Low energy electron emission, injection and charge riequilibrium from plasmonic nanostructures for catalysis applications

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To perform macroscopic measurements of injection, catalytic, solar efficiency a proper device is needed.

In absence of a device excited state spectroscopy offers both microscopic investigtion and quantitative information.

Here we present three different approach to study electron injection based on time resolved spectroscopies in metal nanoparticles/CeO2 systems **(Nano-CNR, Modena).**

1. NIR – UV Fast Transient Absorption Spectroscopy: Information on excited state polulation, joint density of states; flexible experimental set-up for liquid, solid and gas phase, lack of element sensitivity (**EuroFel Support Lab-ISM-CNR**).
2. X-ray Fast Transient Absorption Spectroscopy: information about excited population projected on the absorbing site via local excitation of core levels, in case of correlated systems the excited state absorption is very sensitive to the excited state population via multiplet structure; lack of energetic resolution of density of states **(FERMI@Elettra – BEAR beamline@Elettra)**
3. Time Resolved PhotoEmission Spectroscopy: surface sensitivity, it probes both occupied valence bands and core levels with good energy resolution; High pump laser fluence can induce space charge **(SPRINT-IOM-CNR Trieste)**

- *CeO_2 (cerium oxide or ceria) plays an important role as a TMO catalyst.*
- *fast and reversible changes between 4+ and the 3+ oxidation state of Ce extra electron localized in the Ce 4f levels.*
- *The combination of ceria with metallic NPs can induce modifications of important properties, such as oxygen vacancy formation energy, which may improve the material reactivity,*
- *increasing the prospect of using sunlight for environmental and energy applications.*
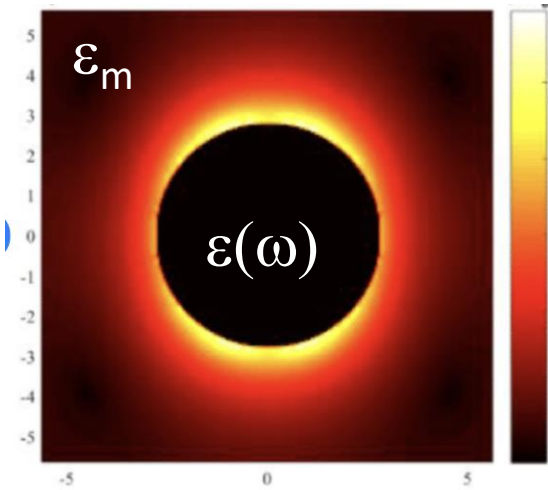
Quasi-electrostatic model (λ>>a)

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}.$$

at resonance

$$\mathrm{Re}\left[\varepsilon\left(\omega\right)\right] = -2\varepsilon_m$$

- near surface field enhancement
- frequency tunability via eleftron density, shape and size
- fast de-excitation (5 – 50 fs)
- complex nano-achitectures with the coupling of plasmon modes
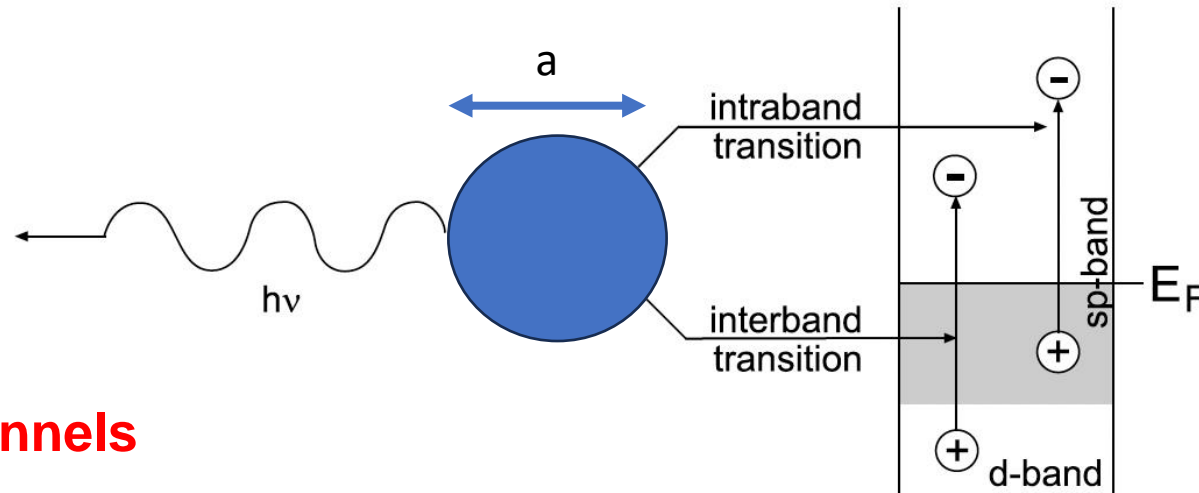- applications in sensors, catalysis, nano-antennas, health.
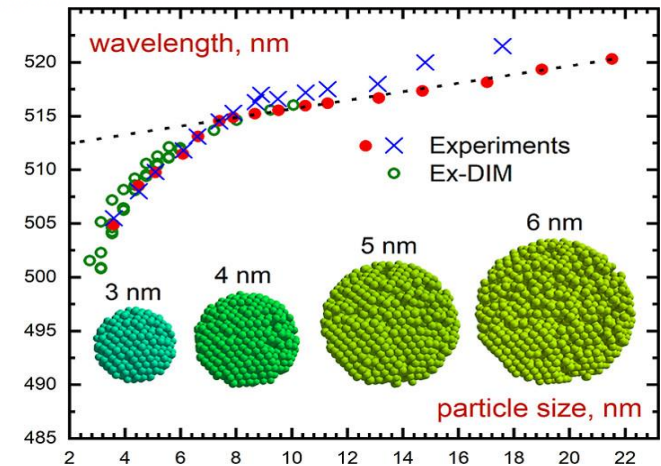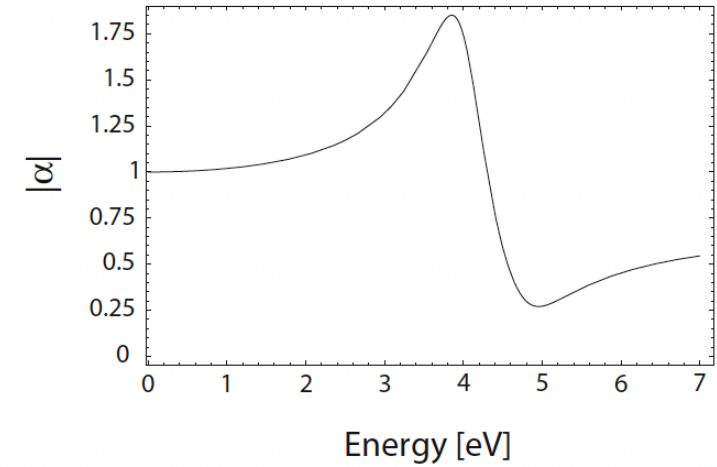
Stefan Maier, Plasmonics, Principles and Applications, Springer, 2007

L. K. Sorensen et al, J. Phys. Chem. C 2022, 126, 39

De-excitation channels

- radiative emission
- Free carrier absorption arising from phonon and defect scattering : phonons ad defects provide the momentum to allow the transition
- Absorption assisted by electron–electron Scattering: dependent on ω^2 , not negligible in the visible range
- Absorption via Landau damping (a.k.a. surface collision assisted absorption): surface effect dominant when the particle size is less than the electron mean free path; dependent on the ratio v_F/a
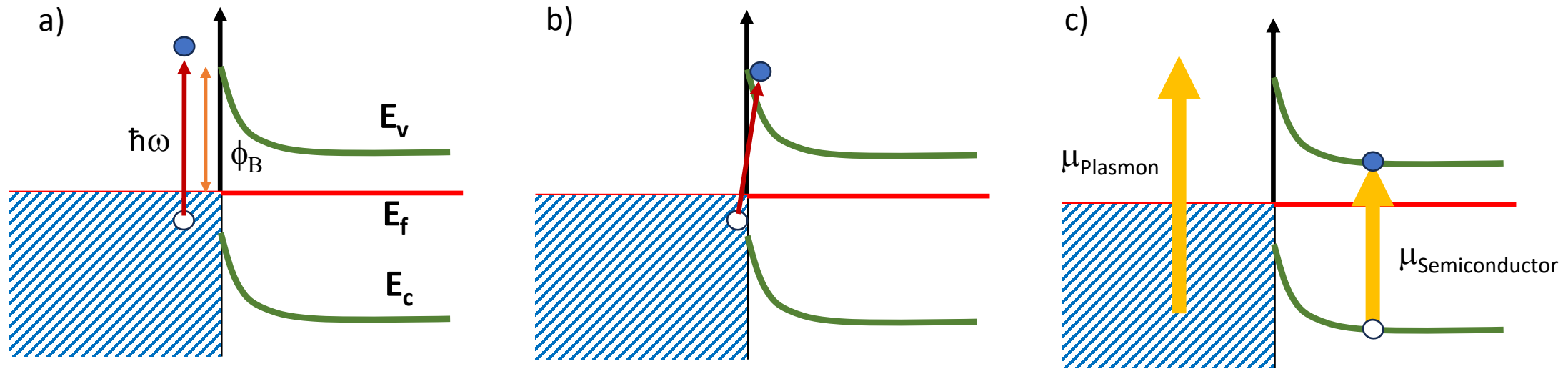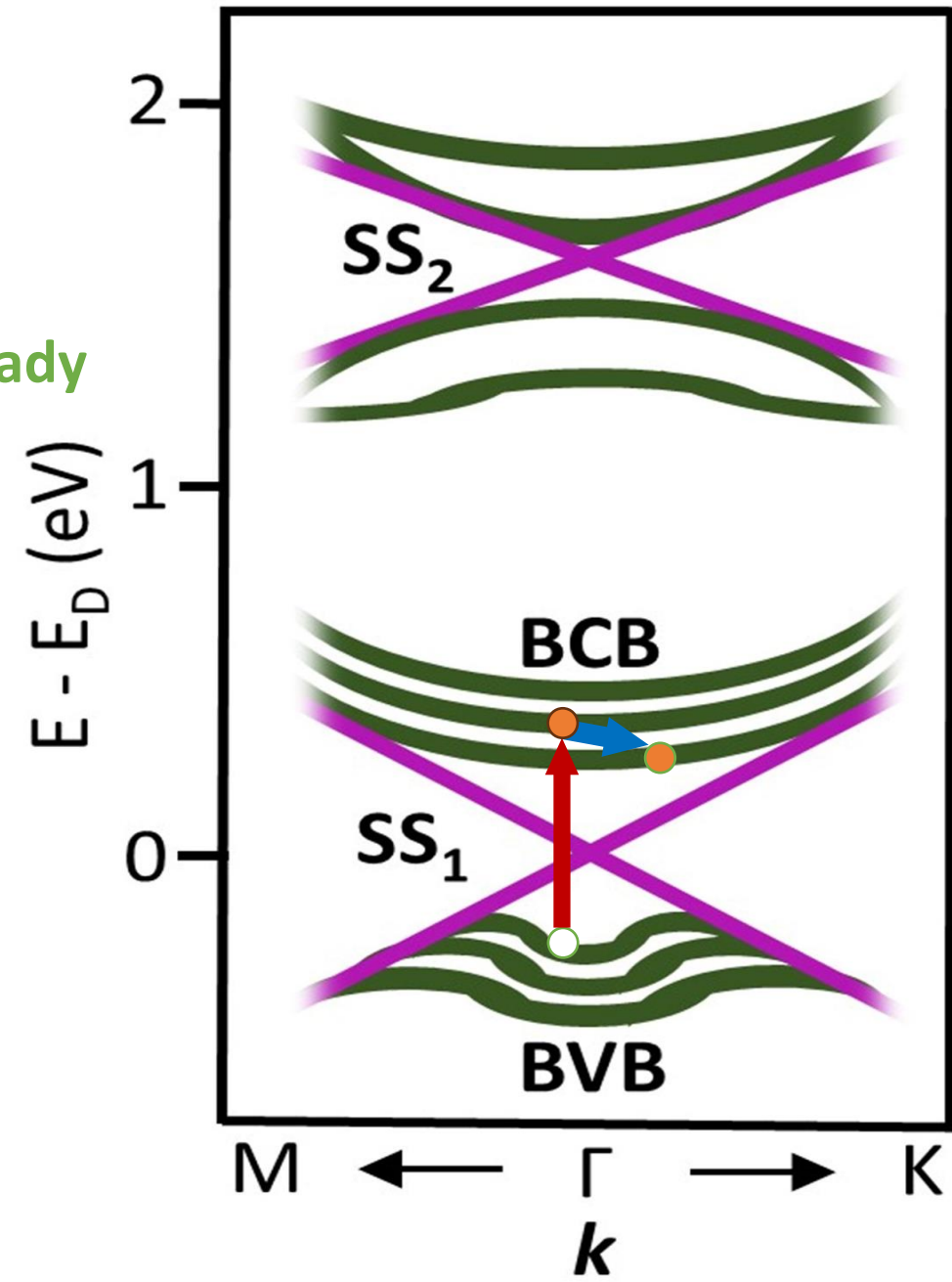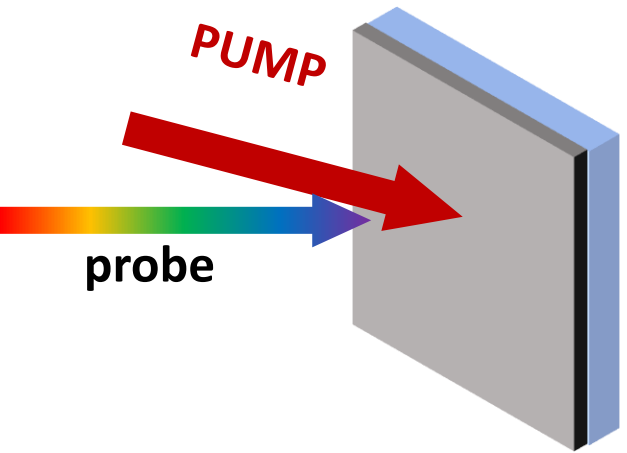
a) Hot electron transfer (T~100 fs): the mechanism is competitive with the e-e scattering

b) Direct injection: (T ~ 10-50 fs) charge separation via interfacial states CT-like

c) Plasmon Induced Energy Transfer: the process, similar to Foster Resonance Energy Transfer, is based on the coherent oscillation of the plasmon electric dipole
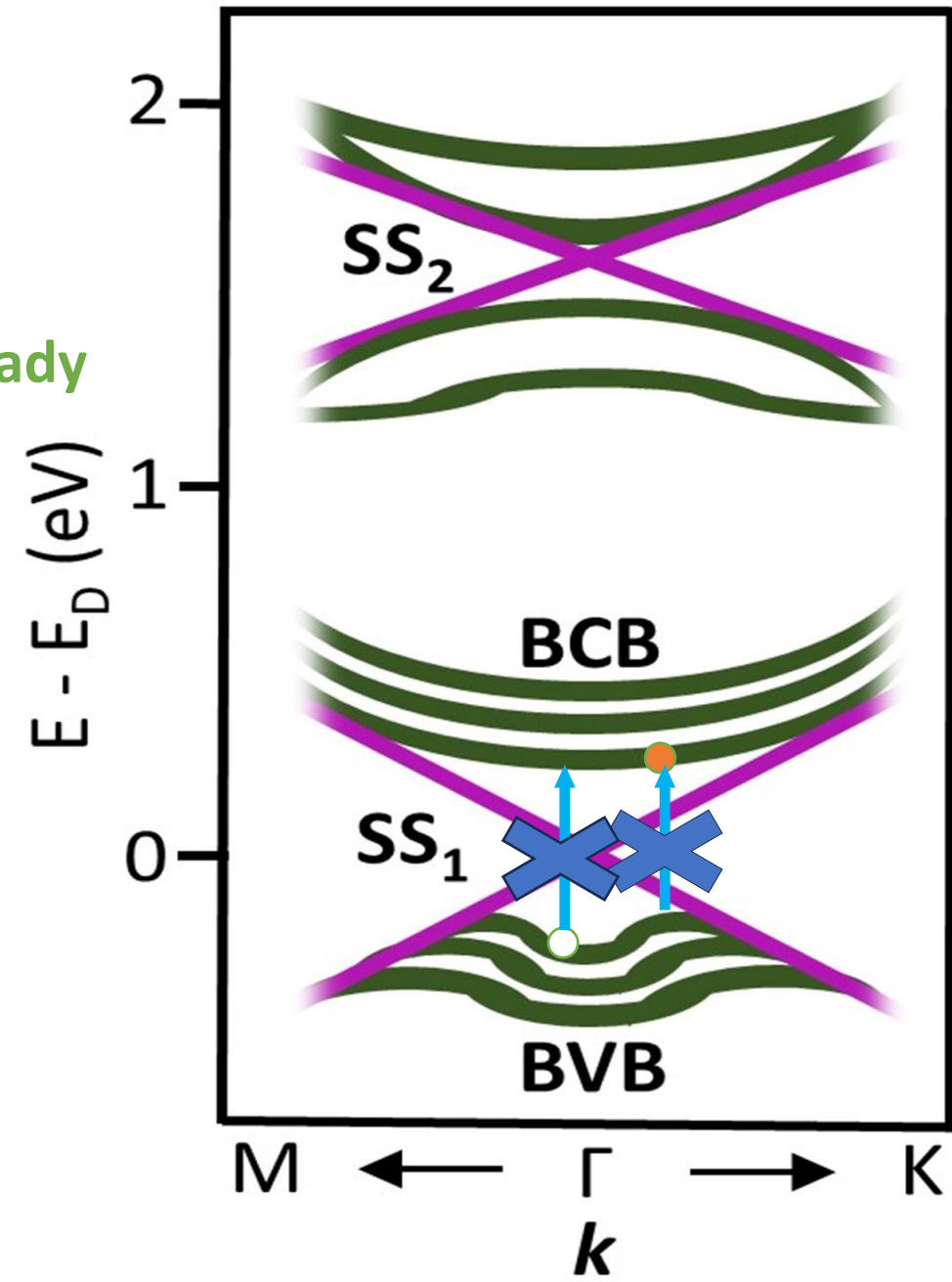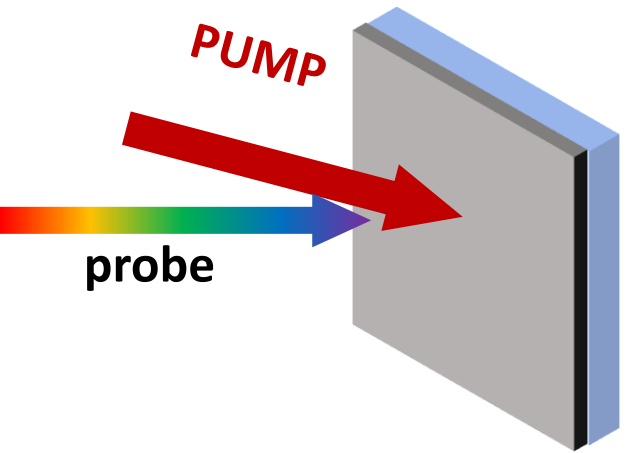
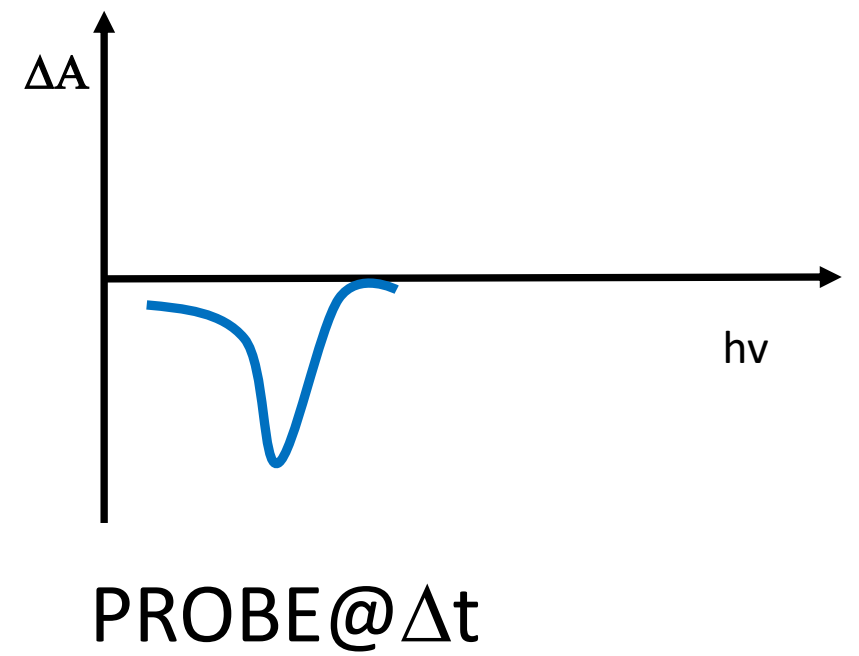ΔA=A_{exc}(Δt)-A_{steady}

Fast Transient Absorption spectroscopy

t=0 PUMP + evolution@Δt

ΔA=A_exc(Δt)-A_steady

$\Delta A = A_{exc}(\Delta t) - A_{steady}$

a) Photo-Bleaching ΔA<0 (Pauli blocking, hole in the initial state)
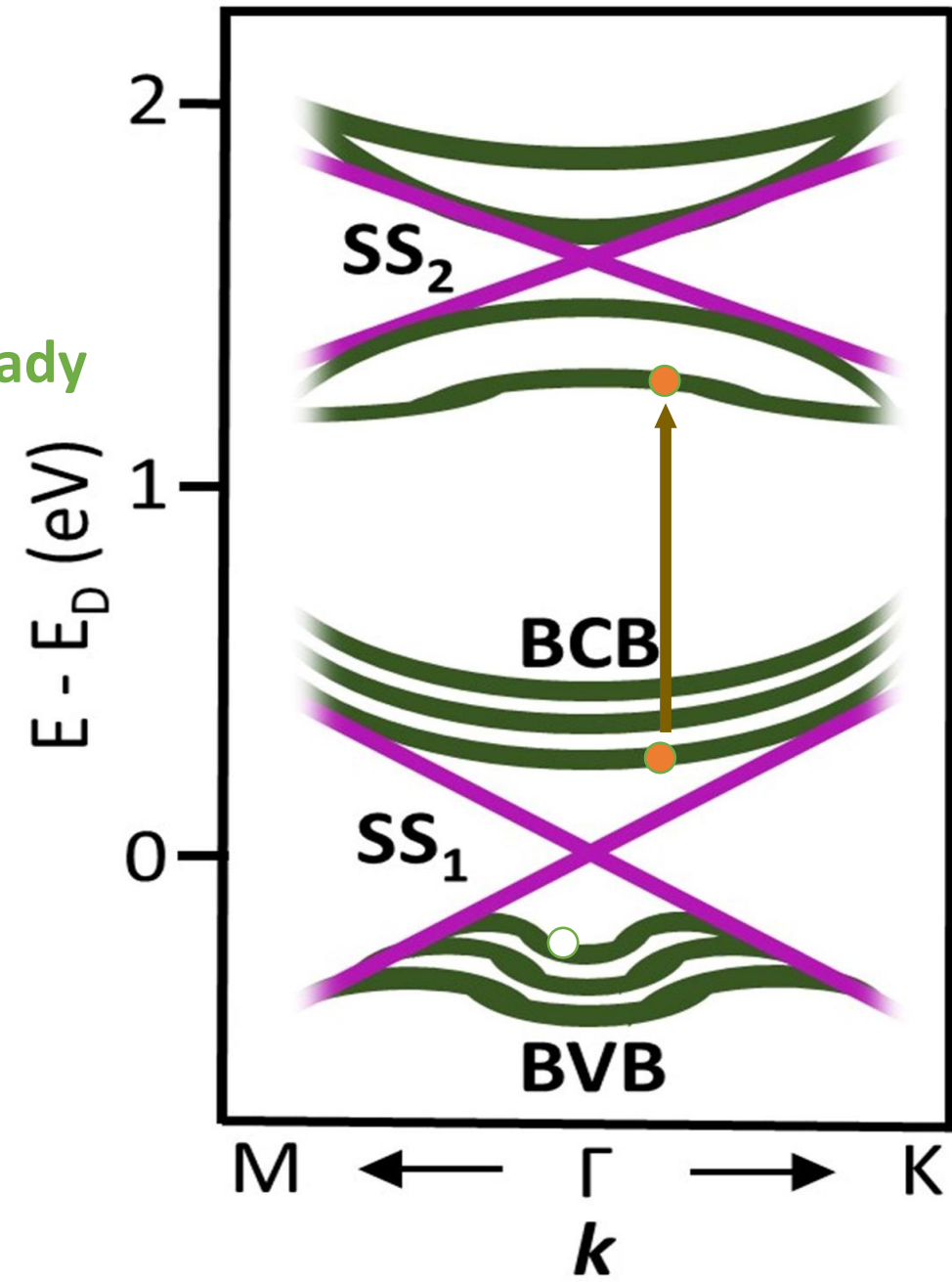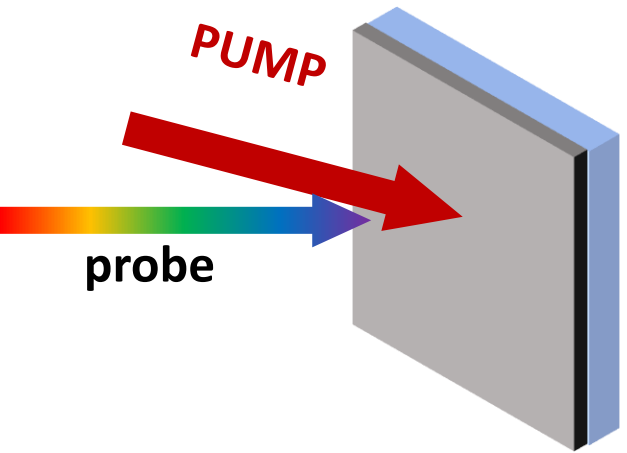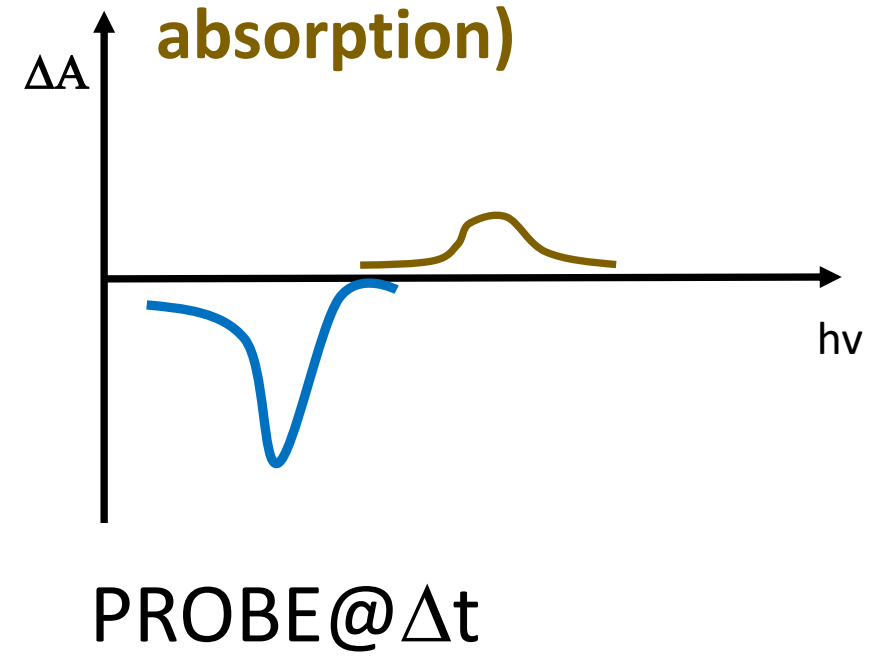
PROBE@Δt

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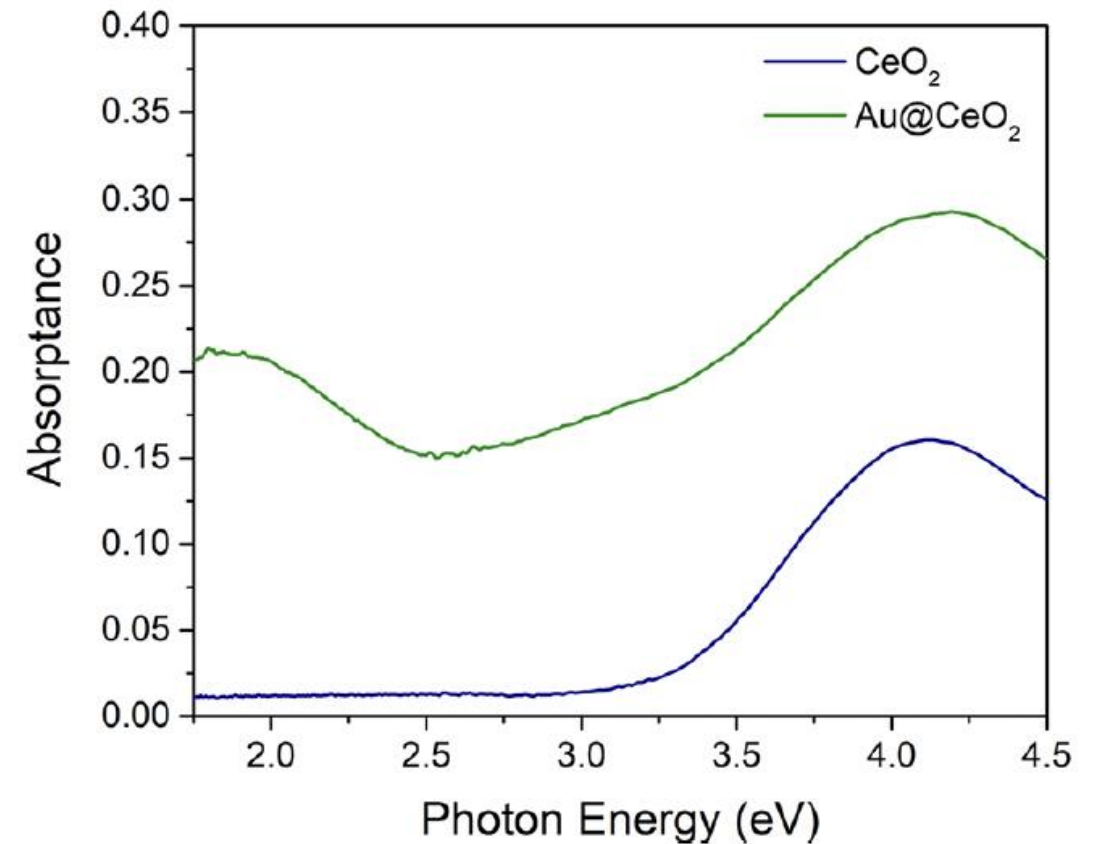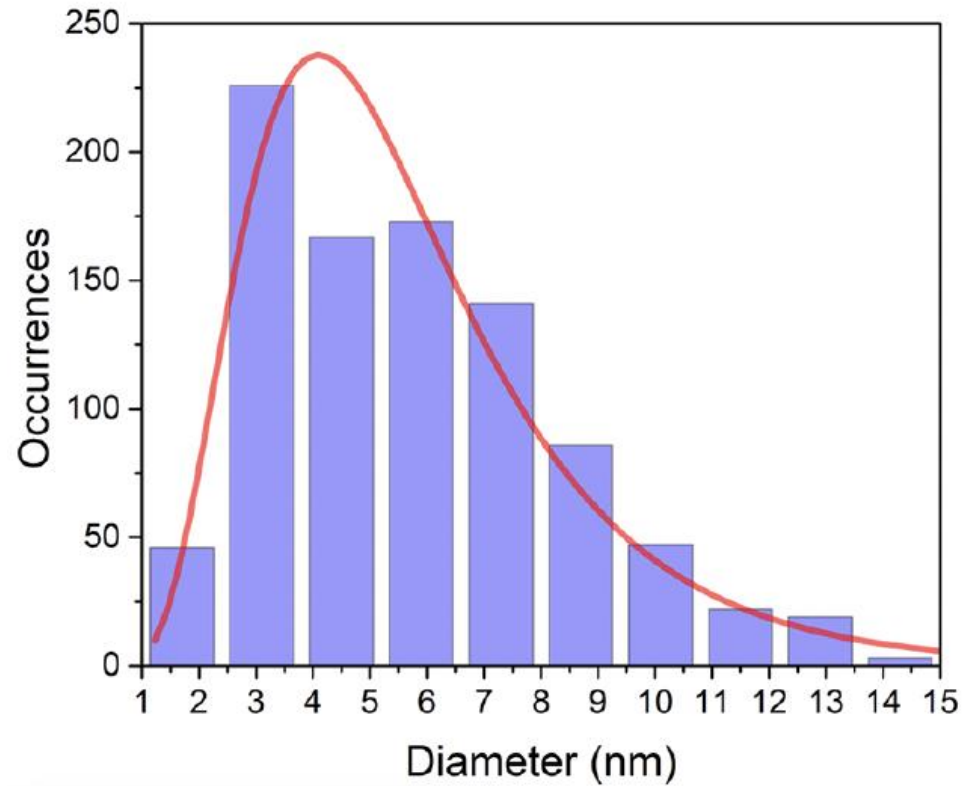
Eleonora Spurio et al, *ACS Photonics* **2023** *10* (5), 1566-1574
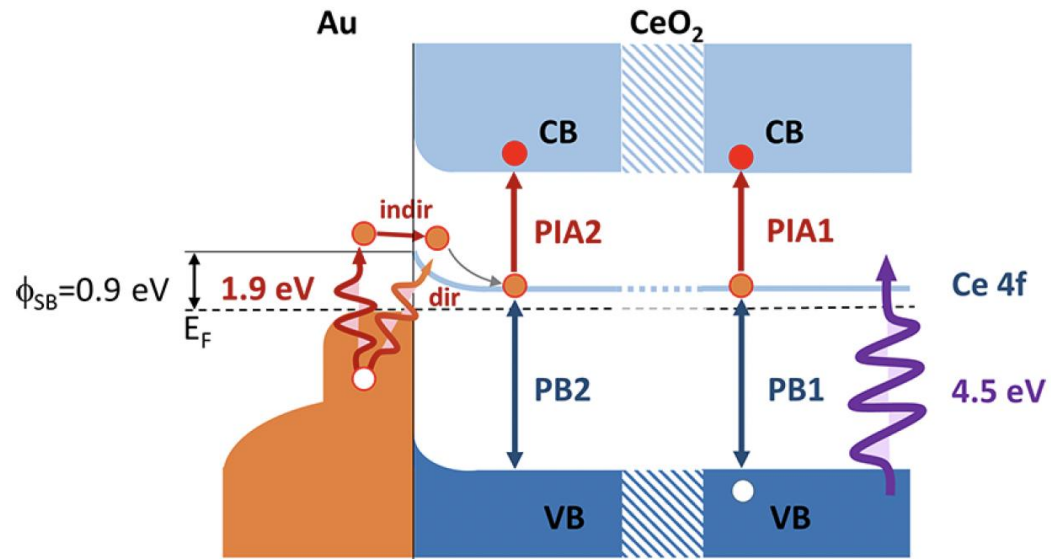
- Clear evidence of the presence of an injected 4f population in CeO2 at 1.9 eV excitation
- Transient signals after thermalization converge, consistent with the 4f population.
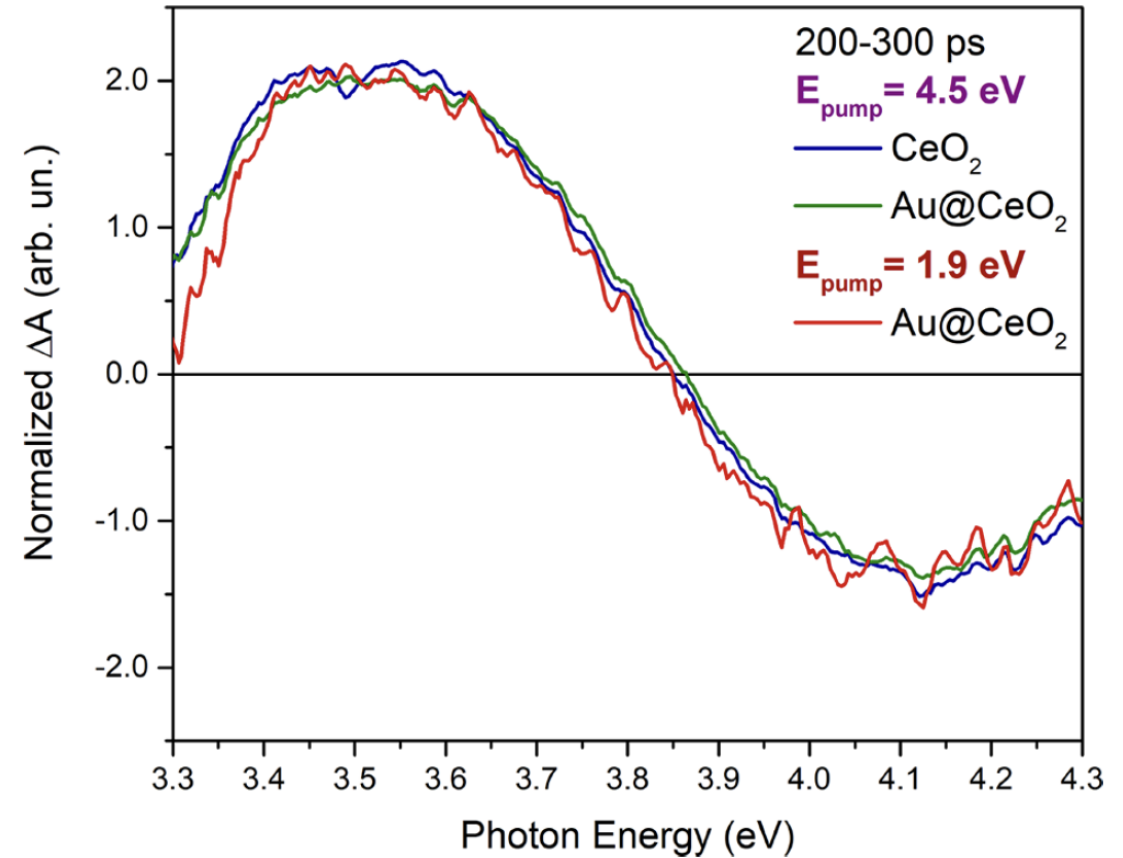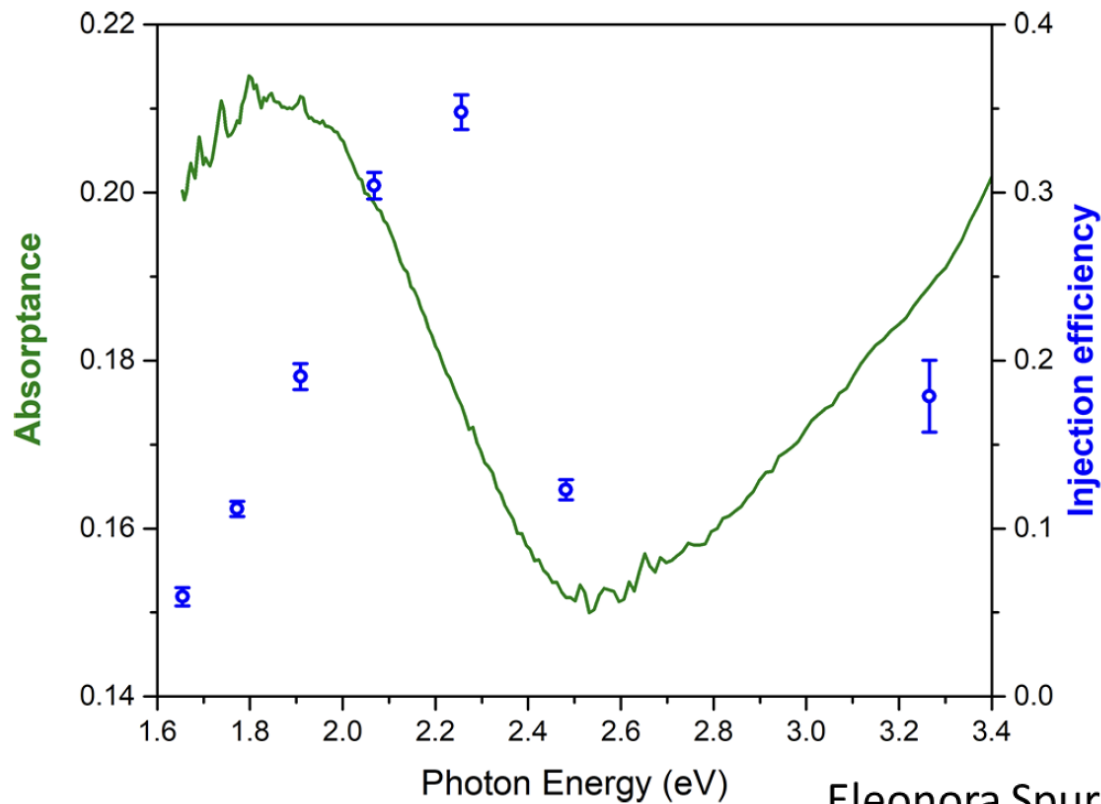
Eleonora Spurio et al, *ACS Photonics* **2023** *10* (5), 1566-1574

Injection efficiency as a function of photon energy

$$relative\ transient\ efficiency \sim \Delta A_{pl}/\Delta A_{int}$$

Injection efficiency changes as a function of photon energy
The maximum of the injection efficiency does not coincide with the maximum of the plasmon absorption.
Possible explanation is the excess energy with respect to the schottky barrier increases the number og hot electrons, the excess energy, the acceptance angle of hot electrons increases with the excess energy

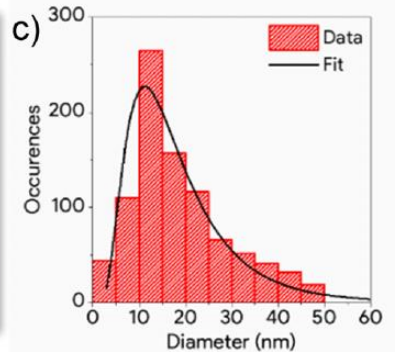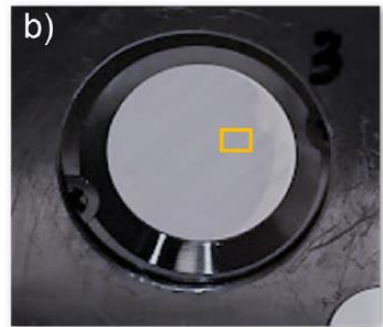Eleonora Spurio et al, *ACS Photonics* **2023** *10* (5), 1566-1574
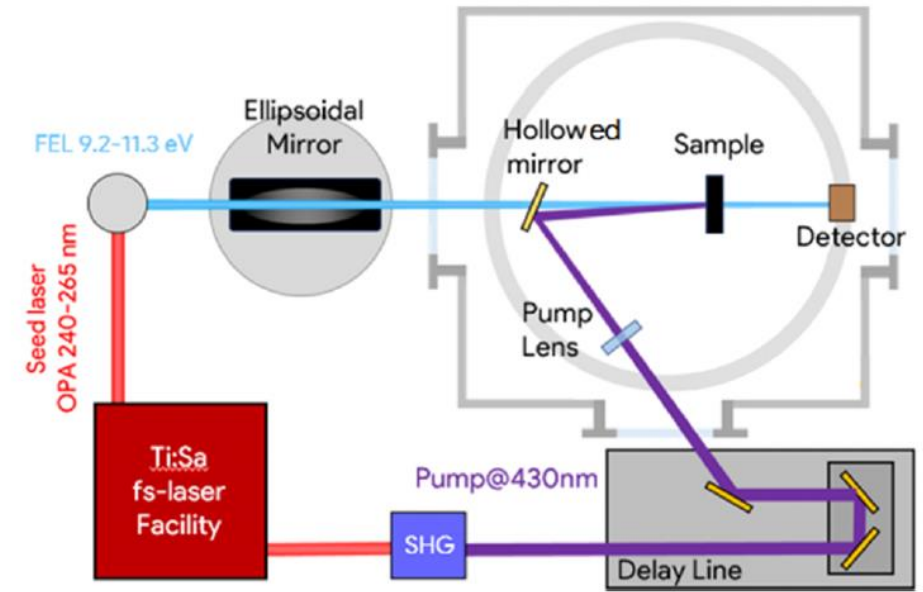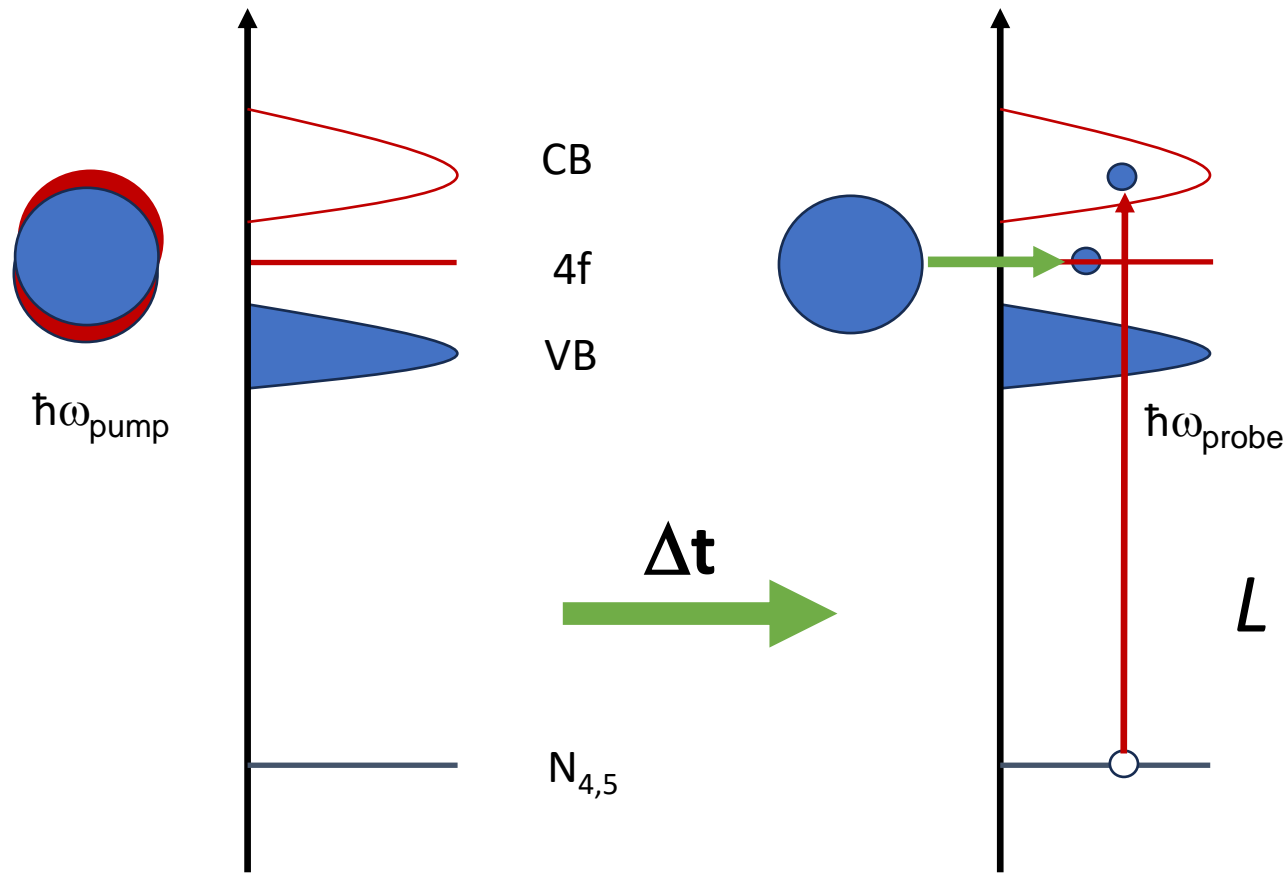
$$L \longrightarrow L\ 4f^{+1}$$

Plan of the experiment
- t= 0 plasmon excitation
- Search for excited states of the type Ce3+ via electron injection as the plasmon dephases
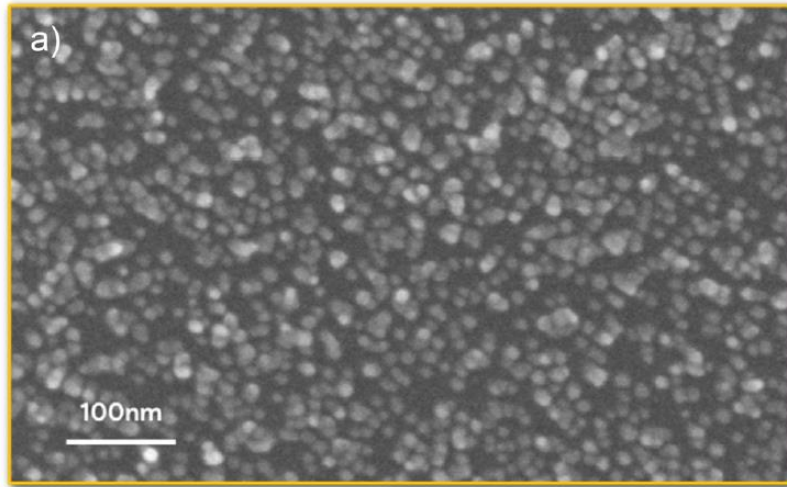
- *The Ag NPs/CeO2 samples were grown at the SESAMo laboratories in Modena on ultrathin (100 nm) parylene-N (Figure 1b).*
- *Mass-selected Ag NPs with an average diameter d of ~20 nm (Figure 1a,c) grown by an inert gas aggregation cluster based on magnetron sputtering.*
- *The NPs were coevaporated with cerium oxide forming a film with embedded NPs*
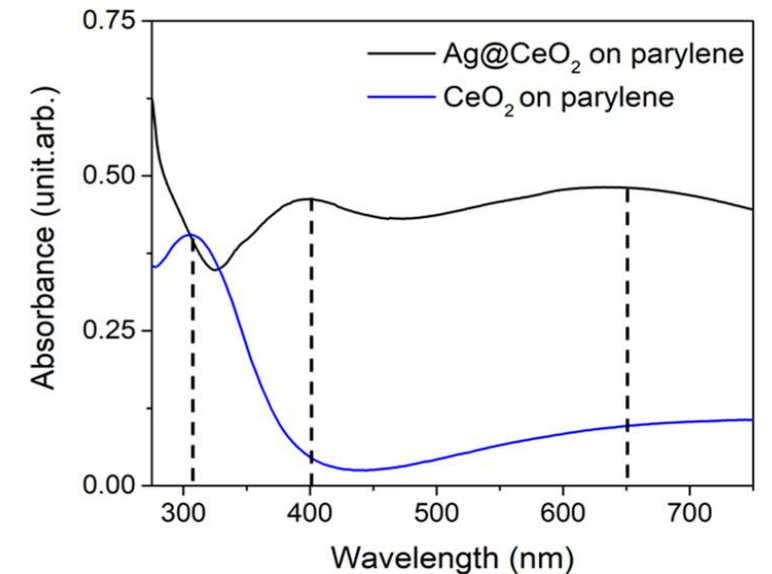
J. S. Pelli Cresi et al., *Nano Letters* **2021** *21* (4), 1729-1734

Strong mix in the ground state between the configurations $L^{-n}4f^n$ in Ce compounds gives rise to a strong difference of the XAS lineshape. After 200 fs a 20% popuplation of Ce3+.

J. S. Pelli Cresi et al., *Nano Letters* **2021** *21* (4), 1729-1734

$$\eta = \frac{n_{el}}{n_{ph}} = \frac{12944 \; electrons}{1.6 \cdot 10^5 \; photons} \sim 8\%$$

- The contribution of the Ce^{3+} 20% spectrum dynamics after 100 ps allows to determine, via the CeO2 volume, the number of injected electrons.
- The absorption coefficient allows to evaluate the number of photons absorbed by the film.

Space Charge Model

L.-P. Oloff et al

J. Appl. Phys. 119, 225106 (2016)

$$\mu(t) = E_{k0} - E_k' = e(V^-(z(t)) - V^+(z(t)))$$

$$V^\pm(z(t)) = \frac{N^\pm e}{4\pi^{3/2}\varepsilon_0}$$

$$\int_0^\infty \frac{\exp\left(-\frac{z(t)^2}{2\sigma_z^2 + q}\right)}{\sqrt{(2\sigma_x^2 + q)(2\sigma_y^2 + q)(2\sigma_z^2 + q)}} \mathrm{d}q$$

J.S. Pelli Cresi et al, *J. Phys. Chem. C* 2022, 126, 11174–11181

- The space charge model provides a quantitative analysis of the holes lifetime in the case of plasmon excitation.
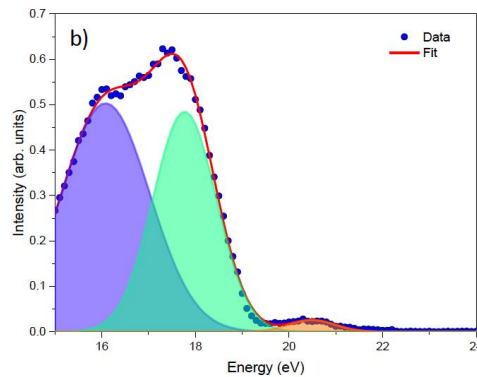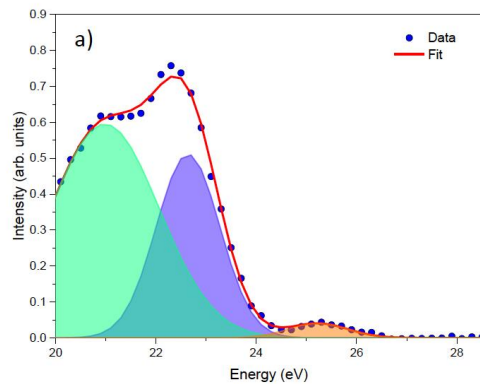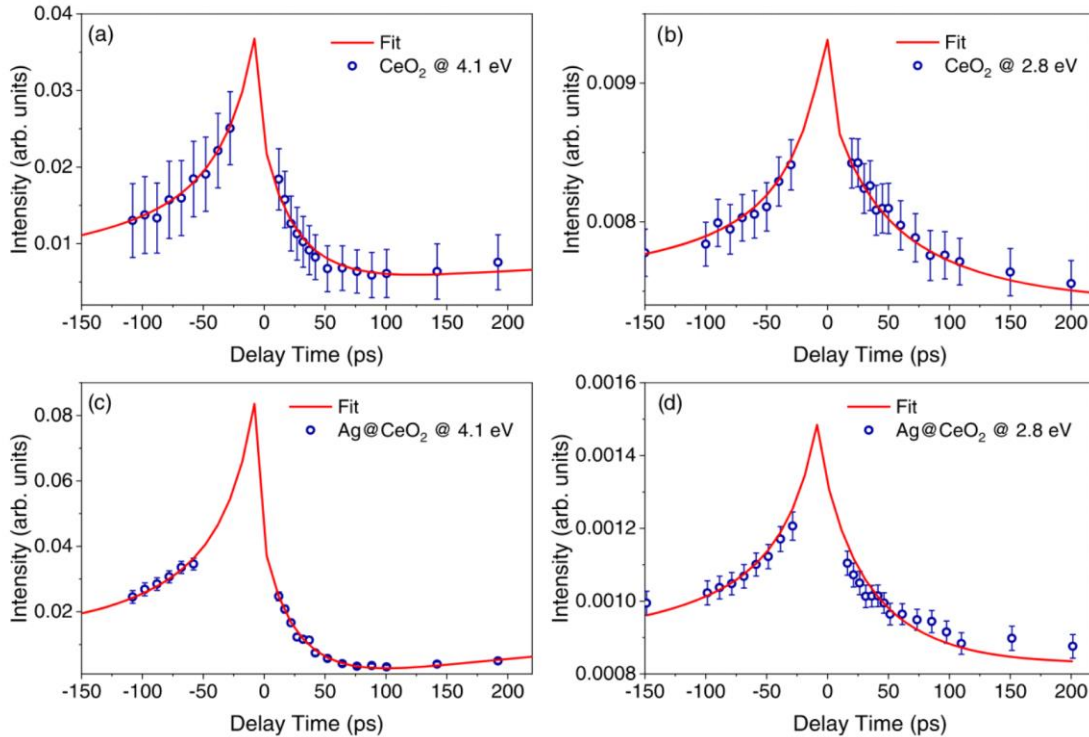- Hole lifetime of Ag@CeO2 excited at plasmon resonance (2.8 eV) is significative higher (300 ps) than that (150 ps) of the non-resonant (4.1 eV) excitation.

J.S. Pelli Cresi et al,

J. Phys. Chem. C 2022, 126, 11174–11181

sample	pump (eV)/fluence (μJ)	hole lifetime (ps)	fraction of holes X	N^-	drain current (pA)
CeO_2	4.1/0.7	150	0.46	2700	104 (2.6 10^4 carriers)
	2.8/0.9	87	0.29	140	27 (6.7 10^3 carriers)
Ag@CeO_2	4.1/0.7	153	0.54	6500	600 (1.5 10^5 carriers)
	2.8/1	300	0.35	1900	320 (8 10^4 carriers)
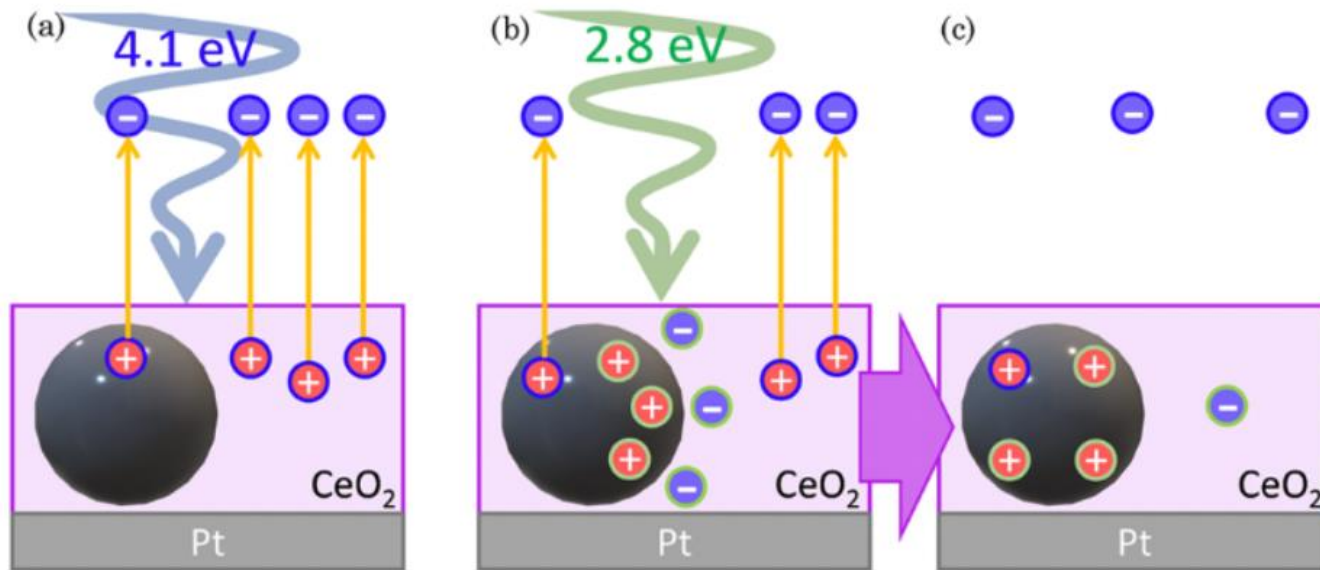
J.S. Pelli Cresi et al,
J. Phys. Chem. C 2022, 126, 11174–11181

After the plasmon de-excitation electrons are injected in CeO2.

Positive ions in CeO2, produced by photoionization, are neutralised by the injected electrons.

The positive charge are mainly localised on the metal particles.

The recharge is provided by CeO2 defects and the 300 ps time scale represent an estimation of the recharging any Ag@CeO2 device based on the plasmon electron injection.

$$\eta = \frac{n_{el}}{n_{ph}} = \frac{12944 \; electrons}{1.6 \cdot 10^5 \; photons} \sim 8\%$$

- The contribution of the Ce^{3+} 20% spectrum dynamics after 100 ps allows to determine, via the CeO2 volume, the number of injected electrons.
- The absorption coefficient allows to evaluate the number of photons absorbed by the film.

What is missing?

In a steady-state or quasi steady-state process recharge process should be taken into account

The flux of electrons from the nanoparticles should be balanced by the recovery of electrons from the semiconductor, otherwise the positive charge on the nanoparticle hampers the emission of electrons lowering the efficiency.

Considering the 300 ps hole lifetime retrieved by the TR-PES as an educated guess of a recharge timescale the efficiency of injection in a steady state could be of the order of magnitude 0.1-0.01%.

A microscopic picture of electron injection in CeO2 due to the plasmon decay of the metal nanoparticle (Au, Ag) via the study of the excited state populatation was presented.

- **Demostration of the electron injection in the 4f states of Ce by NIR-UV (joint density of states) and X-ray (multiplets effects) Transient Absorption Spectroscopy.**

- **Quantitative determination of an efficiency associated to the ultrafast excitation in a quasi equilibrium state (e-e processes and phonon electron processes thermalization) via transient absorption spectroscopy.**

- **Quantitative guess on the re-charge time scale and re-scaling of the transient efficiency.**

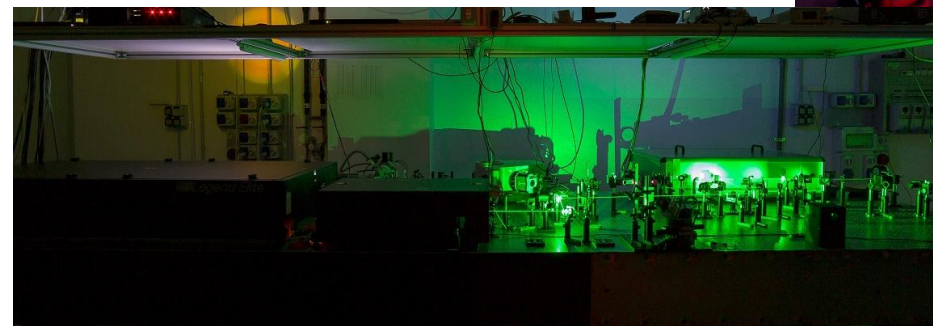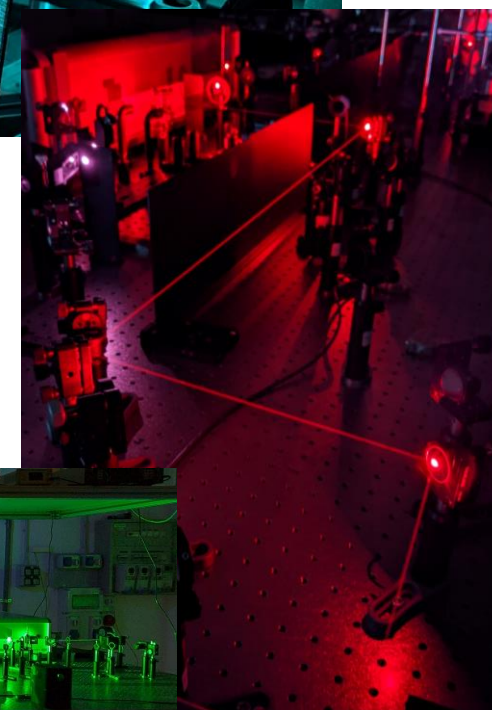- **Device architecture should optimize recharge timescale.**

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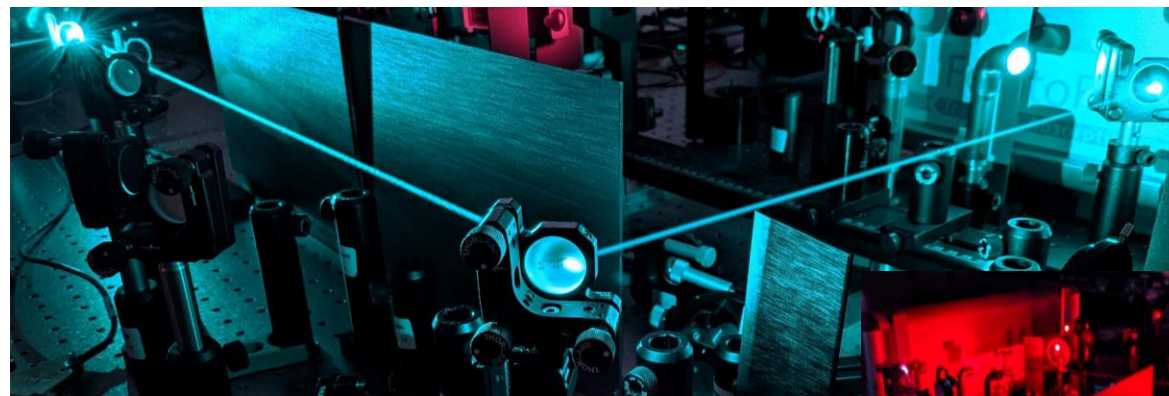
- Femtosecond Transient Absorption Spectroscopy
- PhotoLuminescence steady state and time-resolved

https://www.ism.cnr.it/it/eurofel-support-laboratory-efsl.html

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