Molecular Control of Plasmon Coupling in Self-Assembled Metal Nanoparticles

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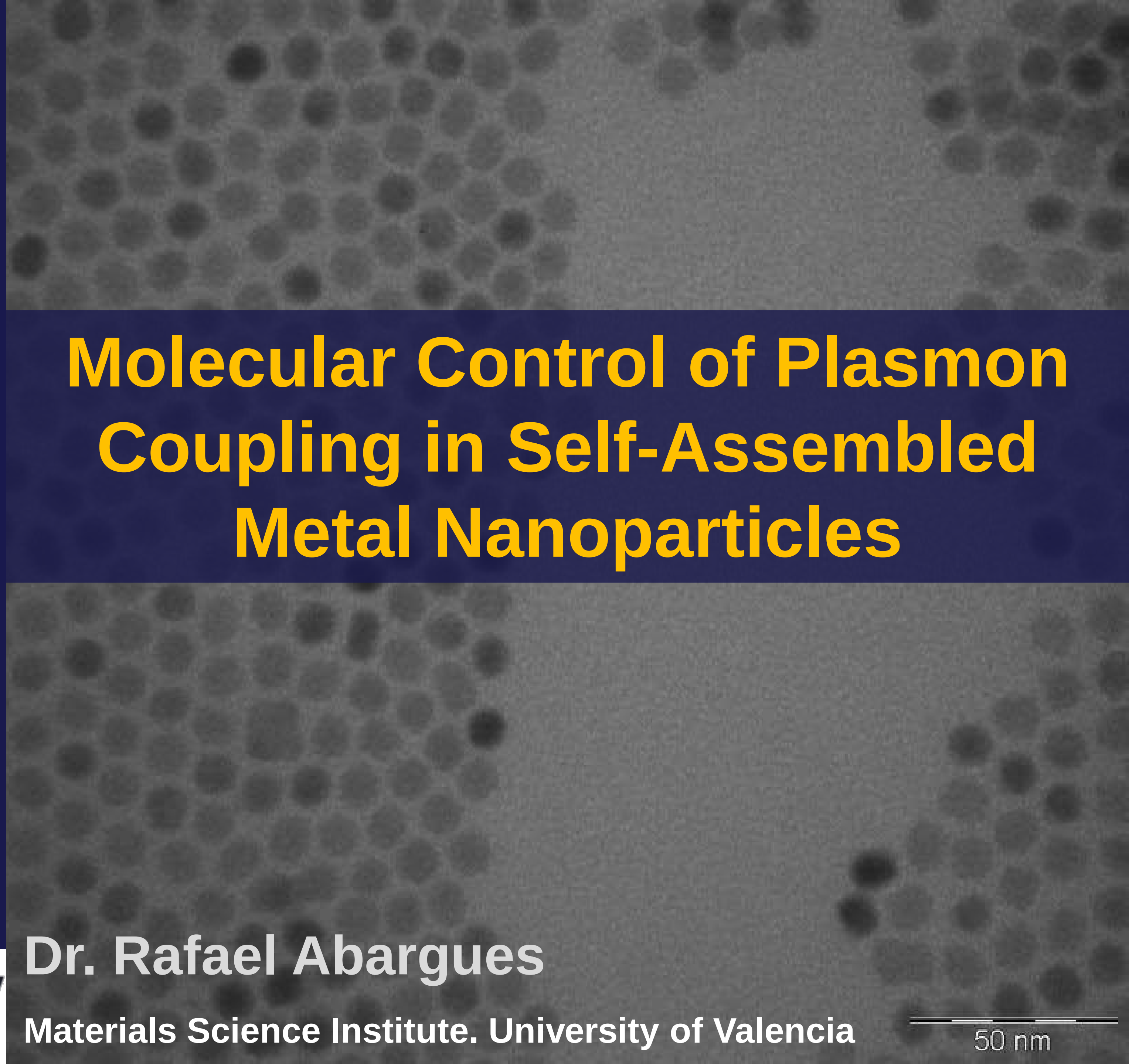


Summary

1. Metal Nanoparticles: Background

2. Self Assembly Approach

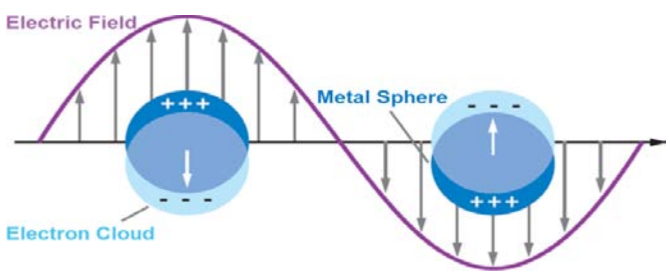
3. Results.

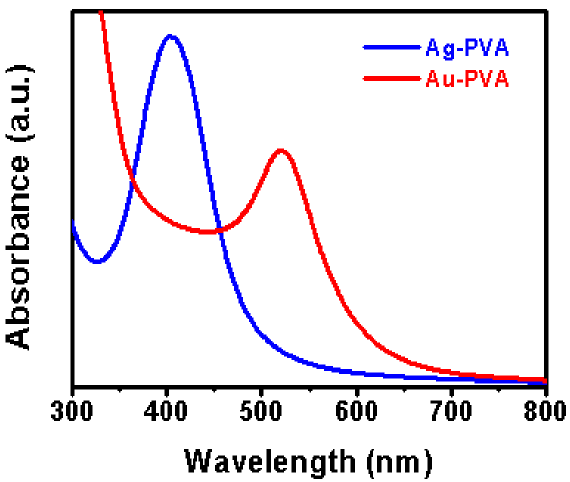
4. Summary

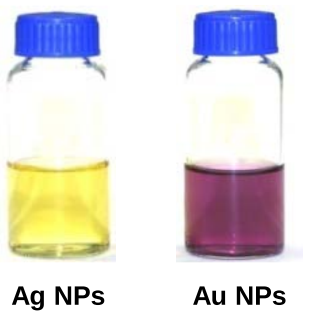
Background — Metal Nanoparticles

- **Noble metal nanoparticles** (NPs) such as Ag, Au and Cu have LSPR in the UV-Vis.

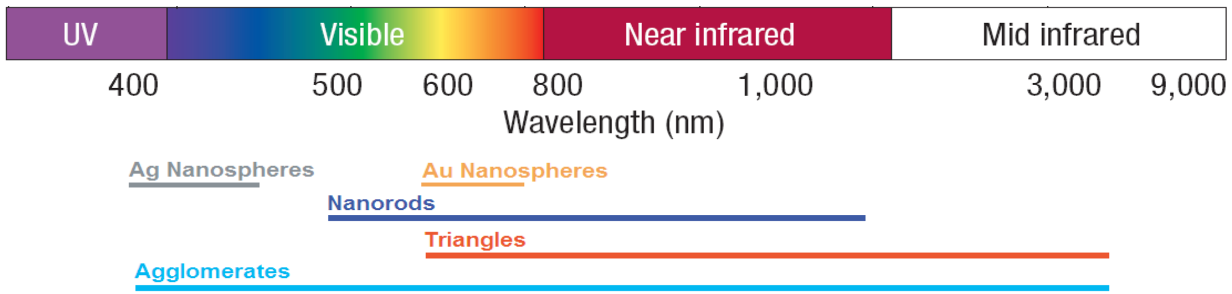
- **Localized Surface Plasmon Resonance** (LSPR) are collective oscillations of the free electrons at the interface between a metallic structure and a dielectric in the presence of an electromagnetic field.



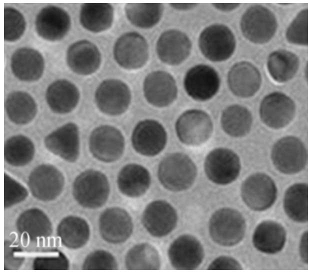


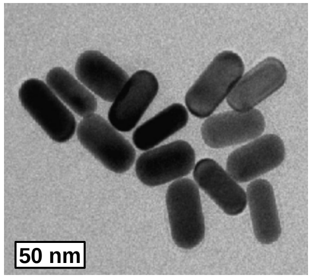


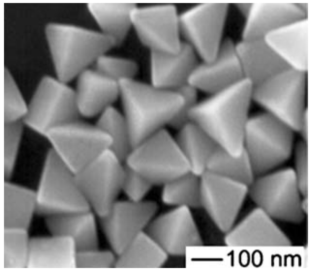
- **Optical properties** are mainly determined by size, shape, and assembly of nanoparticles.

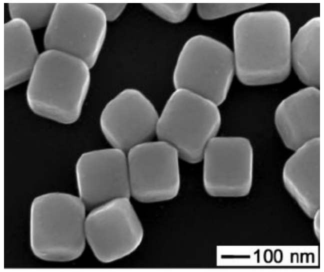


Tailoring Optical Properties: Shape and Size



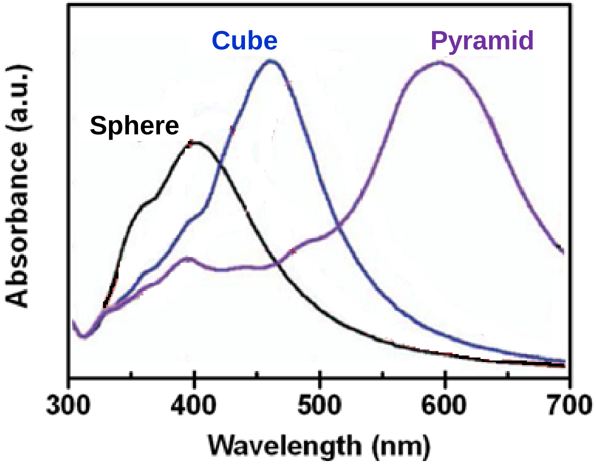




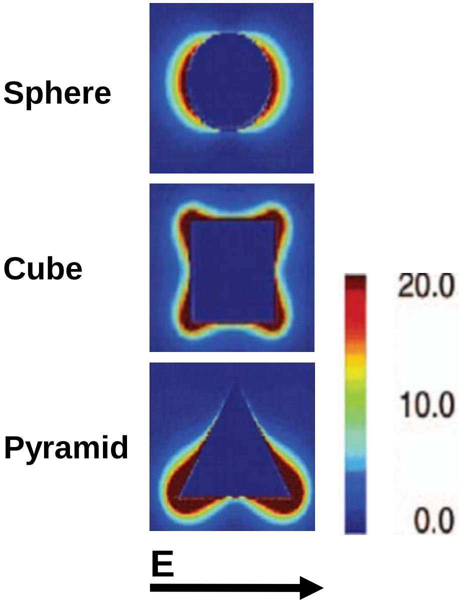


❖ Shape Dependency

Ag Nanoparticles

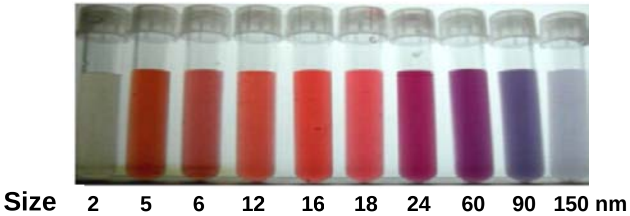


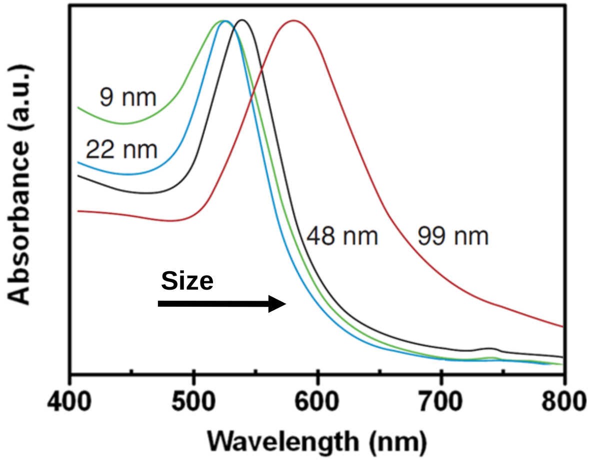
EM Field Enhancement



❖ Size Dependency

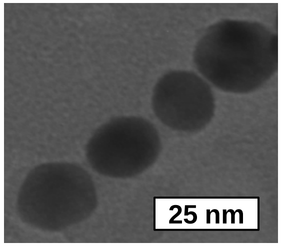
Au Nanoparticles

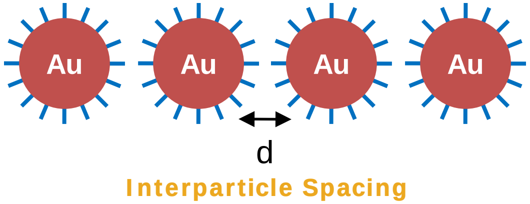


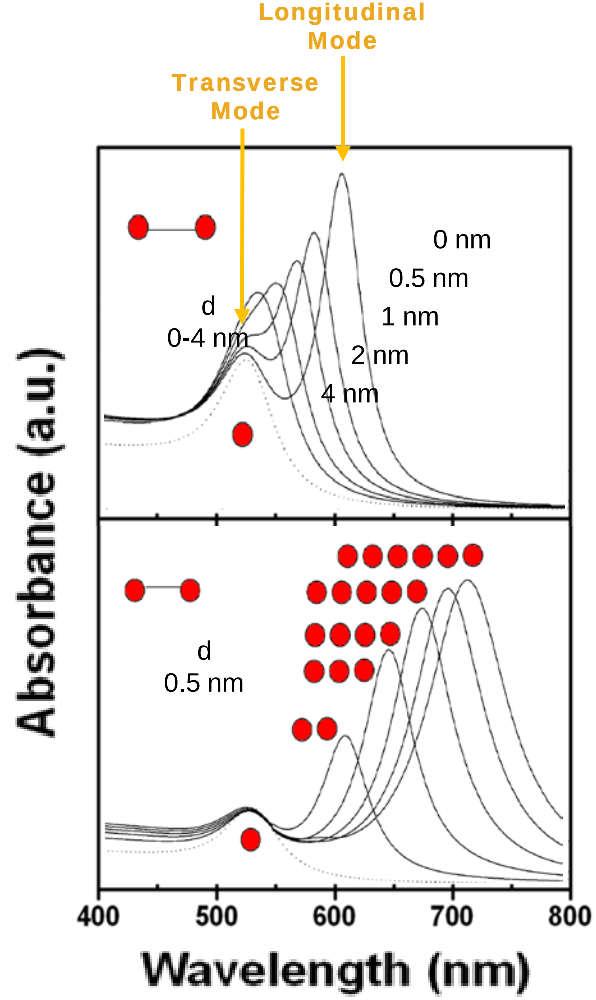


Tailoring Optical Properties: Assembly

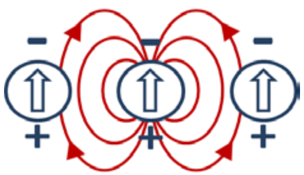
❖ **Plasmon Coupling** when nanoparticles are closely spaced. The dipole field resulting from SPR of a metal NP can induce plasmon oscillations in other neighboring metal NPs via near-field electrodynamic interactions.



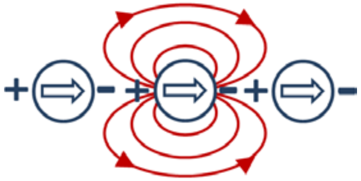


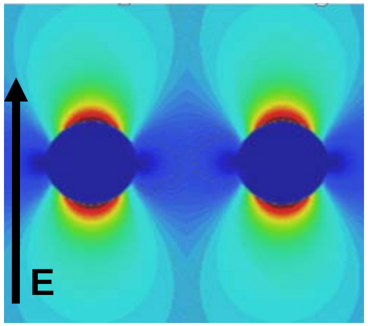


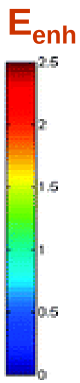
Transverse Coupling Mode (High energy)

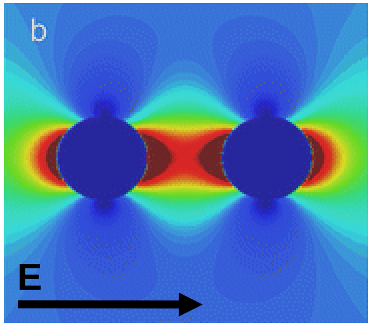


Longitudinal Coupling Mode (Low energy)









Blue-shift plasmon mode

Red-shift plasmon mode

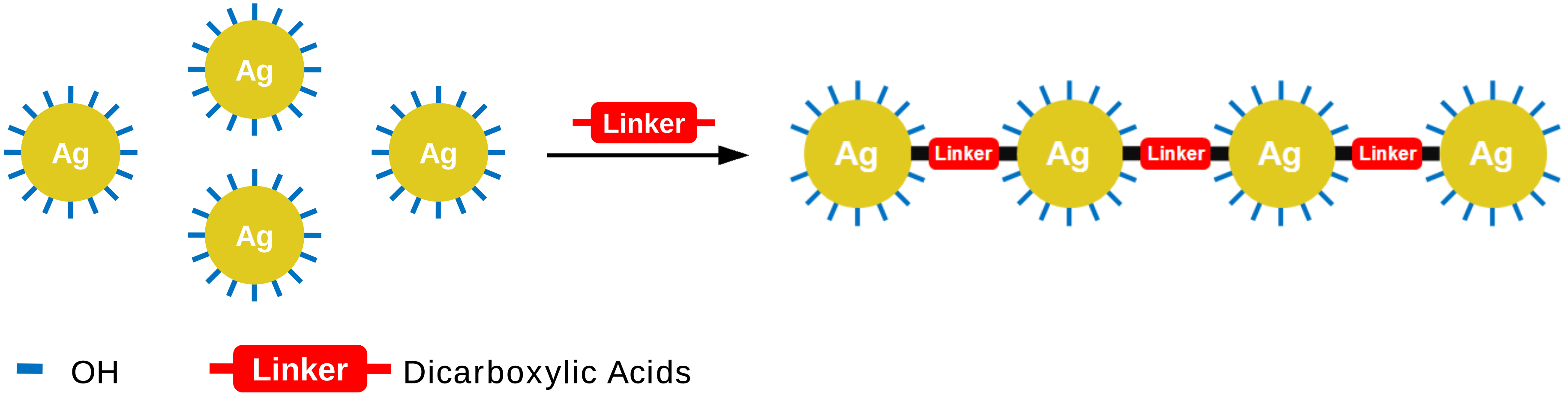
Self-Assembly Approach

❖ **Bottom-up approach:** Nanoparticles as building blocks to form more complex nanostructures with tunable properties.

❖ **Synthetic Strategy:** Covalent binding among Ag or Au Nanoparticles

1) Building Blocks: OH-Terminated Nanoparticles

2) Linkers: Dicarboxylic Acids



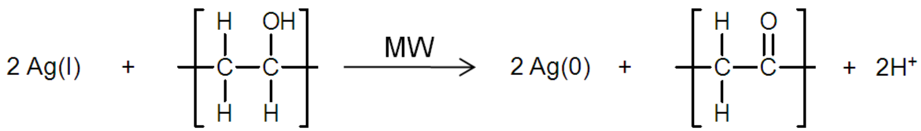
❖ **Advantages:**

❖ Control of the interparticle distance with Linker

❖ Control of the agglomerate sizes: stequiometry, reactant concentration, pH, t and T.

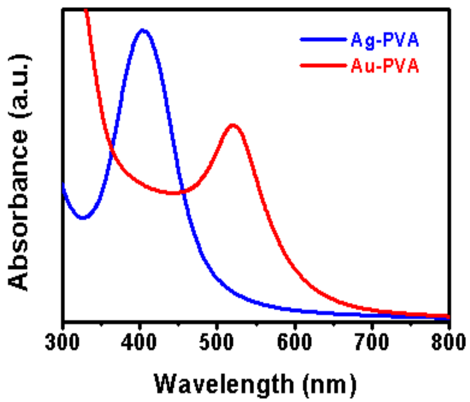
Synthesis of Nanoparticles

❖ **Synthetic Route:** MW-assisted reduction of Ag(I) and Au(III) with Polyvinylalcohol (PVA)

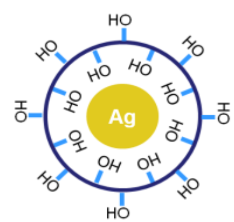


PVA **NPs**

- ❖ Capping agent and Reductor: PVA
- ❖ Metal sources: $AgNO_3$, $HAuCl_4$
- ❖ Solvents: EtOH:H_2O

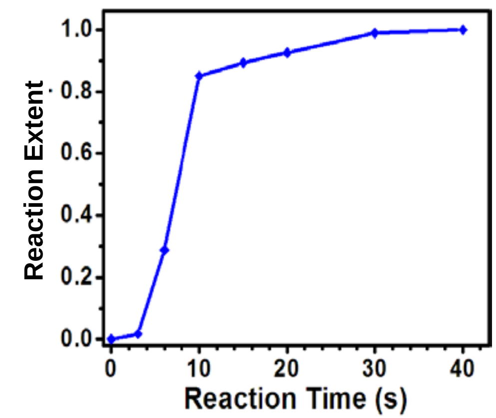


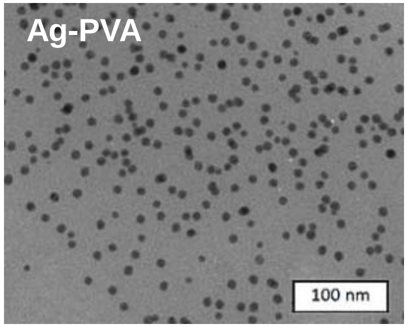
Ag-PVA
(in water)

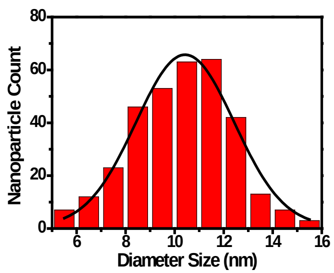


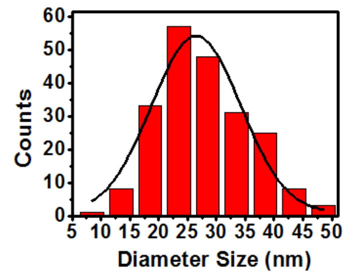
Ag-PVA Nanoparticle
(OH-terminated)

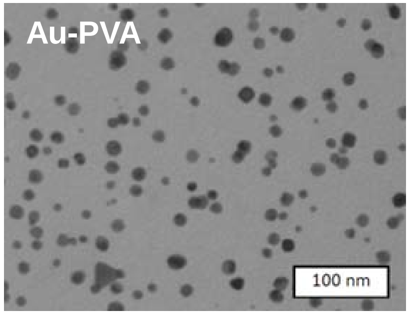
Au-PVA
(in water)







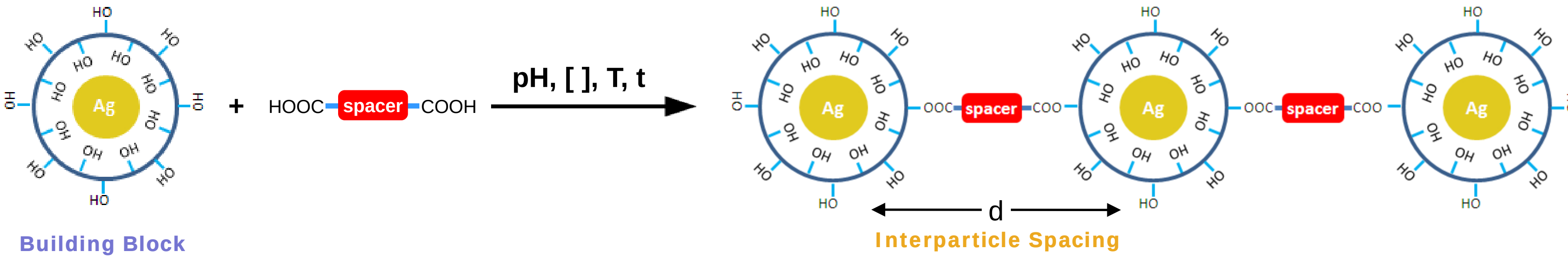




R. Abargues, R.Gradess ,J.Canet-Ferrer , K.Abderrafi ,J.L. Valdés J.Martínez-Pastor. New Journal of Chemistry, **2009**, 33, 913 - 917

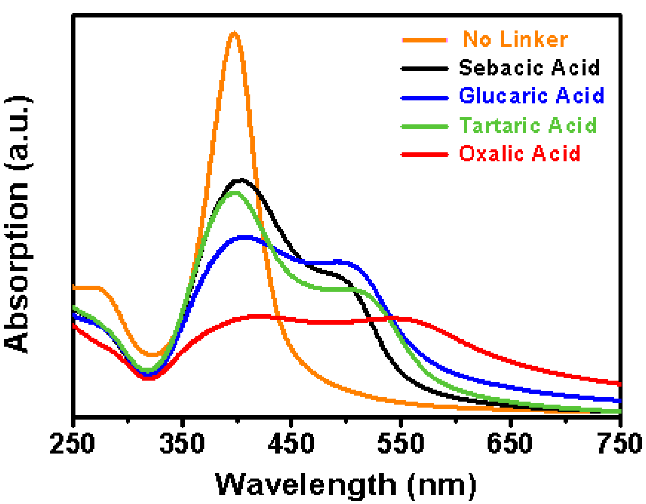
Au and Ag NPs Self-Assembly

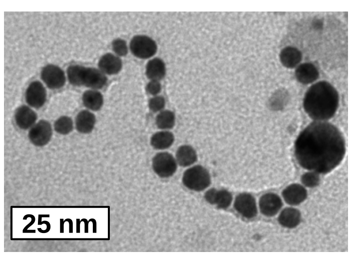
❖ Ag and Au NPs self-assembly based on the crosslinking reaction of PVA with dicarboxylic acids.



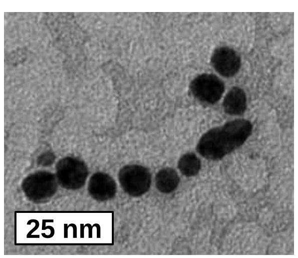
HOOC-Spacer-COOH

Oxalic Acid | Tartaric Acid | Glucaric Acid | Sebacic Acid

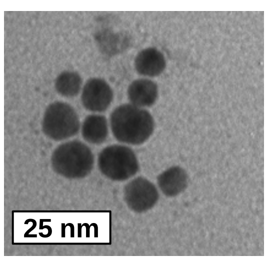




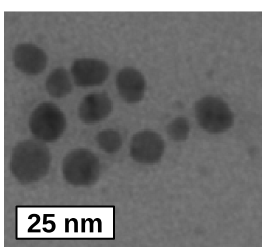
Oxalic Acid



Tartaric Acid



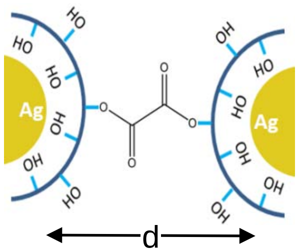
Glucaric Acid



Sebacic Acid

Control of the Interparticle Spacing

HOOC–**Spacer**–COOH

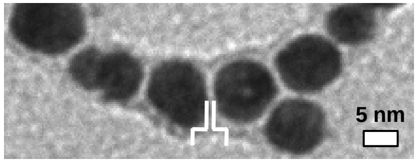


Interparticle Spacing

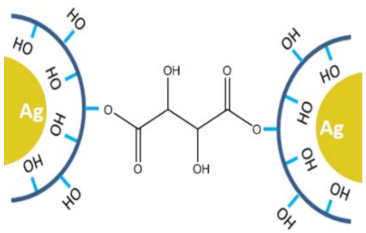
Oxalic Acid

d calc = 0.88 nm

d exp = 0.9 nm



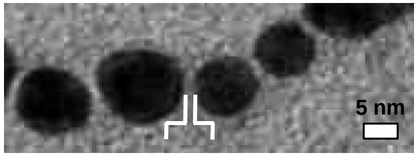
0.9 nm



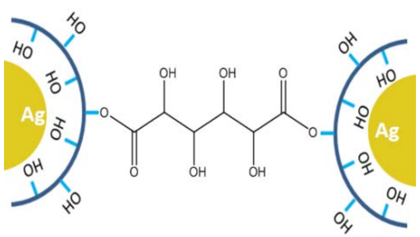
Tartaric Acid

d calc = 1.26 nm

d exp = 1.2 nm



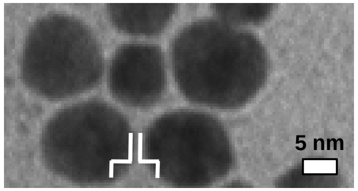
1.2 nm



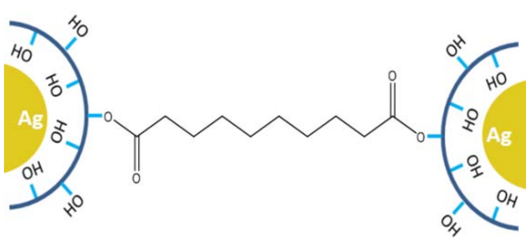
Glucaric Acid

d calc = 1.55 nm

d exp = 1.4 nm



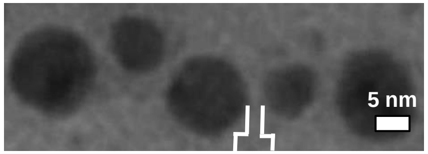
1.4 nm



Sebacic Acid

d calc = 1. 91 nm

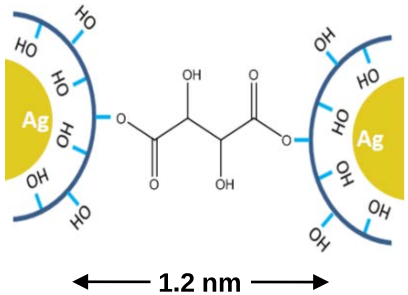
d exp = 1.7 nm

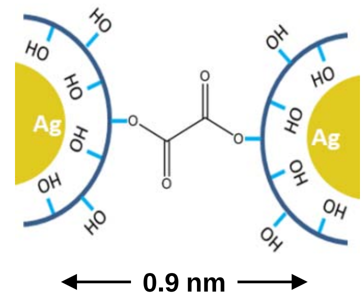


1.7 nm

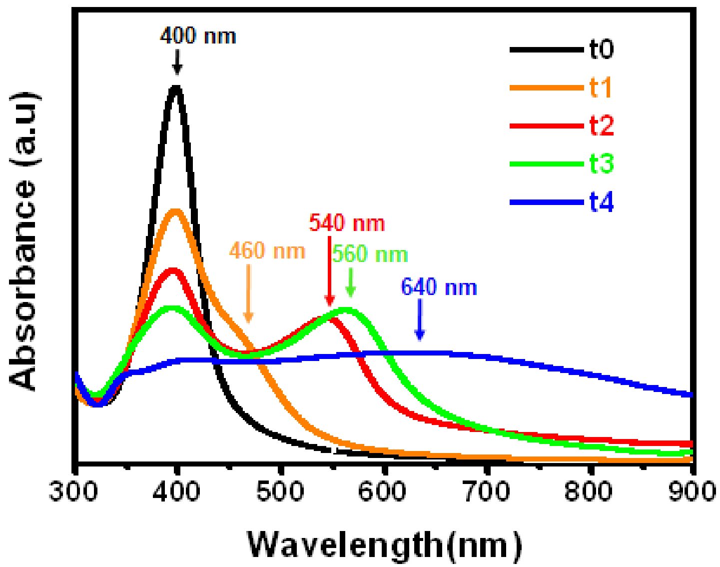
Control of the Assembly Size: Ag-PVA

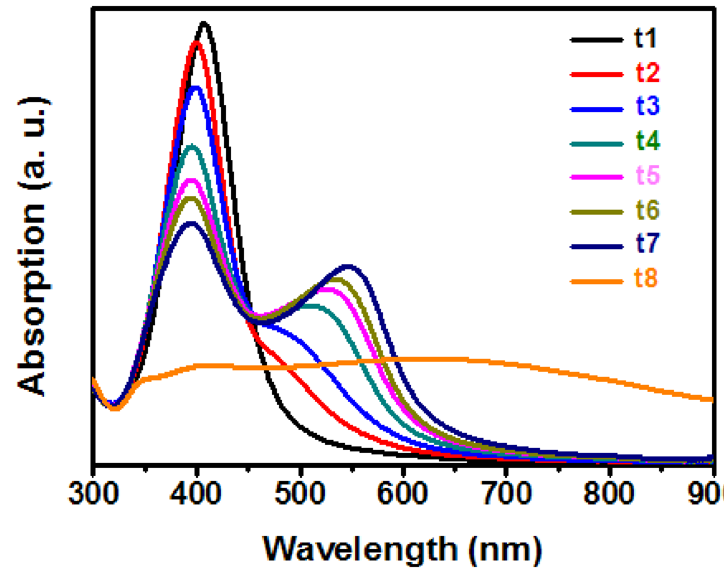
Tartaric Acid

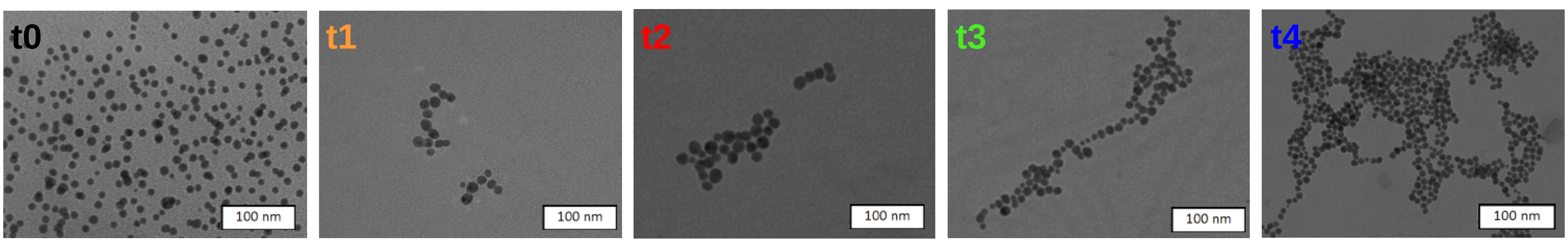




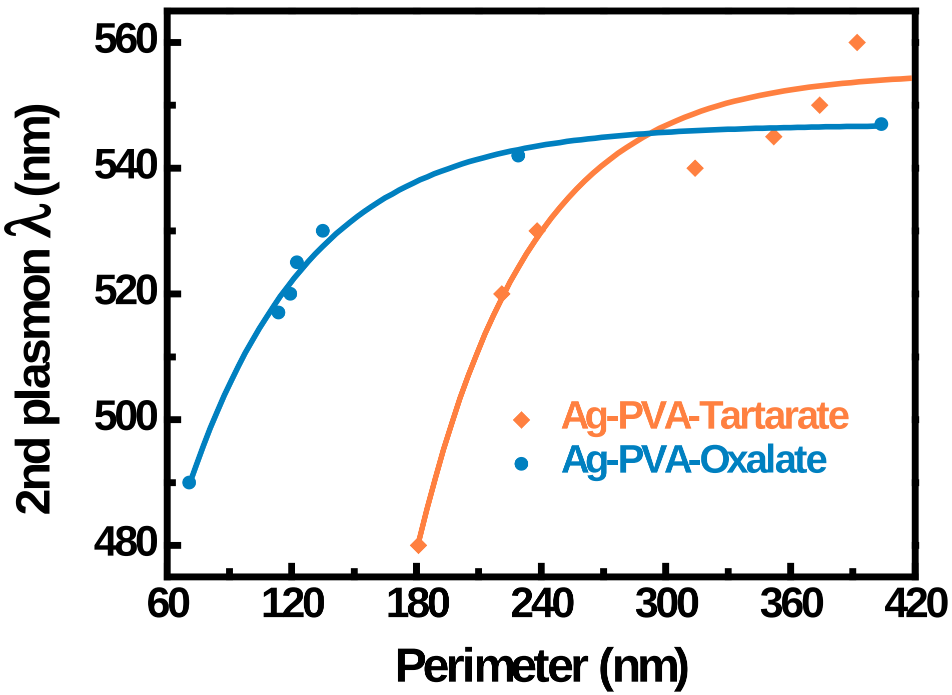
Oxalic Acid



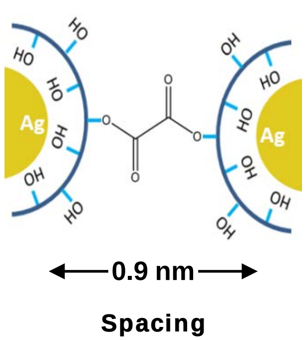




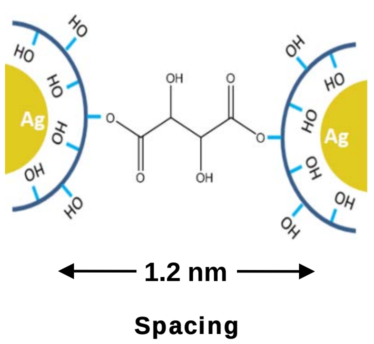
Control of the Assembly Size: Ag-PVA



Oxalic Acid

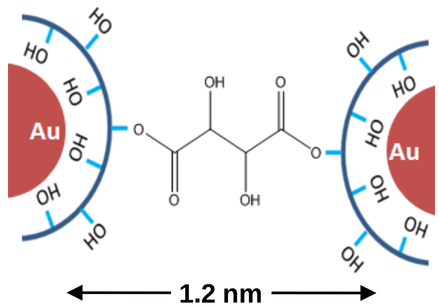


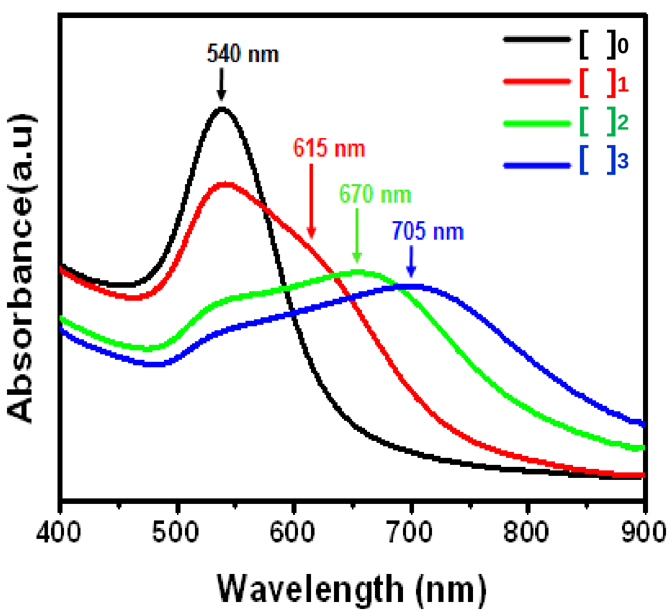
Tartaric Acid

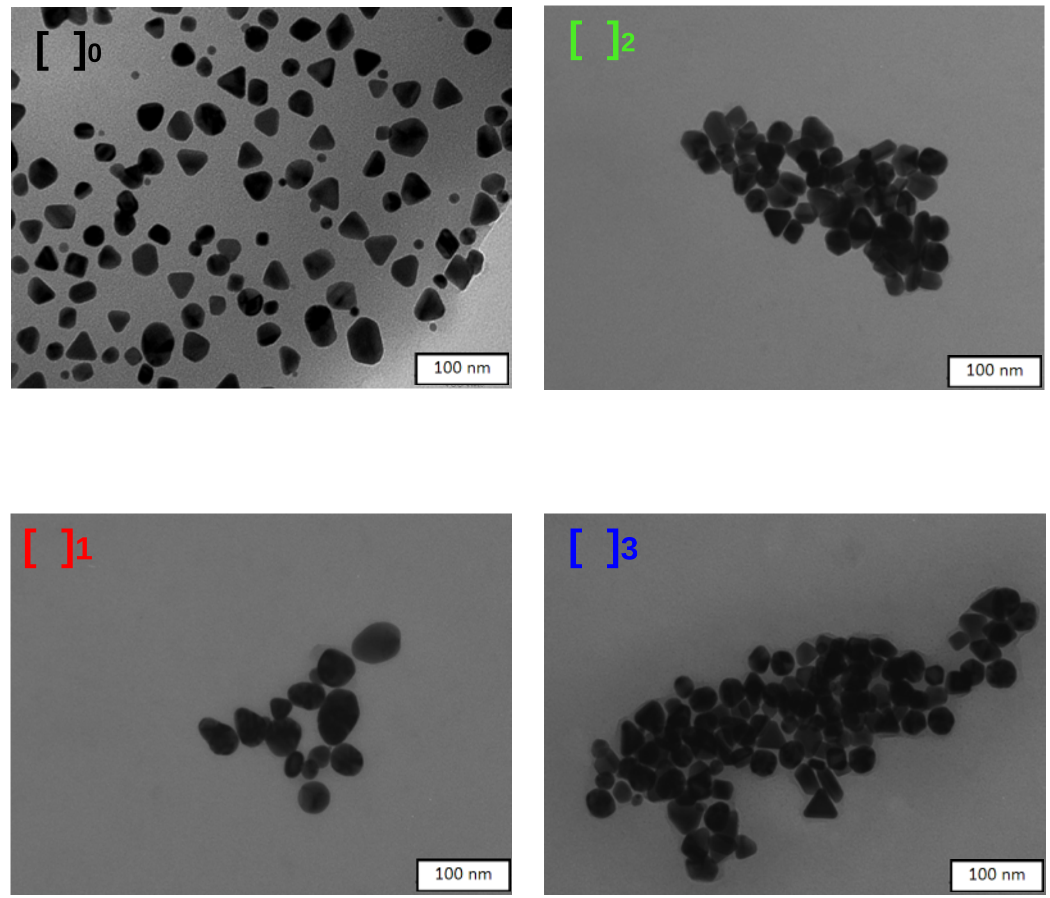


Control of the Assembly Size: Au-PVA

Tartaric Acid







Summary

- Self-Assembly Approach: Covalent binding among Ag or Au Nanoparticles
  - Building Blocks: OH-terminated Nanoparticles
  - Linkers: Dicarboxylics Acids
- Strong plasmon coupling among nanoparticles observed
- Control of the interparticle spacing (from 0.9 to 2 nm) with dicarboxylic acids.
- Facile control of the agglomerate size with the reaction time

Acknowledgments

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