NATIONAL INSTITUTE OF CHEMISTRY

# Plasmonic phenomena and photoelectron generation in Au/$TiO_2$ nanorod arrays for visible light harvesting

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NOWELTIES – 3rd Project Meeting & ATC2 • 16-18 September 2020, Zagreb, Croatia

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# Current research directions

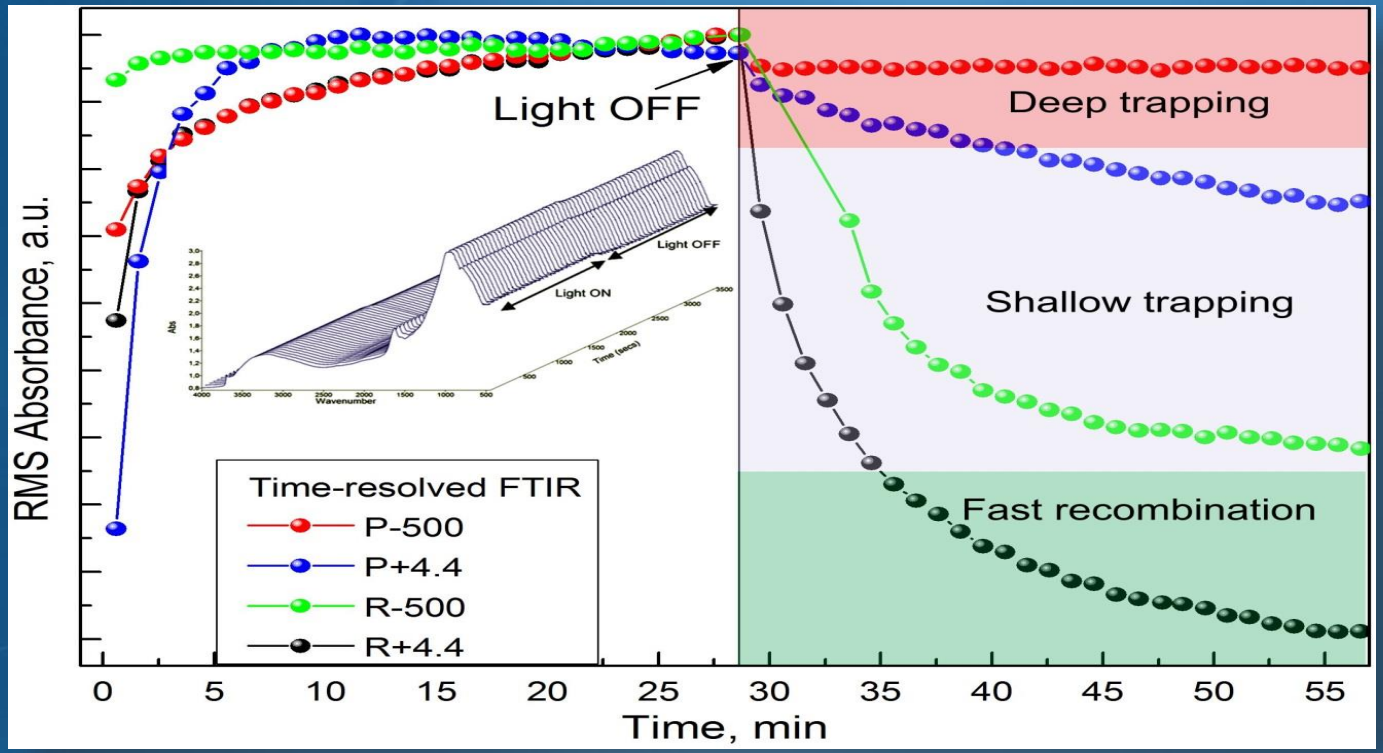
## Enhanced charge separation in heterogeneous photocatalysts

$TiO_2$-$WO_3$ composites
$TiO_2$/reduced graphene oxide composites

## Visible light utilization in photocatalysis

Multicomponent $TiO_2$-$Bi_2O_3$/$(BiO)_2CO_3$ composites
Plasmonic immobilized multisegmented nanorod arrays

# Time resolved FTIR spectroscopy




Time-resolved FTIR measurements for P-$TiO_2$-$WO_3$ and R-$TiO_2$-$WO_3$ composites without and with 4.40 wt. % W. Inset is showing the typical temporal variation in the RMS absorption during light ON and light OFF experiments for R+4.40 composite.

G. Žerjav et al., Appl. Catal. B 209 (2017) 273-284.

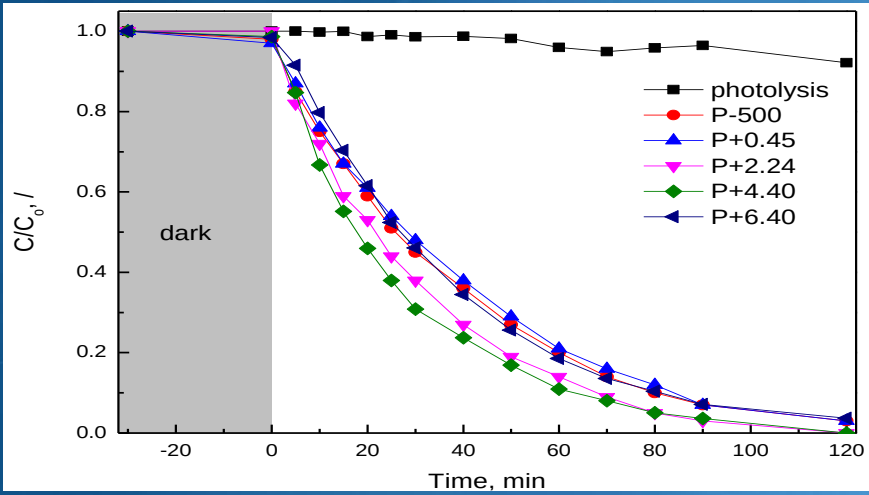
# Photocatalytic oxidation of aqueous bisphenol A (BPA) solution in batch slurry reactor

BPA degradation conditions:

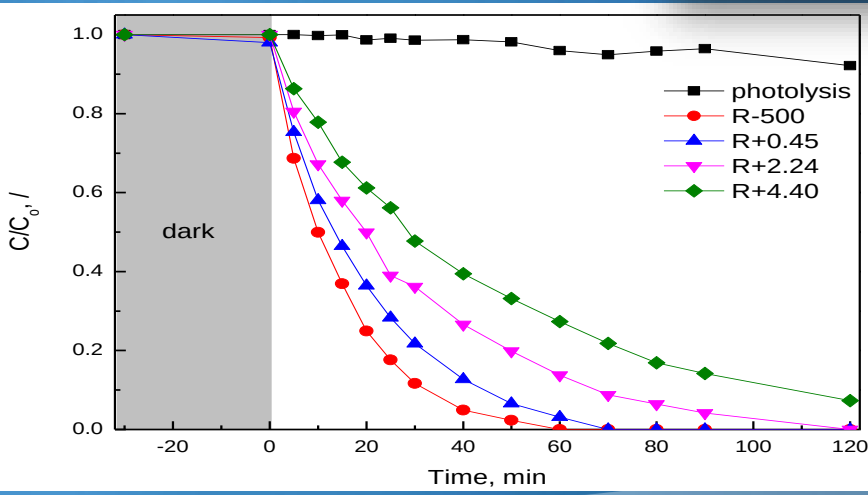
- 10 mg/l of BPA @ t=0
- 20°C, purged with air (45 l/h)
- magnetically stirred (600 rpm)
- catalysts concentration: 62.5 mg/l
- illuminated with UVA Hg lamp (150 W, $\lambda_{max}$=365 nm)

Batch slurry reactor system.

P-$TiO_2$-$WO_3$




R-$TiO_2$-$WO_3$




Photolytic and photocatalytic degradation of BPA in the presence of P-$TiO_2$-$WO_3$ and R-$TiO_2$-$WO_3$ composites with different $WO_3$ loadings irradiated with UV light.

G. Žerjav et al., Appl. Catal. B 209 (2017) 273-284.

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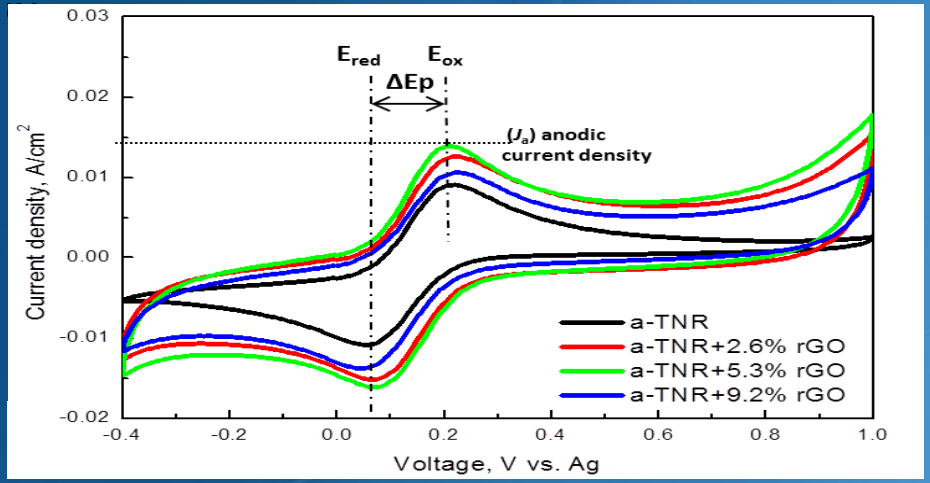
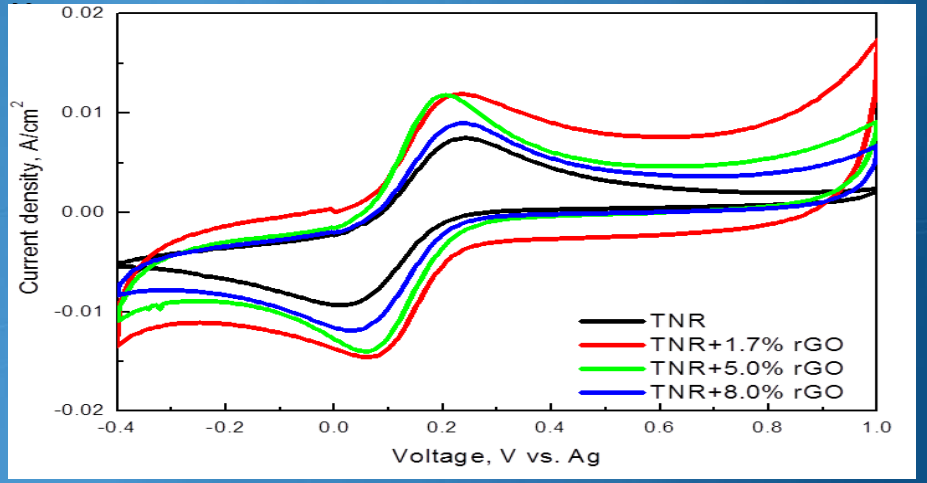
# Cyclic voltammetry (CV) measurements

a-TNR+rGO composites




TNR+rGO composites




Cyclic voltammograms recorded for the a-TNR and TNR composites with different amounts of rGO. The CVs were measured in 0.1 M KCl solution containing 1 mM $K_3[Fe(CN)_6]$ as a redox probe with scanning rate of 50 mV/s.

G. Žerjav et al., Nanoscale 9 (2017) 4578-4592.

# Bisphenol A (BPA) photocatalytic oxidation in batch slurry reactor

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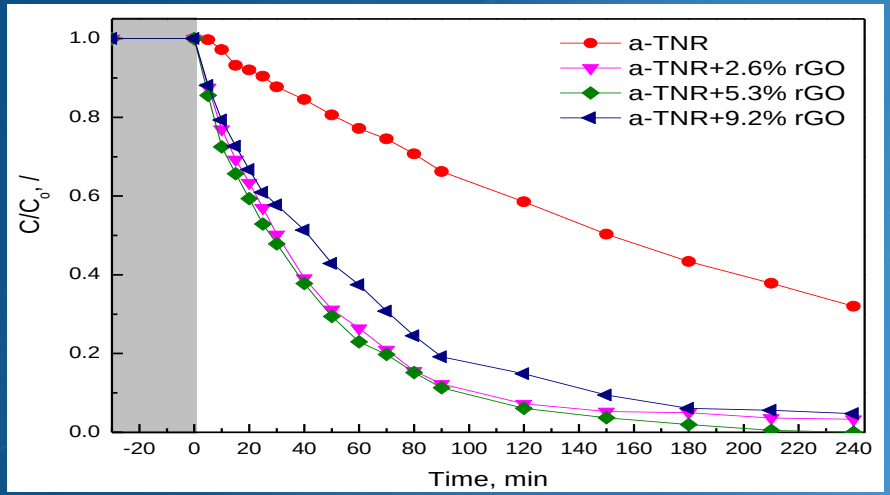
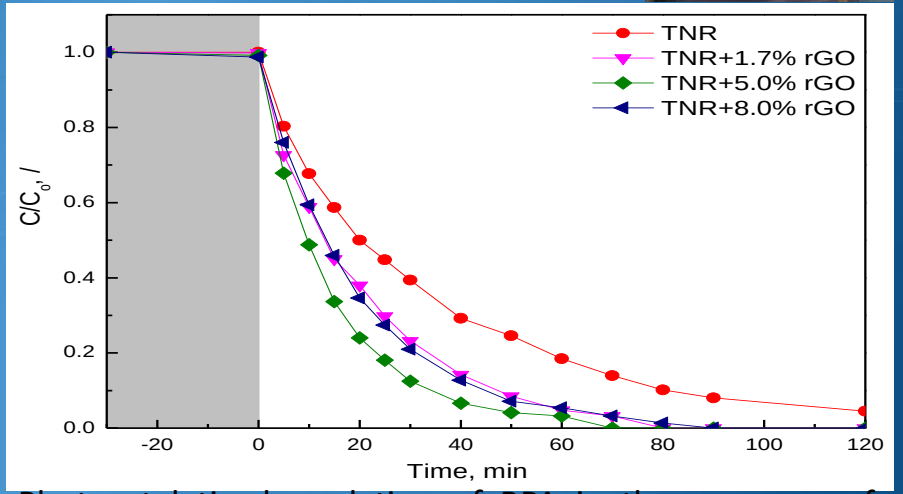
Batch slurry reactor system.

a-TNR+rGO composites




Photocatalytic degradation of BPA in the presence of a-TNR composites with different rGO loadings irradiated with UVA light. The catalyst concentration used in the performed experiments was 62.5 mg/l.

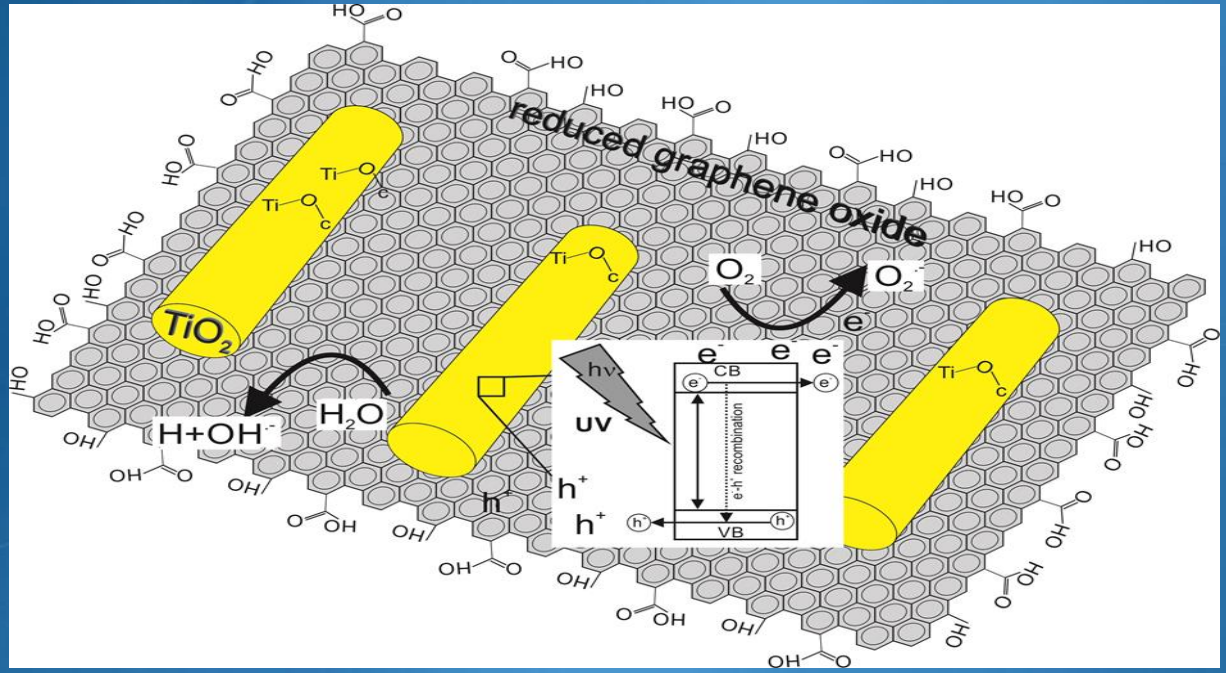
TNR+rGO composites




Photocatalytic degradation of BPA in the presence of TNR composites with different rGO loadings irradiated with UVA light. The catalyst concentration used in the performed experiments was 31.25 mg/l.

G. Žerjav et al., Nanoscale 9 (2017) 4578-4592.

# Proposed mechanism for improved charge separation and migration




Graphical illustration of TNR+rGO composites and possible mechanism for improved charge separation and migration.

G. Žerjav et al., Nanoscale 9 (2017) 4578-4592.

# Current research directions

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Plasmonic immobilized multisegmented nanorod arrays

# Novel plasmonic immobilized multisegmented Au/$TiO_2$ nanorod arrays for solar energy conversion applications

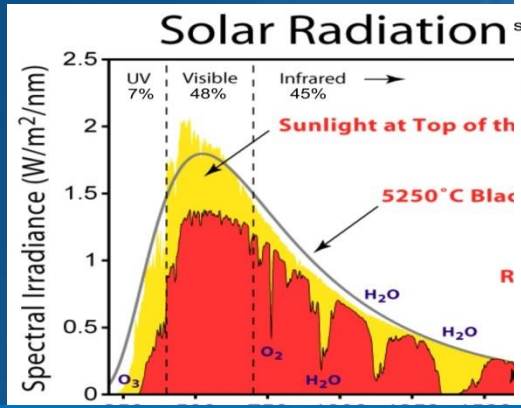
# Plasmonic photocatalyst active under visible + IR radiation

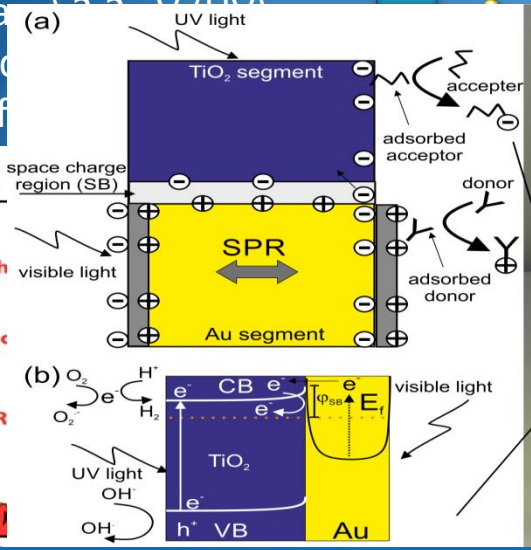
**$TiO_2$**

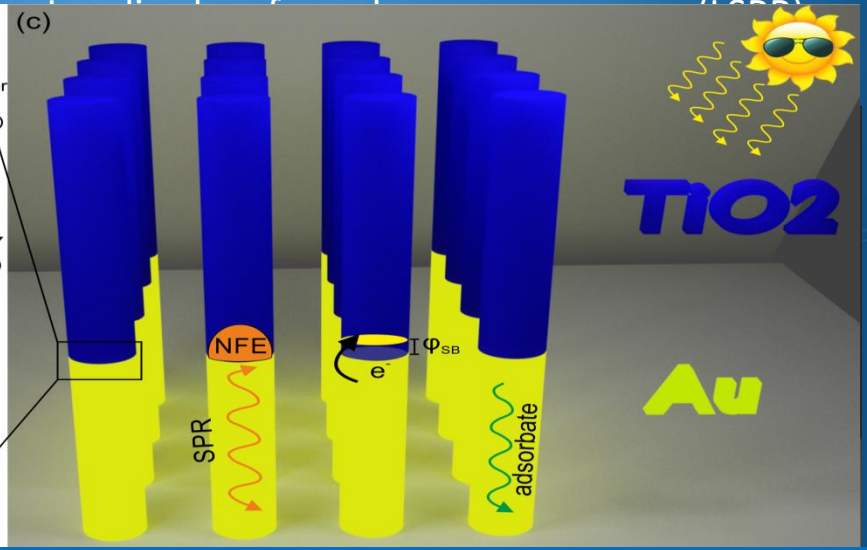
- Semiconductor oxide (SO) (n-type)
- Band gap energy (anata
- Safe, chemically and
  inexpensive and high ef

**Au/Ag/Cu**

- Plasmonic metals (PM)



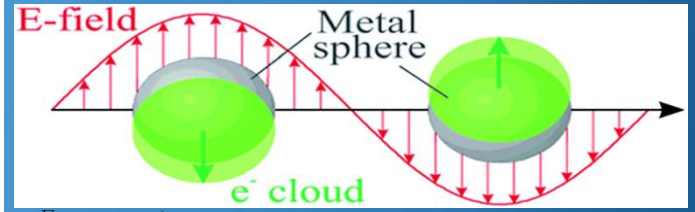



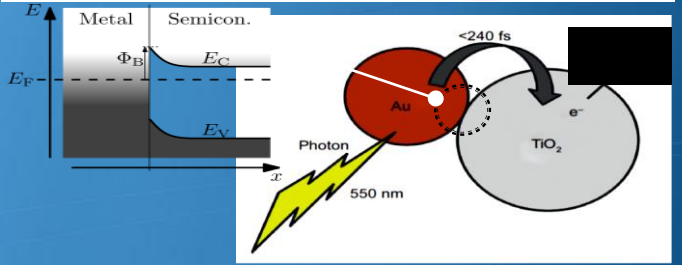

**Coupling of PM with SO**

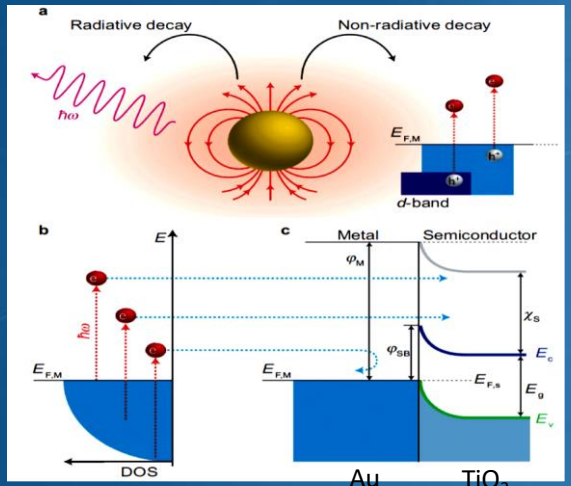
1. The PM (Au) efficiently absorbs solar light through **LSPR** and converts it into energetic e-h pairs in nearby SO ($TiO_2$).
2. Recombination rate of e-h pairs is avoided by the **Schottky barrier** generated at the interface between PM and SO.
3. Photoactivity (efficiency) further depends on energy transfer mechanism from PM to SO: (1) plasmon-induced hot e injection, (2) plasmon-induced resonance energy transfer, and (3) plasmon-induced radiative energy transfer. Optimizing these mechanisms can help to greatly maximize the efficiency.

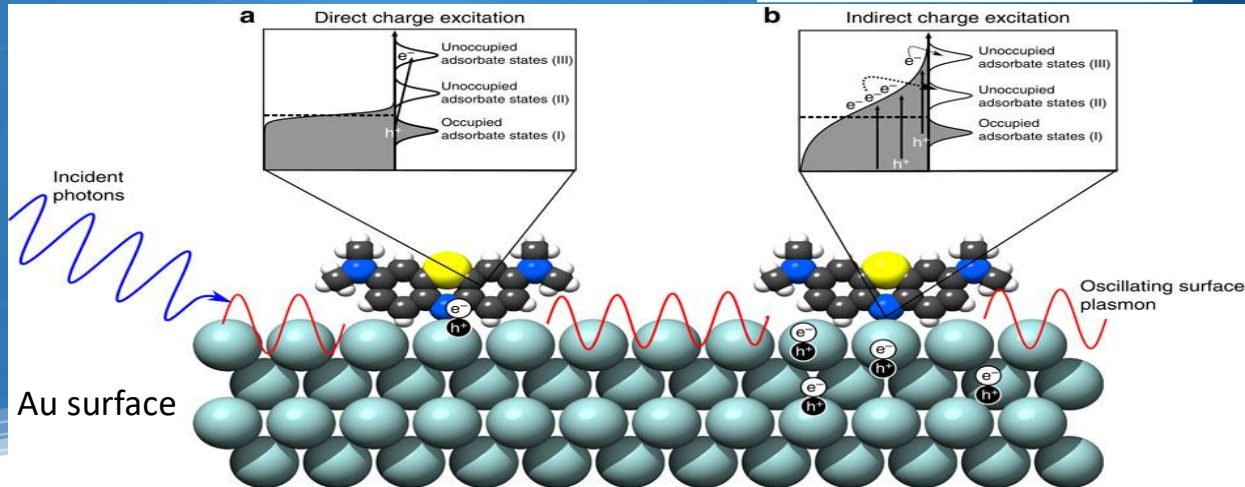
# What is LSPR & plasmon induced hot *e* injection?

- In PM (Au, Ag, Cu), conduction electrons undergo a collective oscillation when excited by light at specific wavelengths, known as localized surface plasmon resonance (LSPR). This results in the unusually strong scattering and absorption of light. LSPR depends on the geometrical shape and size of PM.
- LSPR leads to generate hot e at the surface of PM, which can be injected into SO to create e-h pair. Hot e refers to electrons that are not at thermodynamic equilibrium with the atoms in materials.
- Interface between PM and SO creates a Schottky barrier that prevents reverse electronic motion; the barrier depends on energy band position of both PM and SO.
- Au/$TiO_2$ and Ag/$TiO_2$ composites are great choice due to excellent band alignment.
- The interaction of LSPR with adsorbate orbitals can lead to the injection of energized charge carriers into the adsorbate, which can result in chemical transformations. The energy of the unoccupied states of adsorbates must overlap with the LSPR energy.



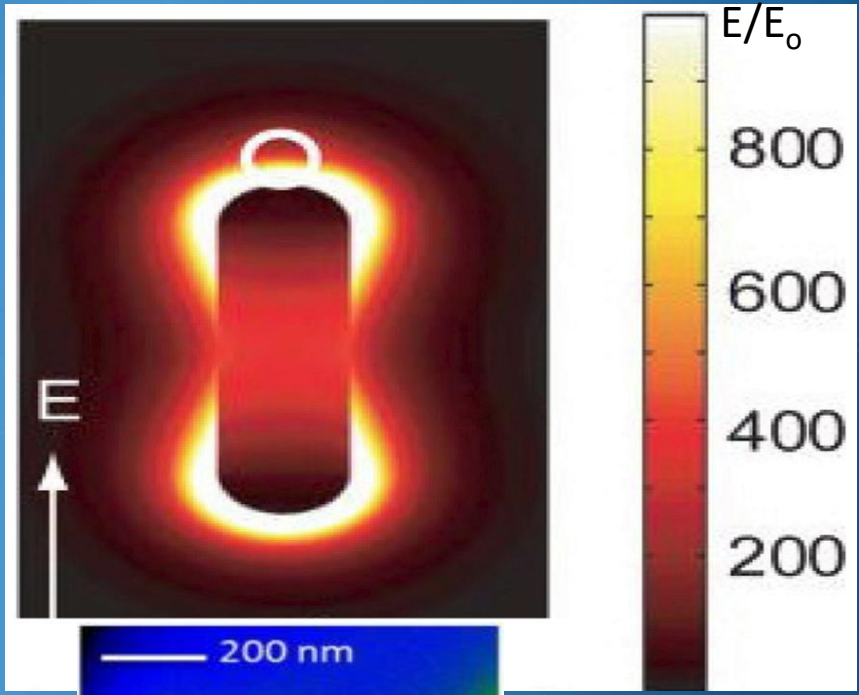



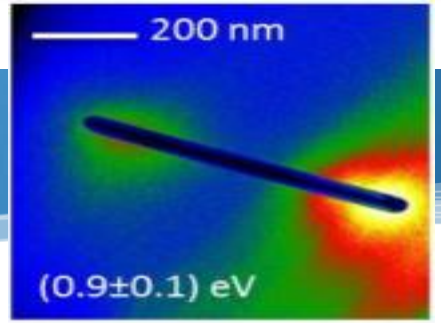




X.-C. Ma, Y. Dai, L. Yu, B.B. Huang, Energy transfer in plasmonic photocatalytic composites, Light Sci. Appl. 5 (2016) e16017.

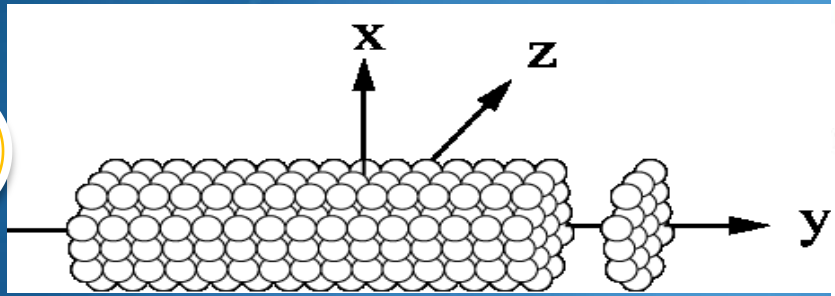
# Plasmon-induced resonance energy transfer

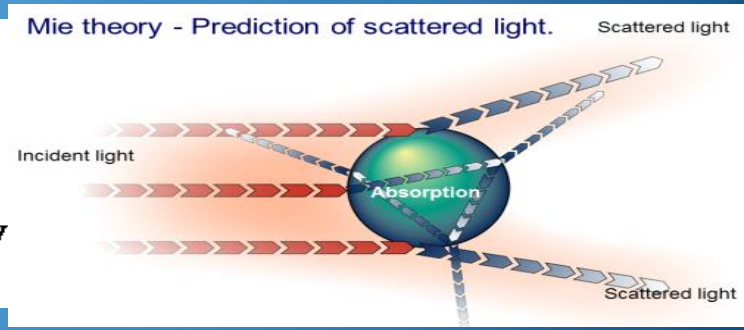
- LSPR can induce near-field enhancement (NFE), the intensity of **NFE is tens to thousands of times that of incident light**. Thus, it can significantly enhance the *e-h* pair generation in the nearby SO.
- Further enhancement is possible using **non-spherical nanoparticles**, where the rod-lightning effect strongly amplifies the electric field at the ends.
- Notably NFE is only few tens of **nm around PM**, and can be varied with geometry and greater in elongated nanostructure (e.g. nanowires).
- For enhancement of catalytic activity **NFE should be stronger inside SO**, which **we** believe can be obtained with heterojunction nanowires having SO in between.
- Experimentally TEM analysis can provide information about NFE; however, computer simulation methods like discrete dipole approximation (DDA) can be used to study the NFE.



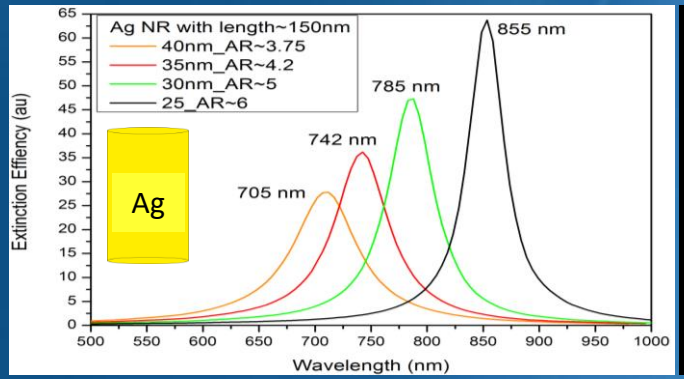
# Discrete dipole approximation (DDA) for light scattering from arbitrary shaped objects

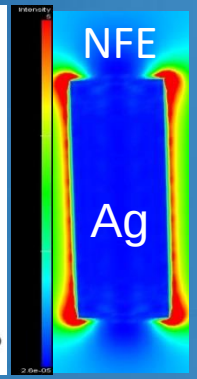


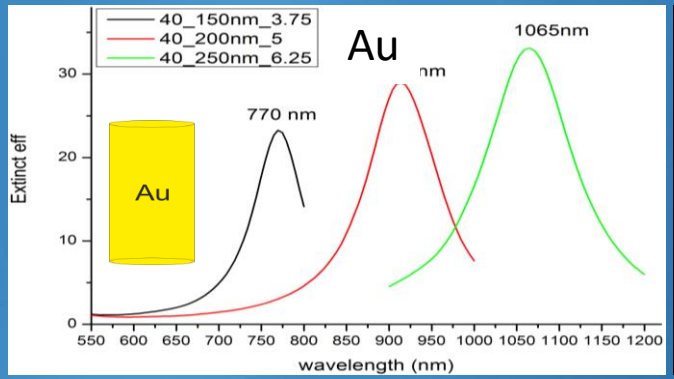



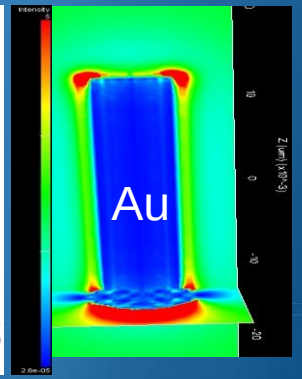

**The discrete dipole approximation** (DDA) is a method for computing scattering of radiation by particles of arbitrary shape and by periodic structures. Given a target of arbitrary geometry, one seeks to calculate its scattering and absorption properties. **Exact solutions to Maxwell's equations are known only for special geometries such as spheres, so approximate methods are in general required.** However, the DDA employs no physical approximations and can **produce accurate enough results, given sufficient computer power**.

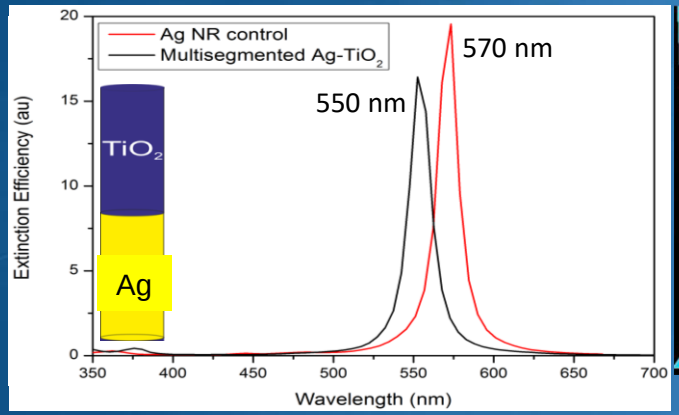
# Optical properties of Ag and Au NRAs in vacuum: DDA simulation

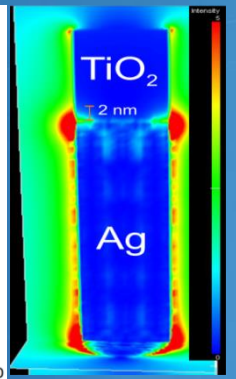


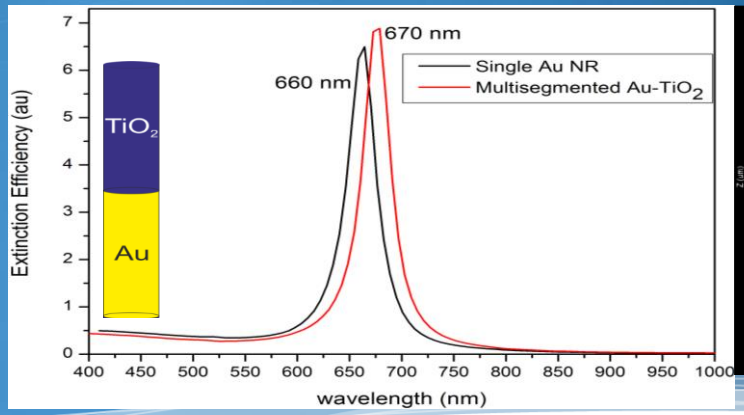



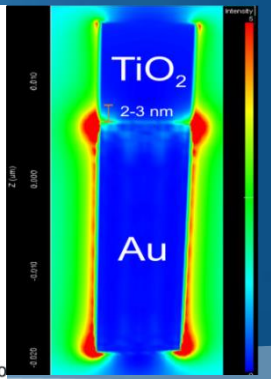



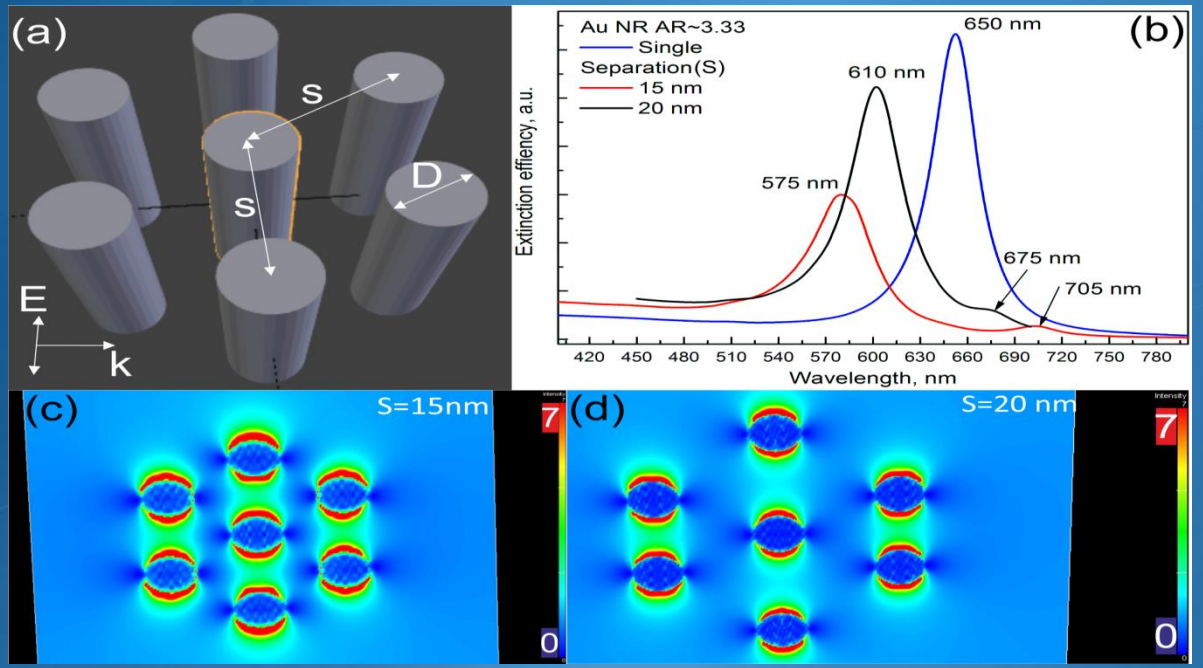

(1994) 1491-1499.




M.S. Arshad et al., J. Mater. Chem. C 5 (2017) 10509-10516.

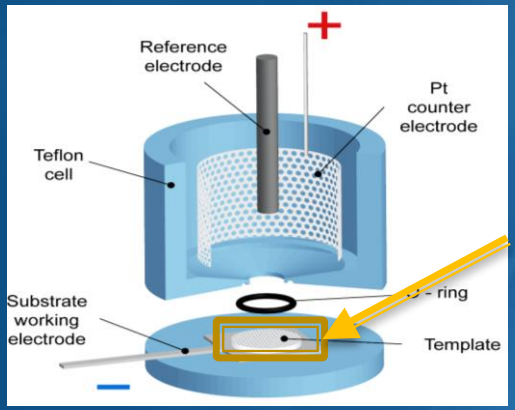
# Optical properties of Ag and Au NRAs in vacuum: DDA simulation

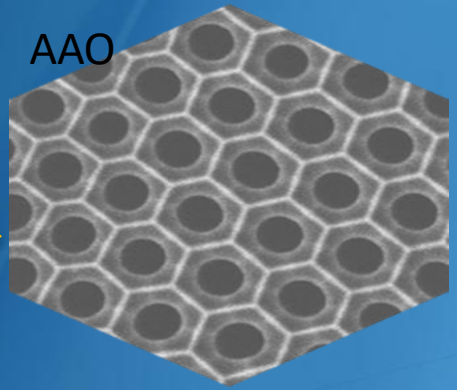



*B.T. Draine, P.J. Flatau, Discrete-dipole approximation for scattering calculations, J. Opt. Soc. Am. A 11 (1994) 1491-1499.*

M.S. Arshad et al., J. Mater. Chem. C 5 (2017) 10509-10516.

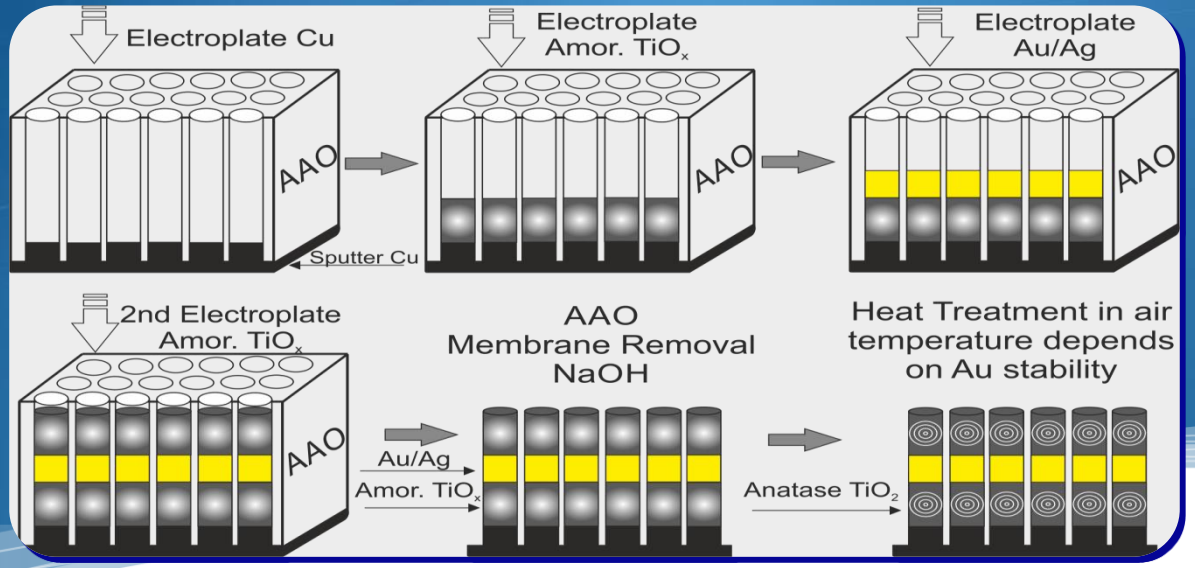
# Fabrication of multisegmented NRAs



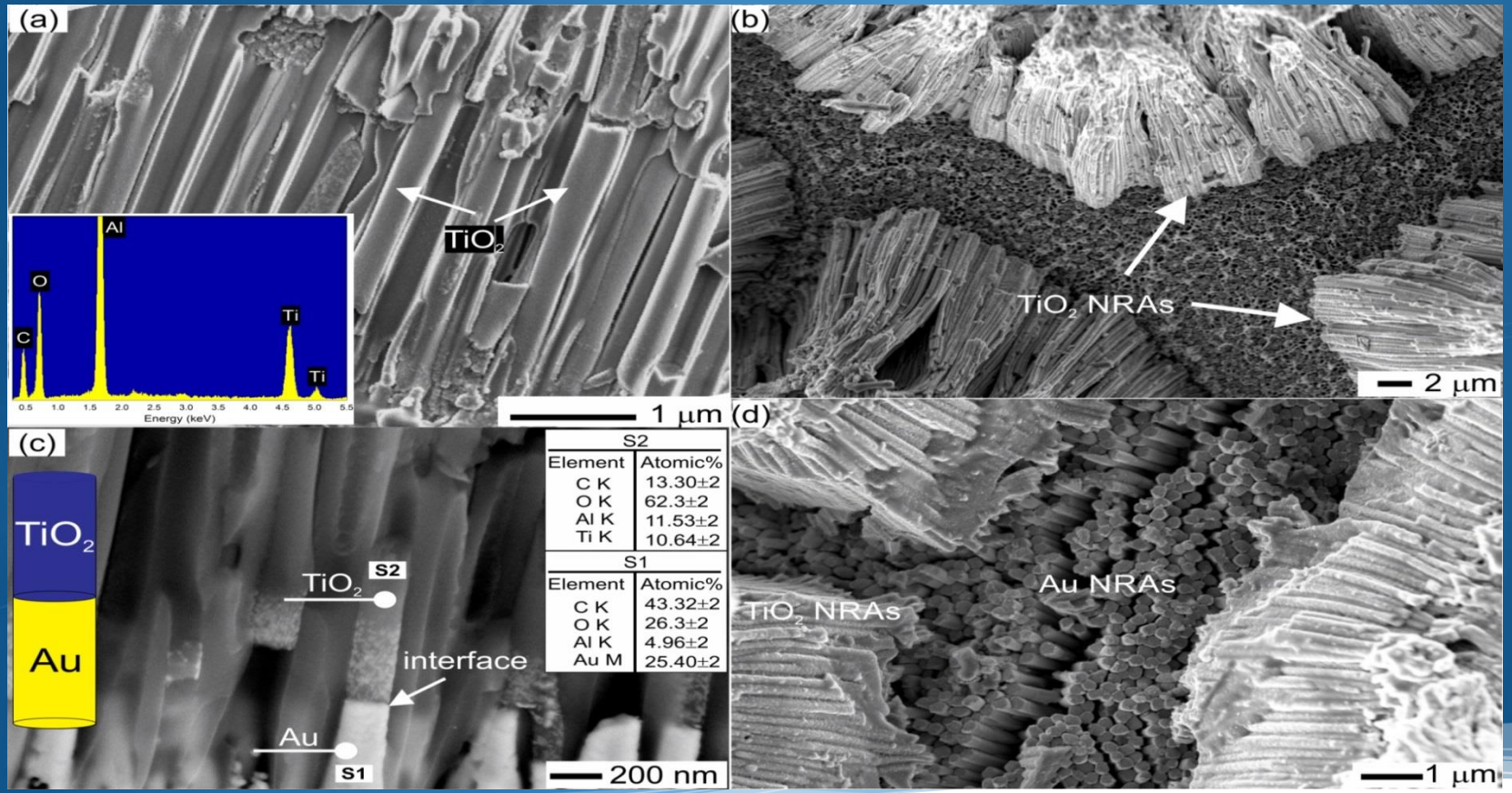




- Multibath technique
- Cu layer sputter (≈100 nm) on one side of mem.

1. Copper platting solution: Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) (100 g/L), ammonium sulfate (20 g/L), and diethylenetriamine (80 mL/L). U=-1.2 V
2. Cu segment at -0.2 V from 0.5 M $CuSO_4$ and 0.67 M $H_3BO_3$ (pH=3.5).

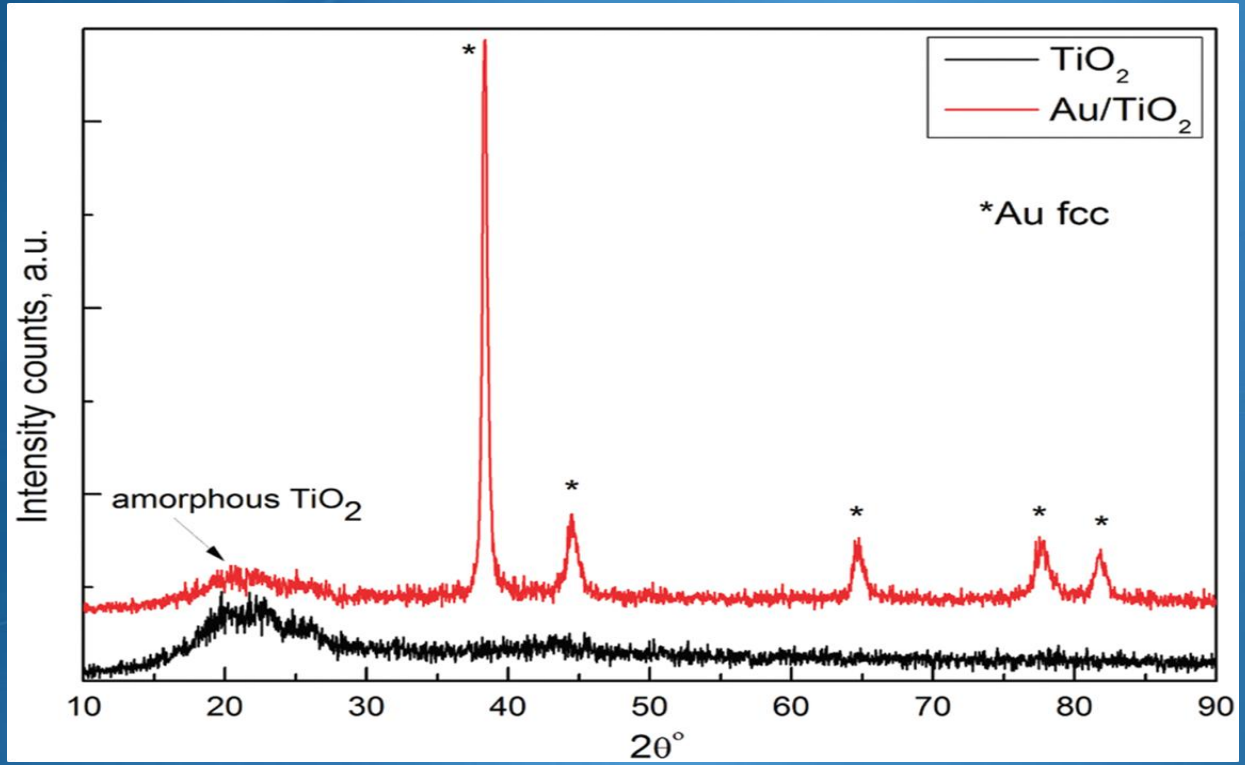


# Free standing $TiO_2$ and Au/$TiO_2$ NRAs




M.S. Arshad et al., J. Mater. Chem. C 5 (2017) 10509-10516.

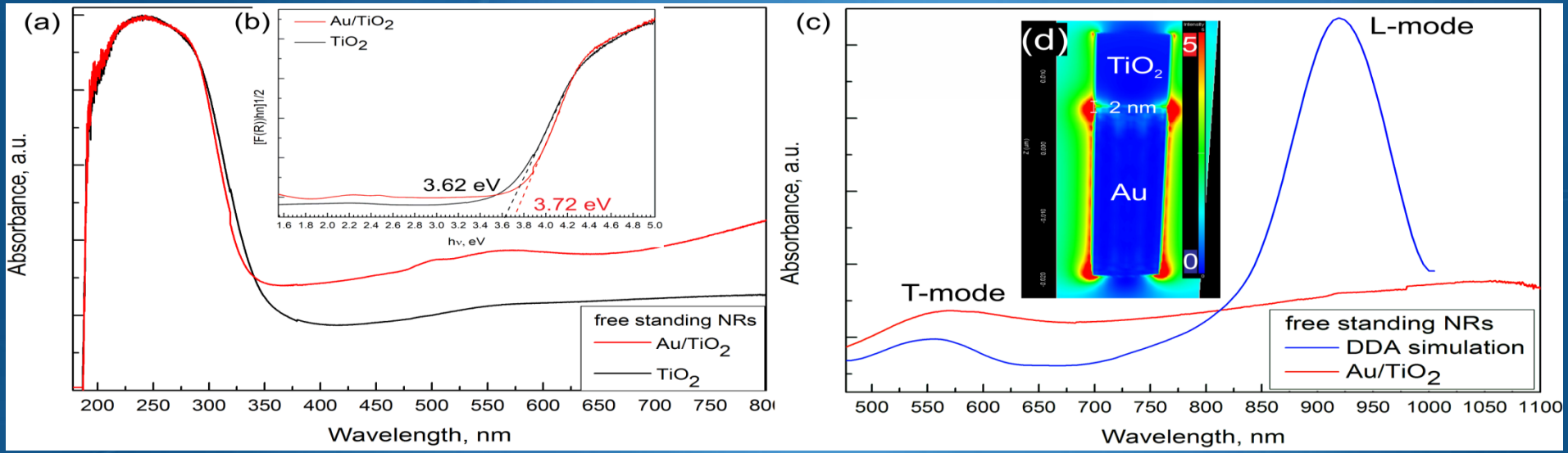
# XRD examination of $TiO_2$ and Au/$TiO_2$ NRAs




XRD patterns of pure $TiO_2$ NRAs and multisegmented Au/$TiO_2$ NRAs.

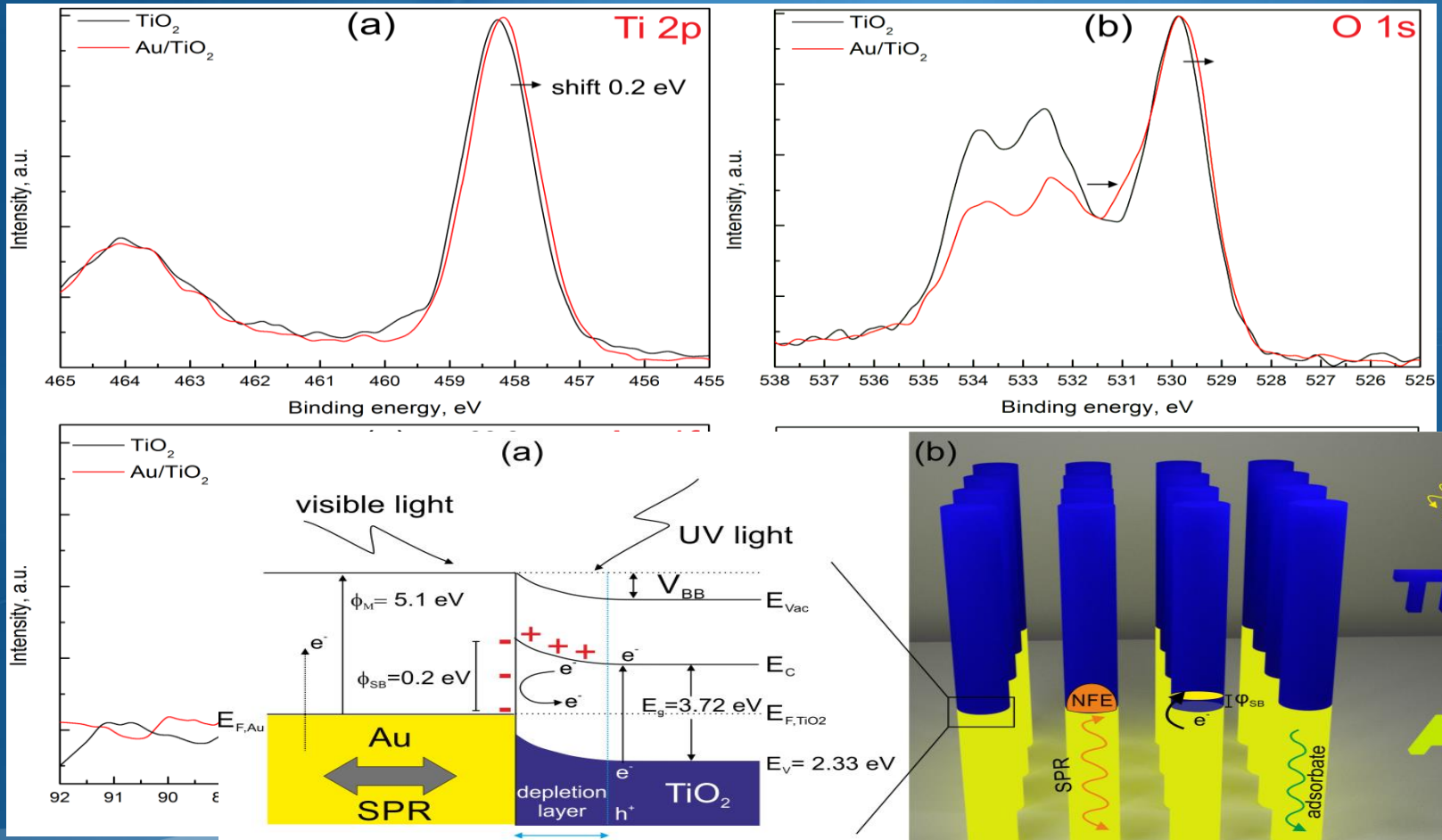
M.S. Arshad et al., J. Mater. Chem. C 5 (2017) 10509-10516.

# UV-VIS examination of $TiO_2$ and $Au/TiO_2$ NRAs

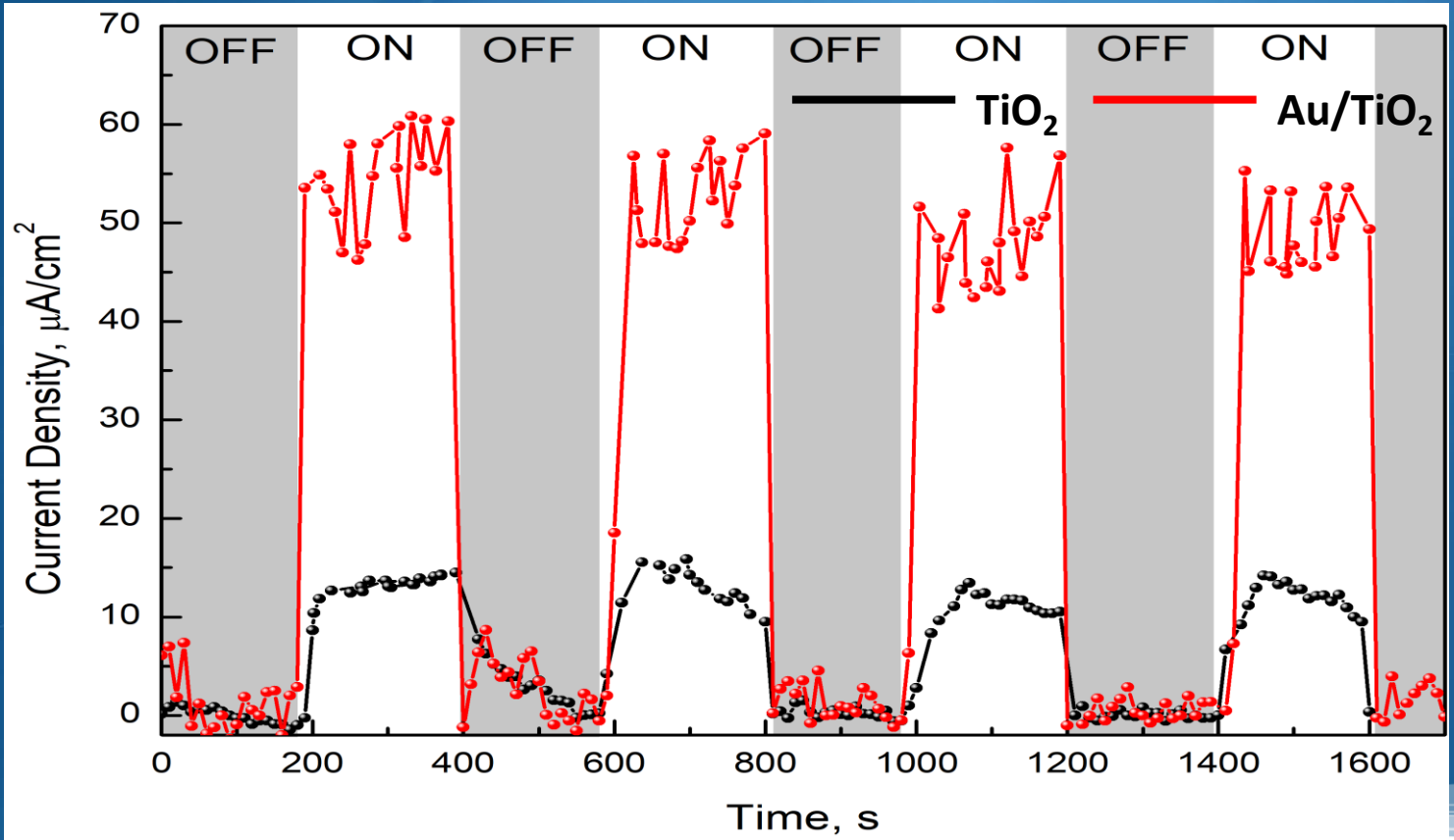



M.S. Arshad et al., J. Mater. Chem. C 5 (2017) 10509-10516.

# XPS examination of $TiO_2$ and $Au/TiO_2$ NRAs



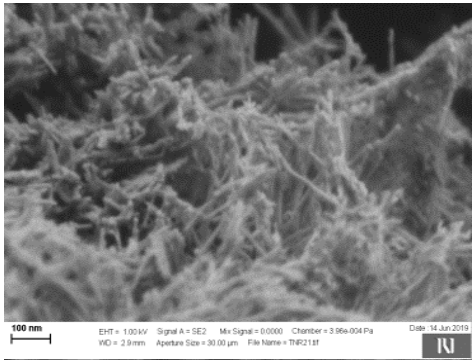
# Photocurrent measurements on $TiO_2$ and $Au/TiO_2$ NRAs



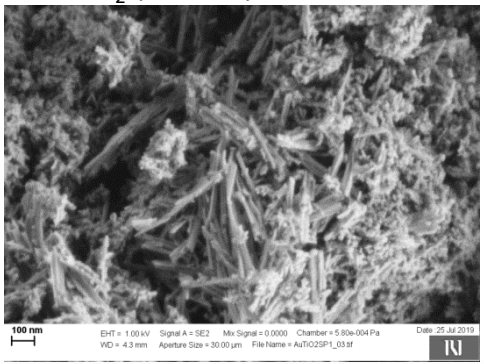

M.S. Arshad et al., J. Mater. Chem. C 5 (2017) 10509-10516.

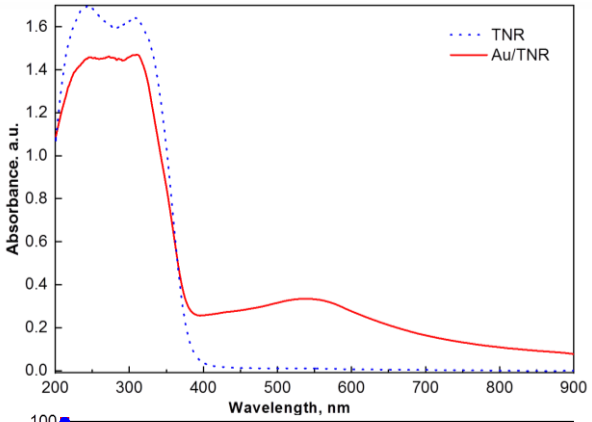
# Recent research activities - $Au/TiO_2$ nanorod catalysts

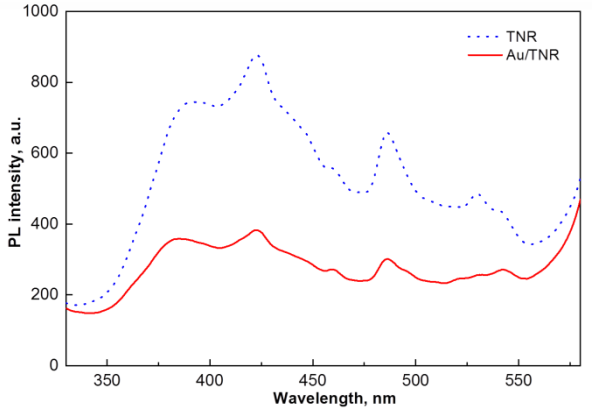
$TiO_2$ nanorods (TNR)

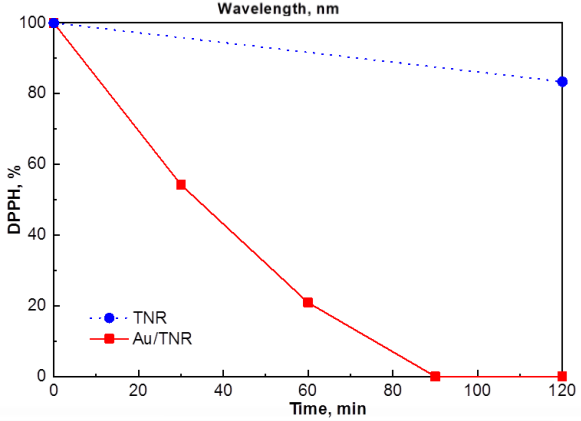


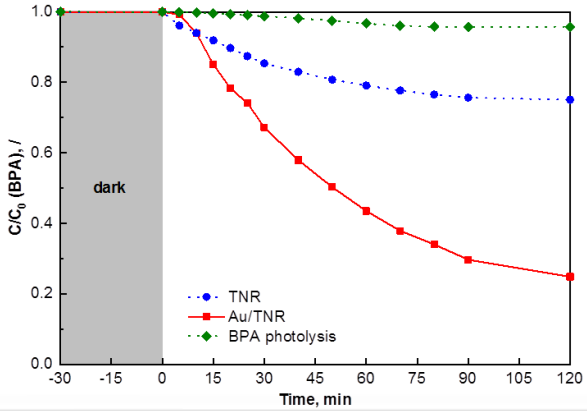

$Au/TiO_2$ (Au/TNR)




G. Žerjav, A. Pintar et al., submitted.

# Take home messages

Pure $TiO_2$ NRAs showed typical optical behaviour; however, **for Au/$TiO_2$ NRAs, transverse and longitudinal plasmon modes were observed using UV-VIS DR analysis**, which correlates closely with theoretical predictions.

XPS results confirmed that Au $4f_{7/2}$ binding energy in Au/$TiO_2$ NRAs is 0.2 eV lower than that in pure bulk Au. **Decreasing of the Au $4f_{7/2}$ binding energy and concurrent increasing of the bond length of $Ti^{4+}$-O species may be taken as direct evidence for charge transfer from oxygen vacancies in $TiO_2$ to Au segments.**

The net charge transfer from $TiO_2$ to Au ceases when charge equilibrium is achieved and forms a **SB at the interface, which is found to be 0.23 eV**.

The generation of light-driven photocurrent from **Au/$TiO_2$ NRAs is 4x higher than that of bare $TiO_2$ NRAs** measured with a photoelectrochemical cell.

# Acknowledgements

SLOVENIAN RESEARCH AGENCY

NATIONAL INSTITUTE OF CHEMISTRY

# Plasmonic phenomena and photoelectron generation in Au/$TiO_2$ nanorod arrays for visible light harvesting

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NOWELTIES – 3rd Project Meeting & ATC2 • 16-18 September 2020, Zagreb, Croatia

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