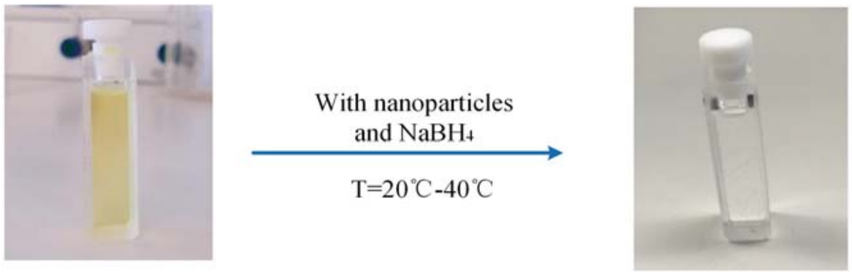


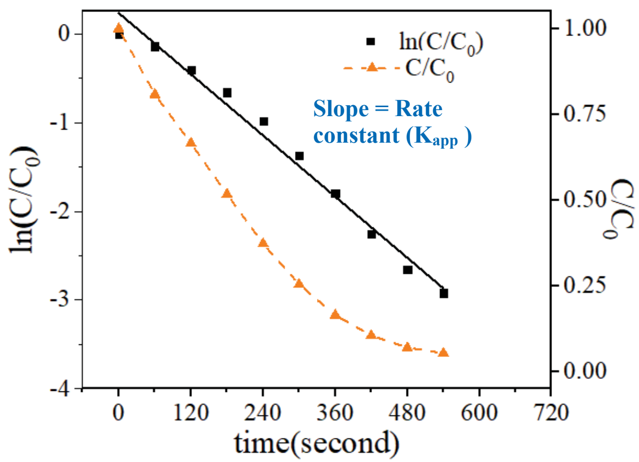
S. Lee, et al.“Versatile and robust synthesis process for the fine control of the chemical composition and core-crystallinity of spherical core-shell Au@Ag nanoparticles “ Nanotechnology, 32, 095604 (2021)

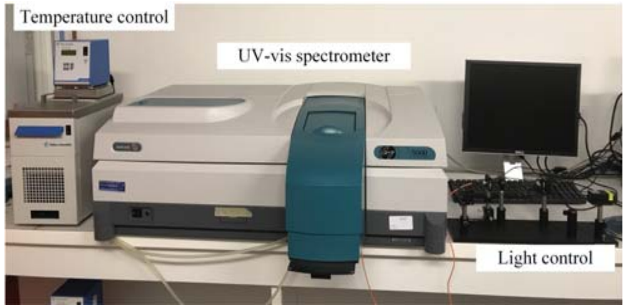
Catalytic activity of Ag and Ag@Pt NPs

Catalytic activity of Ag@Pt NPs: reduction of 4-NP into 4-AP.





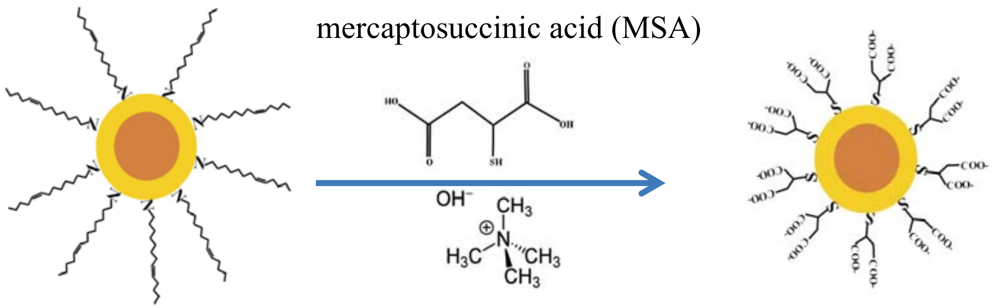




- ➢ Easily monitored by UV-visible spectroscopy
- ➢A pseudo-first order reaction

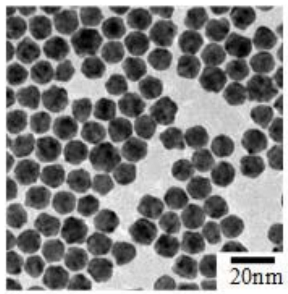
Zhao, et al. Coordination Chemistry Reviews 287 (2015): 114-136.

Transfer of NPs to aqueous phase through ligand exchange

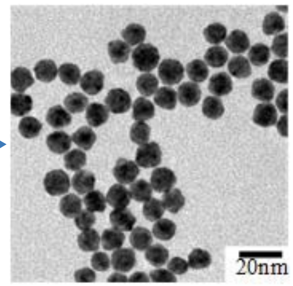


Coated by oleylamine (OLA)

Coated by MSA



Before ligand exchange Ag@Pt NPs in $CHCl_3$

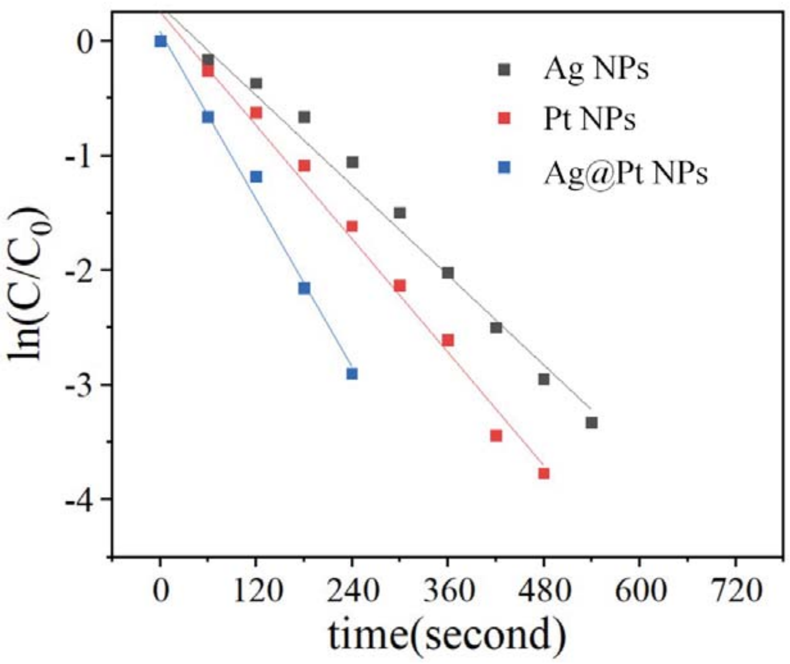


After ligand exchange Ag@Pt NPs in water

EDS measurements

EDS	Pt(%)	Ag (%)	N(%)	S(%)
Before exchange ligand	32.1	52.4	15.5	0
After exchange ligand	35.9	57.4	0.9	5.8

Catalytic activity of Ag@Pt NPs : synergistic effect

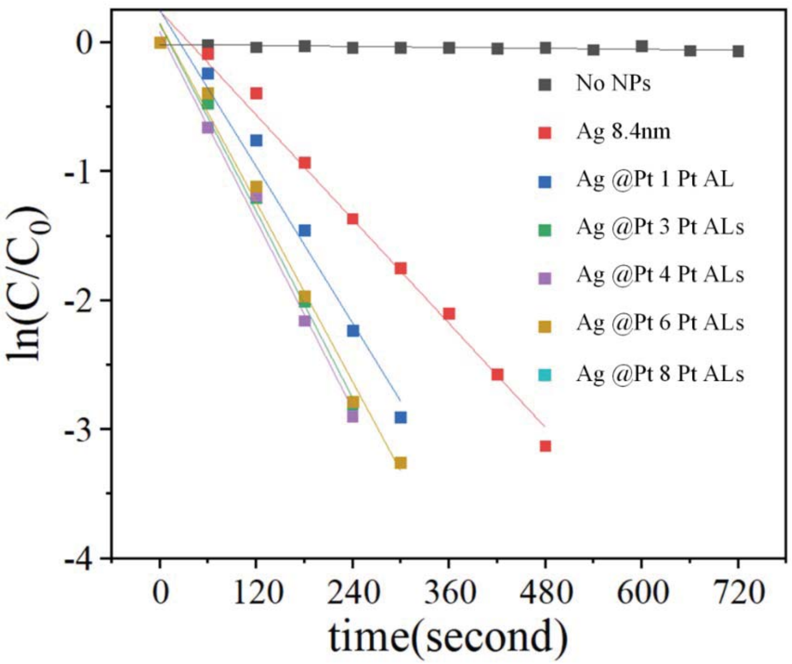


NPs	NP size (nm) e ±0.3 nm	K_{app} (10^{-3} s^{-1})
Ag	8.4	6.7
Pt	9.7	8.3
$Ag_{8.4nm}$@$Pt_{1.1nm}$	10.6	12.5

- **Bimetallic Ag@Pt NPs show higher catalytic activity than monometallic Ag and Pt NPs, highlighting synergistic effect between both metals**

Y . Ma, et al., Core-shell Ag@ Pt nanoparticles supported on sepiolite nanofibers for the catalytic reduction of nitrophenols in water: Enhanced catalytic performance and DFT study, Applied Catalysis B: Environmental 205 (2017) 262-270.

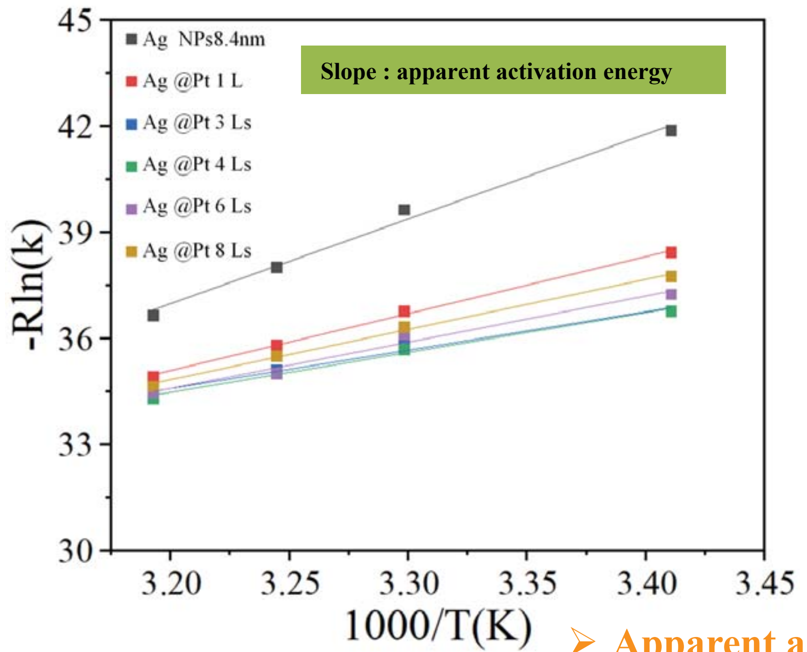
Catalytic activity of Ag@Pt NPs : Pt content effect

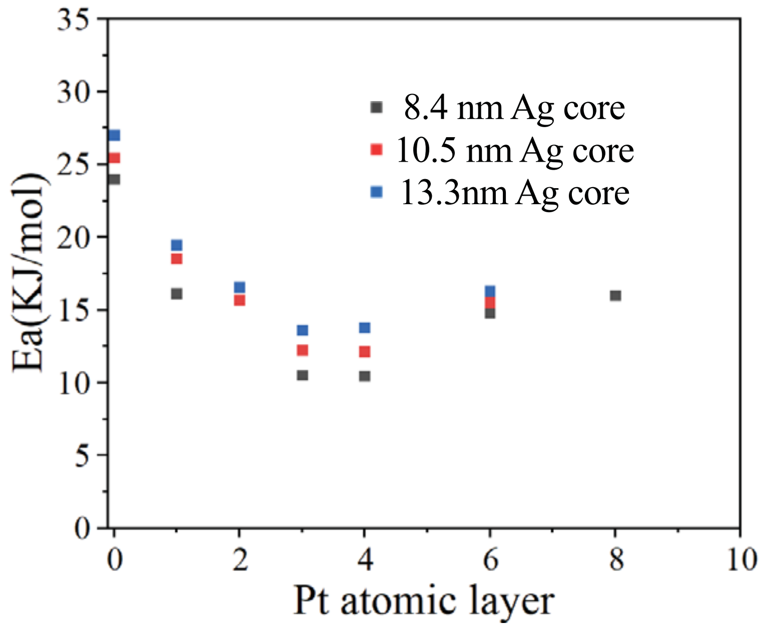


Sample	NP size ±0.5 nm	Shell thickness (nm) e ±0.3 nm	K_{app} (10^{-3} s^{-1})
Ag	8.4	-	6.7
Ag@Pt (8.4nm core)	9.2	0.4 (~1 layer)	10.0
	10.1	0.85 (~3 layers)	12.1
	10.6	1.1 (~4 layers)	12.5
	12.0	1.6 (~6 layers)	11.3
	12.8	2.0 (~8 layers)	10.1

- K_{app} increases as the Pt thickness increases up to 4 atomic layers and then decreases beyond that thickness

Catalytic activity of Ag@Pt NPs : Ag size effect



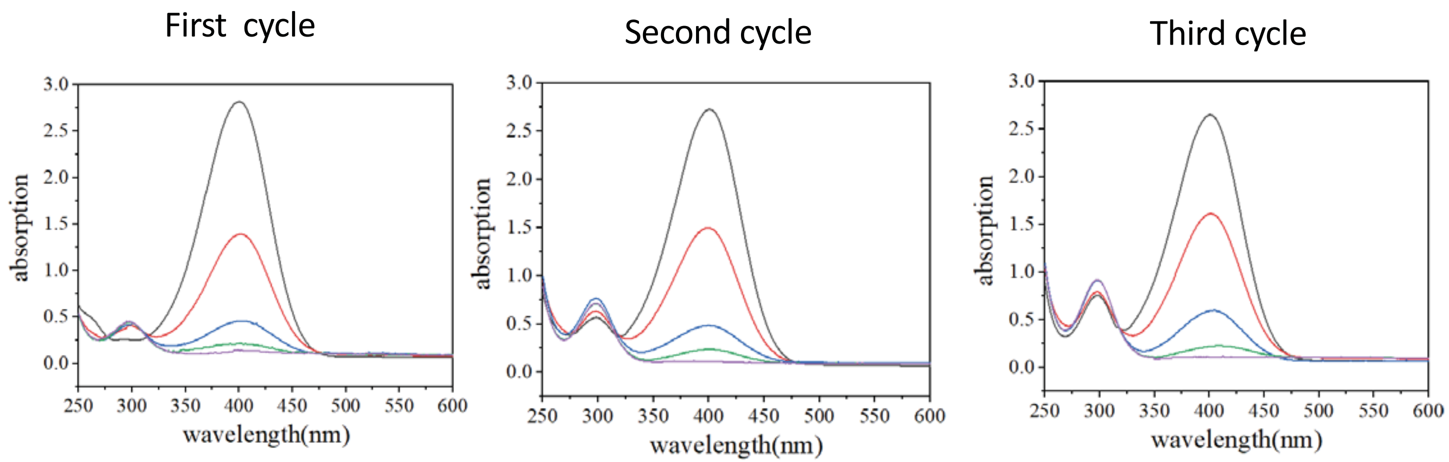


Arrhenius equation

$$k = Ae^{-E_a/RT}$$

- Apparent activation energy is depended on both Pt thickness and core size
- $Ag_{8.4nm}$@Pt NPs with the smallest core size present the greatest reactivity

Recycling catalytic activity of Ag@Pt nanocatalysts

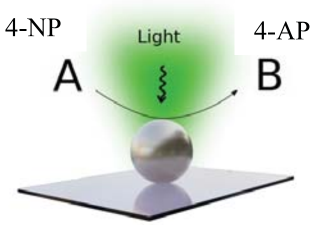


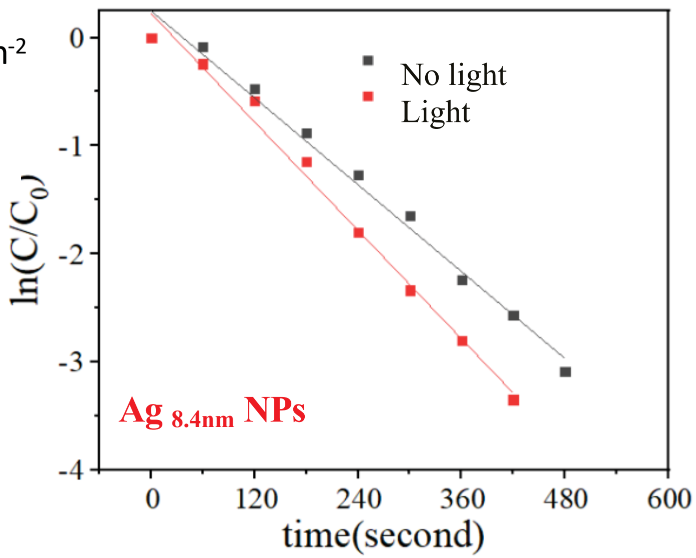
	First	Second	Third
k_{app} (min^{-1})	0.72	0.70	0.68

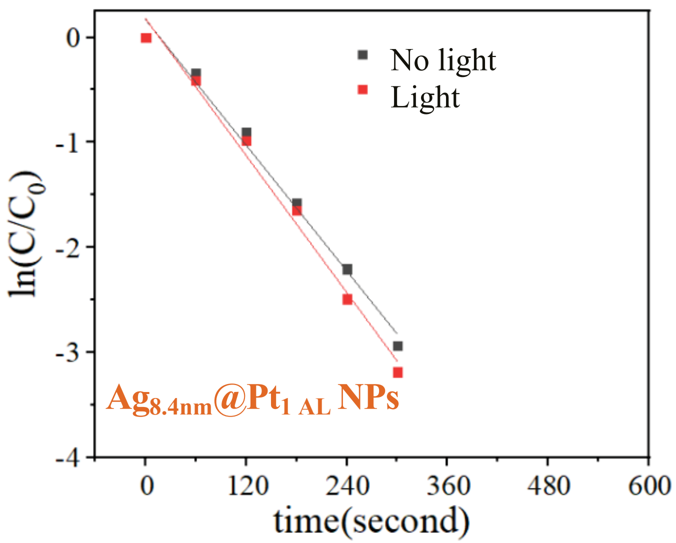
- **Ag @Pt NPs are shown to have a good stability and could be reused without significant loss of activity after running 3 recycling**

Catalytic activity of Ag and Ag@ Pt NPs : plasmonic effect

λ_{exc}=405 nm, I=1Wcm^{-2}





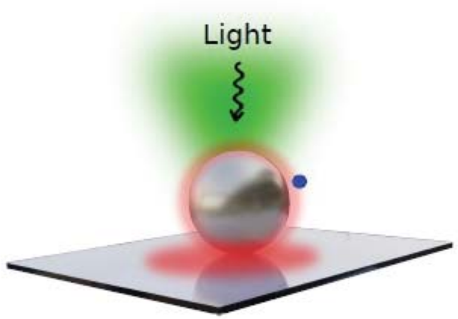


- **Laser illumination increases catalytic activity of Ag NPs**
- **for Ag@Pt NPs, this effect is very weak**

Sample	K_{app} (10^{-3} s^{-1}) (Error, R^2)	
	light	No light
$Ag_{8.4nm}$	8.2	6.7
$Ag_{8.4nm}@Pt_{1\ AL}$	10.5	10

Catalytic activity of Ag NPs : plasmonic effect

❖ Heat generation?



(c) Photo-induced heating

$$\Delta T_{NP} = \frac{\sigma_{abs} I}{4\pi R K_{water}} = 3.3 \text{ K}$$

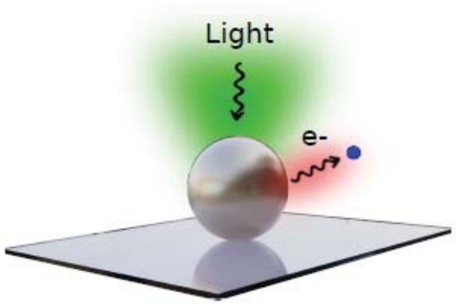
$I = 1 W/cm^2$; $\sigma_{abs} = 10^{-16}\ m^2$; R NP radius ; $K_{water} = 0.59$ W.K.m^{-1}

➢ Δk~0.4% according to the Arrhenius equation

➢ **The increase in reactivity observed with pure Ag NPs is not due to LSPR heating effect**

G. Baffou et al. , Thermo-plasmonics: using metallic nanostructures as nano-sources of heat, Laser & Photonics Reviews 7(2) (2013) 171-187.

❖ Hot electron excitation?



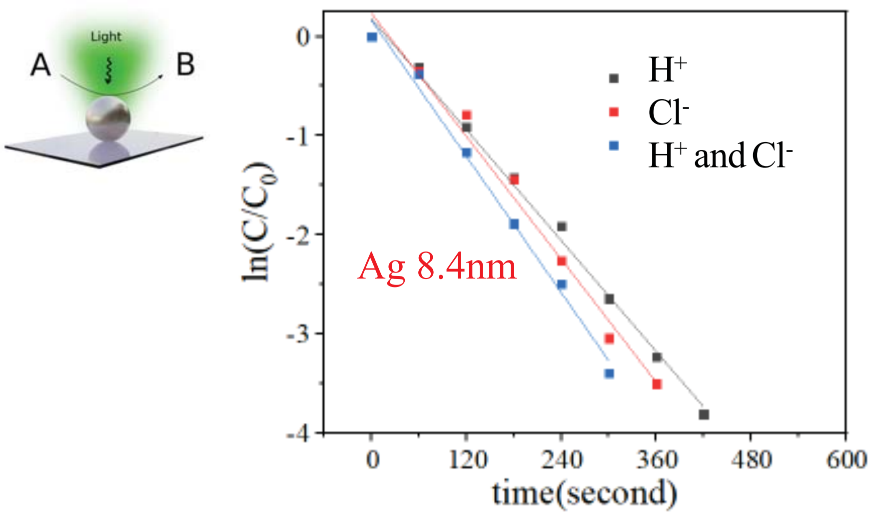
(b) Hot electron transfer

Hot electron reduction can explain the improvement observed under irradiation, which may remain moderate for the following reasons:

- They are primarily emitted at regions of intense electromagnetic field (hot spots), which are much more intense on anisotropic NPs or NPs with sharp edges or Organized NPs.
- The number of hot electrons available per molecule remains limited due to high rate of charge–carrier recombination
- An oxidation counter-half-reaction may be necessary to balance the hot electron-induced reduction reaction

W.Xie and al. Nat comm,2015 , DOI: 10.1038/ncomms8570

Optimization of 4-NP to 4-AP conversion for Ag NPs



Conditions	K_{app} (10^{-3} s^{-1})
Water	8.4
H_2SO_4	10.3
HCl	11.2
KCl	9.1

- Best conditions for the conversion of 4-NP to 4-AP : laser irradiation resonant to the SPR of Ag seeds and addition of $HCl_{(aq)}$
- Leading to an increase in K_{app} of 67%

Optimization of 4-NP to 4-AP conversion for Ag NPs

❖ **4-NP to 4-AP conversion optimized in aqueous HCl:**

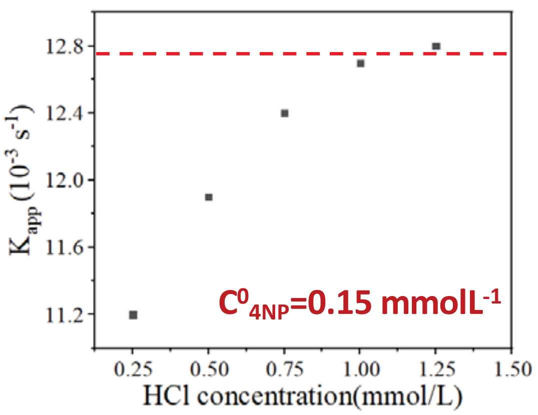
$$Ag_{(s)} \xrightarrow{h\nu} Ag^{+}(aq) + e^{-}$$ (generation of hot e⁻)

$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl_{(s)}$$ (precipitate of photosensitive AgCl)

$$AgCl_{(s)} \xrightarrow{h\nu} Ag_{(s)} + Cl.$$ (photodissociation of AgCl and regeneration of Ag atoms)

➢ Under light illumination halide ions allow the photo-recycling of Ag and the generation of supplementary hot electrons improving the catalytic reduction of 4NP.

Proton promote conversion of 4-NP to 4-AP under light irradiation:



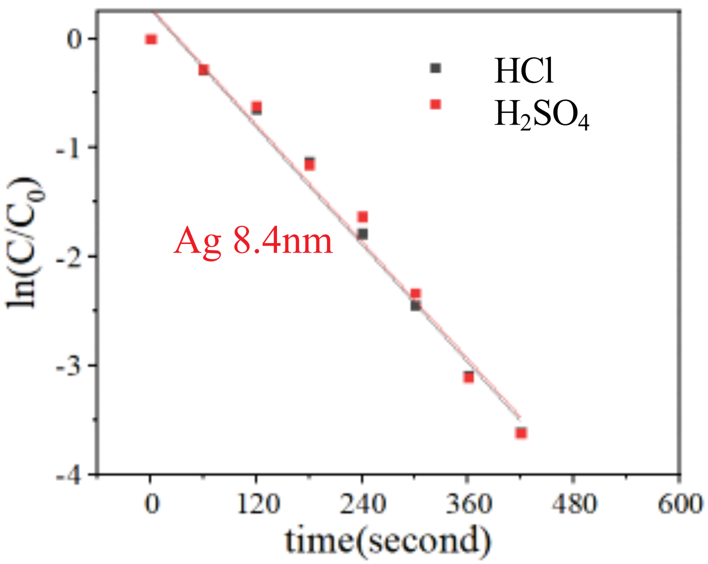
$$Ph - NO_2 + 6e^{-} + 6H^{+} \rightarrow Ph - NH_2 + 2H_2O$$

➢ An additional supply of protons for the conversion of 4-NP is founded to improve the catalytic efficiency of Ag NPs.

Optimization of 4-NP to 4-AP conversion for Ag NPs

$$Ph - NO_2 \; + 6e^- + 6H^+ \rightarrow Ph - NH_2 \; + 2H_2O$$

No light

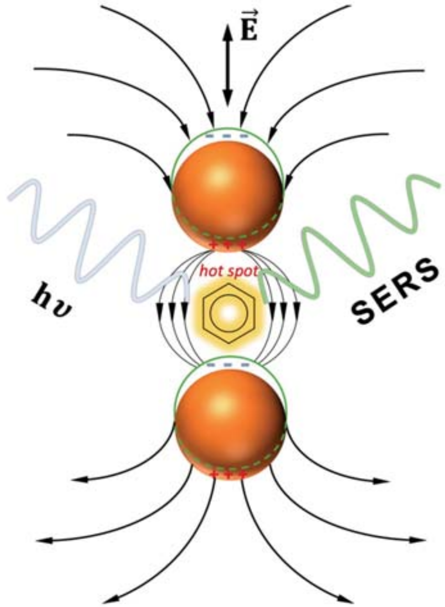


Conditions	K_{app} (10^{-3} s^{-1})
Water	6.7
H_2SO_4	9.1
HCl	9

- Cl^- has no contribution in absence of light
- The addition of $H^+_{(aq)}$ improves significantly the catalytic activity of AgNPs

Plasmonic photo-catalytic activity of supported Ag@Pt supercrystals (SCs)

Plasmonic photo-catalytic activity of Ag@Pt SCs

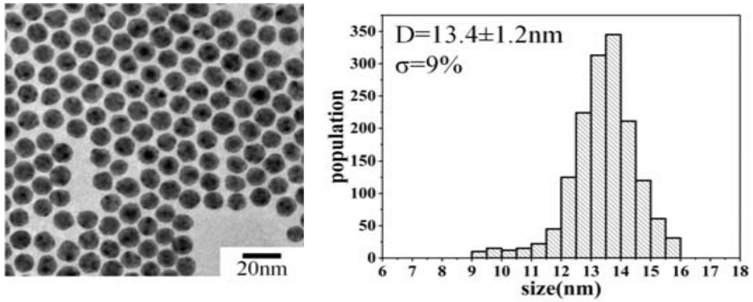


❖ Catalysis of hydrogen evolution reaction (HER), $2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$

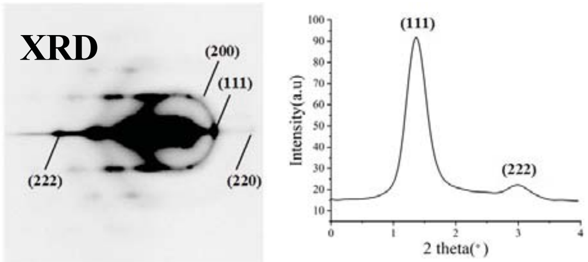
L. Chapus, et al. Chem.Phys.Chem 18, 1 – 11 (2017).

supported Ag@Pt SCs: chatracterization

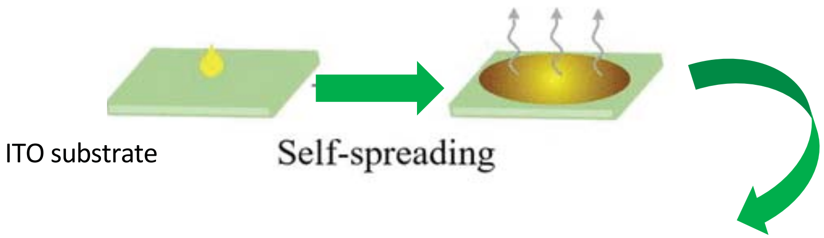
Ag@Pt NPs

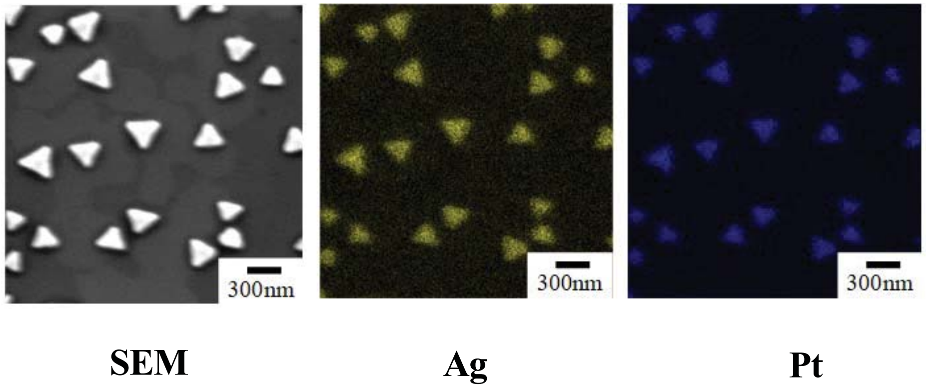


Pt thickness (nm)	EDS composition for NPs		EDS composition for superlattices	
	% Ag	% Pt	% Ag	% Pt
0.35	83	17	82	18



➢ A spontaneous organization at 2D and 3D

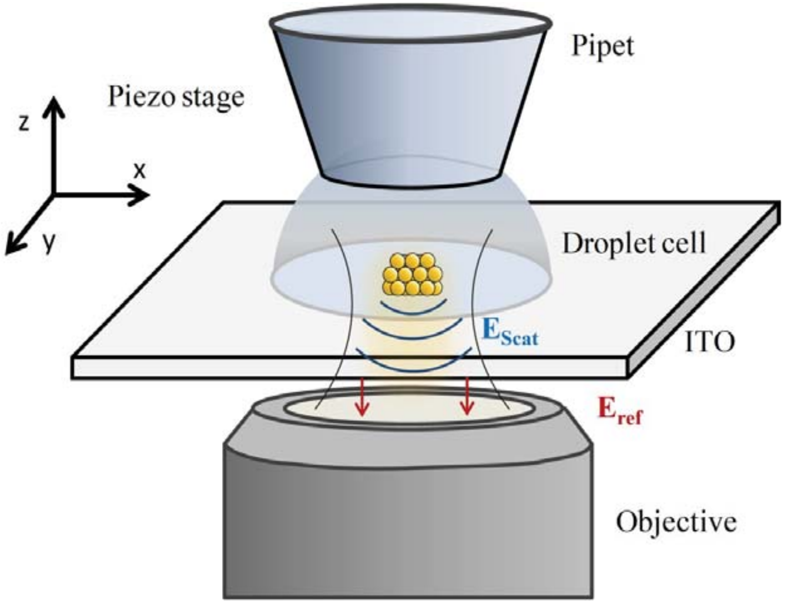


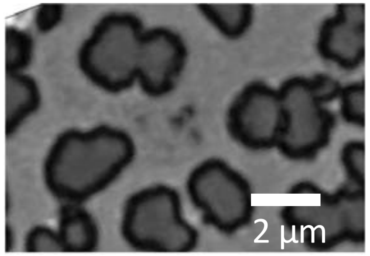


Plasmonic photo-catalytic HER activity of supported Ag@Pt SCs

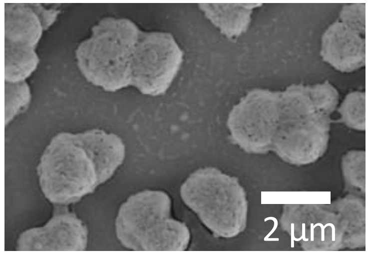
❖ Set up coupling with Optical and Electron Microscopy

Catalysis of hydrogen evolution reaction (HER), $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$





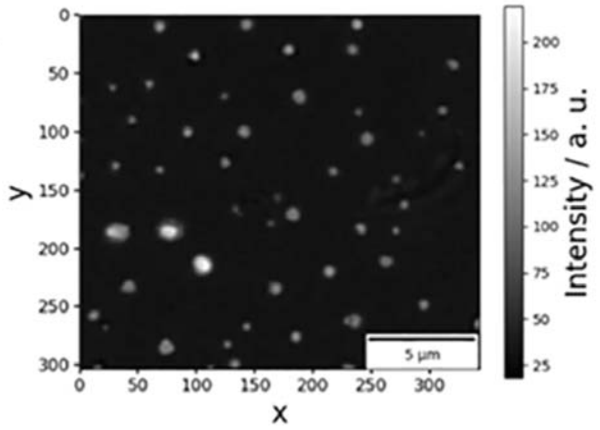
Optical image

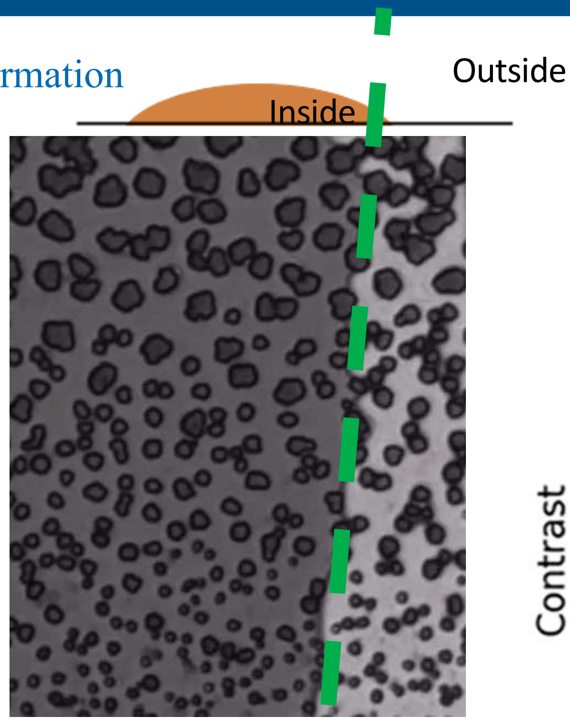


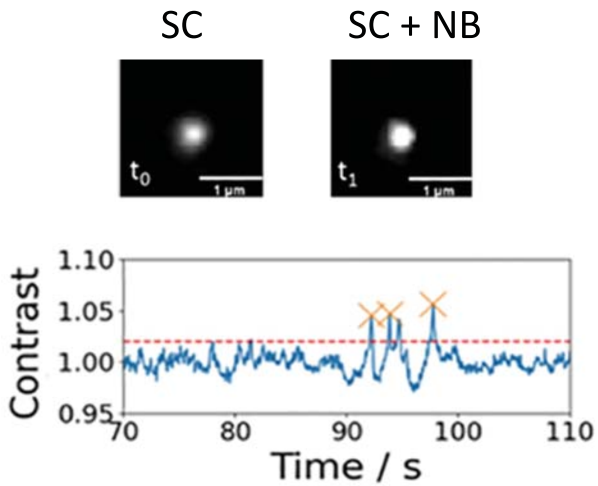
SEM image

J.F. Lemineur et al. *ACS nano* 15.2 (2021): 2643-2653.

Optical monitoring of H_2 gas NBs formation



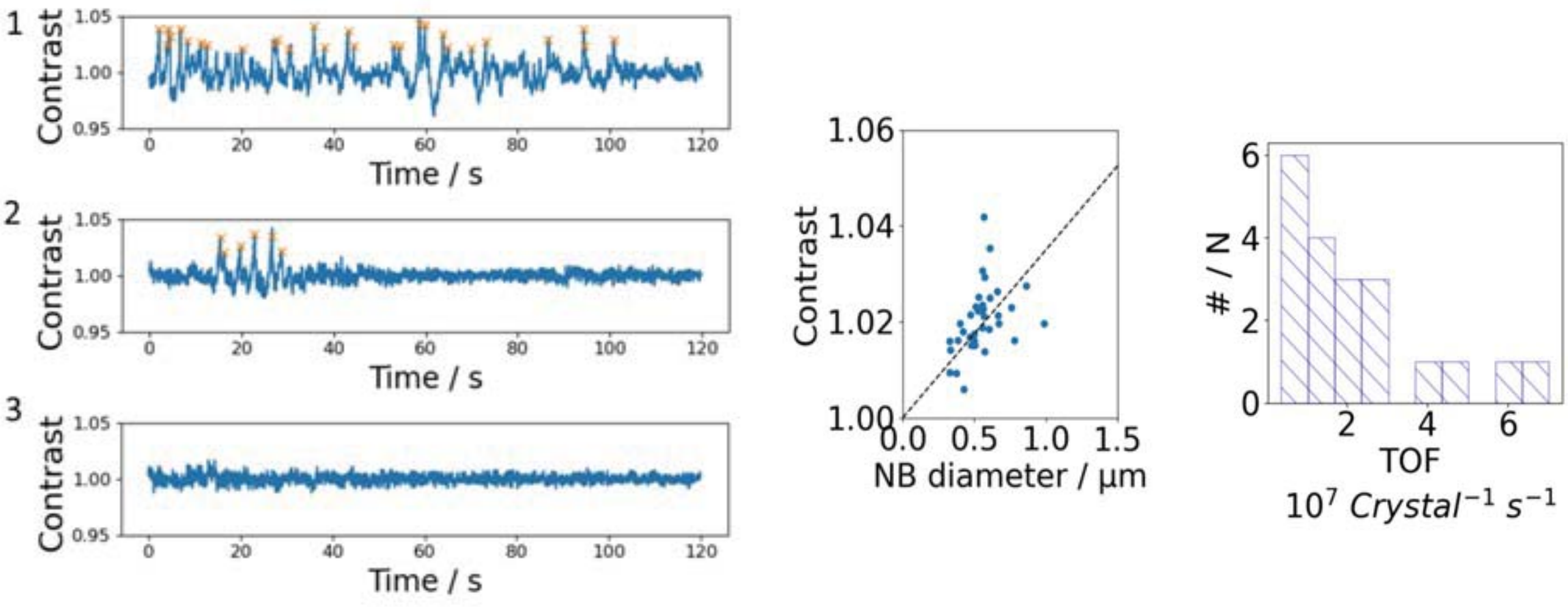




- ➢ **The NBs on single supercrystal increases slightly optical signal**
- ➢ **Optical intensity profiles show the formation and detachment of NBs**

Y. Fan et al., Adv.Mater. 2305402 (2023)

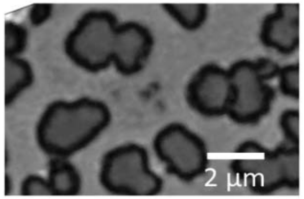
Plasmonic photo-catalysis at single supercrystals



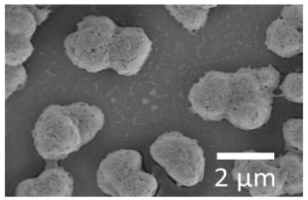
- Three distinct behaviors at a single SCs: activity, intermittent activity and non activity
- The turn over frequency (TOF) is in the range of around 0.6 10^6 H_2 molecules per SC per seconde

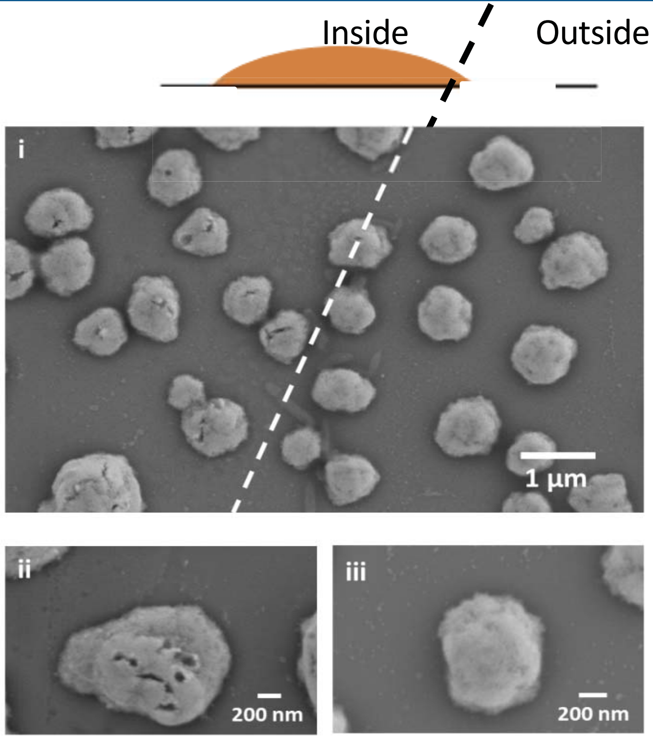
Supercrystal erosion

Optical microscopy

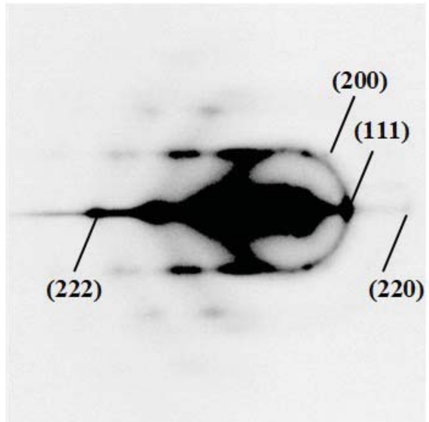


Electron microscopy





SAXS



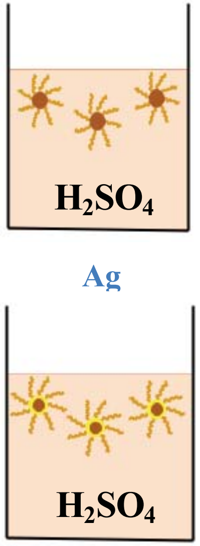
Production of H_2 leads to the supercrystal erosion favored by:

- **A weakening of the crystalline scaffold consistent with the presence of crystal defects (stacking faults)**
- **A chemical weakening such as the corrosion by the HER reaction**

SC and NP corrosion

❖ Evolution of NP SPR upon H_2SO_4 environment

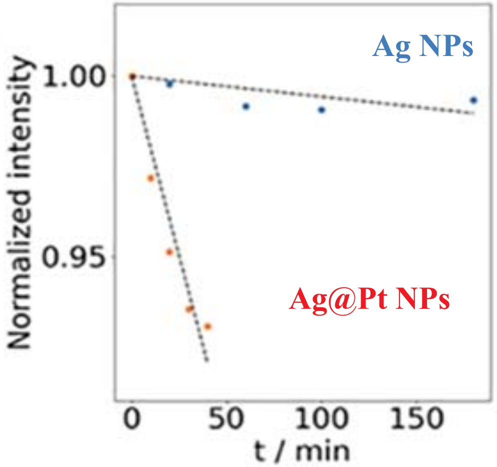
❖ Bubbles formation and Ag oxidation



Ag

Ag@Pt NPs

hν



Ag@Pt NPs

H_2 Bubbles

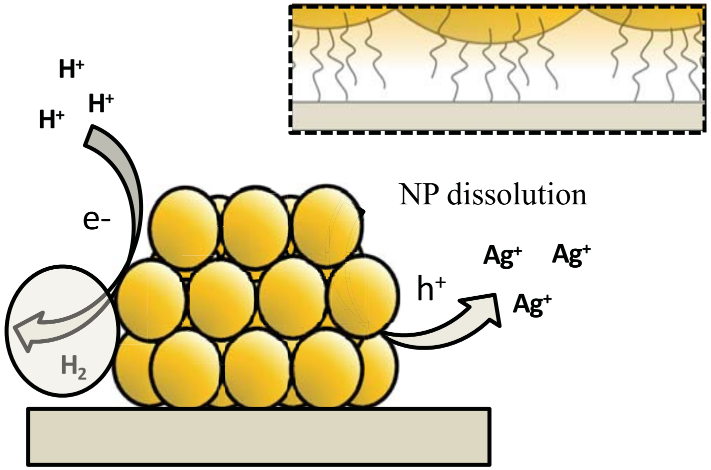
Add KCl

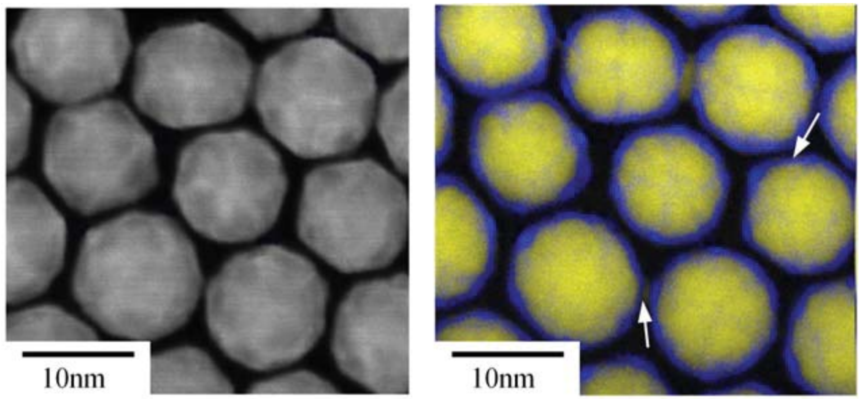
Precipitate of AgCl

➢ **HER step is accompanied by the oxidation of Ag into Ag^+**

Mechanism of plasmon assisted hydrogen production at the core shell NP surface

- HER step is accompanied by the oxidation of Ag into Ag^+





$$\begin{cases} Ag \xrightarrow{h\nu} Ag^+ + e^- \\ 2H^+ + 2e^- \rightarrow H_2 \end{cases}$$

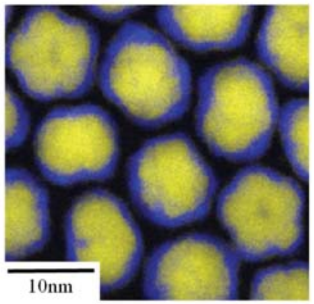
(generation of e^- and h^+)

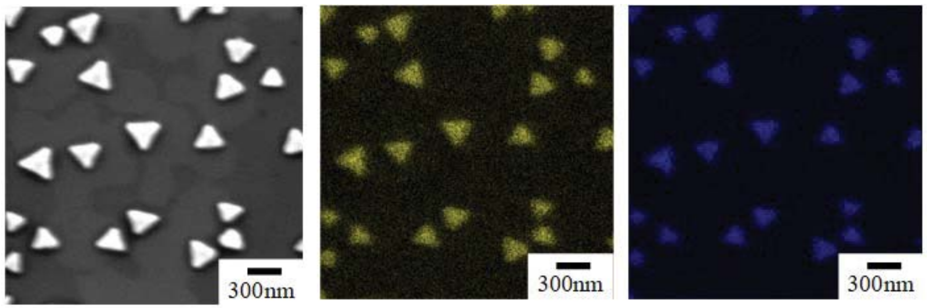
- The counterpart anodic reaction appears to be the oxidation of the less noble metal of the Ag@Pt NPs

Y. Fan et al., Adv.Mater. 2305402 (2023)

Conclusions & perspectives

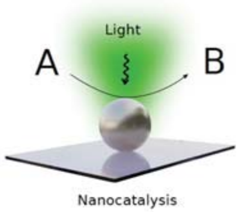
- The catalytic activity and plasmonic effects of isolated Ag and Ag@Pt NPs , and 3D organized Ag@Pt NPs into supercrystals (SCs) were investigated.
- SCs made of Ag@Pt NPs exhibit higher light harvesting than isolated Ag@Pt NPs and provide a good platform for plasmonic catalysis
- To better understand the processes involved in plasmonic catalysis, we have recently developed a new optical platform enabling the measurement of different signals: photoluminescence or Raman.





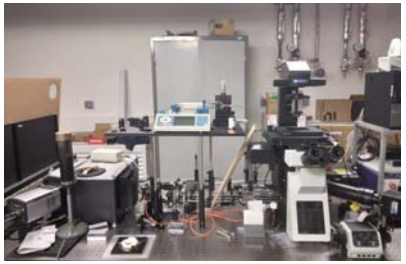
Conclusions & perspectives

in-situ plasmonic catalysis: reactivity of self-assembled NPs



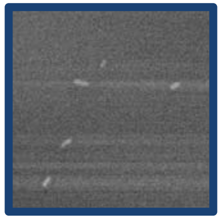
➢ **Challenges:**

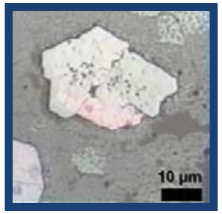
- Disentangle photothermal and hot e- contributions.
- Nanothermometry to address local temperatures at the nanoscale.
- In-situ catalytic activity monitoring using optical signal
- Strategies to enhance hot-e generation: plasmonic coupling



Morphology:

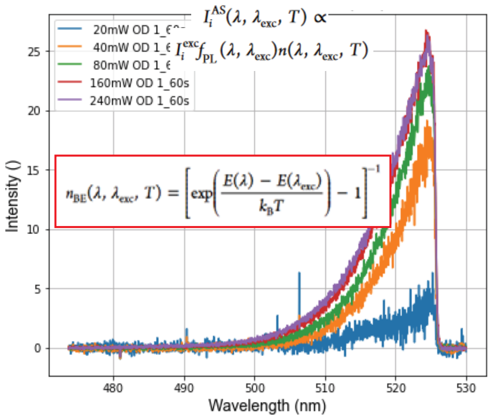
Single NPs
NP supercrystals
Electronic imaging





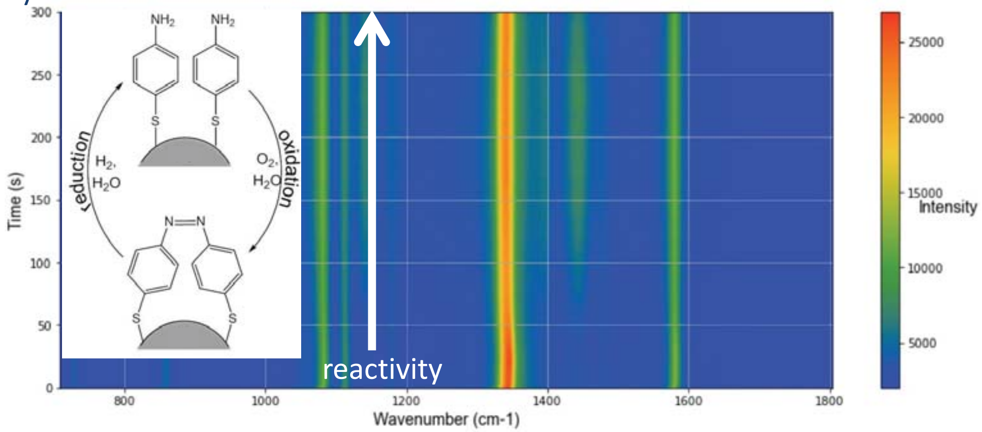
Local temperature under irradiation:

Optical readout, anti-Stokes thermometry



In-situ reactivity:

Raman scattering



Aknowlegments

Dr Suyeon Lee
Dr Yinan Fan
Dr Adrien Girard (MCF)
Dr Caroline Sazemann (MCF)

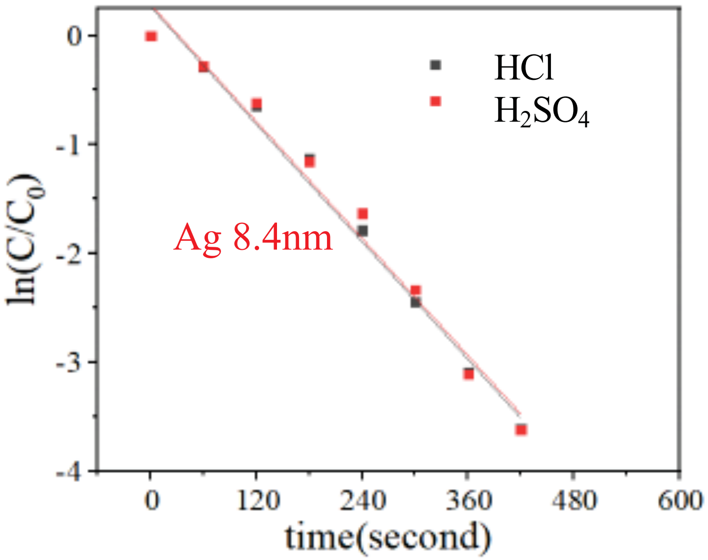
Pierre-Antoine Albouy
Michael Waals

Dr Frederic Kanoufi
Dr Jean-François Lemineur
Dr Jean-Marc Noël

Optimization of 4-NP to 4-AP conversion for Ag NPs

$$Ph - NO_2 \; + 6e^- + 6H^+ \rightarrow Ph - NH_2 \; + 2H_2O$$

No light



Conditions	K_{app} (10^{-3} s^{-1})
Water	6.7
H_2SO_4	9.1
HCl	9

- Cl^- has no contribution in absence of light
- The addition of $H^+_{(aq)}$ improves significantly the catalytic activity of AgNPs