Tunable Photoemission and Photocatalytic Activity of Au-ZnO Nanostructures

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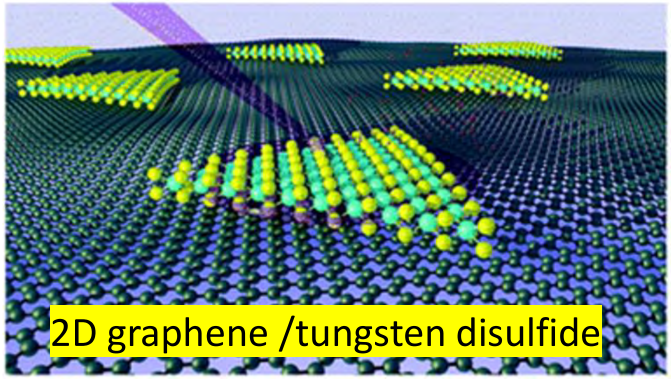
Photocatalysis is powerful, sustainable and cheap technology for energy production and environment remediation

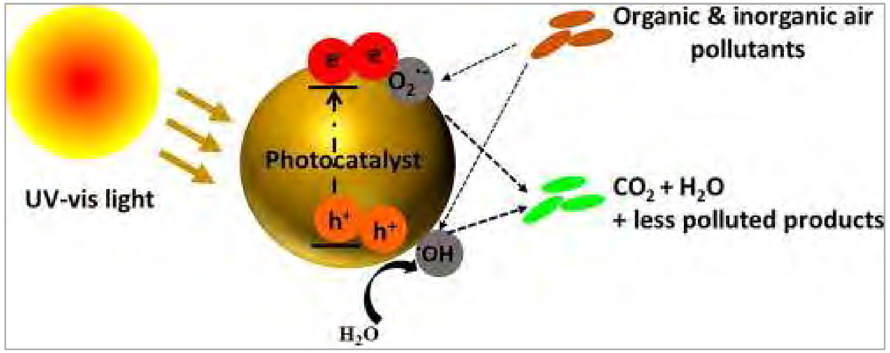
Energy production, storage and conversion



2D graphene /tungsten disulfide

Si-doped Li batteries

Pollutant degradation



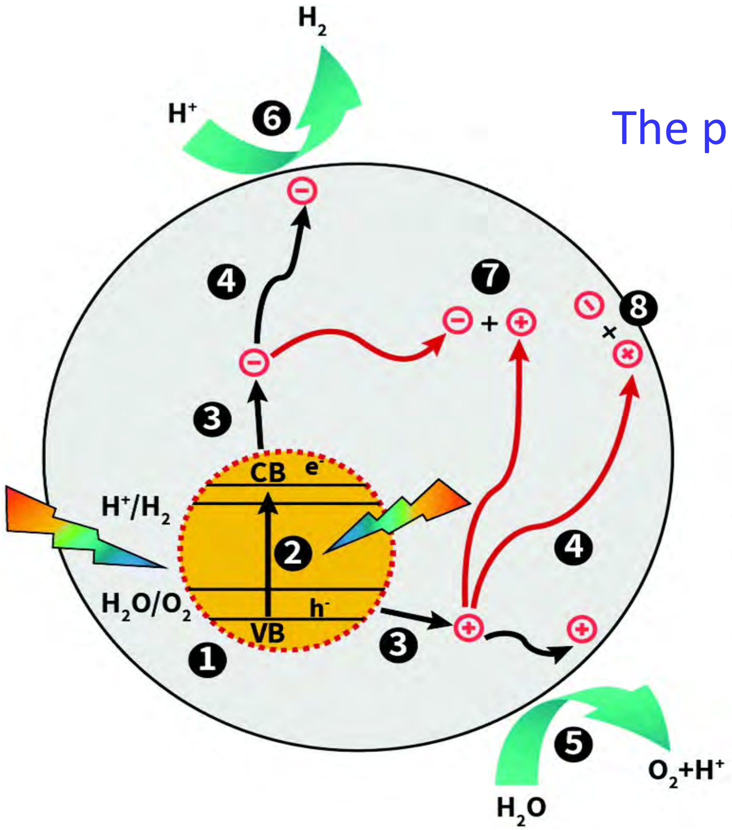
ZnO-doped surfaces

- Pham, H. D. et al. (2021). *Materials Letters*, *288*, 129355.
- Hoang, A. T.et al. (2023). *ACS Sustainable Chemistry & Engineering*, *11*(4), 1221-1252.

Limitations for photocatalysts!

A process using a material called photocatalyst that absorbs light energy to promote chemical reactions

Photocatalytist = Semiconductor



The photocatalytic fundamental process :

1. Light irradiation
2. Electron-hole generation
3. Electron-hole separation
4. Electron-hole transportation to the surface
5. Oxidation reaction and O_2 generation
6. Reduction reaction and H_2 generation
7. Bulk recombination
8. Surface recombination

Water splitting mechanism

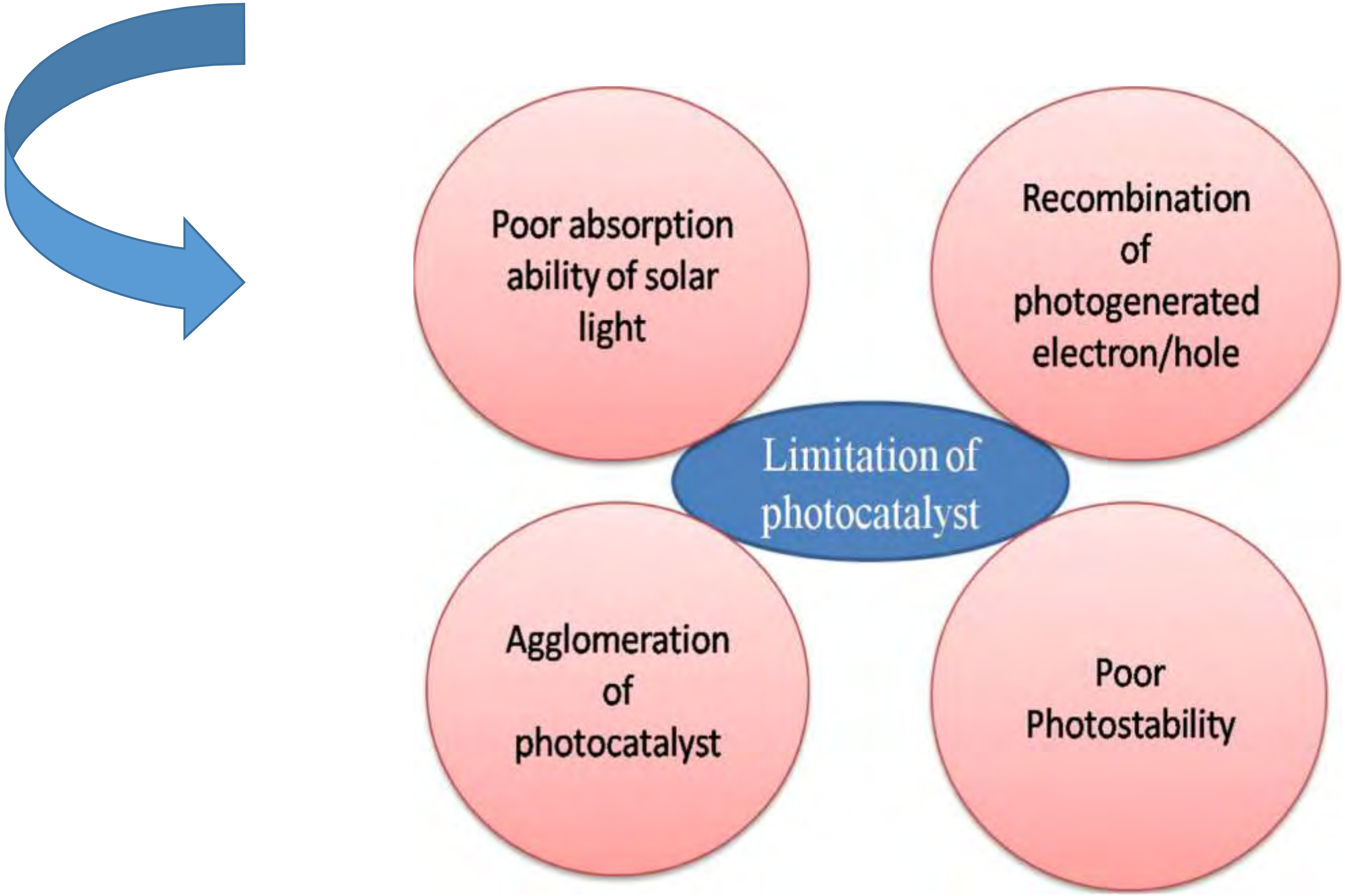
Kumar, A., et al. (2022). Small, 18(1), 2101638.
Saravanan, R. et al. (2017). Nanocomposites for visible light-induced photocatalysis, 19-40.

What's challenging in photocatalysis

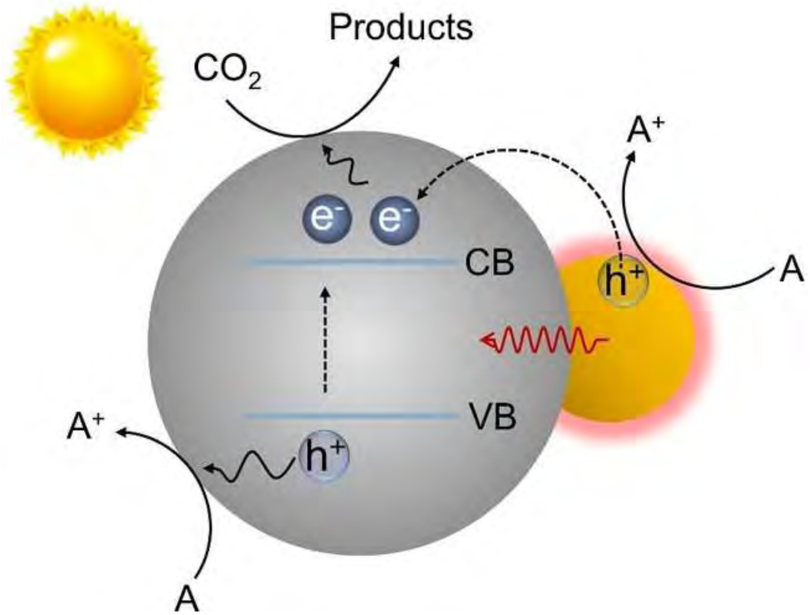
Requirements for a photocatalyst:

- **Chemical reactivity:** robust material with high surface energy and coordination sites
- **Selectivity:** For example selective oxidation of NO to NO_2 and not to another product
- **Stability:** resistance to temperature, surrounding impurities, etc.
- **Activity:** if all previous features are insured, the catalyst is able to promote a reaction
- **Long life span: number of reaction cycles**

Non-homogenous and Defect-rich photocatalyst



Metal-semiconductor heterojunction

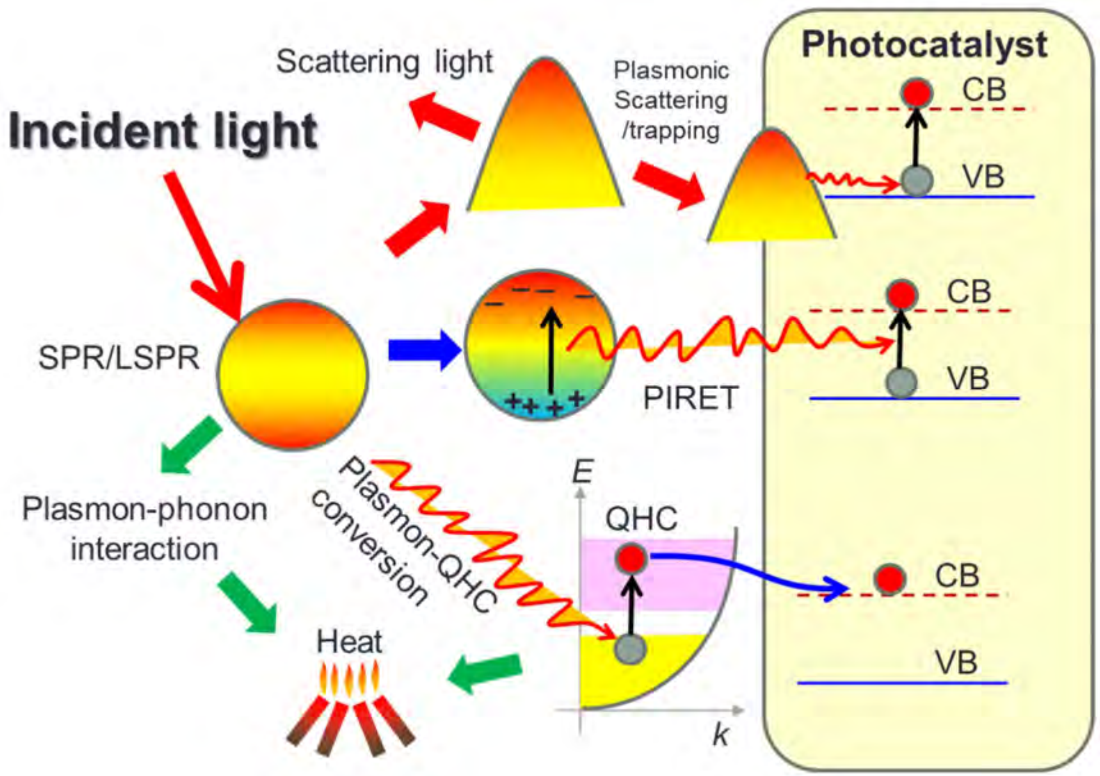


- harness **a broader range of the solar spectrum**, allowing for more efficient use of sunlight.
- offer greater control over reaction **selectivity**
- can operate under **milder conditions**, reducing energy consumption and costs.

Kapoor, A. et al. (2022). *International Journal of Hydrogen Energy*, *47*(40), 17544-17582.

Plasmonic photocatalysis: mechanistic issues

The plasmonic energy transformations of hot electrons in photocatalysis



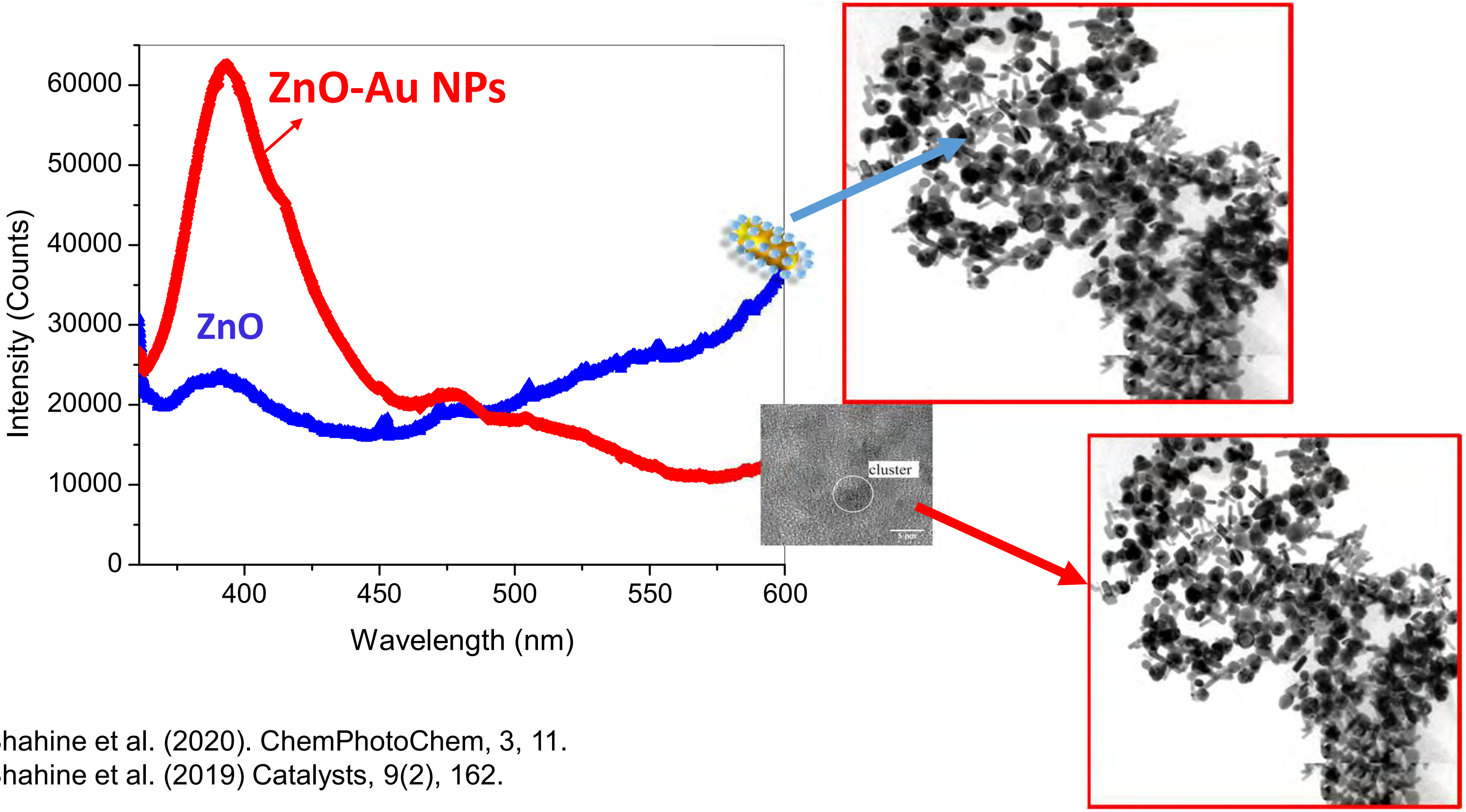
- **Light scattering**
- **Local EF enhancement induced-hot electron injections**
- **Local heat generation**

- The dynamics in surface plasmons is still incomplete with information lacking on the detailed mechanism

Lin, Z. et al. (2015). *Nanoscale*, *7*(9), 4114-4123.
Shahine, I., Jradi, S., Beydoun, N., Gaumet, J. J., & Akil, S. (2020). ChemPhotoChem, 3, 11.

Limitations for nanostructures prepared in liquid medium

Characterization of solutions doesn't allow good understanding of heterojunction mechanisms : need for synthesis optimization

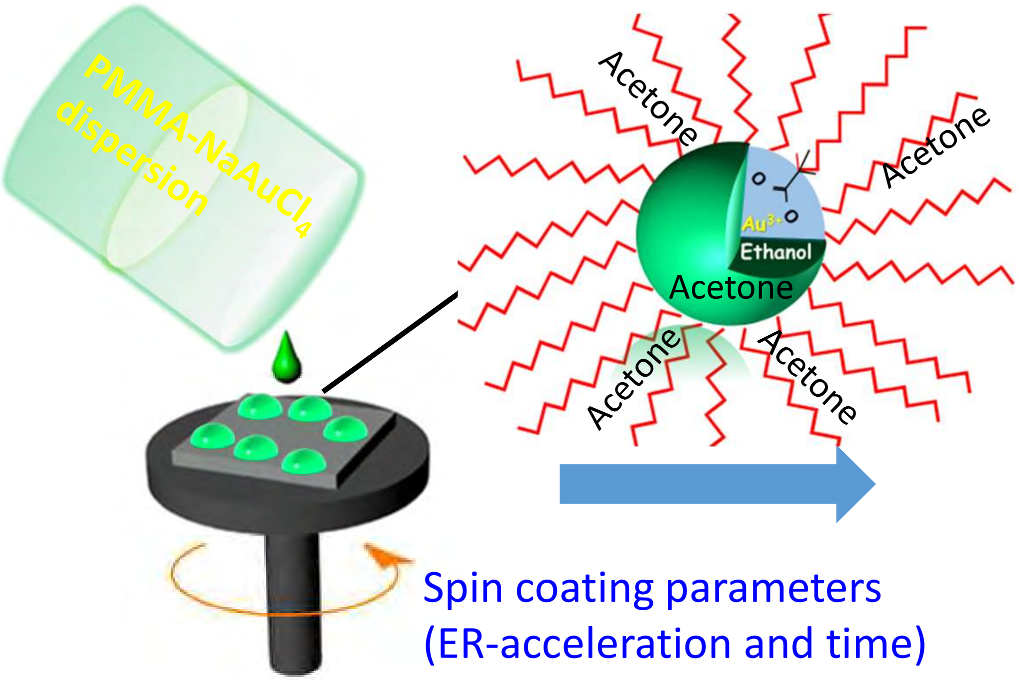


- Shahine et al. (2020). ChemPhotoChem, 3, 11.
- Shahine et al. (2019) Catalysts, 9(2), 162.

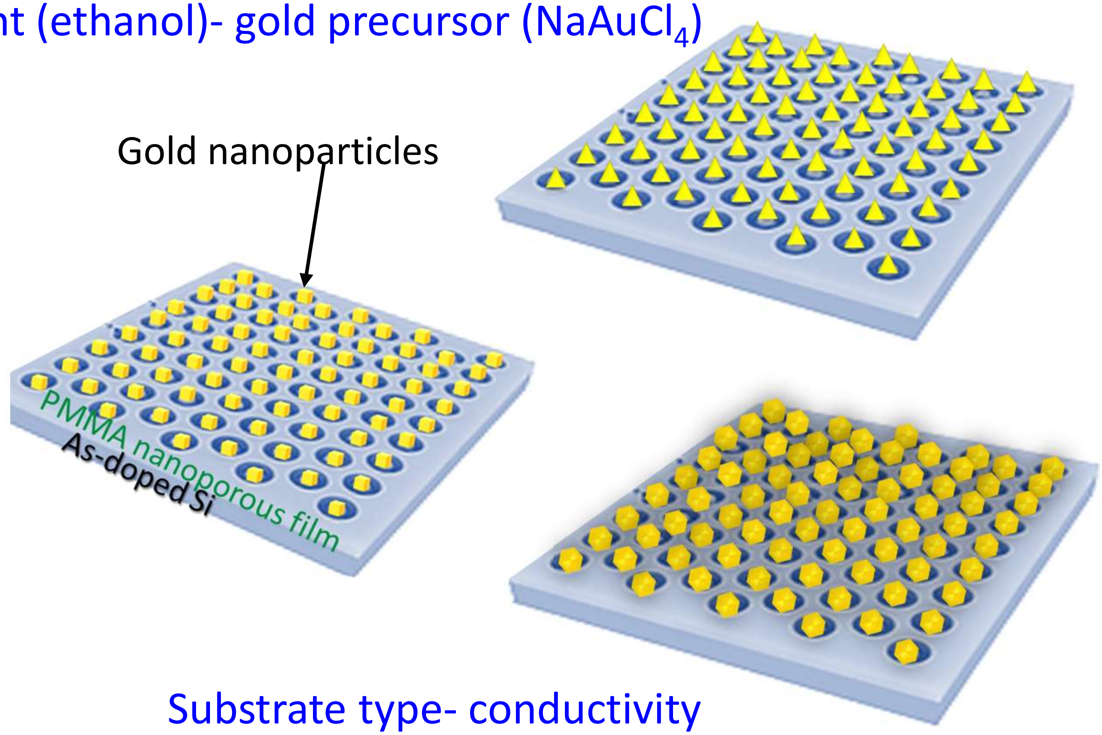
Shape-controlled synthesis of gold nanoparticles

Experimental approach

Dispersion composition: PMMA solvent (acetone), PMMA non-solvent (ethanol)- gold precursor ($NaAuCl_4$)



Spin coating parameters
(ER-acceleration and time)



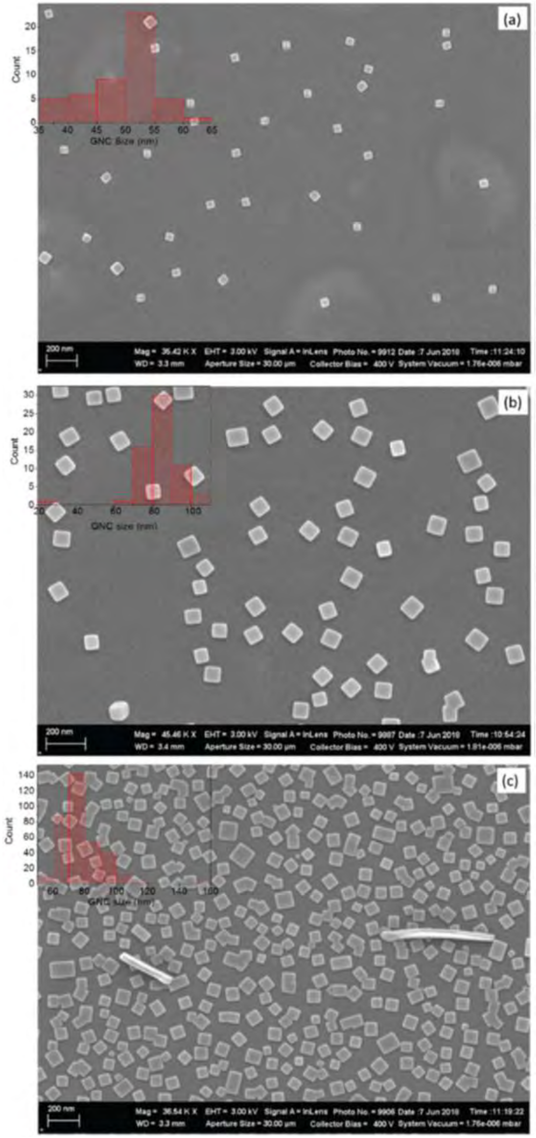
Substrate type- conductivity

Spin-coating induced the formation of Au^{3+}-loaded PMMA micelles

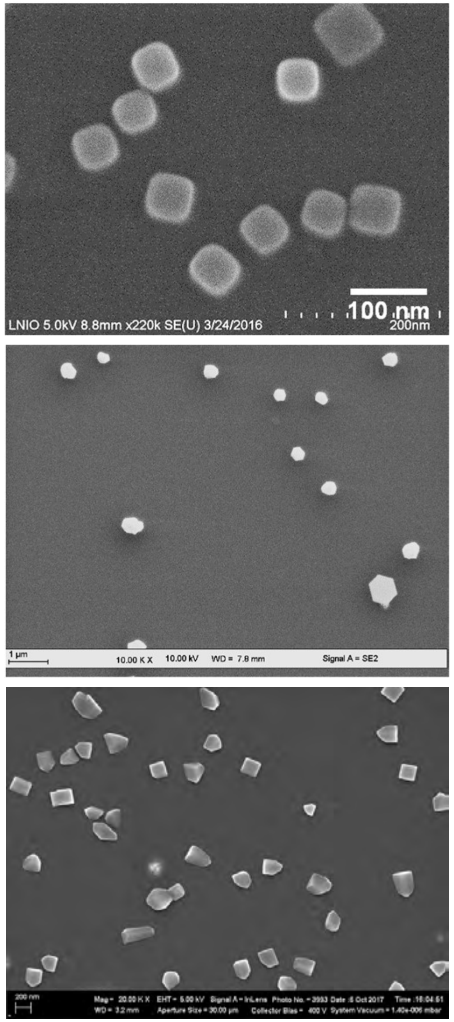
Vapor induced phase separation allows a spontaneous formation of monodisperse gold nanoparticles

Omar, R., et al., 2017. Journal of Materials Chemistry C, 5(41), 10813-10821.

Engineering plasmonic nanomaterials for photocatalysis



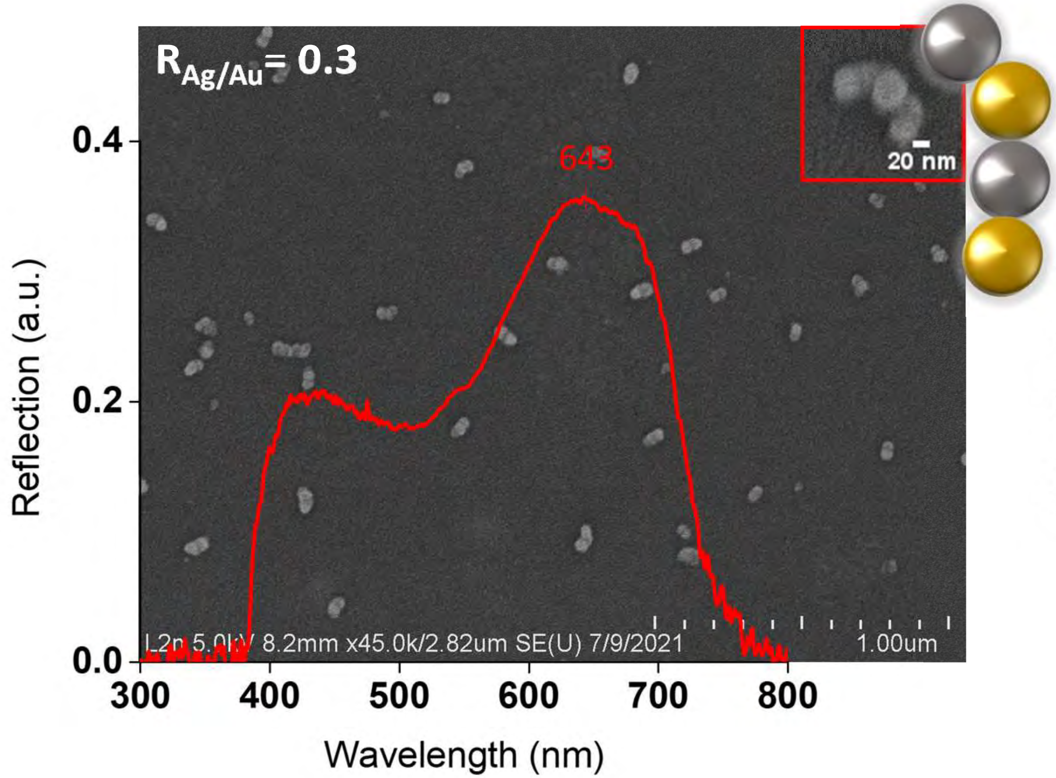
Shape control
Gold nanoparticles

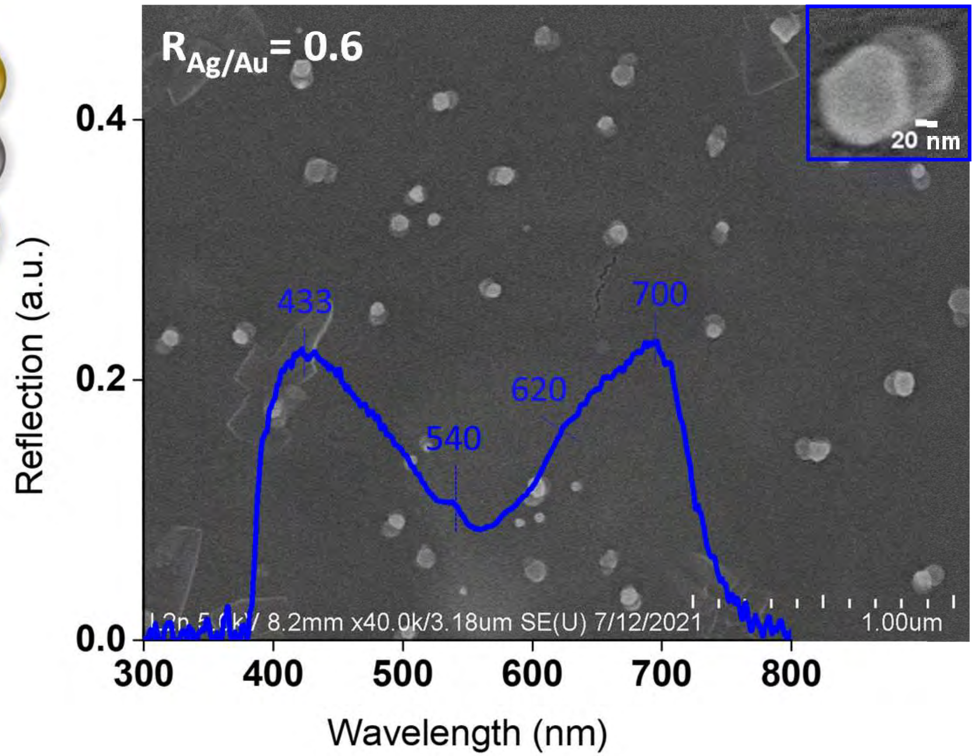


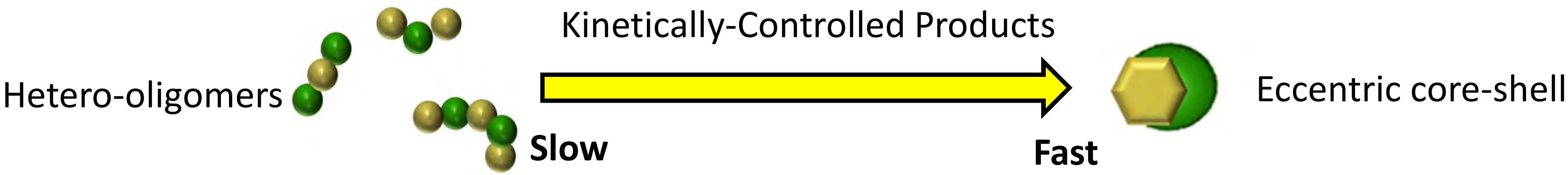
-Fahes et al. (2023). SoftMatter, 19, 321.

-Akil, S., Omar, R., Kuznetsov, D., Shur, V., En Naciri, A., & Jradi, S. (2021). *Nanomaterials*, *11*(7), 1806.

Anisotropic shape-controlled Ag/Au bimetallic nanostructures



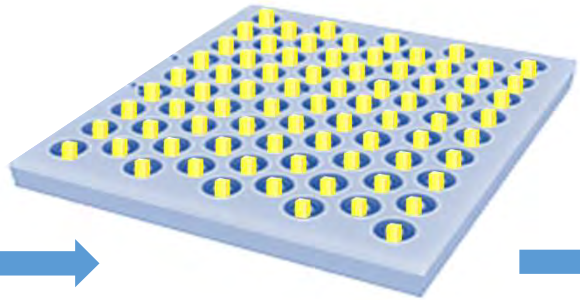




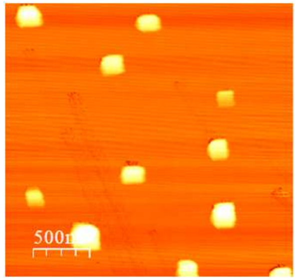
-Fahes et al. (2022). Sensors and biosensors Reasearch, 38, 100528.
-Fahes et al. (2021). Nanomaterials, 11(8), 2055.

Engineering Au-ZnO nanostructures by a Surface-based synthesis strategy

Spin-coating induced the formation of Au^{3+}-loaded PMMA micelles

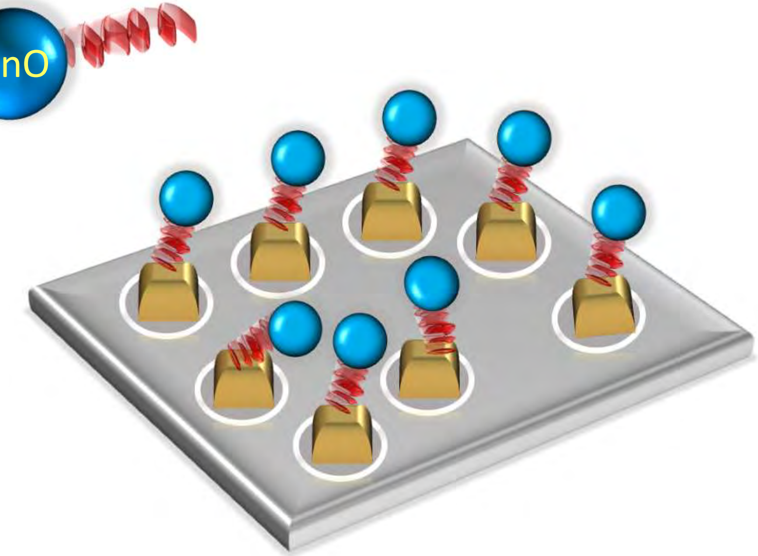


Au Nanocubes



AFM shows cubic Au NPs loading polymer nanostructured thin layer

Protein origami

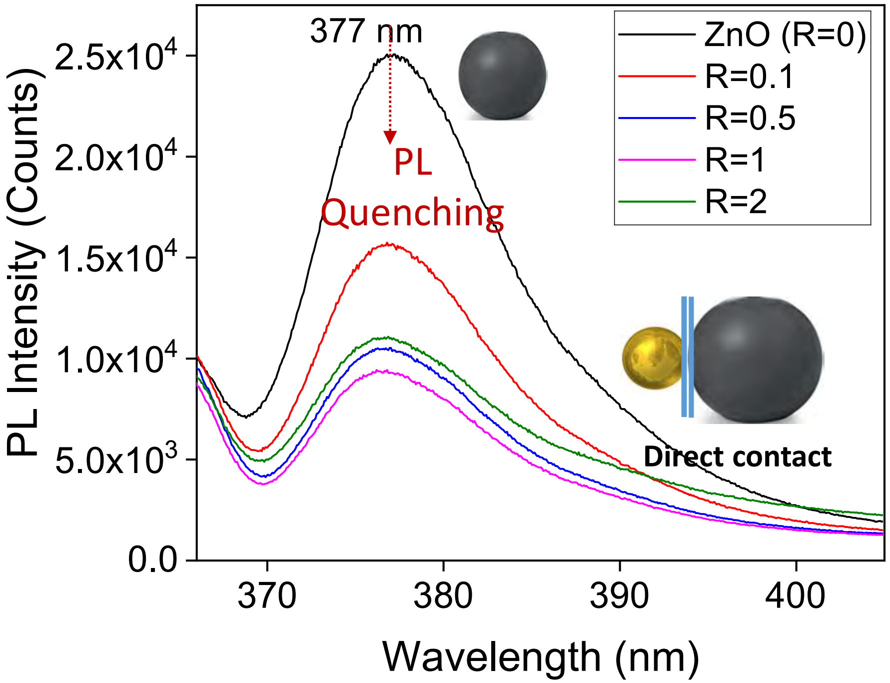


Large area chip device :
Protein length mediated charge transfer at the heterojunction

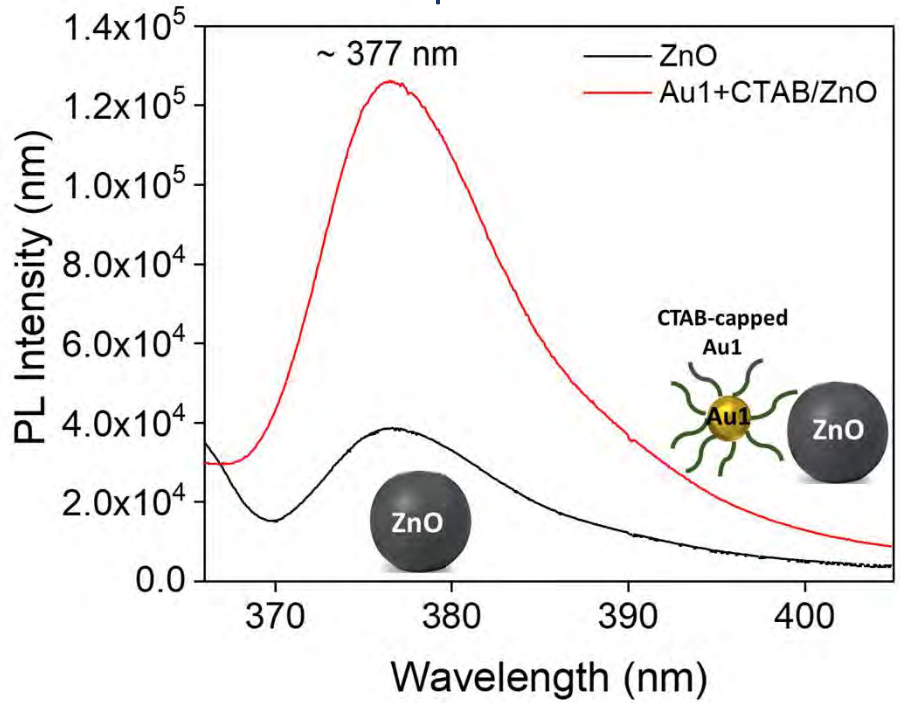
-Fahes A. et al. (2023). SoftMatter, 19, 321.
-Fahes A. et al. (2022). Sensors and biosensors Reasearch, 38, 100528.
-Akil S. et al. (2021). Nanomaterials, 11(7), 1806.
-Fahes A. et al. (2021). Nanomaterials, 11(8), 2055.

From quenched to enhanced photolumincence

Pure Au-ZnO NPs



CTAB separated Au and ZnO



- Au-ZnO junction

  → Formation of Schottky barrier

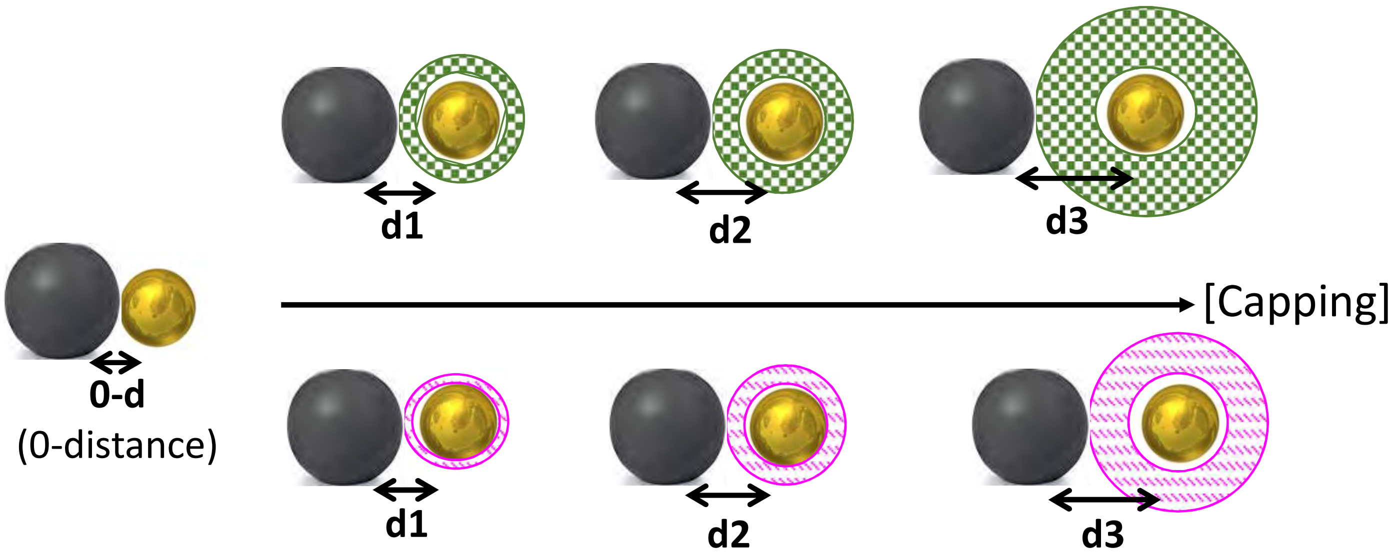
- PL enhancement → e^- transfer into ZnO
- CTAB capping of AuNPs

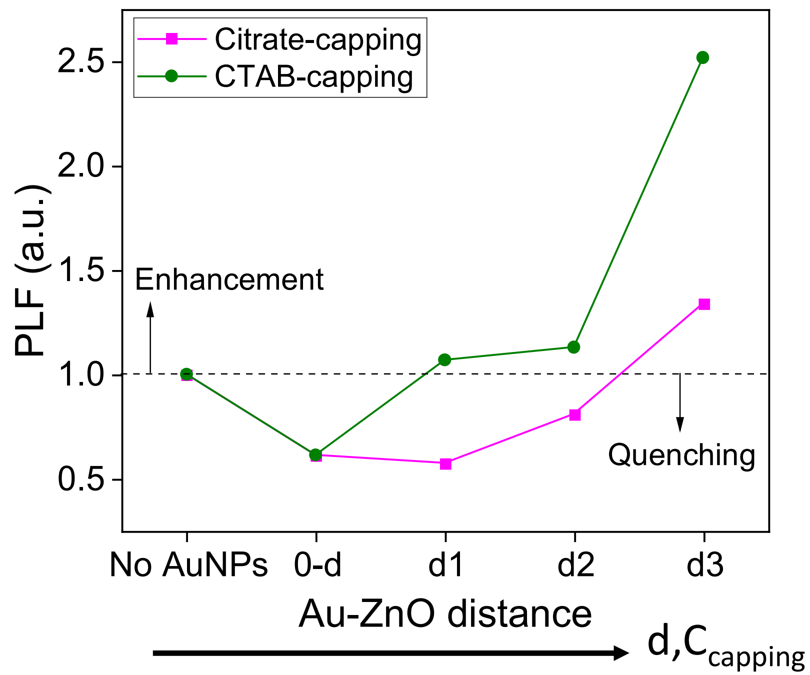
  →Creating distance between ZnO and AuNPs

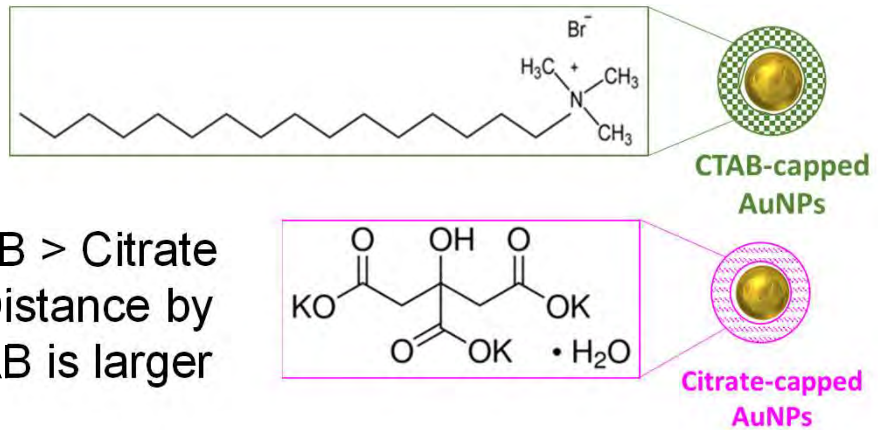
  →Schottky barrier effect is reduced by the separation distance

What's the optimal heterojunction distance for photocatalysis

Effect of distance determined by capping agent concentration





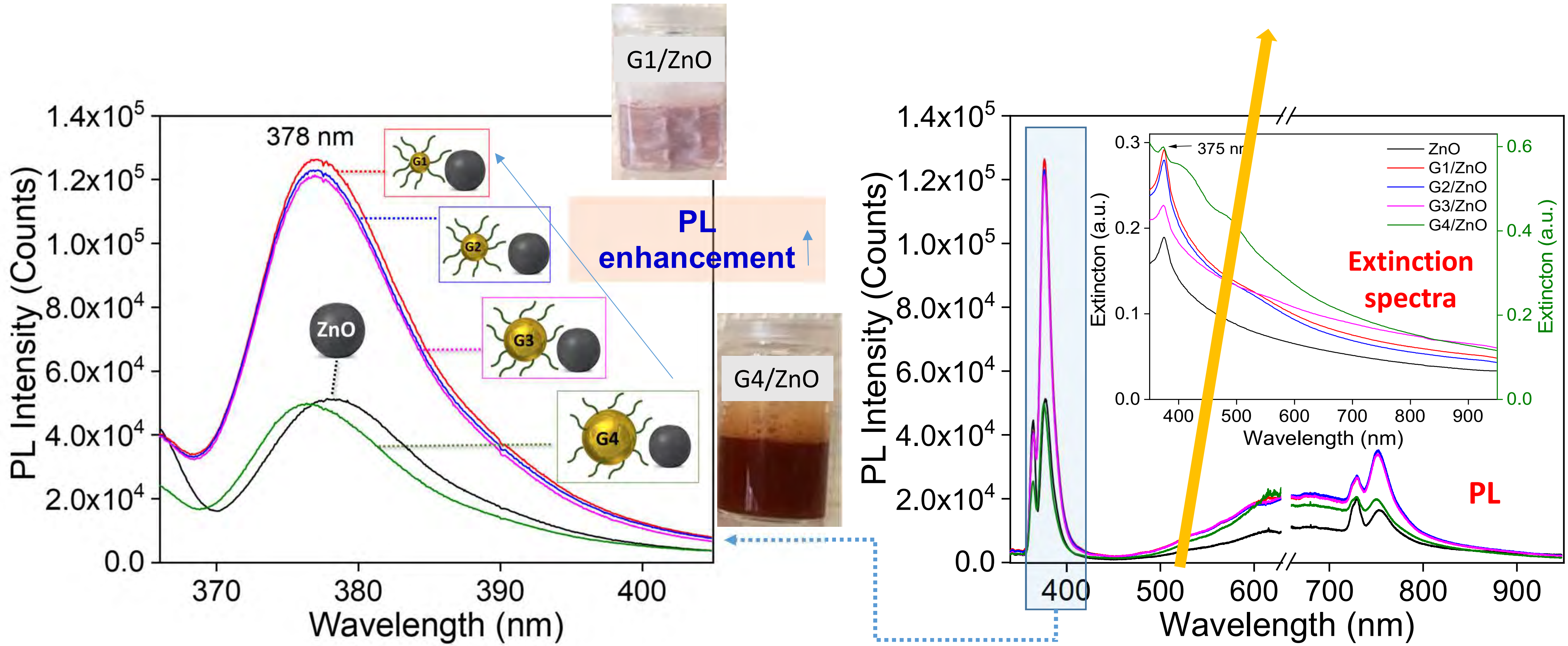


CTAB > Citrate
→ Distance by CTAB is larger

- Optimum interparticle distance
- Inter-charge transfer between AuNPs ↓
- Au-ZnO interactions ↑

→ PL enhancement ↑

Effect of AuNPs size



➢ PL enhancement under UV irradiation → Indirect charge transfer from AuNPs into ZnO NPs

Shahine, I., Beydoun, N., Gaumet, J. J., Bendeif, E. E., Rinnert, H., Magri, P., ... & Akil, S. (2019). Catalysts, 9(2), 162.

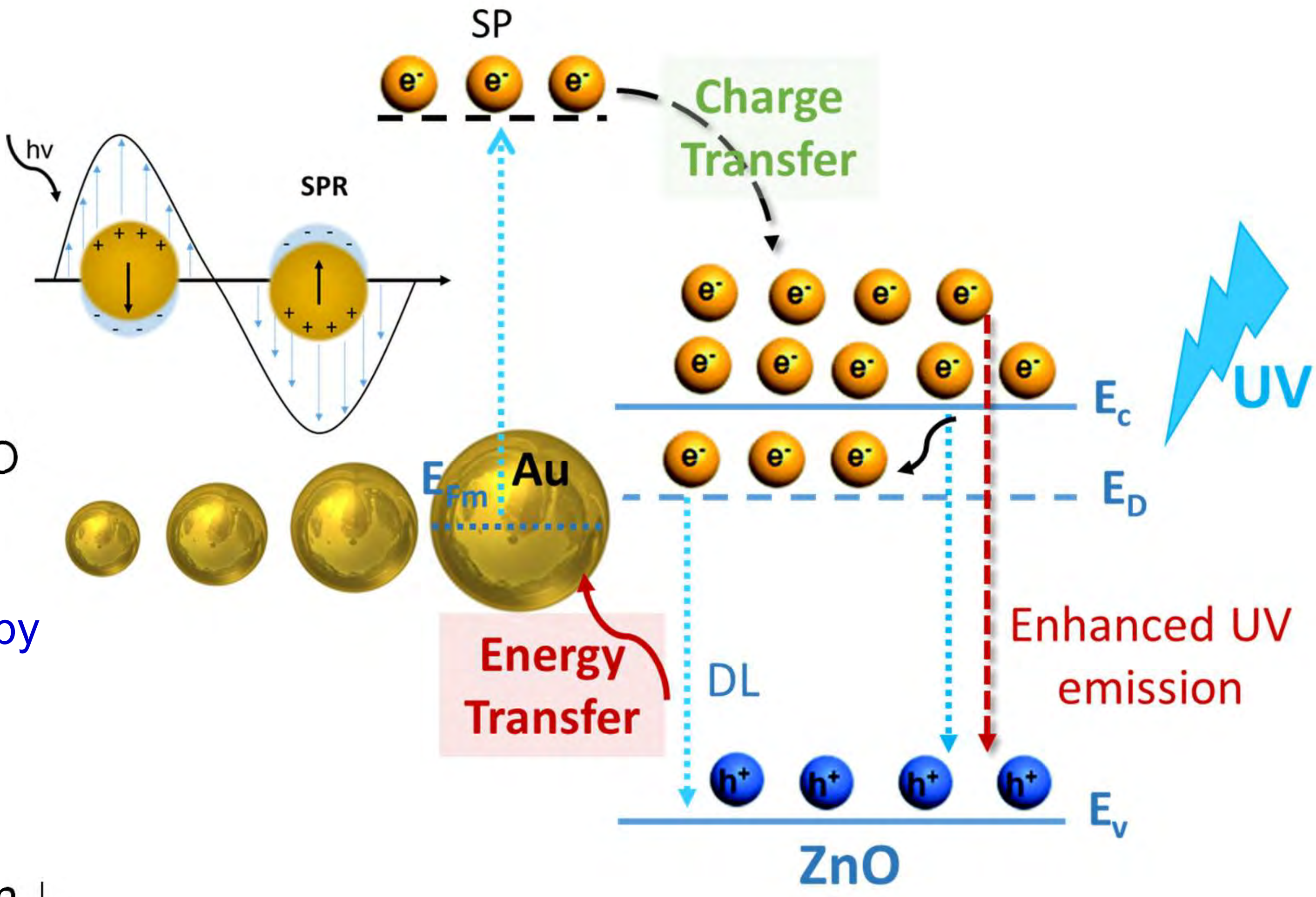
Mechanism of PL enhancement

- Visible defect luminescence is absorbed by AuNPs (due to spectral overlap)
- Hot electrons in AuNPs are produced and transferred into ZnO

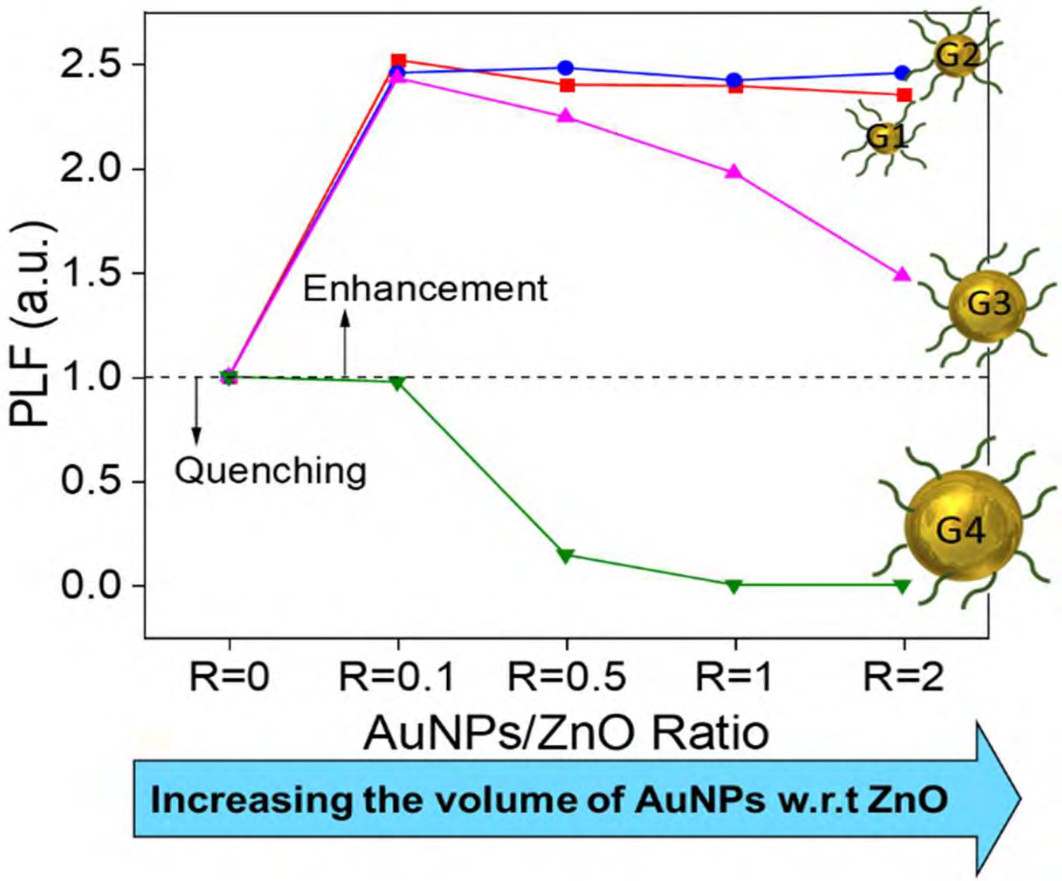
→ Indirect charge transfer induced by energy transfer

- As AuNPs size ↑
  - Au-ZnO interfacial interaction ↓
  - AuNPs Abs ↓ , hot e^- ↓

  → Less PL enhancement

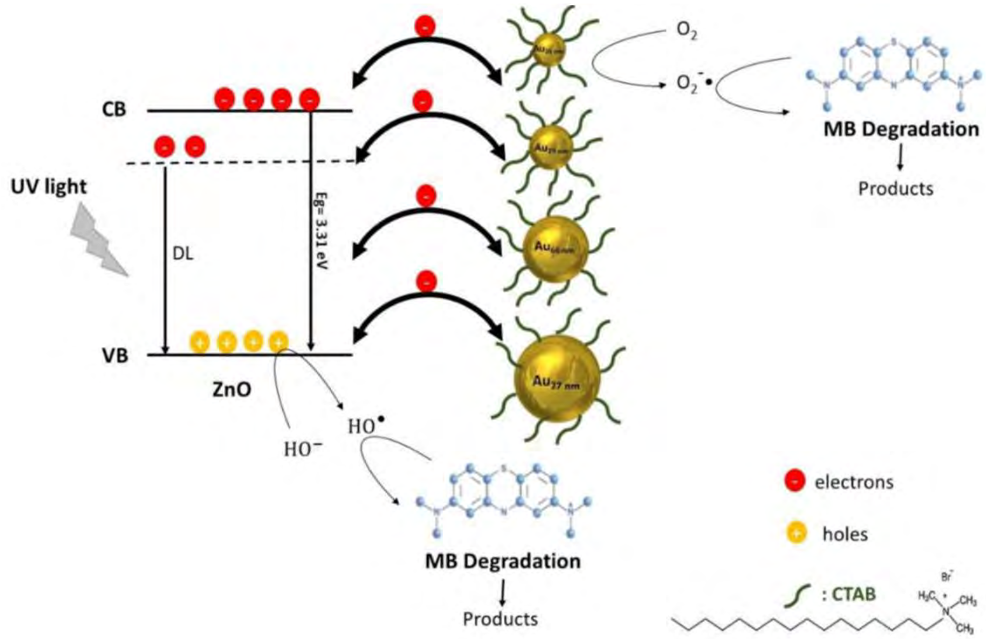


Photocatalytic activity: Methylene blue degradation



Low quantities of small AuNPs:

Enhance the PL and PC activities



Conclusions

The charge transfer (CT) based PL and PC is

- Defect mediated mechanism
- Plasmon structural features dependent
- Junction distance dependent

Enhancement: Optimum distances created by the gold's capping agent facilitated the indirect CT (AuNPs to ZnO) to enhance the PL by PIRET effect.

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