Insights from Single Particle Spectroscopy of Plasmonic Nanostructures

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CHEMISTRY

Optica Webinar April 18, 2025

Acknowledgements

<u>Collaborators:</u>

Christy Landes (UIUC)
Naomi Halas (Rice)
Peter Nordlander (Rice)
Jen Dionne (Stanford)
Tim Lian (Emory)
Greg Hartland (Notre Dame)
Peter Rossky (Rice)
Martin Zanni (Wisconsin)
Sean Roberts (UT Austin
Ben Levine (Stony Brook)
Wei-Shun Chang (UMass Dartmouth)
Many more…

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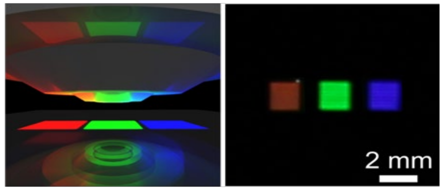
Ben Levine (Stony Brook)
Wei-Shun Chang (UMass Dartmouth)
Many more…

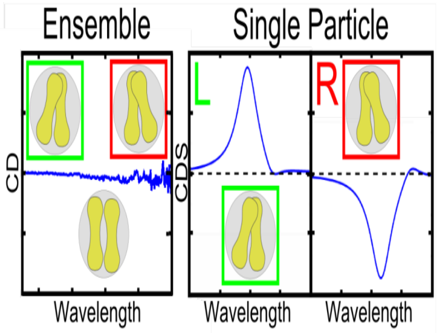
Link lab research: Single-particle spectroscopy of plasmonic nanostructures to remove heterogeneities in to gain detailed insight into structure-function relationships

Plasmon Coupling in Nanoparticle Arrays



Aluminum Plasmonic Pixels

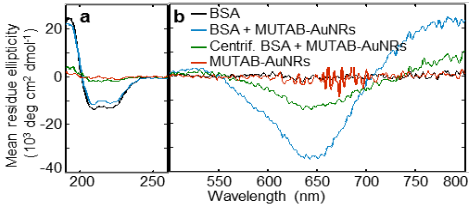
ACS Nano 10, 1108 (2016)

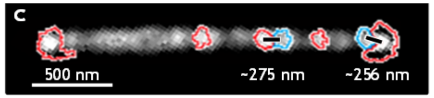


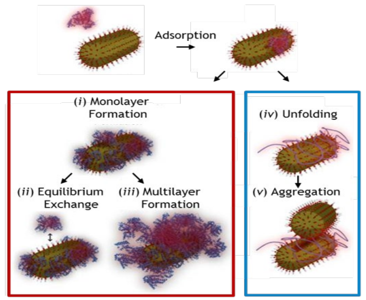
Chiral Assemblies

ACS Nano 10, 6180 (2016)
PNAS, 117, 16143 (2020)

Quantifying Nanoparticle-Protein Interactions



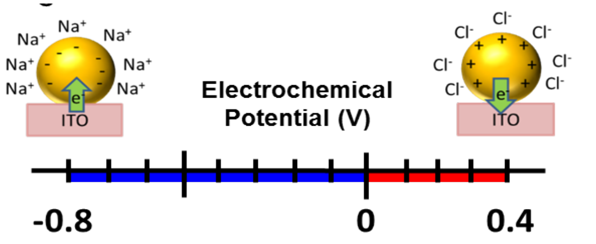


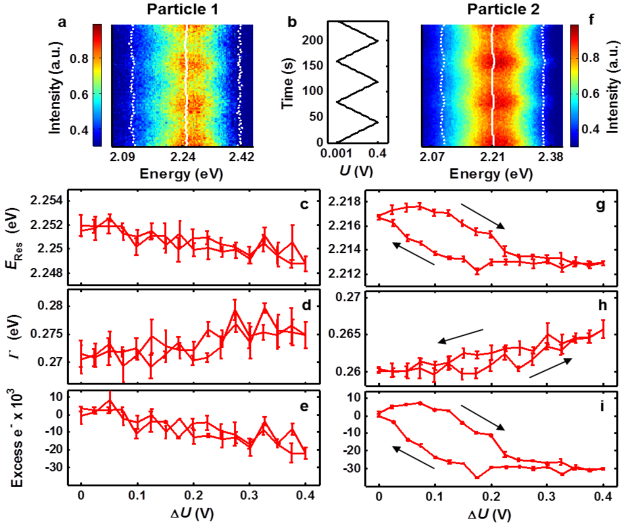


Composition and Structure of the Protein Corona

ACS Nano 10, 2103 (2016)
Science 365, 1475 (2019)

Single-Particle Electrochemistry

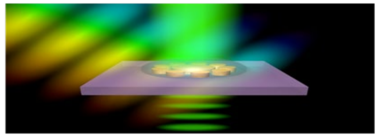


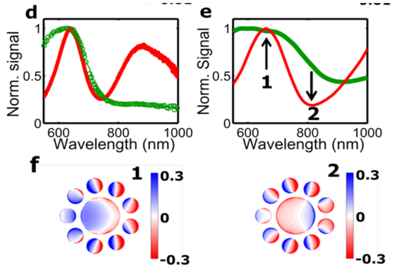


Optical read-out of particle charging

J. Phys. Chem. B 118, 14047 (2014)
J. Phys. Chem. Lett., 12, 2516 (2021)

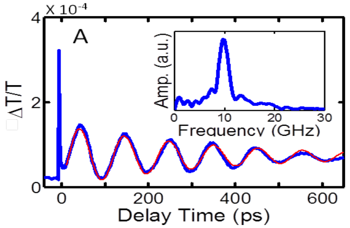
Energy Relaxation in Nanostructures





Photothermal Spectroscopy

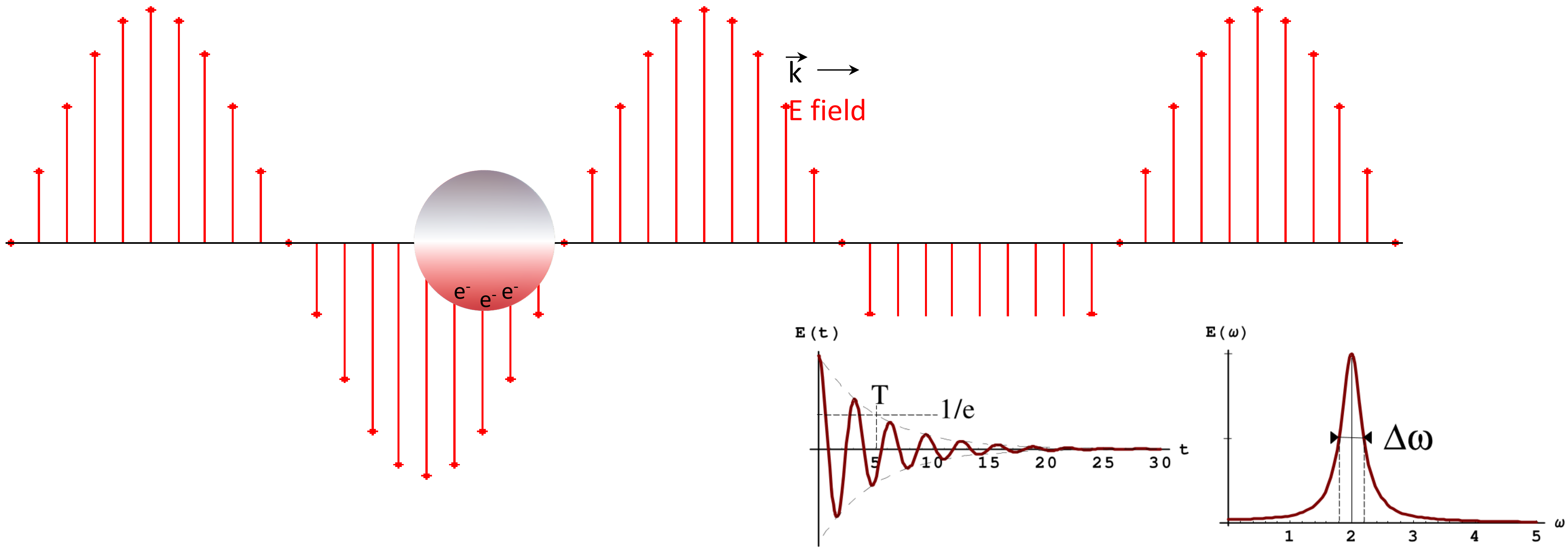
Nano Lett. 16, 6497 (2016)
Nano Lett., 21 , 5386 (2021)



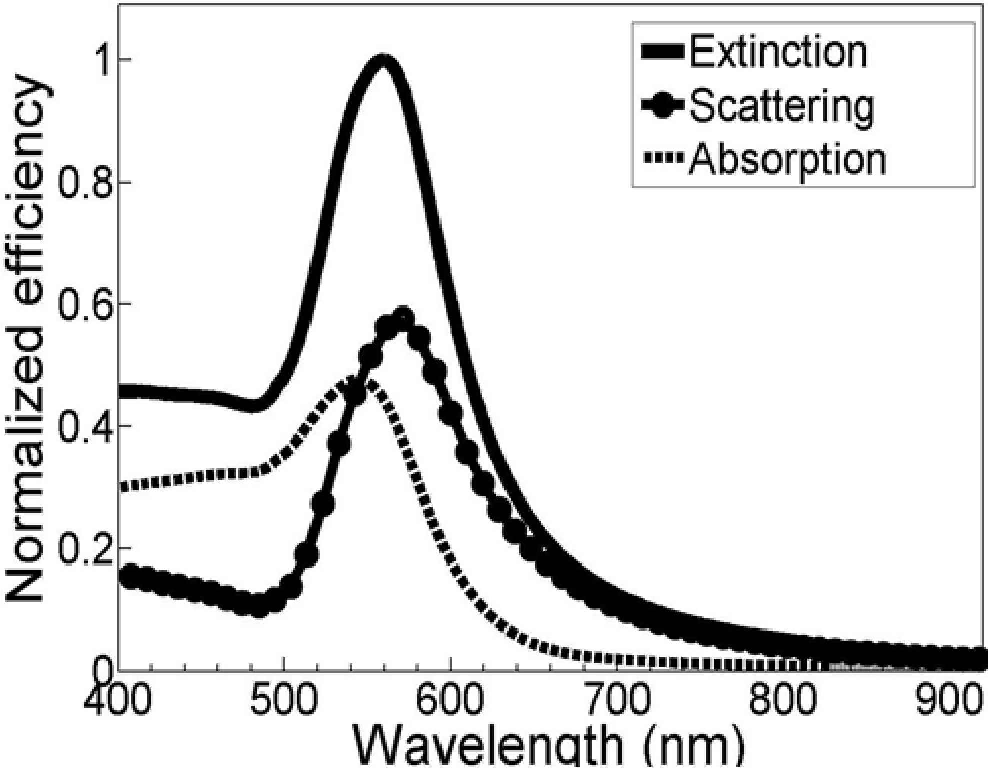
Ultrafast Relaxation Dynamics
Nature Communications 2015

Localized Surface Plasmons

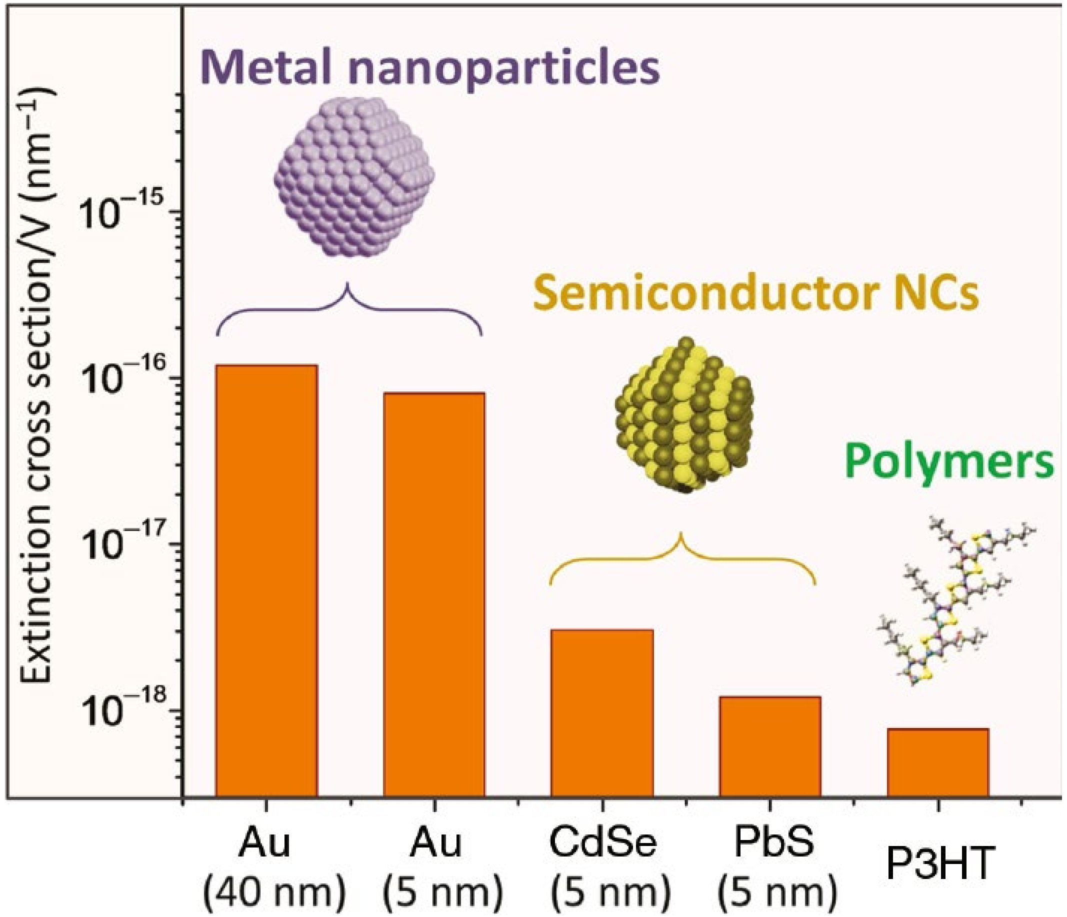
Coherent oscillation of conduction electrons coupled to incident electromagnetic field, described by an underdamped driven oscillator



Converting photons to hot electrons with plasmons

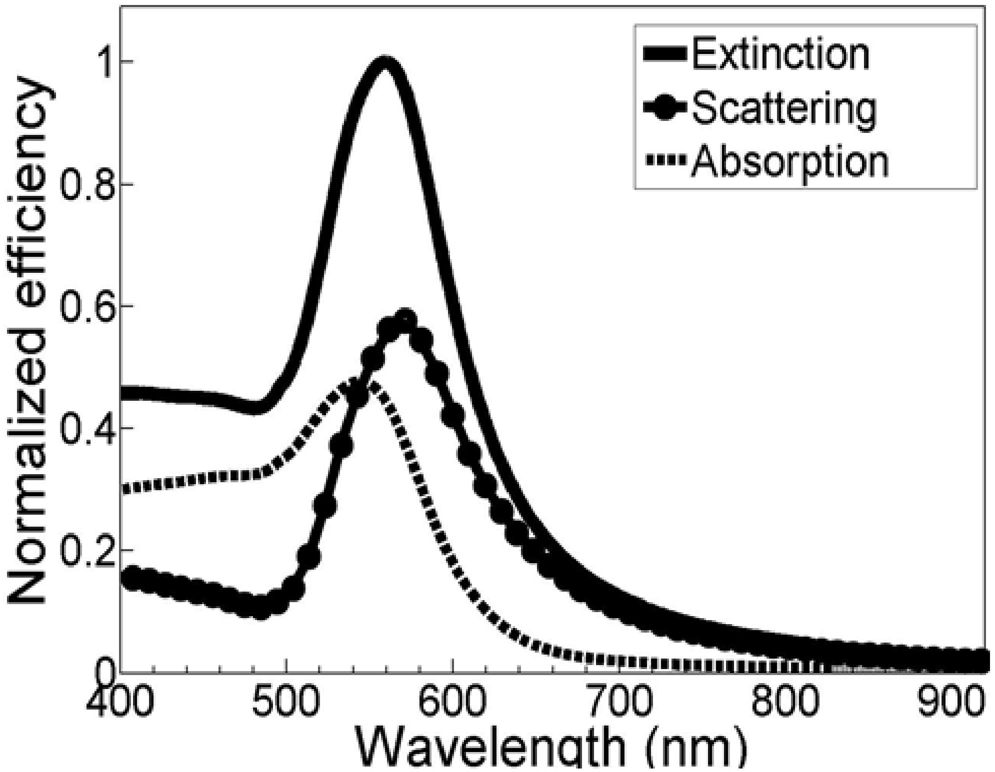


G. Mie, Ann. Phys. 25, 377 (1908)

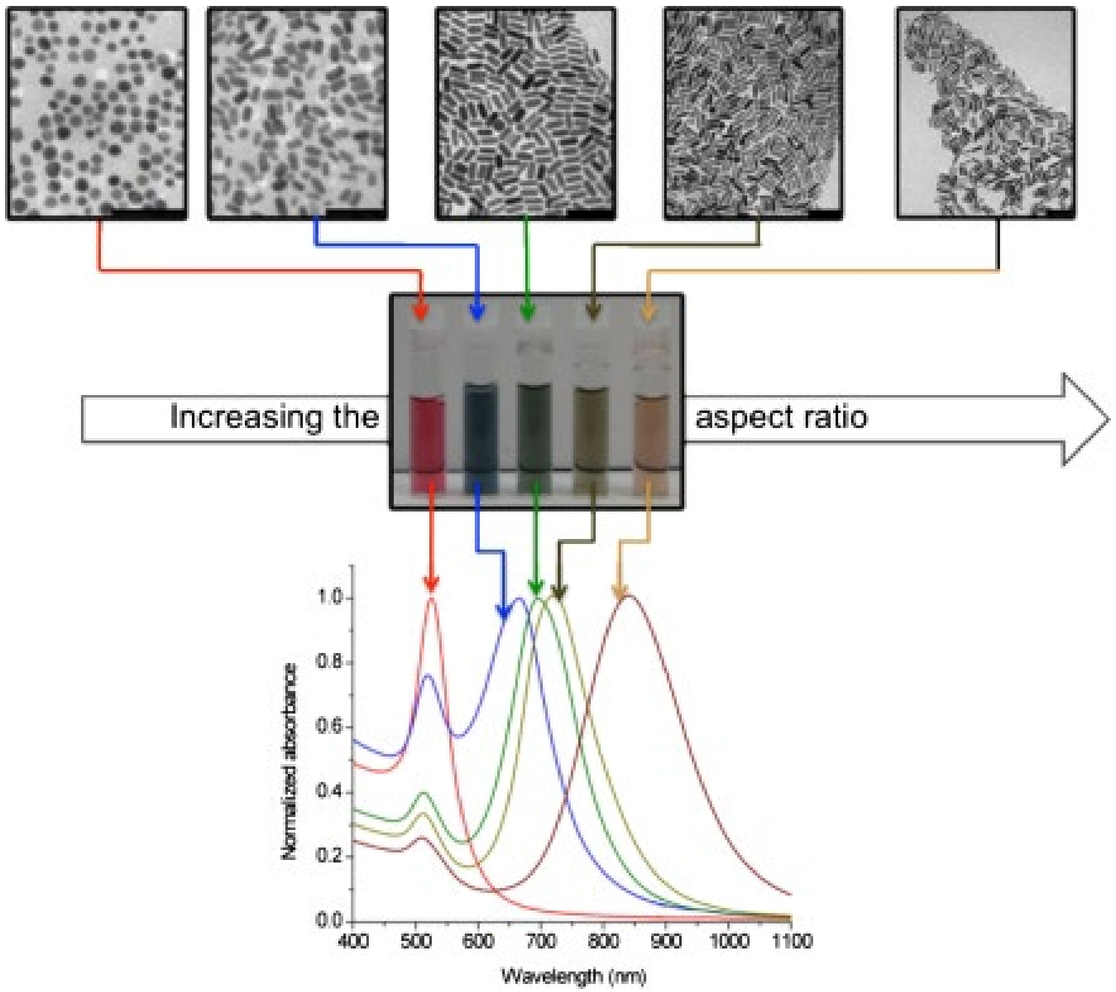


Kholmicheva, et al. *Nanophotonics* **2018**, *8*, 613

Converting photons to hot electrons with plasmons

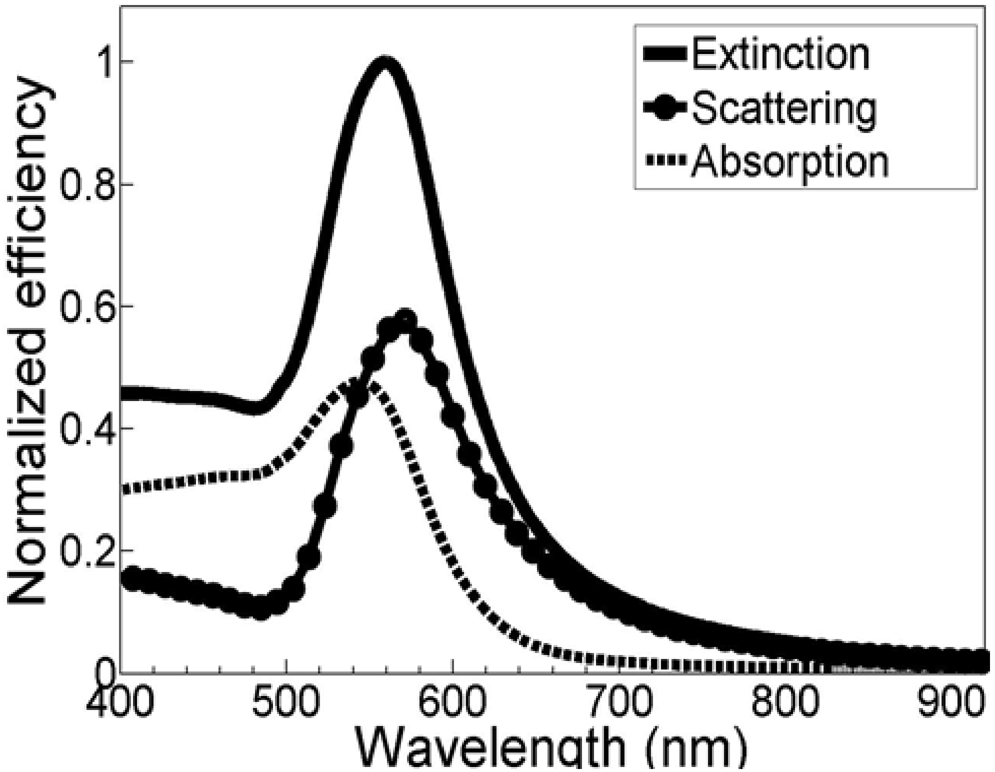


G. Mie, Ann. Phys. 25, 377 (1908)

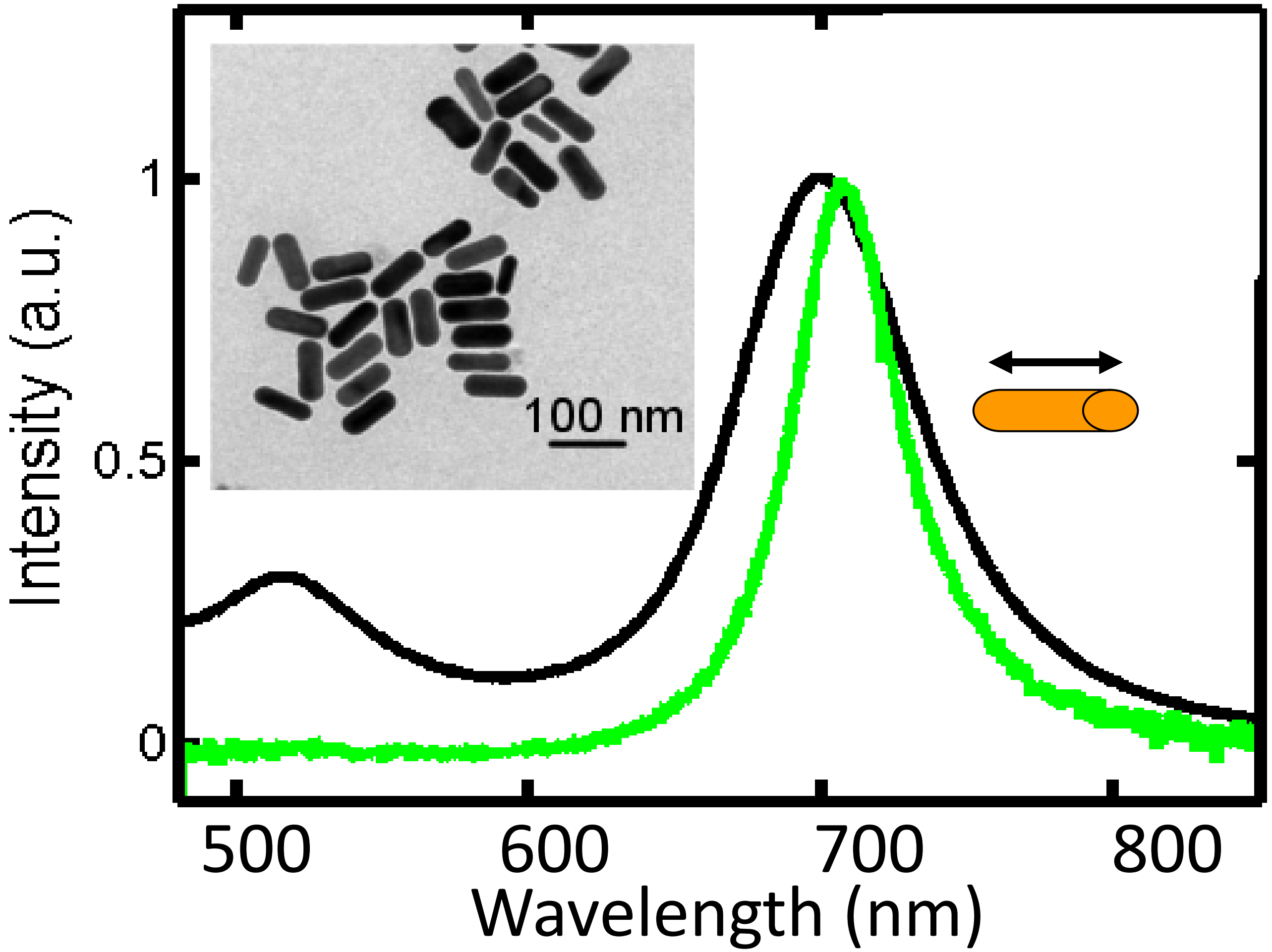


Alkilany, Murphy, *J. Nanopart. Res.* **2010**, *12*, 2313

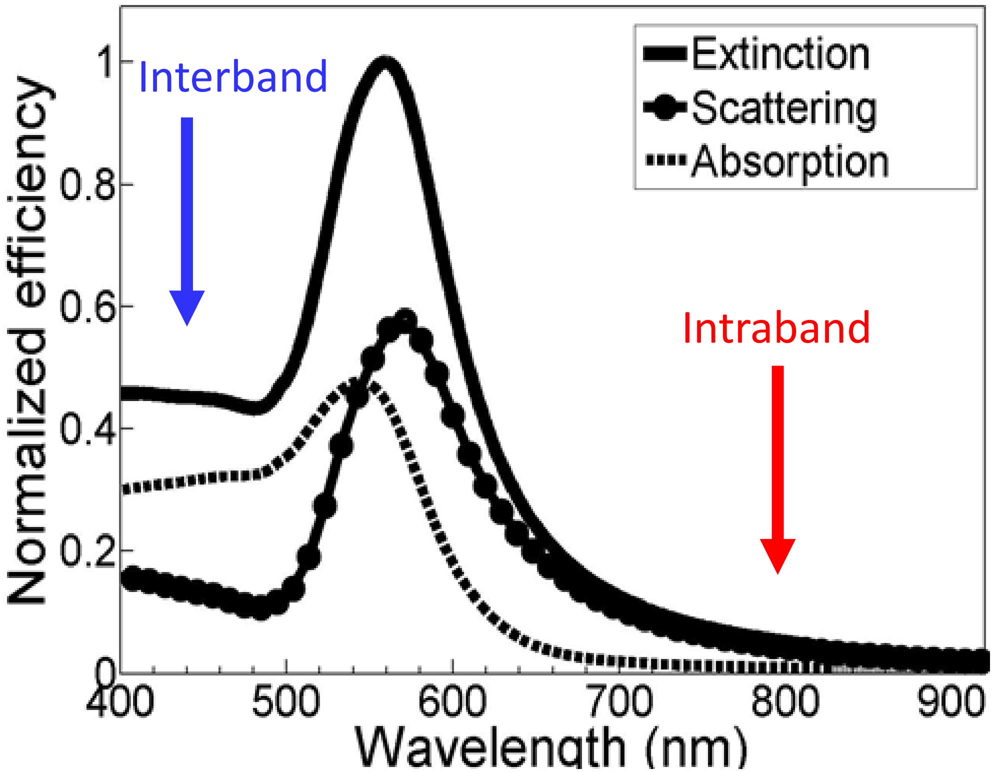
Converting photons to hot electrons with plasmons



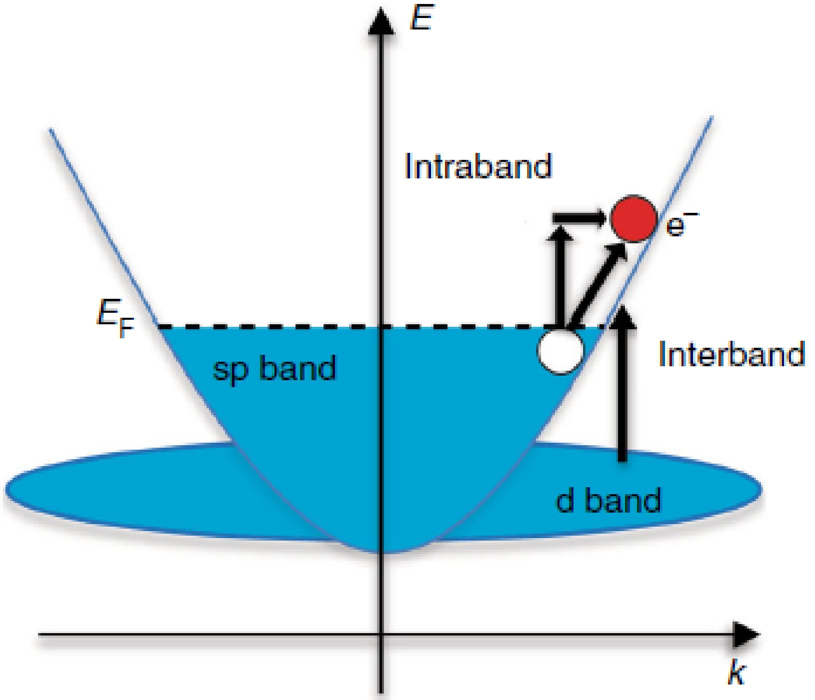
G. Mie, Ann. Phys. 25, 377 (1908)



Photon absorption beyond plasmons



G. Mie, Ann. Phys. 25, 377 (1908)



Govorov, Wiederrecht, Gray, Harutyunyan, *Nat. Commun.* **2018**, *9*, 1853

Outline

1) Charge transfer at metal – semiconductor interfaces

2) Photoemission into water

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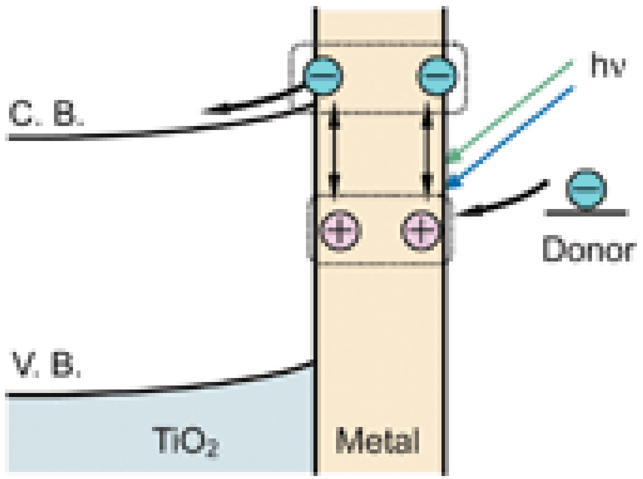
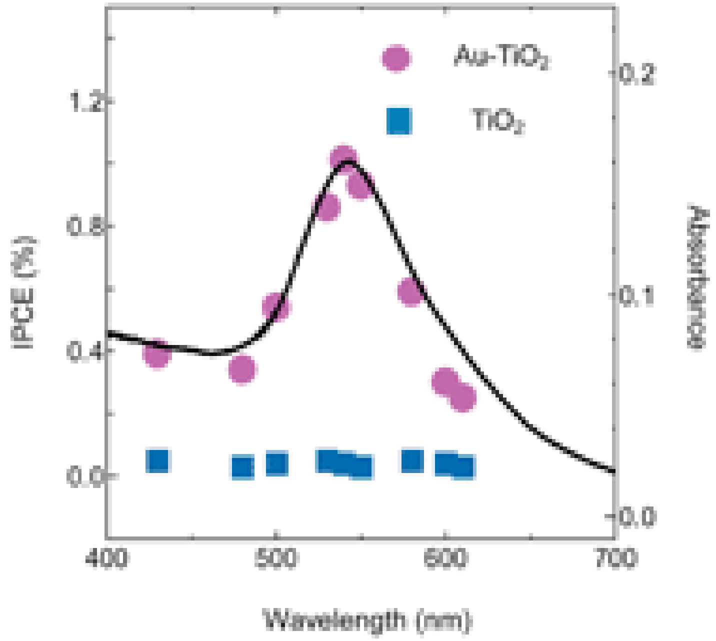
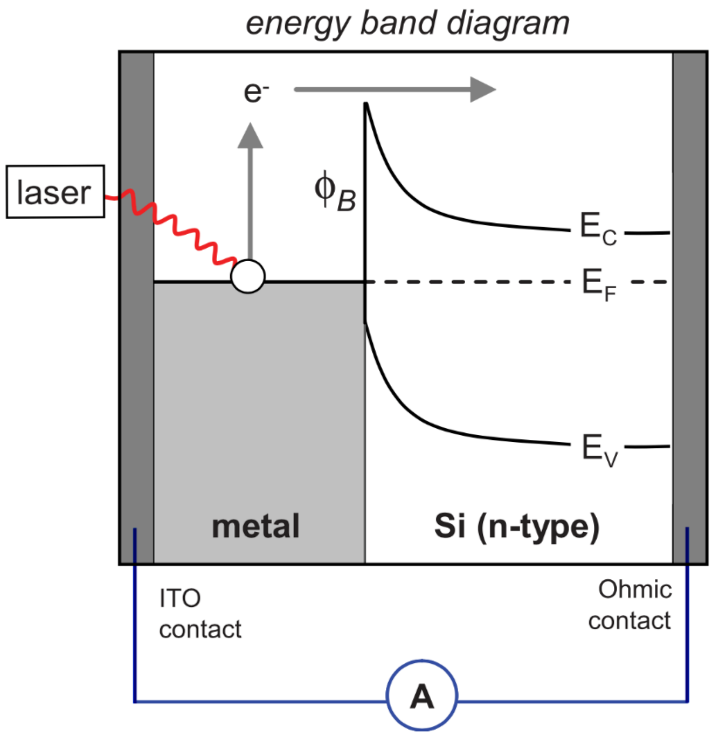
2) Photoemission into water

Charge transfer at metal-semiconductor interfaces: Overcoming semiconductor bandgaps with lower photon energy plasmons







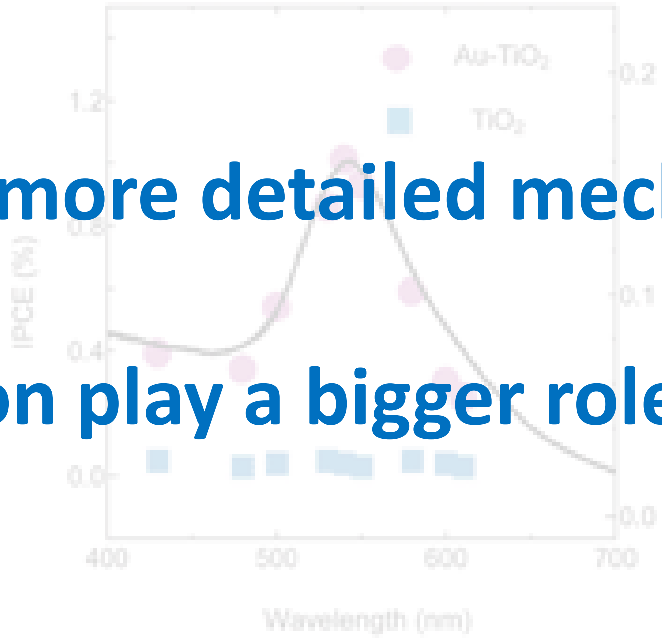
Tatsuma, *Chem. Commun.* **2004**, 1810

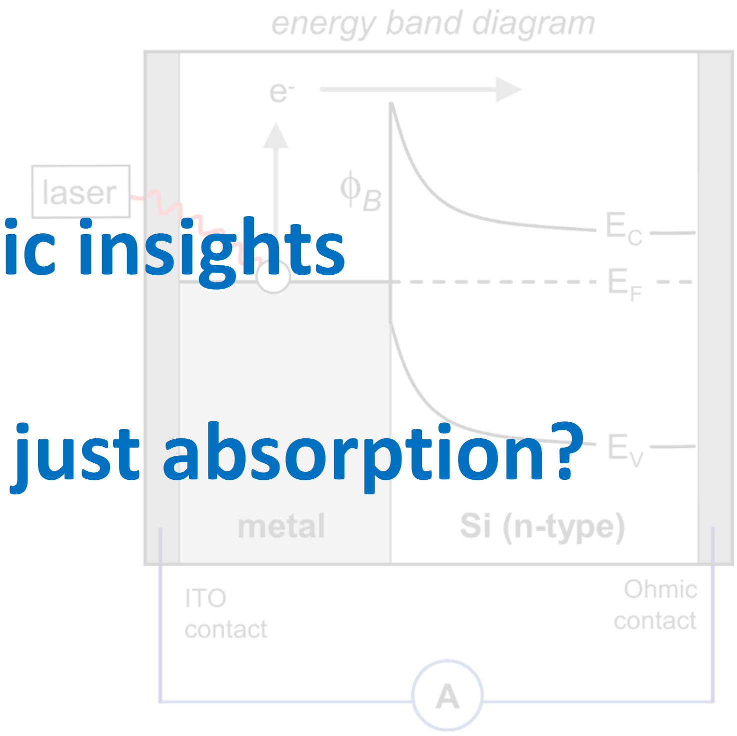
Nordlander, Halas, *Science* **2011**, *332*, 702

Advantage: Large tunable cross sections determining hot carrier energies; band offsets and not bandgaps are important

Disadvantages: Often low yields

Charge transfer at metal-semiconductor interfaces: Overcoming semiconductor bandgaps with lower photon energy plasmons





1) We need more detailed mechanistic insights

2) Does the plasmon play a bigger role than just absorption?

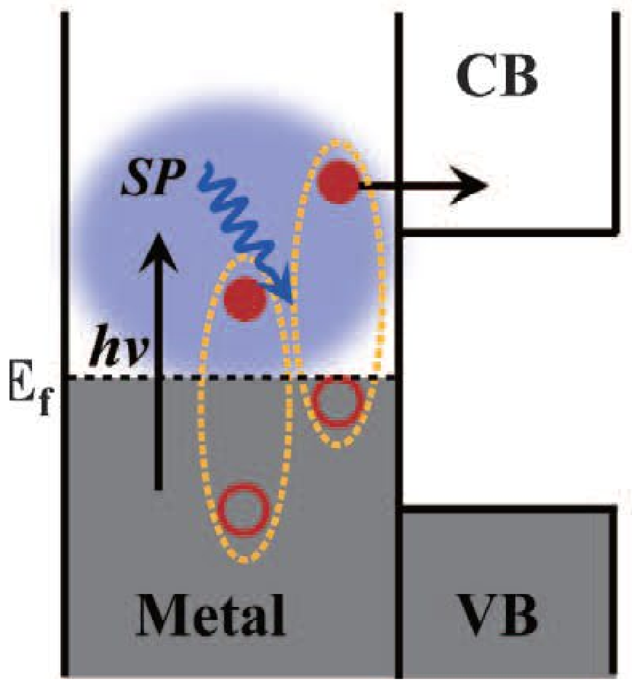
Tatsuma, *Chem. Commun.* **2004**, 1810

Nordlander, Halas, *Science* **2011**, *332*, 702

Advantage: Large tunable cross sections determining hot carrier energies; band offsets and not bandgaps are important

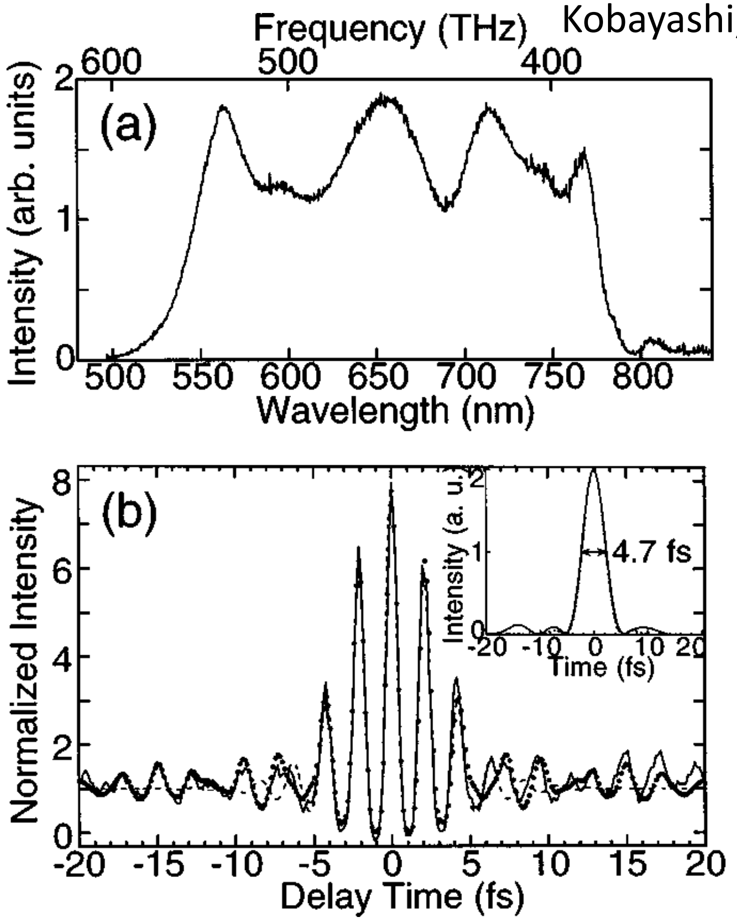
Disadvantages: Often low yields

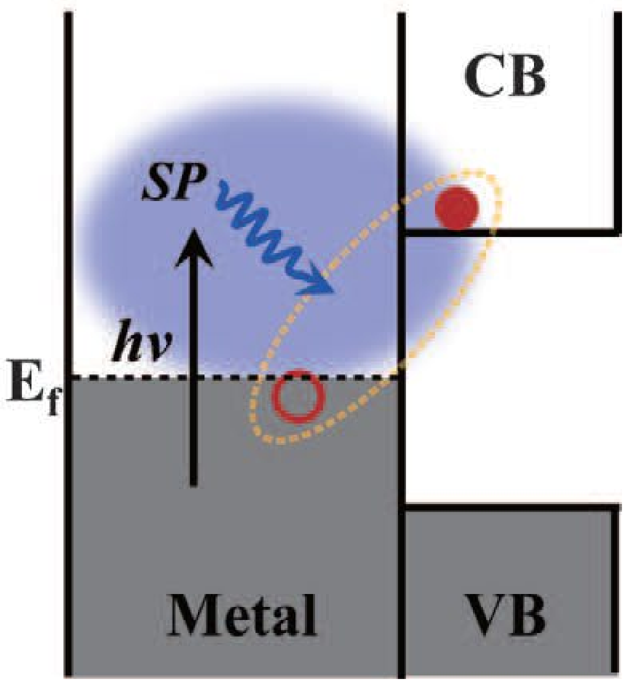
Plasmon induced charge transfer at metal-semiconductor interfaces – direct vs. indirect pathways



Lian, *Science* **2015**, *349*, 632

Kobayashi, Appl. Phys. Lett. *1999*, *74*, 2268





>24% efficiency

BUT, how can we distinguish these mechanisms when both are expected to be less than 100 fs?

Plasmon dephasing

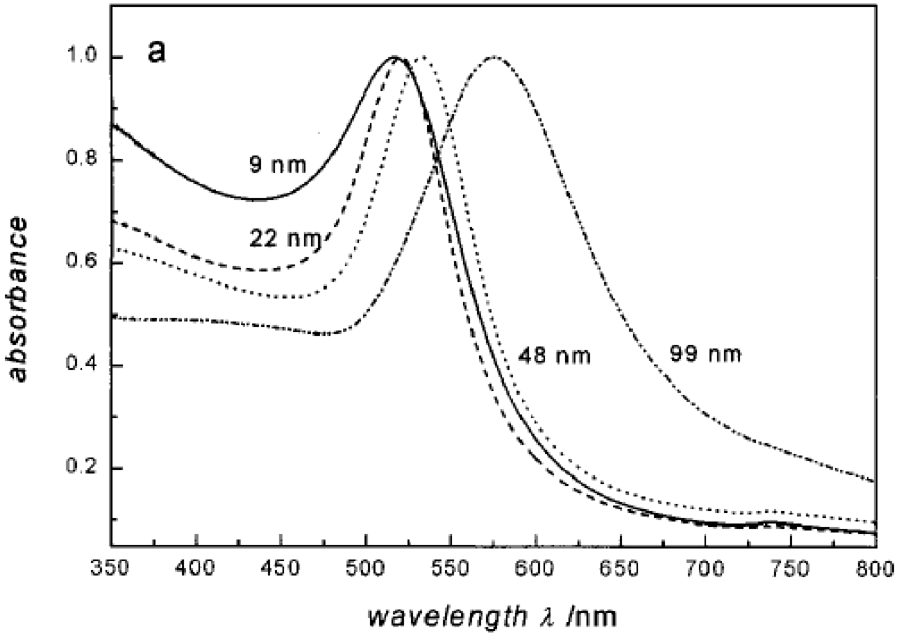
$$\Gamma = \gamma_b + \Gamma_{rad} + \Gamma_{surf}$$

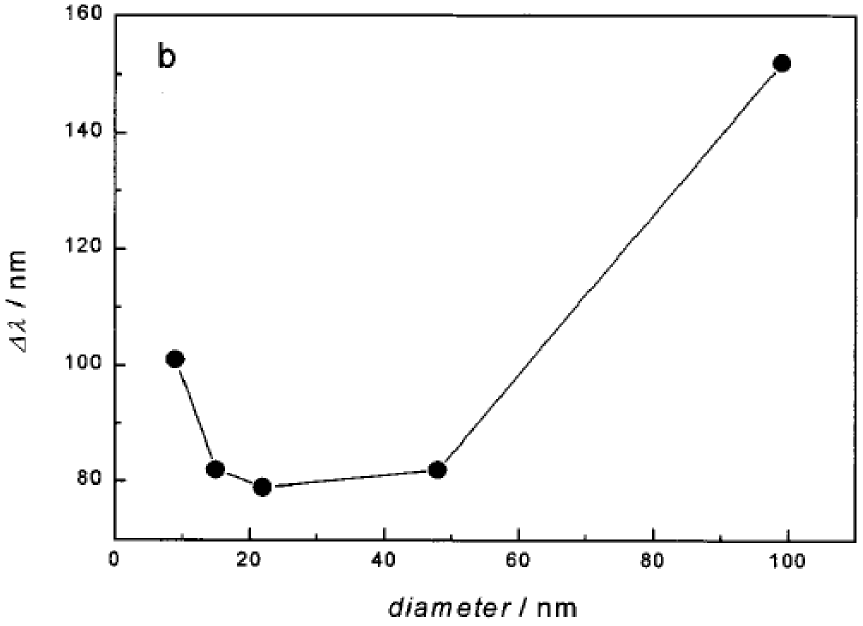
$$\Gamma_{total} = \gamma_b + 2\hbar\pi V + \frac{A_{surf} \cdot v_F}{l_{eff}}$$

4212 *J. Phys. Chem. B* **1999,** *103,* 4212–4217

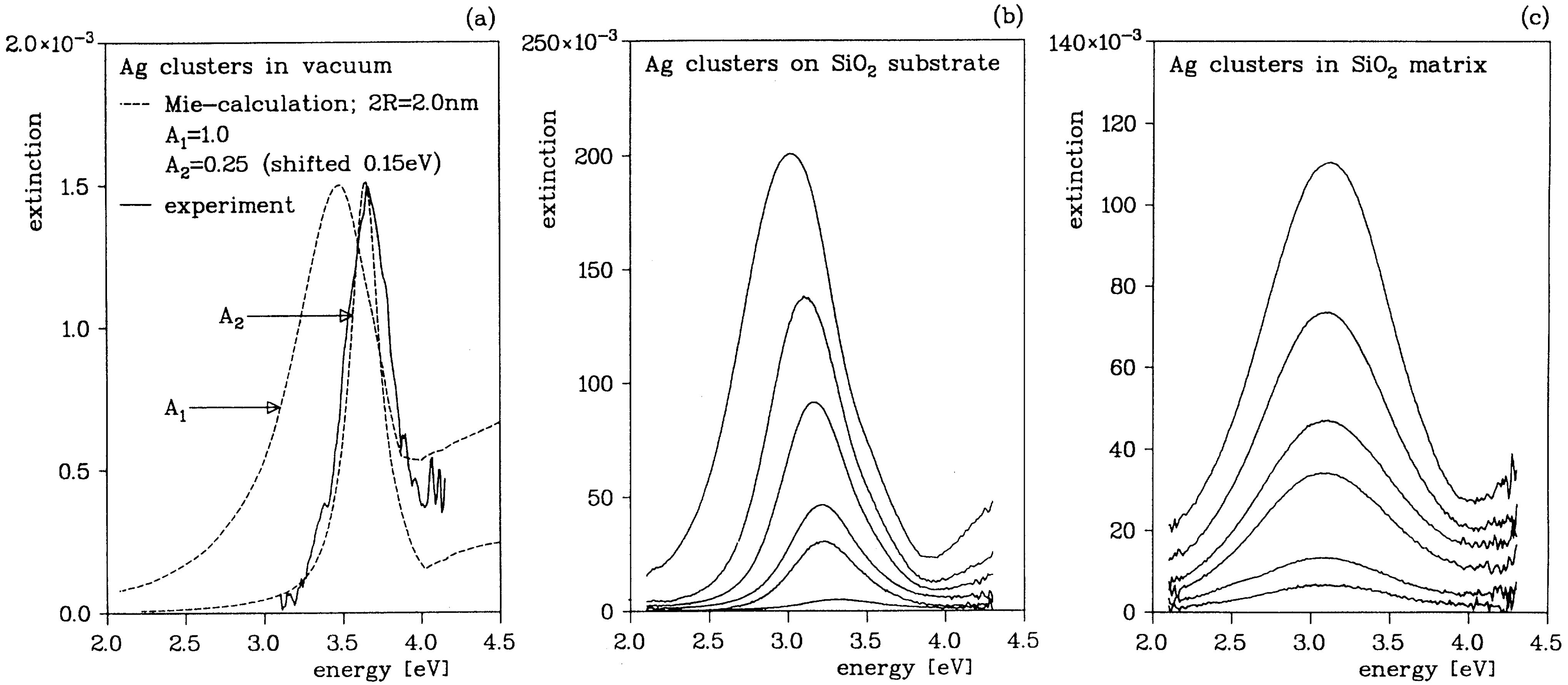
Size and Temperature Dependence of the Plasmon Absorption of Colloidal Gold Nanoparticles

Stephan Link and Mostafa A. El-Sayed*





Additional plasmon decay – chemical interface damping (CID)

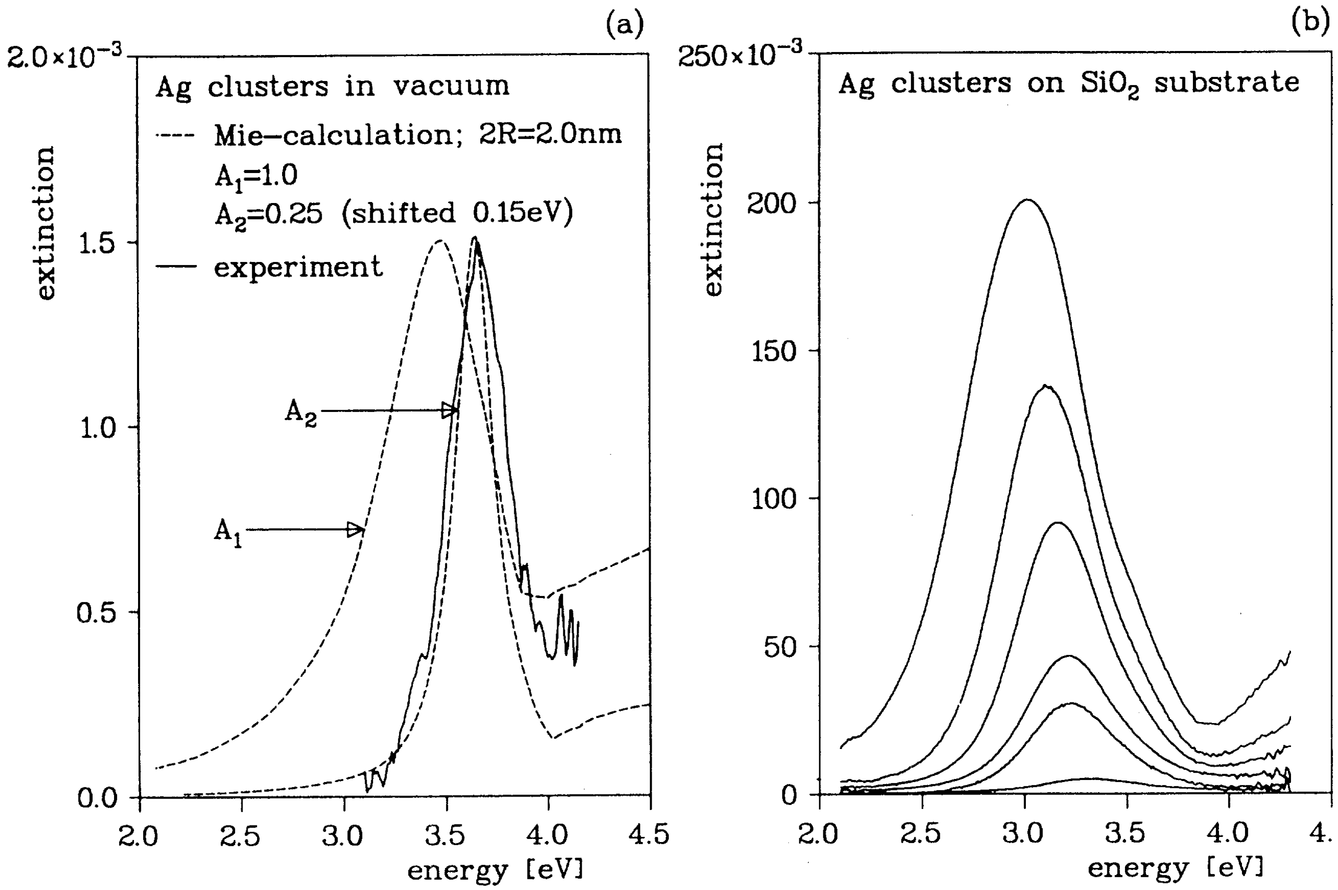


Kreibig, Vollmer, *Phys. Rev. B* **1993**, *48*, 18178

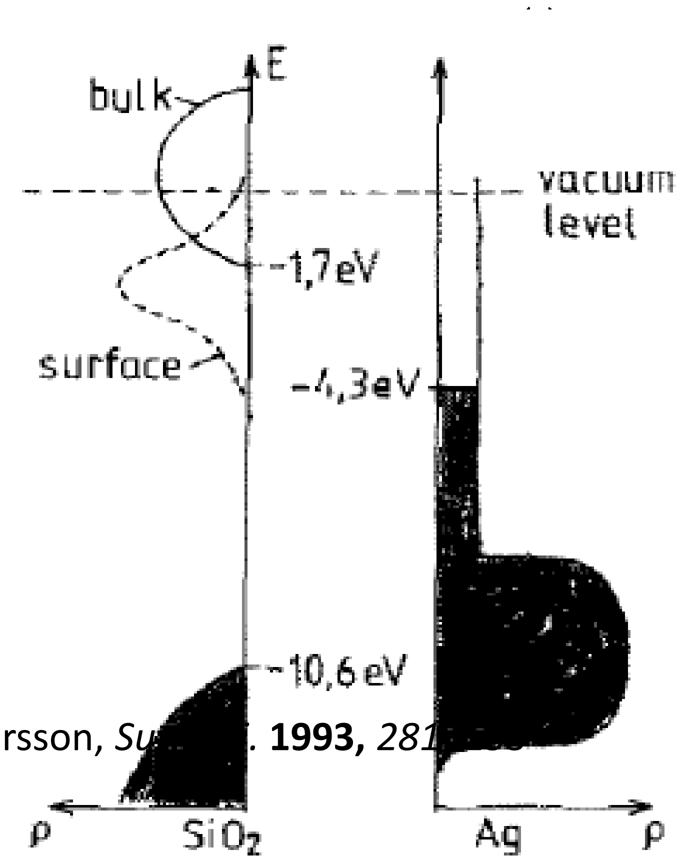
Additional plasmon decay – chemical interface damping (CID)

$$\Gamma = \gamma_b + \Gamma_{rad} + \Gamma_{surf} + \Gamma_{CID}$$

$$\Gamma_{total} = \gamma_b + 2\hbar\pi V + \frac{A_{surf} \cdot v_F}{l_{eff}} + \Gamma_{CID}$$

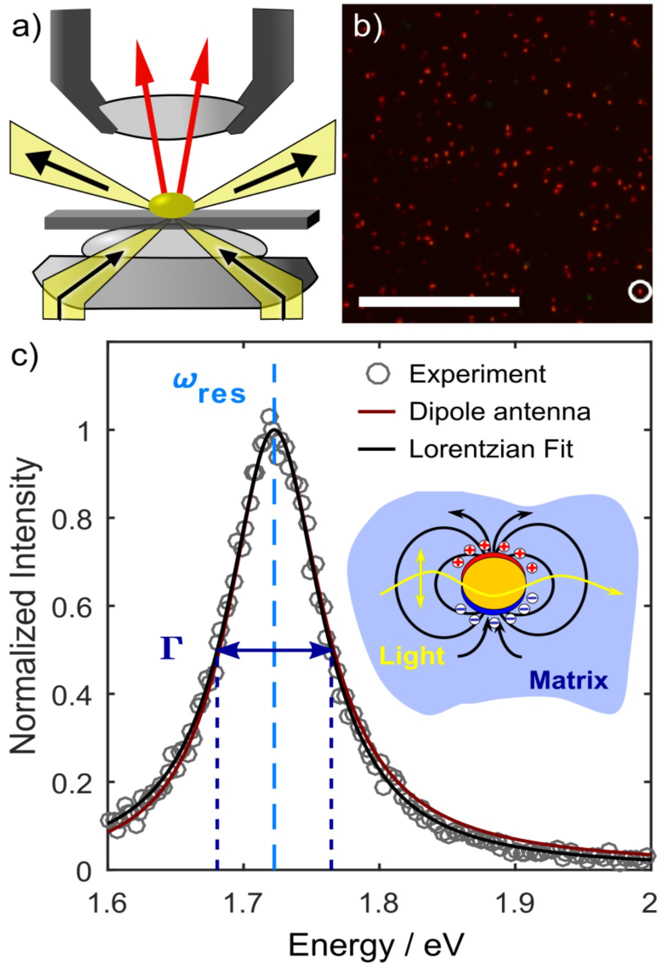


Kreibig, Vollmer, *Phys. Rev. B* **1993**, *48*, 18178



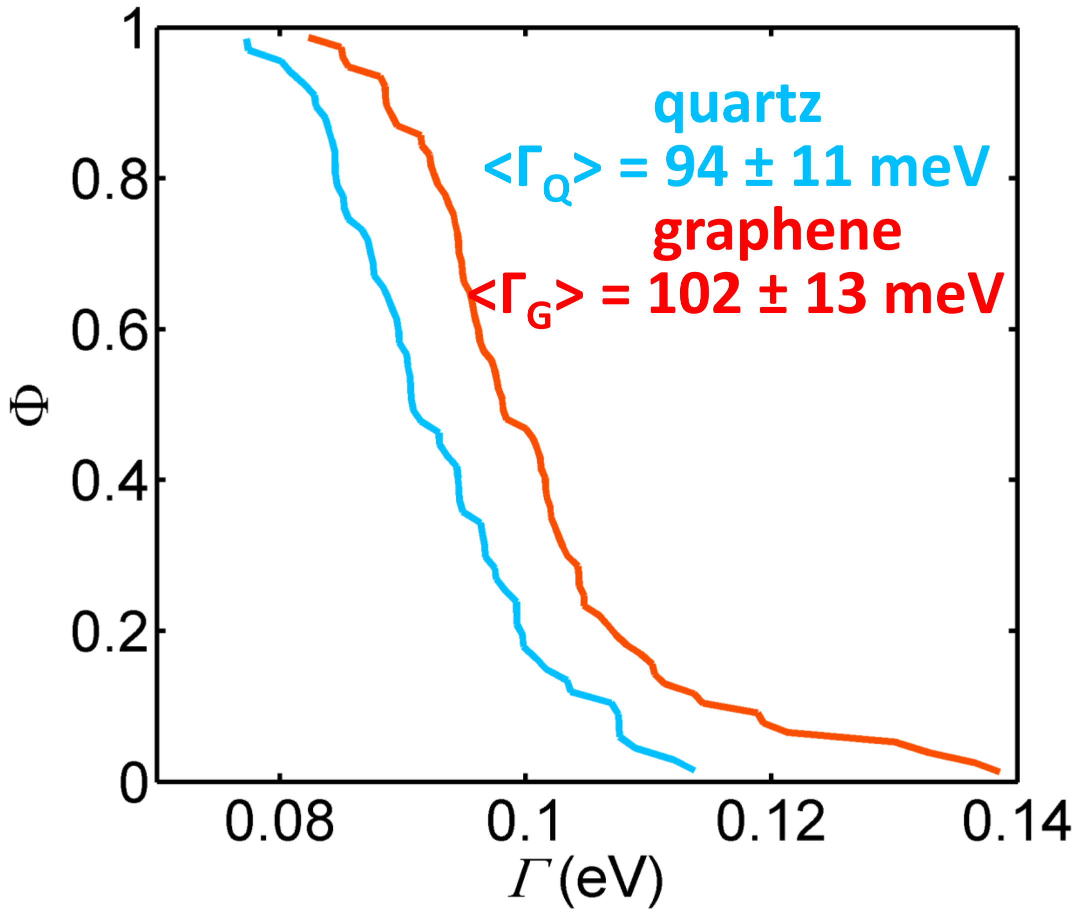
Persson, *Su* . **1993**, *281*

Homogeneous Linewidth from Single Particle Spectroscopy



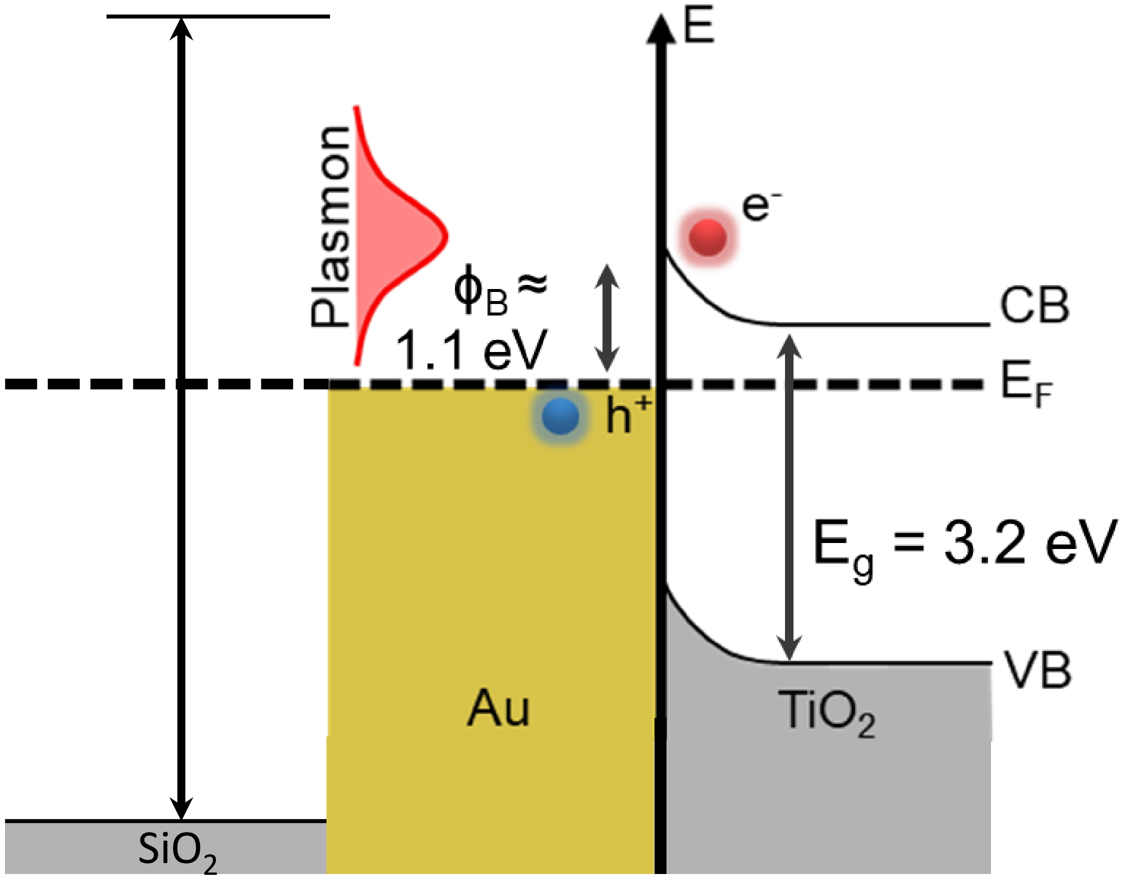
Foerster, Link, Soennichsen et al.,
ACS Nano 11, 2886 (2017)

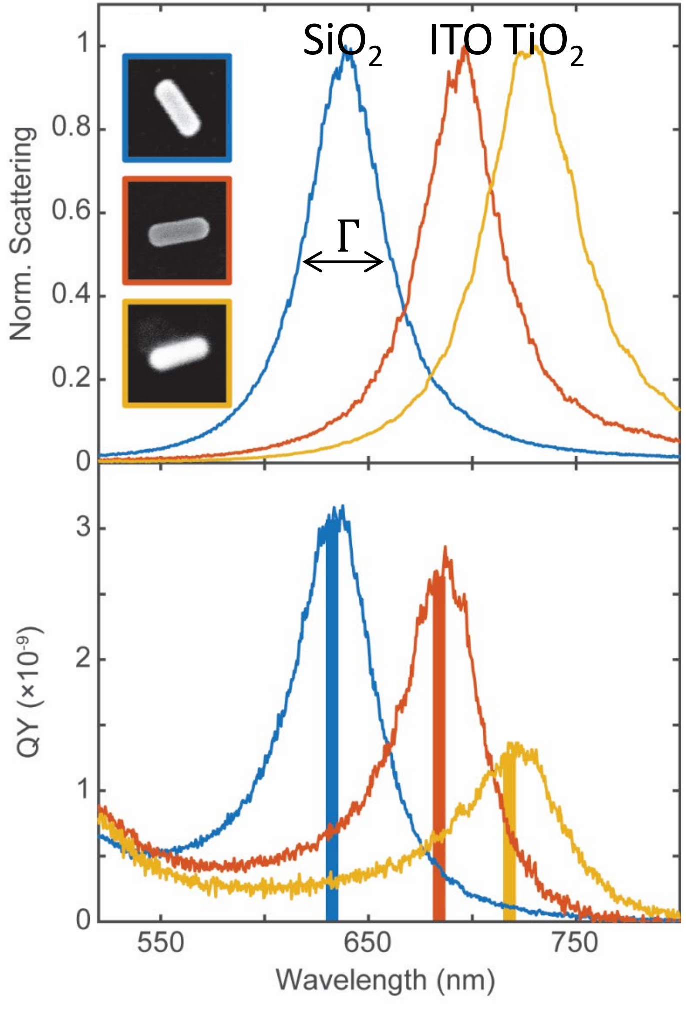
CID of gold nanorods on graphene



Hoggard, Chang, Ajayan. Link et al., ACS Nano *7*, 11209 (2013)

Au-TiO_2 interfaces: Chemical interface damping of gold nanorods on SiO_2 and TiO_2 substrates

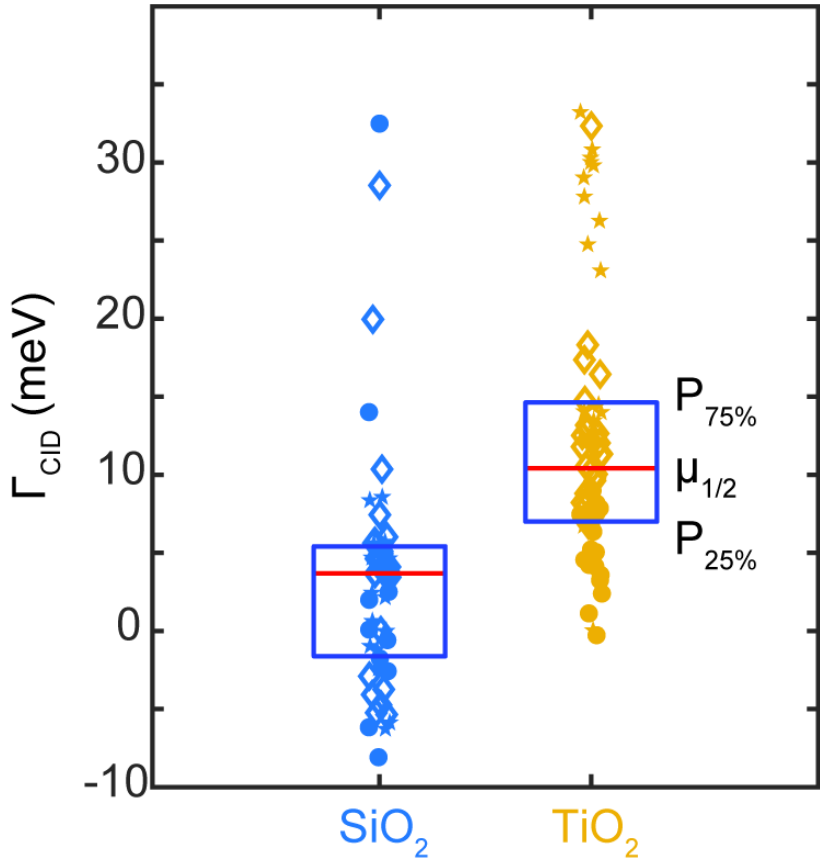


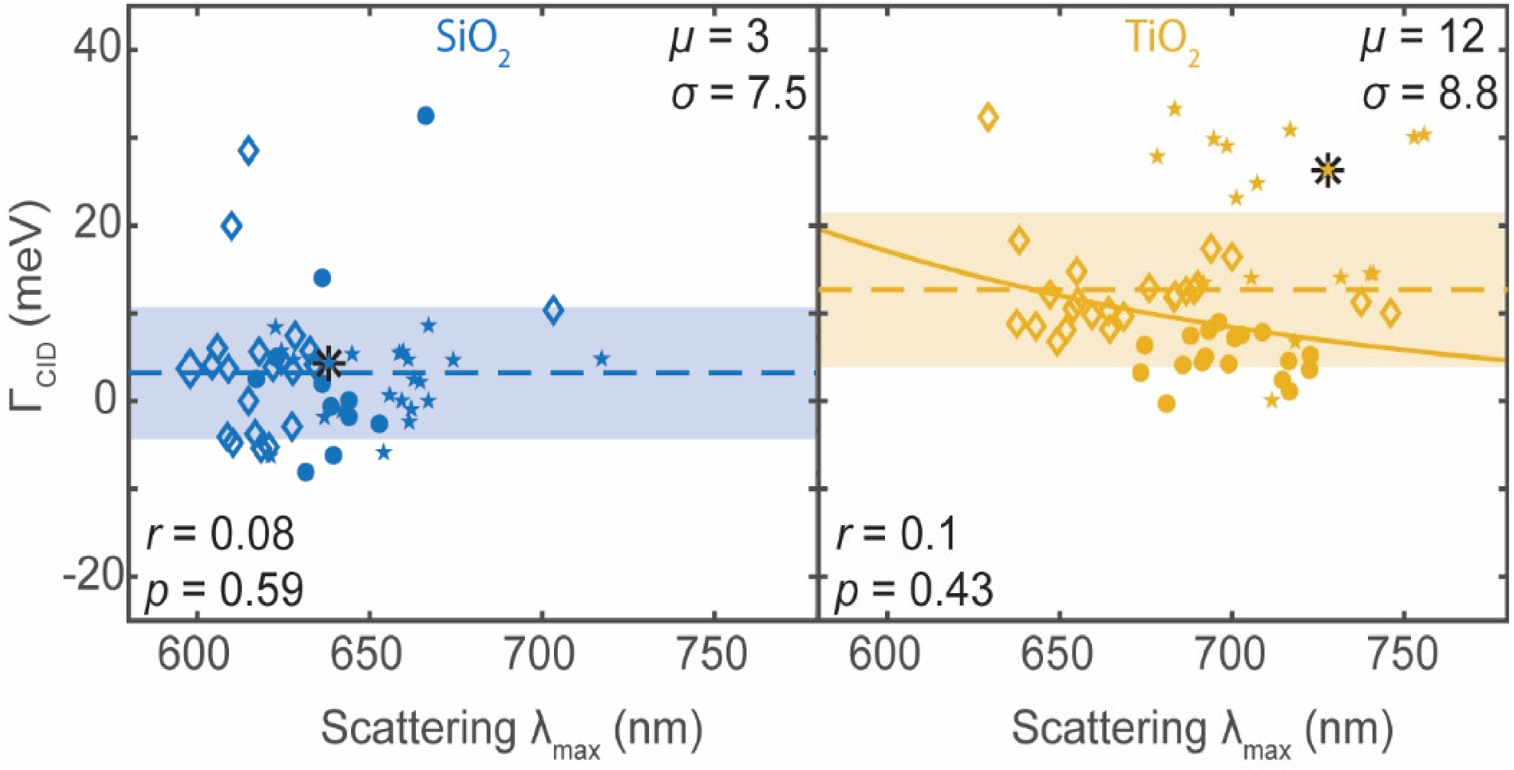


Lee, Landes, S. Link et al., J. Chem. Phys. 156, 064702 (2022)

Chemical interface damping reveals plasmon energy independent charge transfer for the TiO_2 substrate

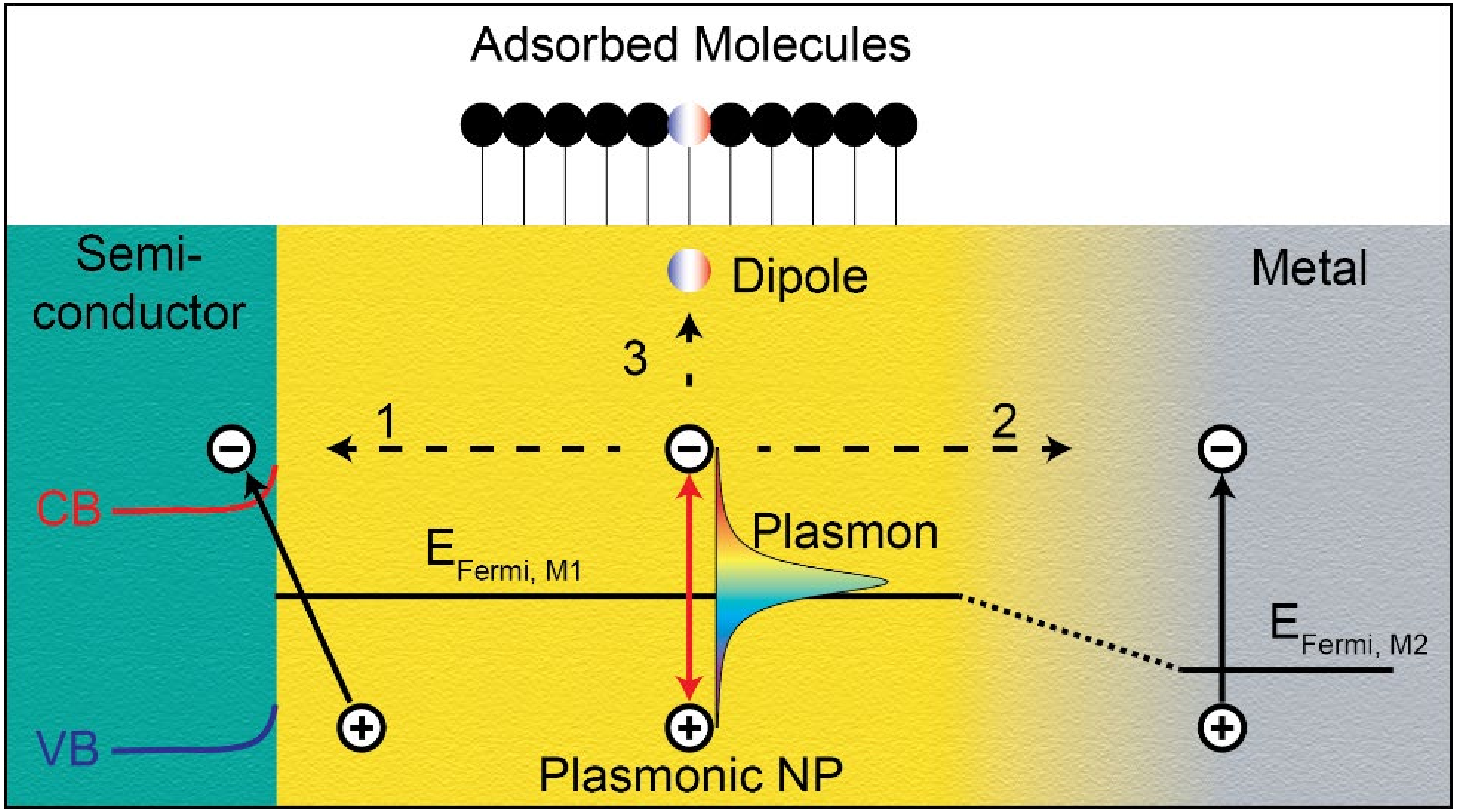
After correction for bulk and radiation damping based on SEM correlated nanorod size





Lee, Landes, S. Link et al., J. Chem. Phys. 156, 064702 (2022)

Only chemical Interface damping is insufficient to prove plasmon induced *direct* charge transfer



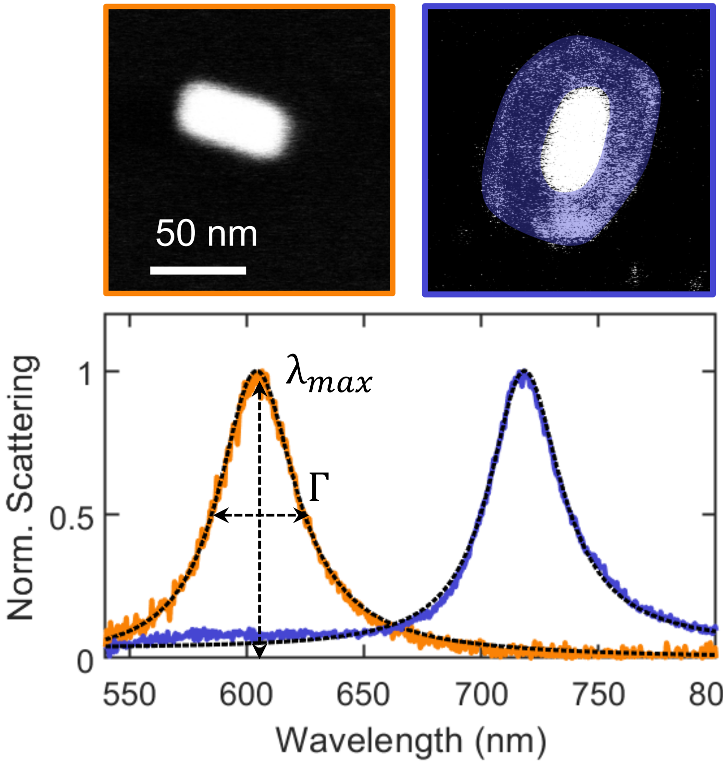
Additional plasmon decay mechanism:
-Charge transfer
-Energy transfer
-Surface induced dipole scattering

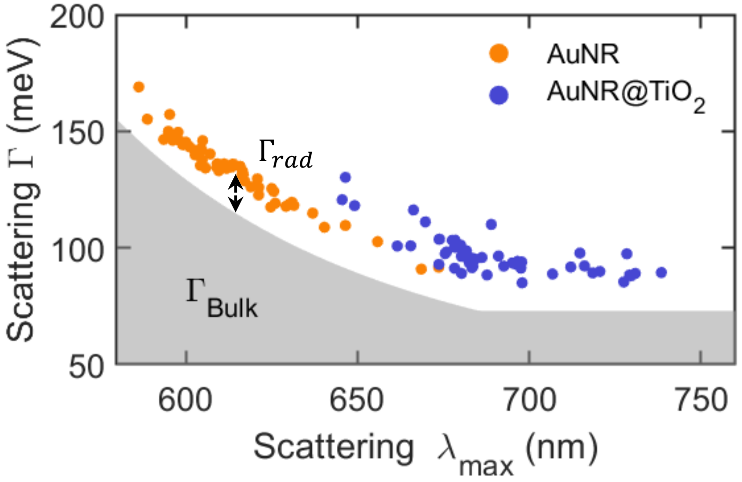
ACS Nano 7, 11209 (2013)
ACS Nano, 11, 2886 (2017)
ACS Nano 11, 12346 (2017)
J. Colloid Interface Sci. 532, 143 (2018)
J. Phys. Chem. C 122, 19116 (2018)
Sci. Adv. 5, av0704 (2019)
Nano Lett. 20, 3338 (2020)
ACS Nano 15, 9522 (2021)
Acc. Chem. Res. 54, 1950 (2021)
J. Chem. Phys. 156, 064702 (2022)
ACS Nano 17, 18280 (2023)
J. Phys. Chem. Lett. 14, 8235 (2023,)
Sci. Adv. 10, eadp3353 (2024)

Need complementary method: IR transient absorption spectroscopy (to give total charge injection)

Lee and Link, Acc. Chem. Res. 54, 1950 (2021)

Gold nanorods overcoated with a TiO_2 shell: chemical interface damping determines the yield of *direct* electron transfer

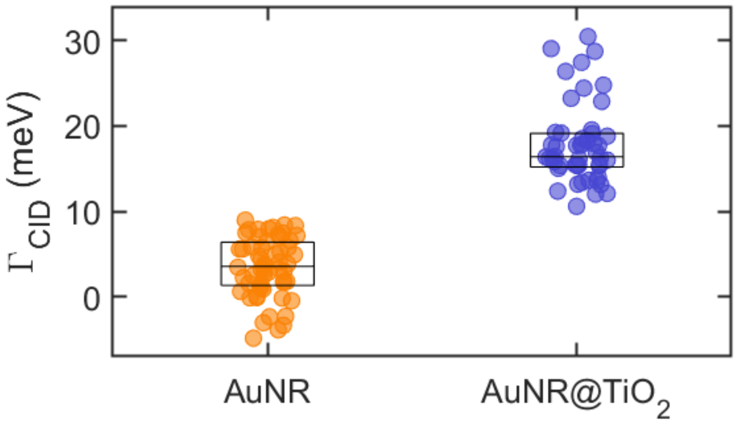




$$\Gamma_{\mathrm{AuNR}} = \Gamma_{Bulk} + \Gamma_{rad}$$

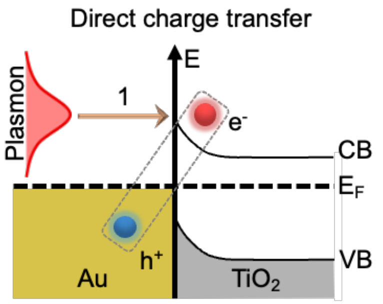
$$\Gamma_{\mathrm{AuNR@TiO_2}} = \Gamma_{Bulk} + \Gamma_{rad} + \Gamma_{CID}$$

$$\eta_{CID} = \frac{\Gamma_{CID}}{\Gamma}$$



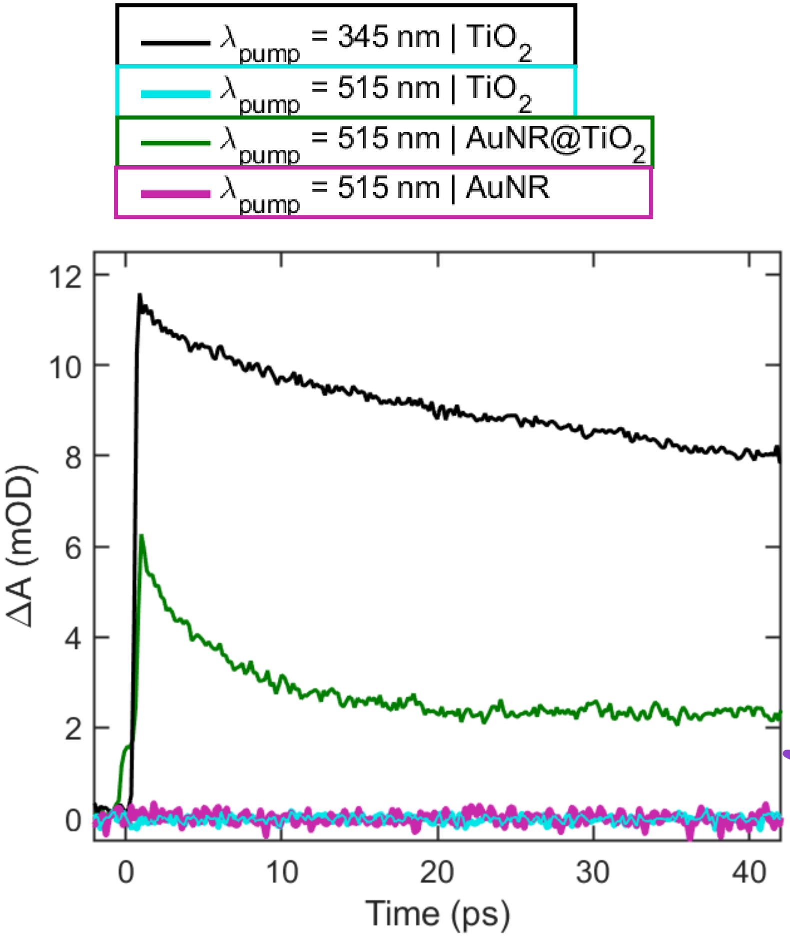
	Γ_{CID} (meV)
AuNR	3.4 ± 3.5
$AuNR@TiO_2$	20.7 ± 4.7

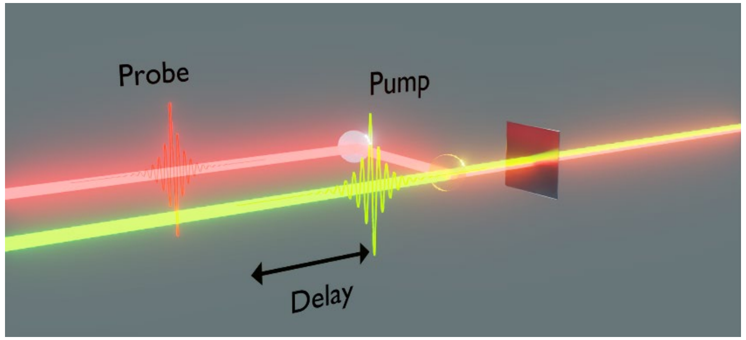
$\eta_{CID} = 19 \pm 4\%$

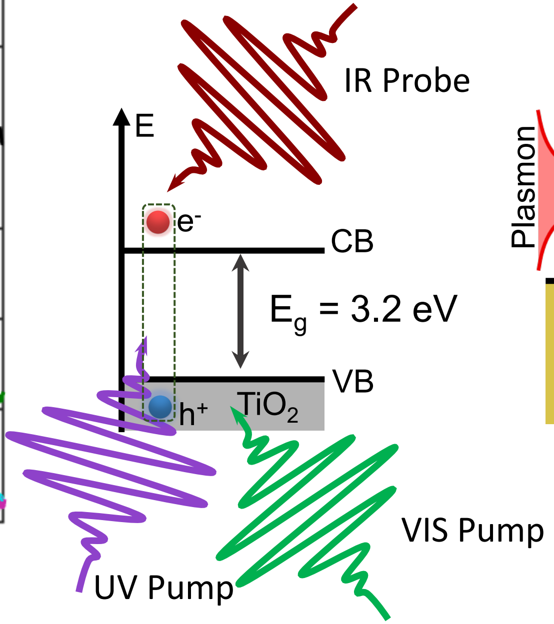


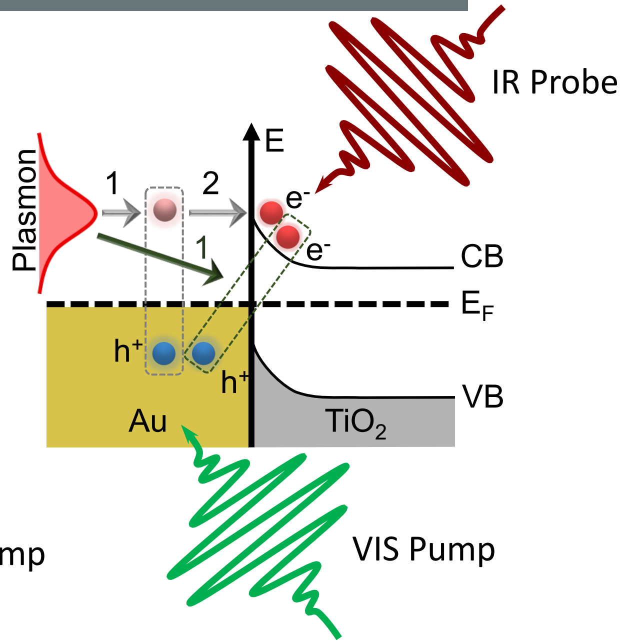
Ostovar, Lee, Dionne, Landes, Zanni, Levine, Link et al., Sci. Adv. 10, eadp3353 (2024)

IR transient absorption spectroscopy probes the *total*/free carriers within the TiO_2 conduction band





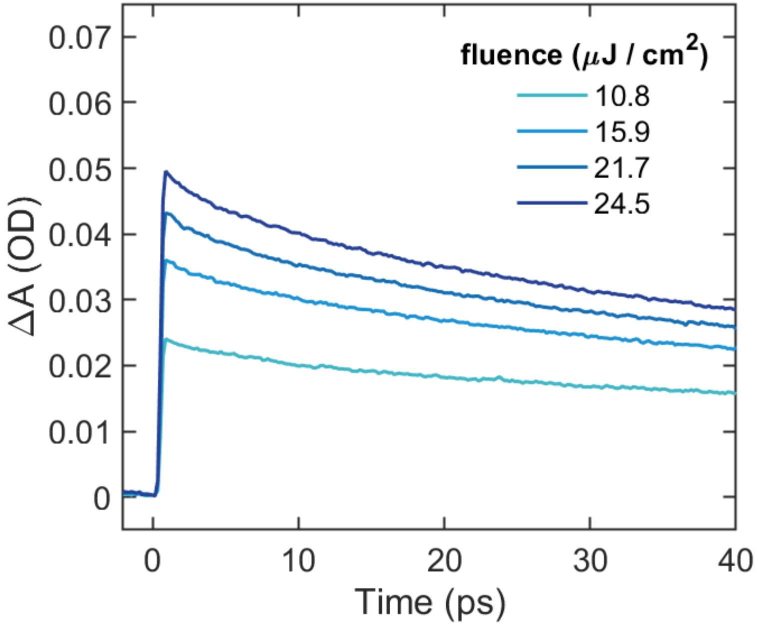




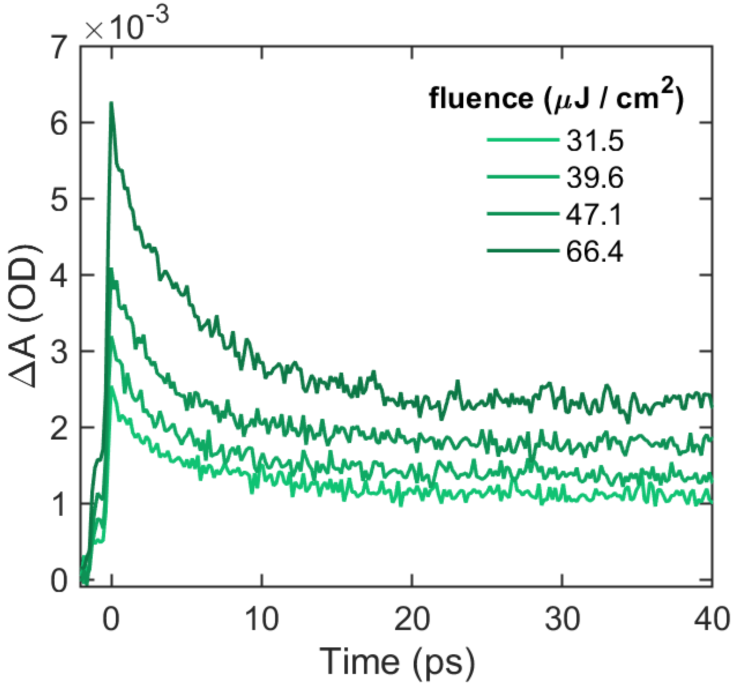
Ostovar, Lee, Dionne, Landes, Zanni, Levine, Link et al., Sci. Adv. 10, eadp3353 (2024)

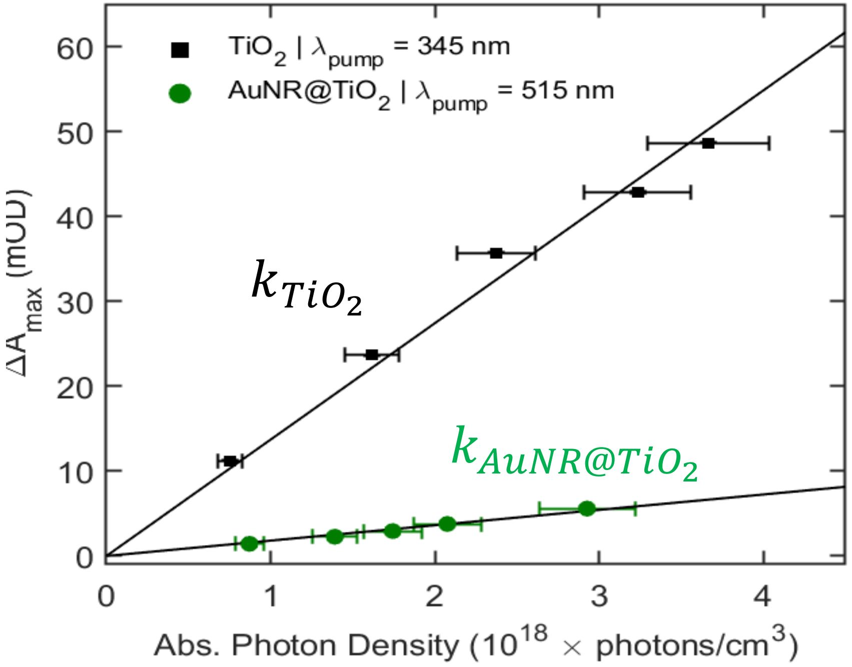
IR transient absorption (TA) spectroscopy probes the *total*/free carriers within the TiO_2 conduction band

TiO_2 – 345-nm excitation



AuNR@TiO_2 – 515-nm excitation

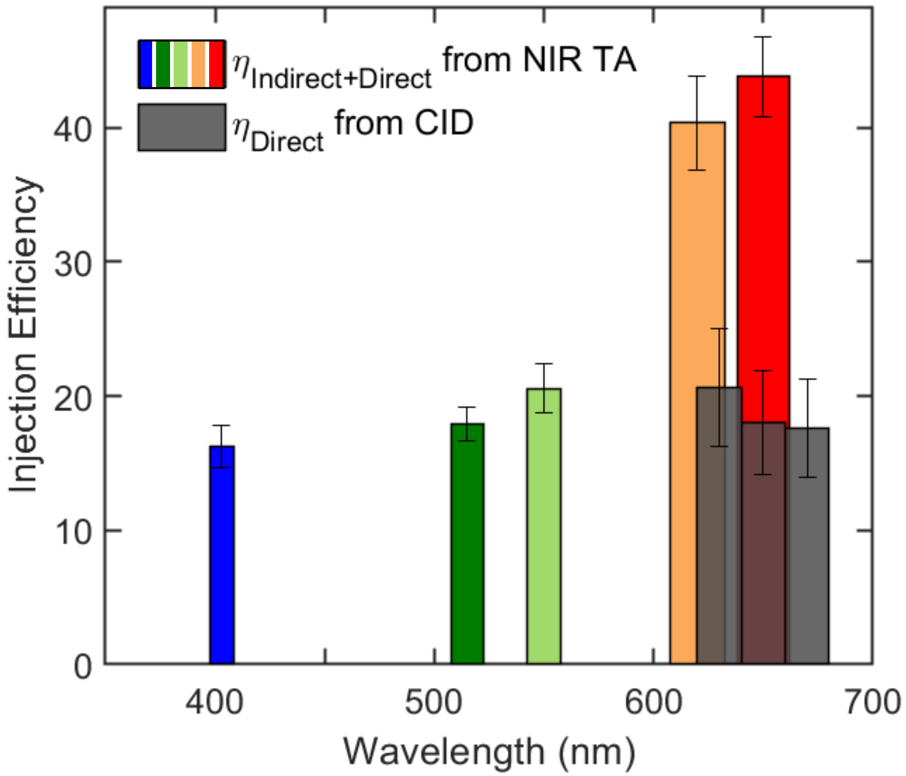




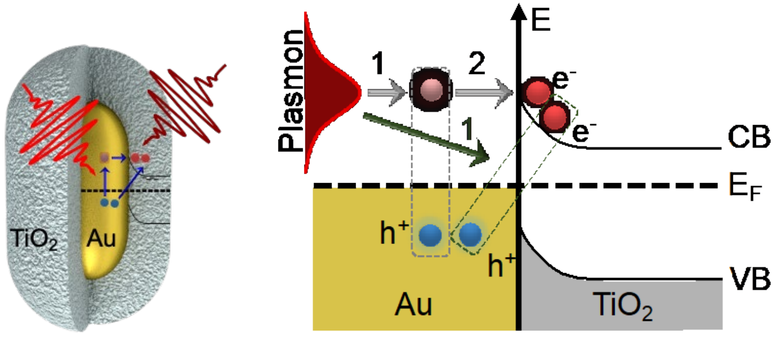
$$\eta_{inj} = \eta_{direct+indirect} = \frac{k_{AuNR@TiO_2}}{k_{TiO_2}} = 15 \pm 6\ \%$$

Ostovar, Lee, Dionne, Landes, Zanni, Levine, Link et al., Sci. Adv. 10, eadp3353 (2024)

Injection efficiency as a function of excitation wavelength: *direct* decay pathway only possible at plasmon resonance



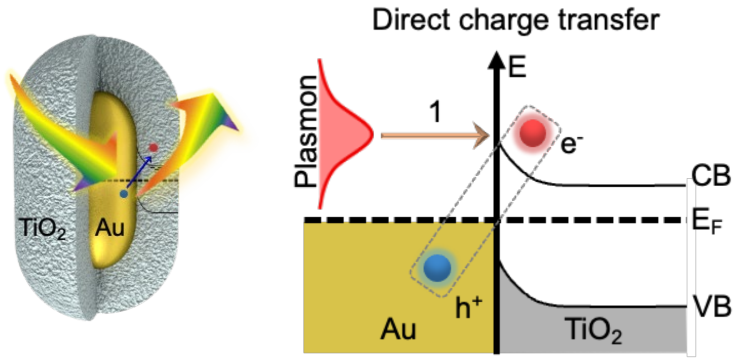
At plasmon excitation:



$\eta_{direct+indirect} = 44 \pm 3\%$

Furube et al.: 40%

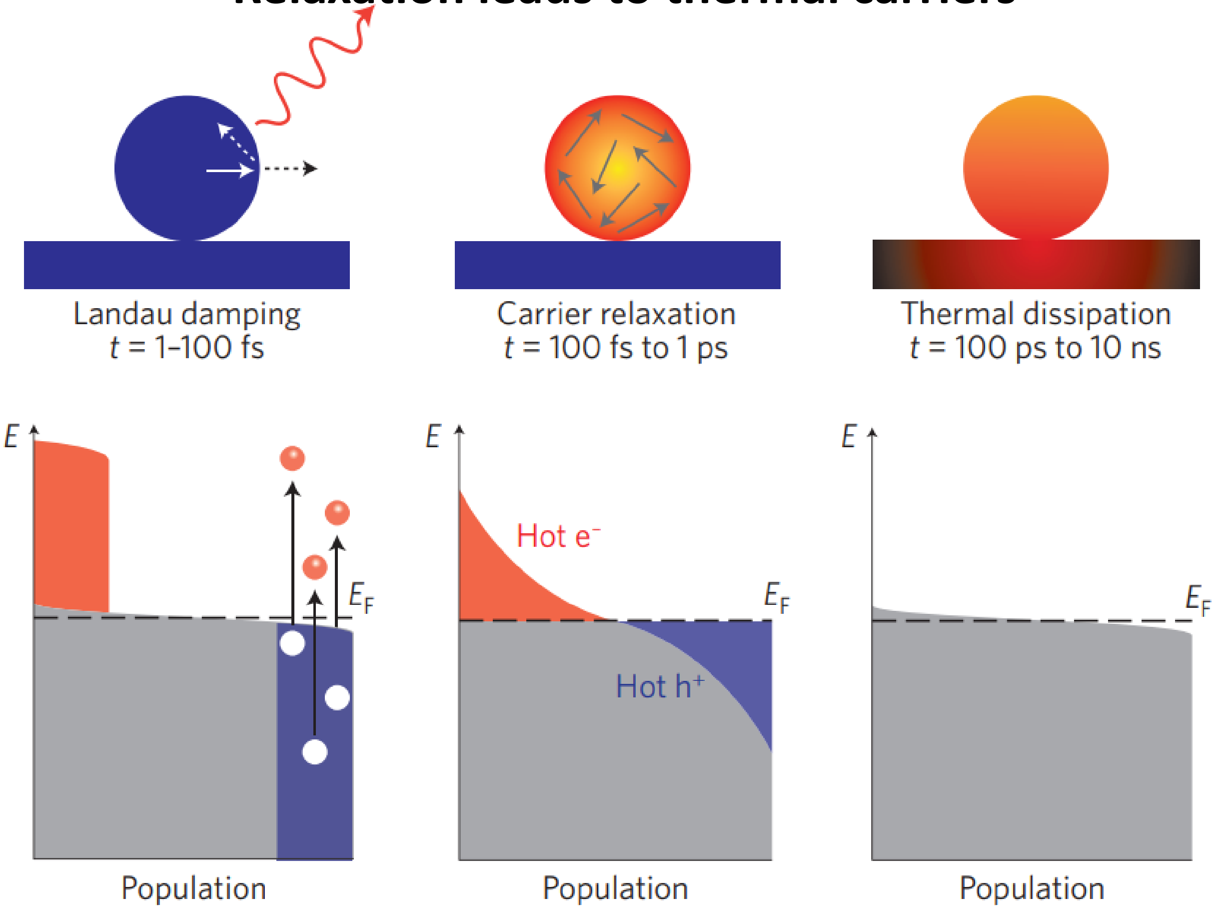
J. Am. Chem. Soc. 129, 14852 (2007)



Ostovar, Lee, Dionne, Landes, Zanni, Levine, Link et al., Sci. Adv. 10, eadp3353 (2024) $\eta_{direct} = 19 \pm 4\ \%$

Dynamics of metal excited carriers: Ultrafast visible pump-probe spectroscopy

Relaxation leads to thermal carriers



Brongersma, Halas, and Nordlander, *Nat. Nanotechnol.*, **2015**, *10*, 25

JOURNAL OF CHEMICAL PHYSICS VOLUME 111, NUMBER 3 15 JULY 1999

Electron dynamics in gold and gold–silver alloy nanoparticles: The influence of a nonequilibrium electron distribution and the size dependence of the electron–phonon relaxation

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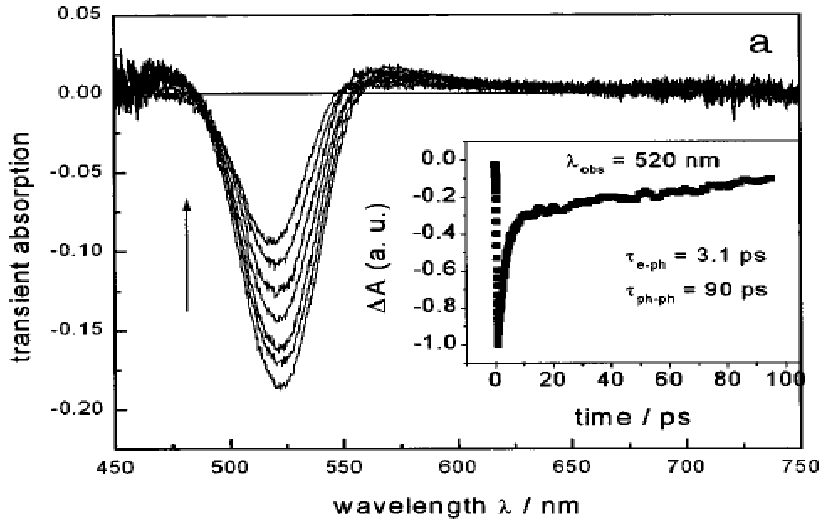


Dynamics of metal excited carriers: Ultrafast pump-probe spectroscopy

Two-temperature model

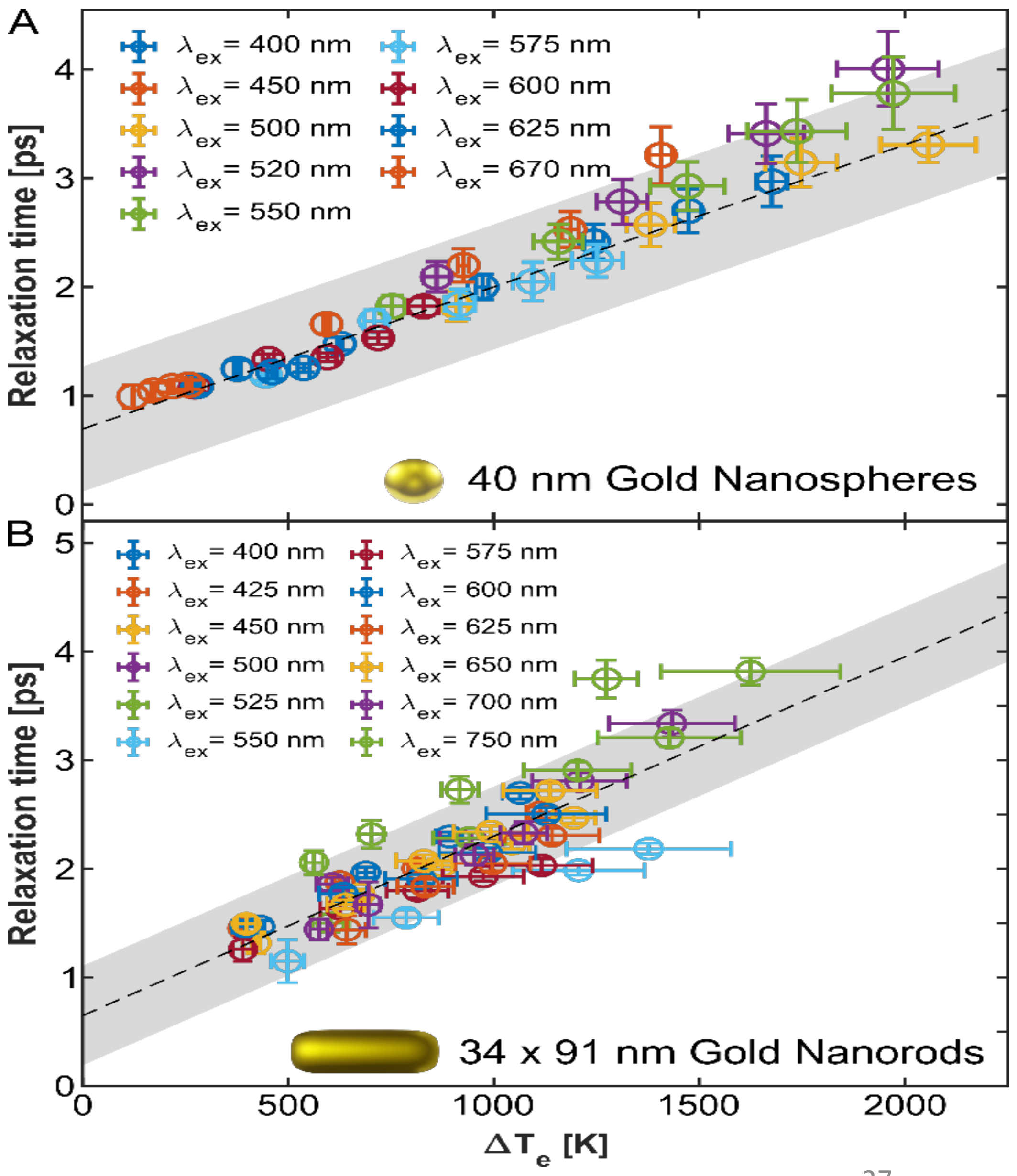
$$\tau_{e\text{-}ph} = \gamma(\Delta T + T_0)/g$$

⬇

$$\tau_{e\text{-}ph} = \gamma\Delta T/g + \gamma T_0/g$$

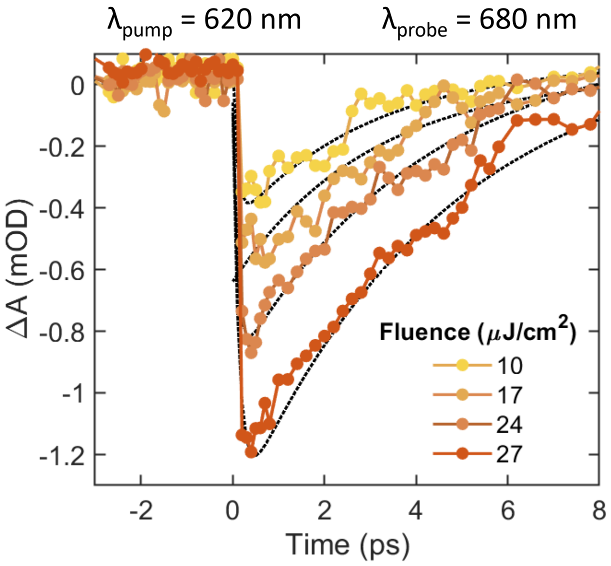
$\tau_{e\text{-}ph} \propto \Delta T$ → pump power + absorption cross section

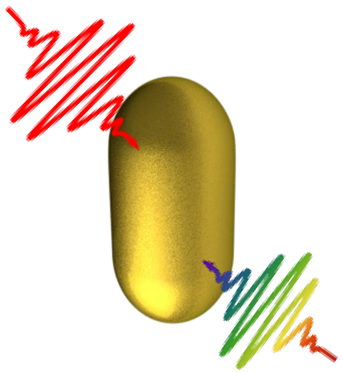
γ: electron heat capacity
g: electron-phonon coupling constant
T_0: ambient temperature
ΔT: increase of the electronic temperature



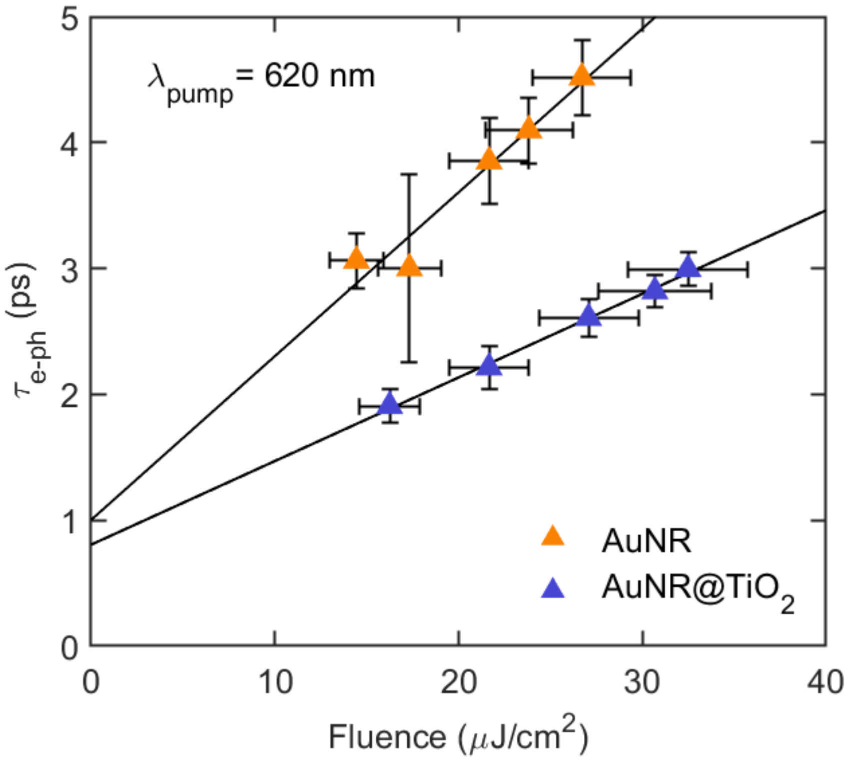
Chiang, Bruncz, Hartland, Link, et al.
J. Phys. Chem. C 127, 21176 (2023)

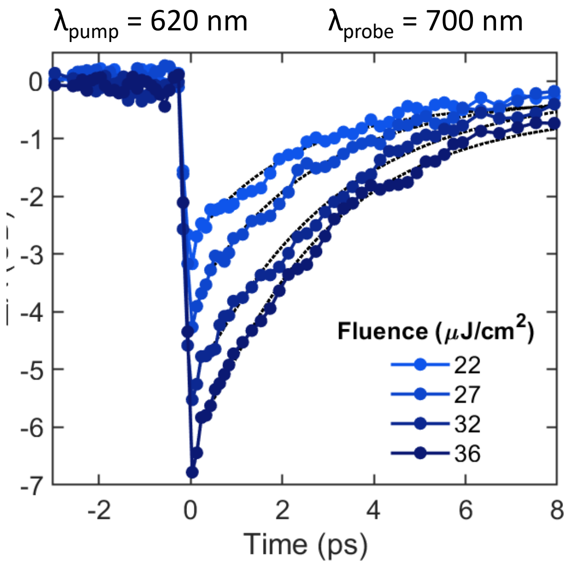
Visible transient absorption spectroscopy reveals charge transfer through changes in electron-phonon scattering

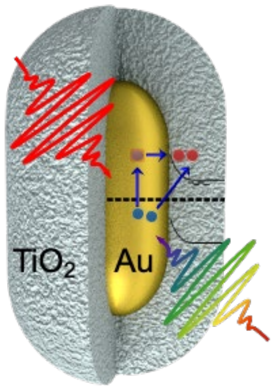




Comparing slopes indicates that $AuNR@TiO_2$ becomes half as hot, implying ~ 50% total charge injection

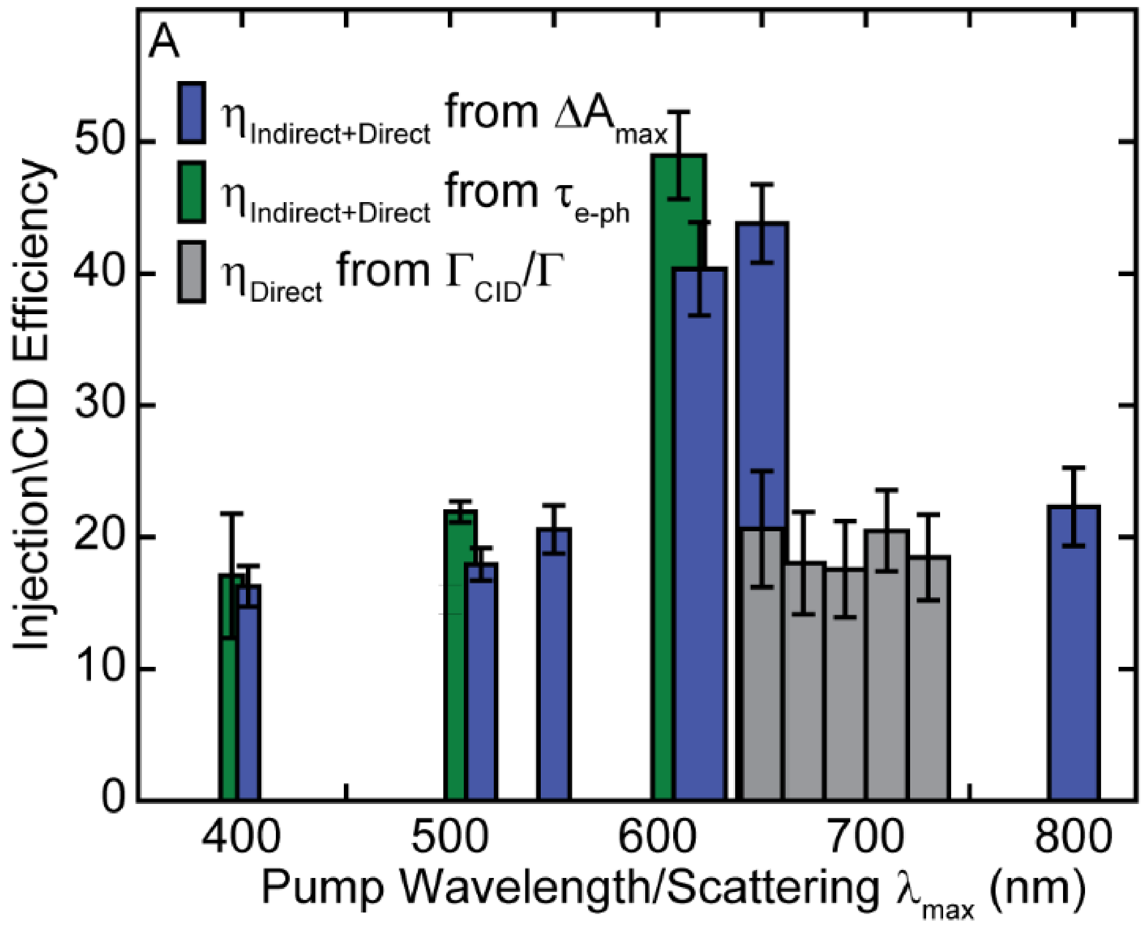


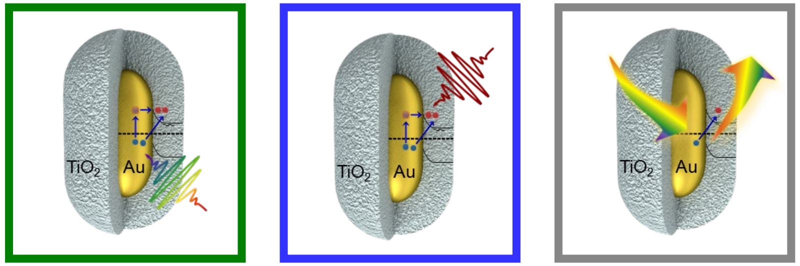




Ostovar, Lee, Dionne, Landes, Zanni, Levine, Link et al., Sci. Adv. 10, eadp3353 (2024)

Both direct and sequential charge transfer occur – plasmon enhancement through chemical interface damping





- VIS transient absorption data determines the amount of absorbed energy that is lost to the TiO_2
- NIR transient absorption spectroscopy probes the total charge injection via free electron absorption in theTiO_2 conduction band
- Single-particle spectroscopy quantifies charge injection via plasmon decay only

Plasmon damping into interfacial charge separated states is a significant/efficient decay pathway

Ostovar, Lee, Dionne, Landes, Zanni, Levine, Link et al., Sci. Adv. 10, eadp3353 (2024)

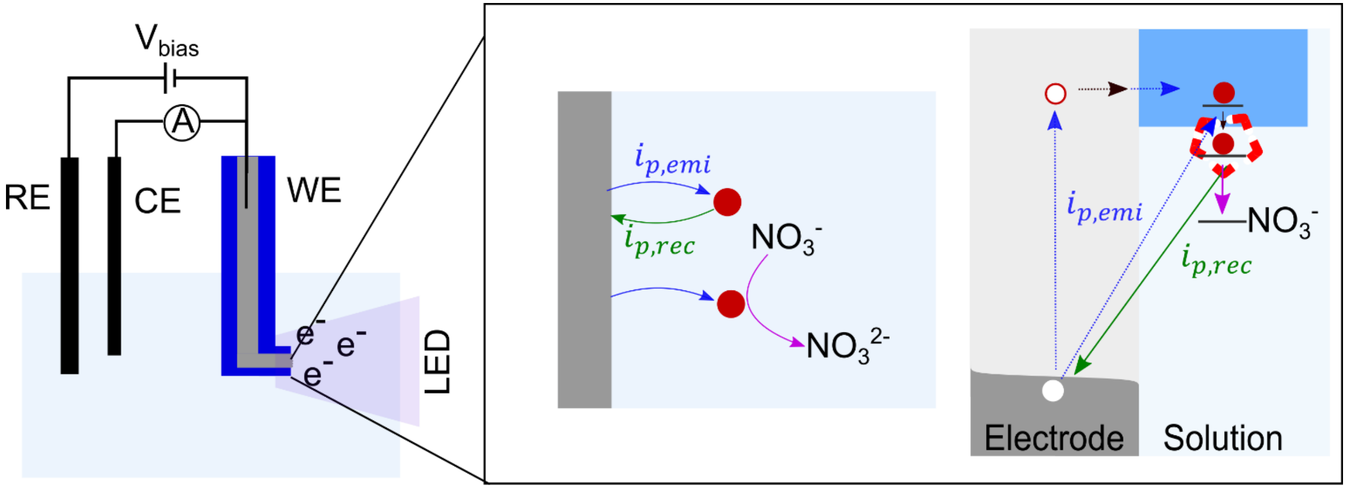
Outline

1) Charge transfer at metal – semiconductor interfaces

2) Photoemission into water

Photoemission can be detected electrochemically

Electron scavengers prevent recombination



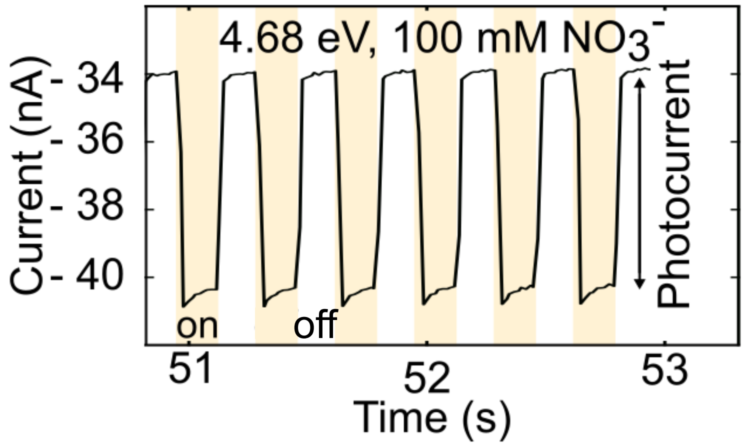
Emission: $M + \hbar\omega \rightarrow e^- + h^+$ $\quad i_{p,emi}$

Reaction: $e^- + NO_3^- \rightarrow NO_3{}^{2-}$

Recombination: $e^- + h^+(M) \rightarrow M$ $\quad i_{p,rec}$

Overall: $\boldsymbol{i_p = i_{p,emi} + i_{p,rec}}$

Photocurrent gives emission yield



- NO_3^- prevents recombination
- Photocurrent proportional to photoemission yield:

$$i_p = n_{e^-_{(aq)}} F$$

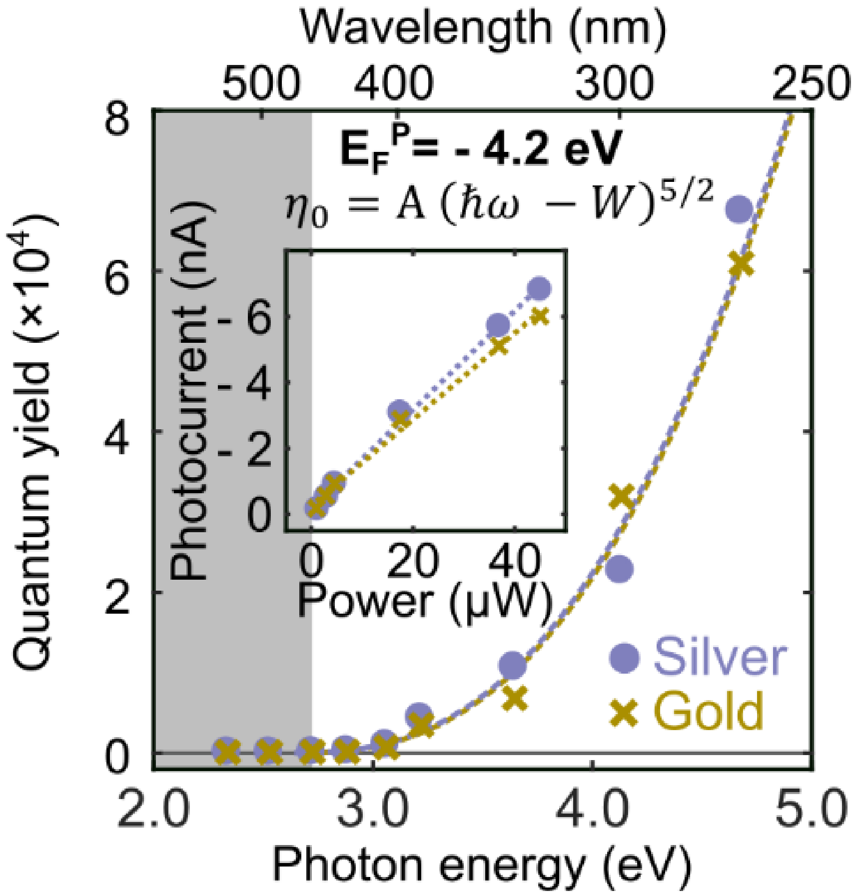
(F = 96485 A s mol^{-1})

External quantum yield: $$\eta = \frac{i_p(A) \times \hbar\omega(eV)}{P\ (W)}$$

Al-Zubeidi, Roberts, Dionne, Rossky, Landes, Link et al., PNAS 120, e2217035120 (2023)

Emission from smooth electrodes follows 5/2 power law

Photoemission spectrum



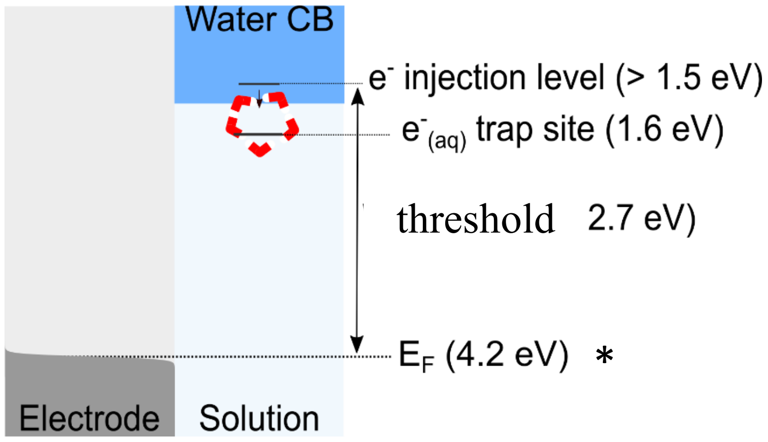
Quantum efficiency depends on excess energy above threshold:

$$\eta_0 = A\,(\hbar\omega - W)^{5/2}$$

Fit reveals threshold:

$$W = 2.7\ \text{eV}$$

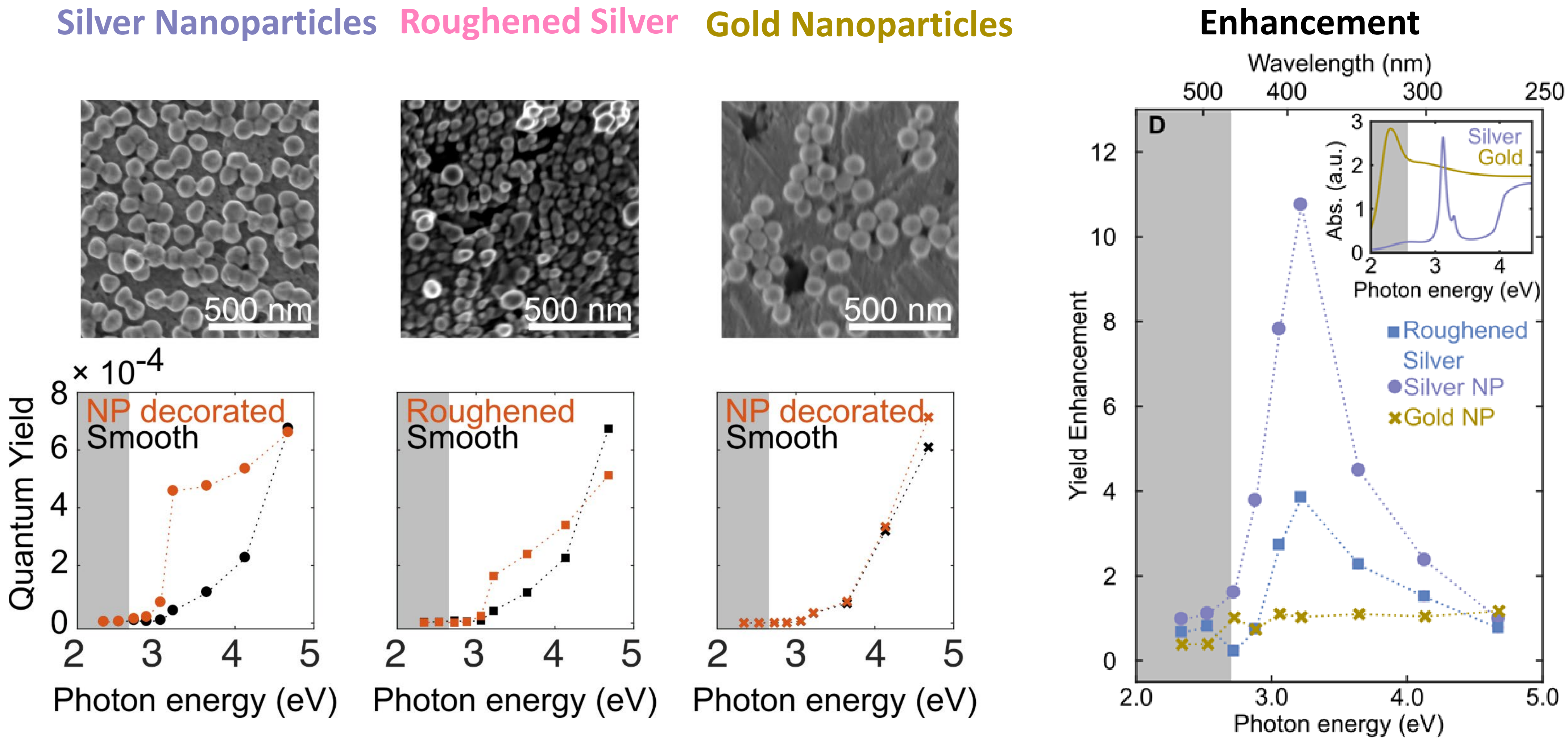
Threshold agrees with e^- injection level:



* 4.2 eV = - 0.3 V vs SHE

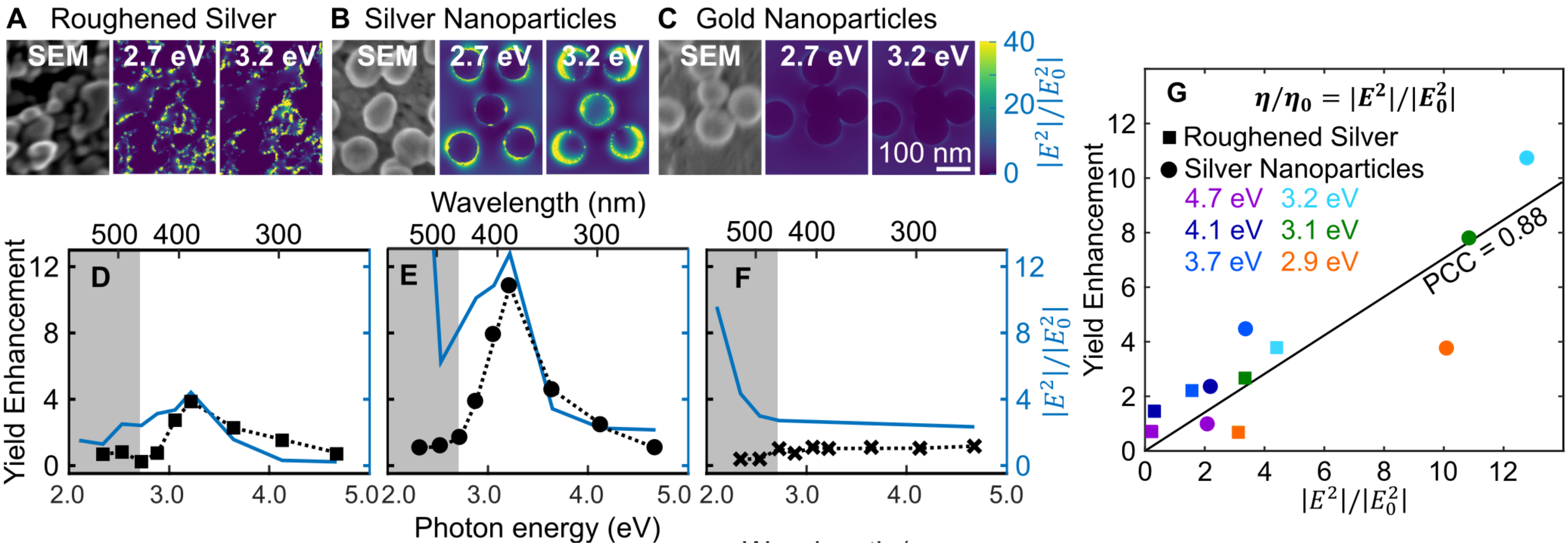
Al-Zubeidi, Roberts, Dionne, Rossky, Landes, Link et al., PNAS 120, e2217035120 (2023)

Nanoparticle decorated electrodes enhance photoemission



Al-Zubeidi, Roberts, Dionne, Rossky, Landes, Link et al., PNAS 120, e2217035120 (2023)

Emission scales with field enhancement



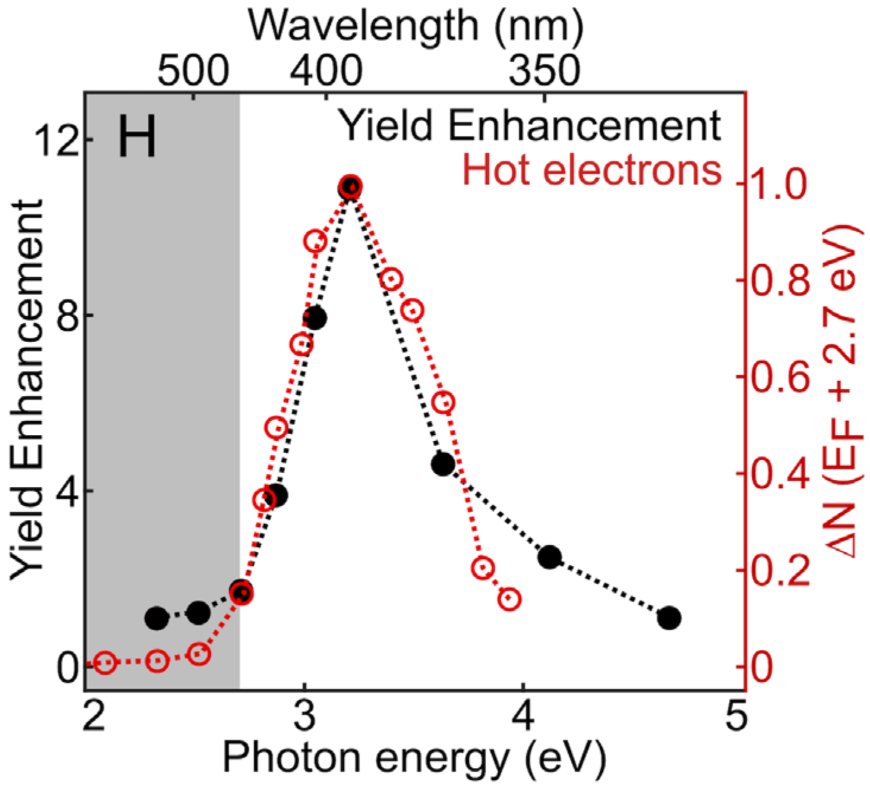
Photoemission scales linearly with field enhancement

Al-Zubeidi, Roberts, Dionne, Rossky, Landes, Link et al., PNAS 120, e2217035120 (2023)

Plasmons produce solvated electrons through field-enhanced hot electron generation in an indirect bulk emission process

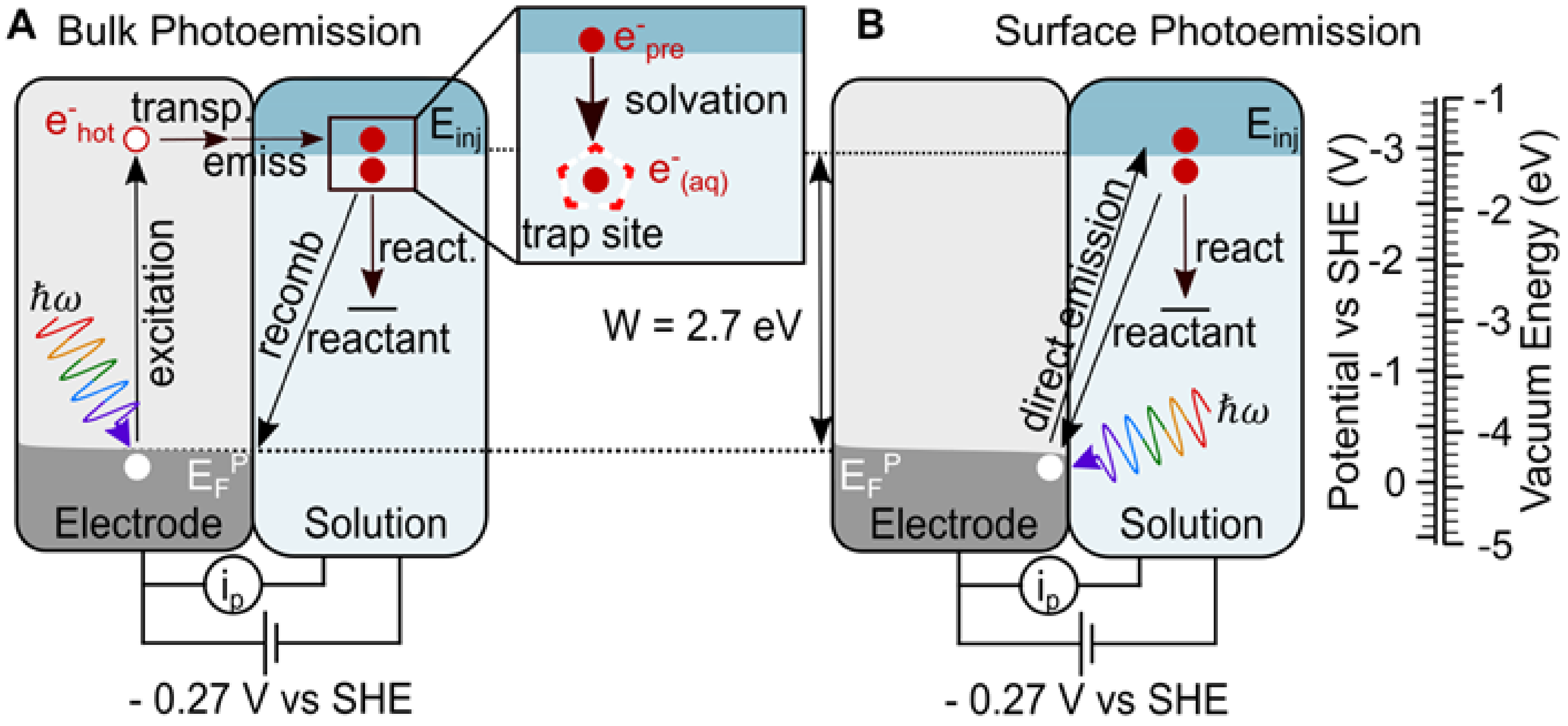
Field-enhancement increases generation of hot carriers

$$\eta_{bulk} \propto n(e^{-}{}_{hot}) \propto |E_{int}|^2$$



Al-Zubeidi, Roberts, Dionne, Rossky, Landes, Link et al., PNAS 120, e2217035120 (2023)

Plasmons produce solvated electrons through field-enhanced hot electron generation in an indirect bulk emission process



Hot e⁻ generation
Hot e⁻ transport to interface
Emission across interface

Direct injection through surface scattering of e⁻ with photon

Increase yields with:
-Smaller nanostructures
-Coupled modes

Need larger potential windows or higher energy resonances

Al nanoparticles in organic solvent: Solti, Nordlander, Halas et al., *J. Am. Chem. Soc.* **2022**, *144*, 20183

Al-Zubeidi, Roberts, Dionne, Rossky, Landes, Link et al., PNAS 120, e2217035120 (2023)

Conclusions

1) **Charge transfer at metal – semiconductor interfaces**

Plasmons open up direct charge transfer process thereby enhancing charge injection efficiency

1) **Photoemission into water**

Plasmons drive solvated electron generation through enhanced fields (indirect pathway)

THANK YOU!!!

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