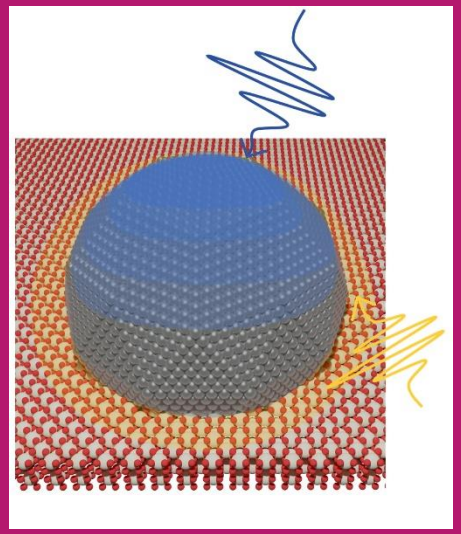
Dynamics of charge excitations in metal-oxide nanostructures for energy conversion

Paola Luches, Istituto Nanoscienze - Consiglio Nazionale delle Ricerche, Modena



Federico Boscherini, University of Bologna

Patrick O'Keeffe, Daniele Catone, Flash.it ESFL, CNR-ISM, Roma

Jacopo Stefano Pelli Cresi, Emiliano Principi, FERMI ELETTRA, Trieste

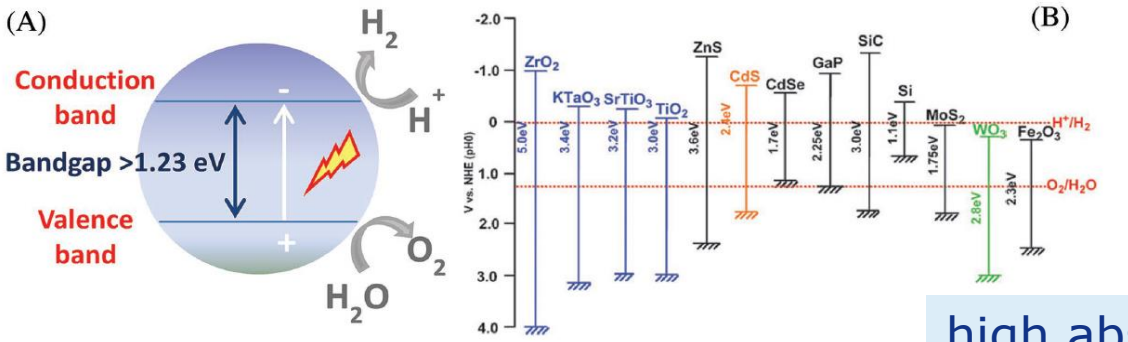
S. D'Addato, University of Modena and Reggio Emilia, Italy

S. Benedetti, A. di Bona, CNR-NANO, Modena, Italy

Oxide-based materials for photocatalysis

stable and abundant materials

catalysis + solar light
= photocatalysis



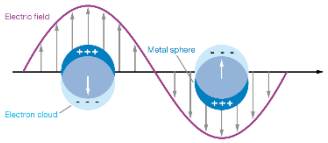
S. Y. Tee et al. Adv. Sci.4, 1600337 (2017).

high absorption CS in the visible range

E_{BG} in the UV for several oxides → low efficiency for solar light absorption

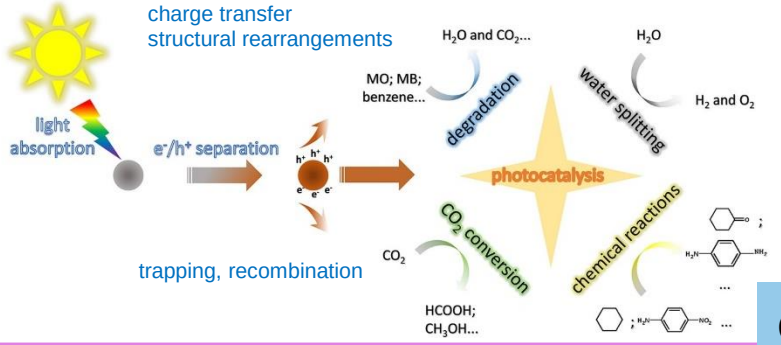
Strategies to increase visible light absorption:

- introduce dopants or defects
- reduce dimensionality
- ternary or mixed oxides
- coupling with plasmonic nanoparticles



LSPR

Light absorption + conv. into chemical energy

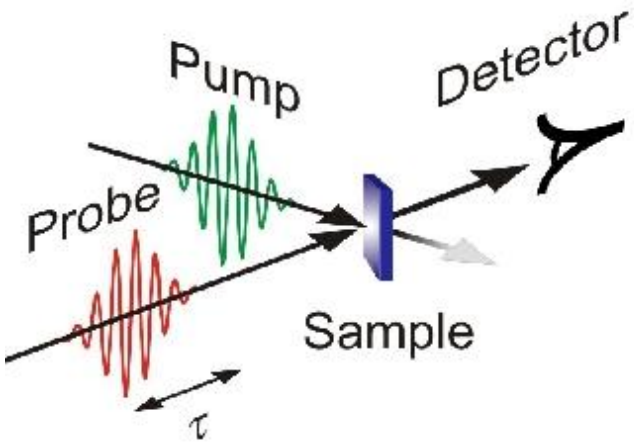


M. Han et al. Nano Today 19, 201 (2018).

understand and optimize light-induced functionalities

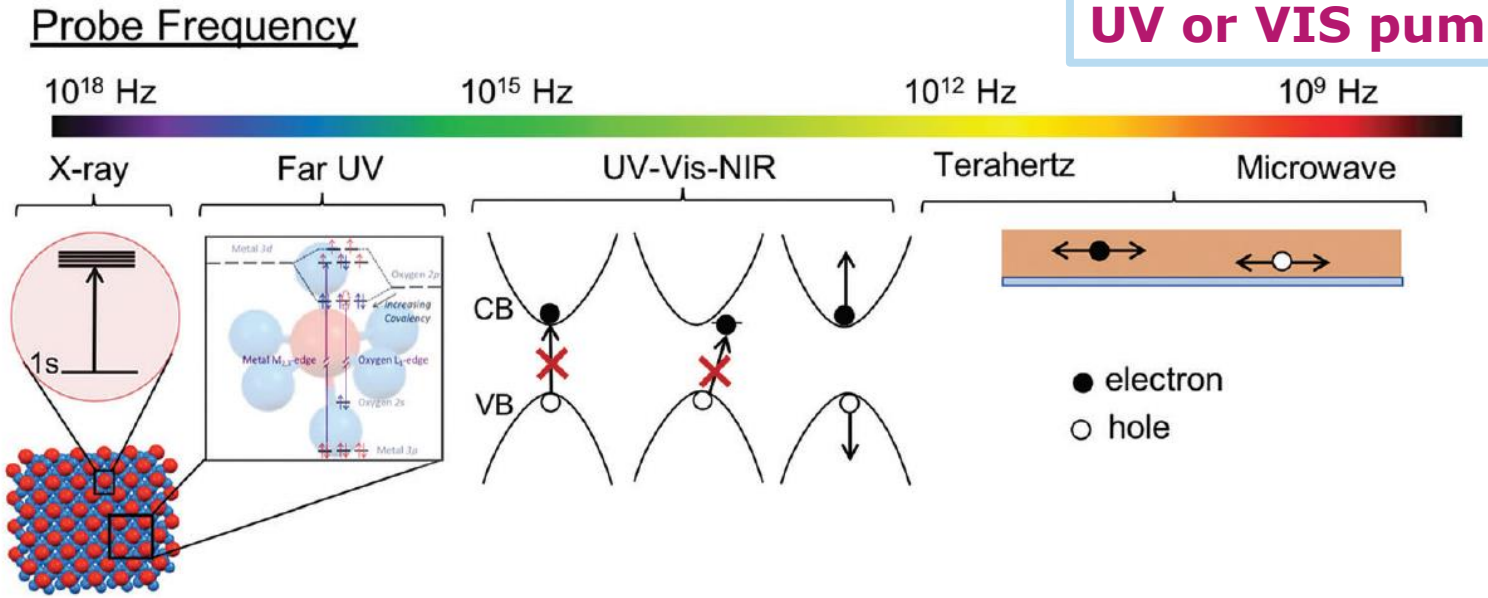
dynamic studies using ultrafast techniques

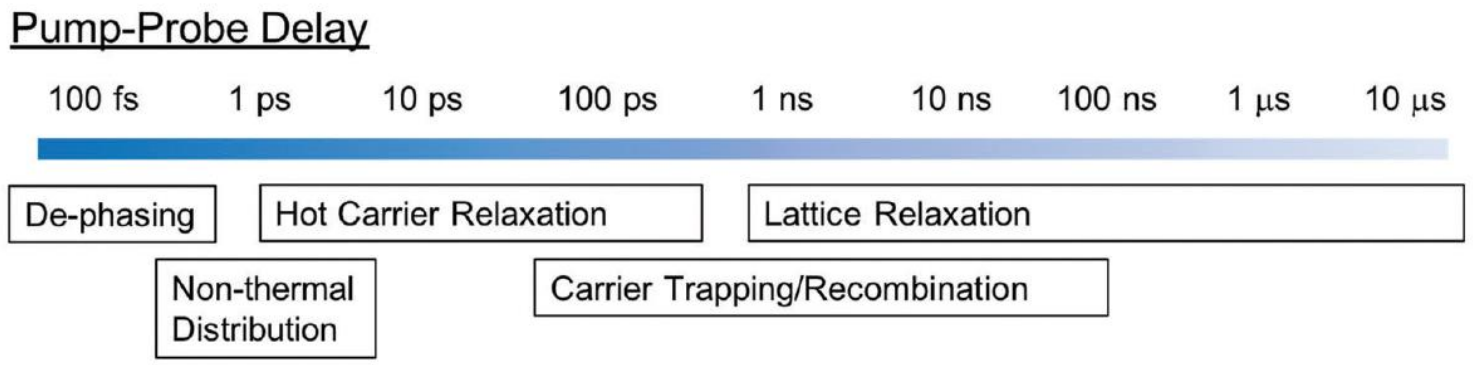
Pump-probe spectroscopies



TRANSIENT ABSORPTION SPECTROSCOPIES

UV or VIS pump

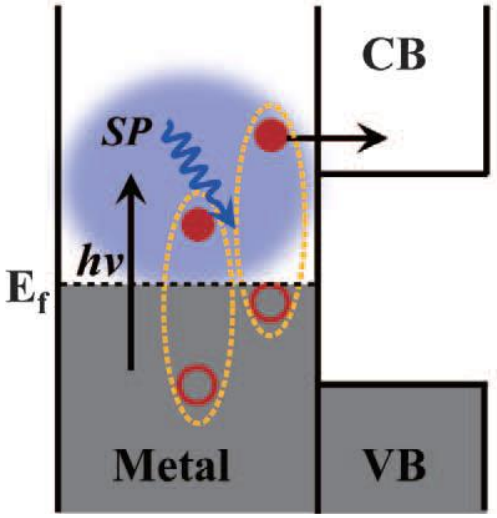




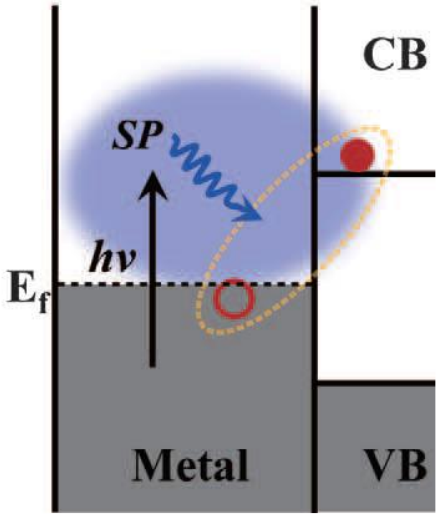
K. E. Knowles et al. J. Mater. Chem. C *6, 11853 (2018).*

Semiconducting oxides + plasmonic NPs

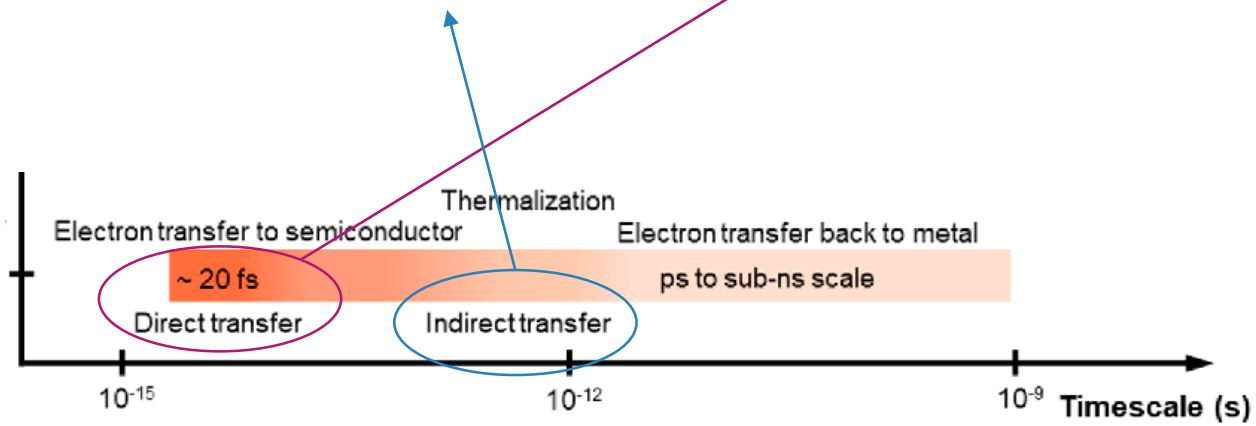
INDIRECT HOT e^- INJECTION



DIRECT INJECTION



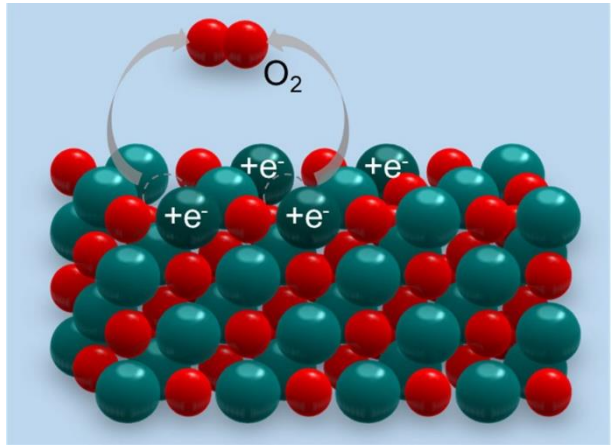
K. Wu et al. Science 349, 632 (2015)

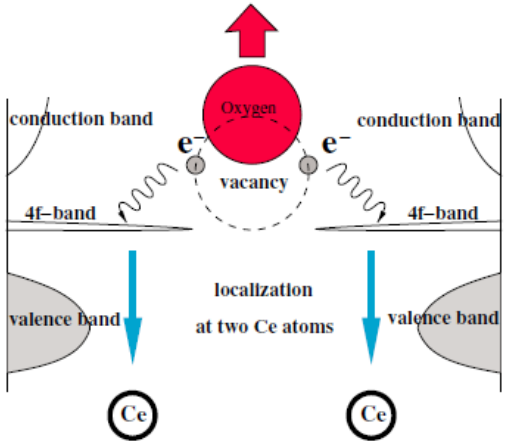


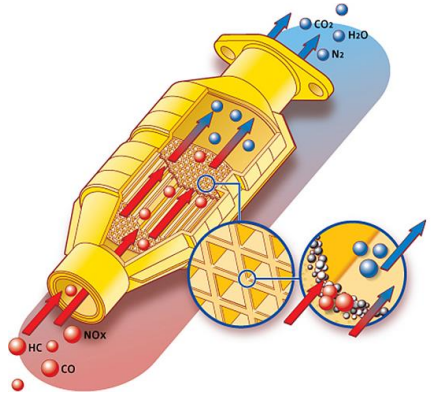
Y. Zhang et al. Chem. Rev. 118, 2927 (2018)

Cerium oxide based materials

CeO_2 - reducibility

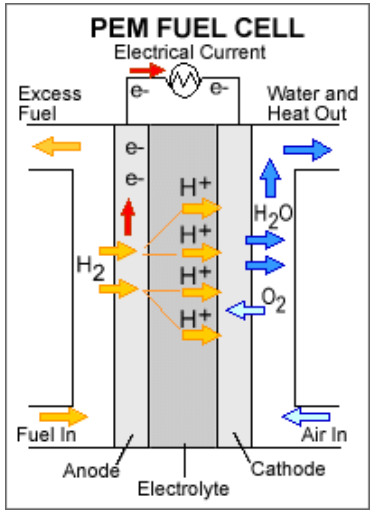




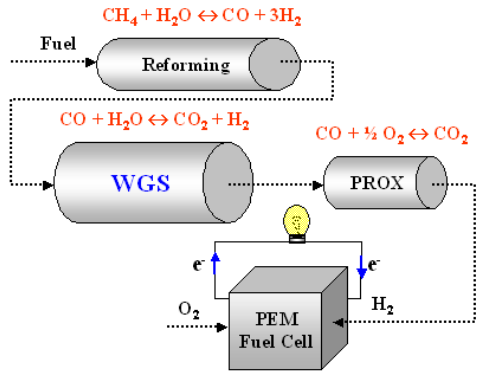


three-way catalytic converters

CO oxidation+ deNO_x

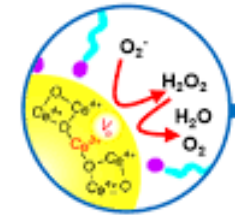


fuel cell electrodes



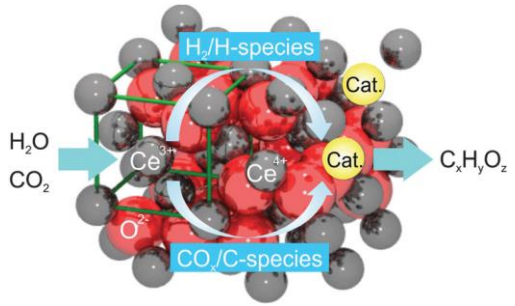
H_2 purification

Water-gas shift reaction & CO prox



Recyclable ROS-scavenging activity

antioxidant additive in biomaterials

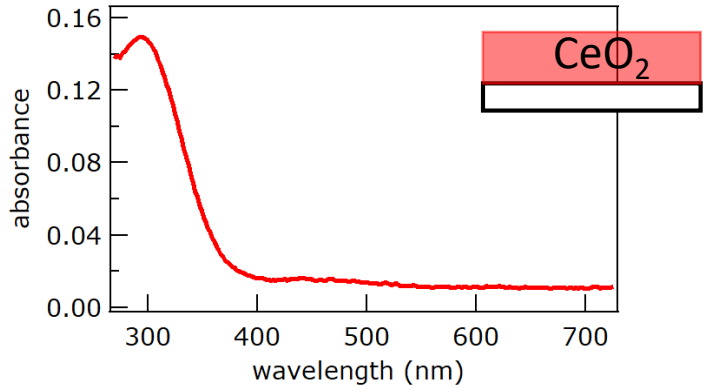


F. Lin et al, Energy Environ. Sci., 2016,9, 2400 (2016).

conversion of CO_2 into fuels

E_{BG} =3.2 – 4.0 eV

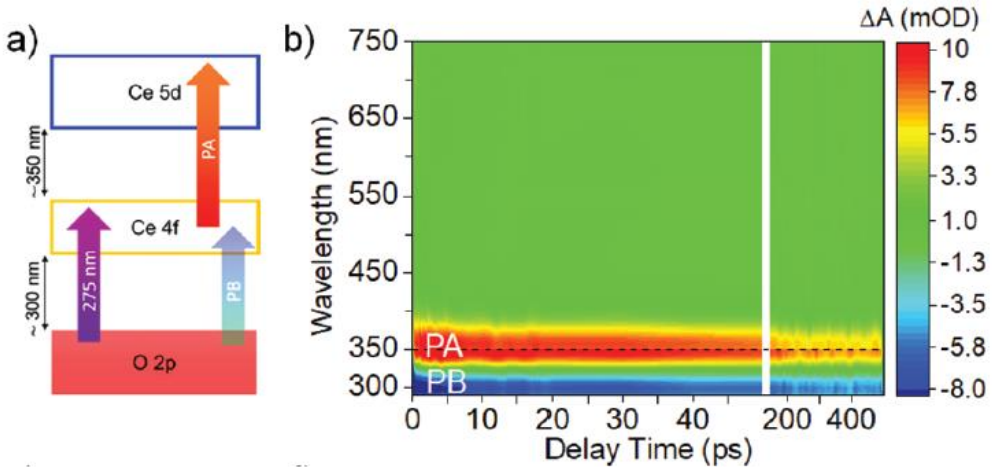
Dynamics of excited states in cerium oxide



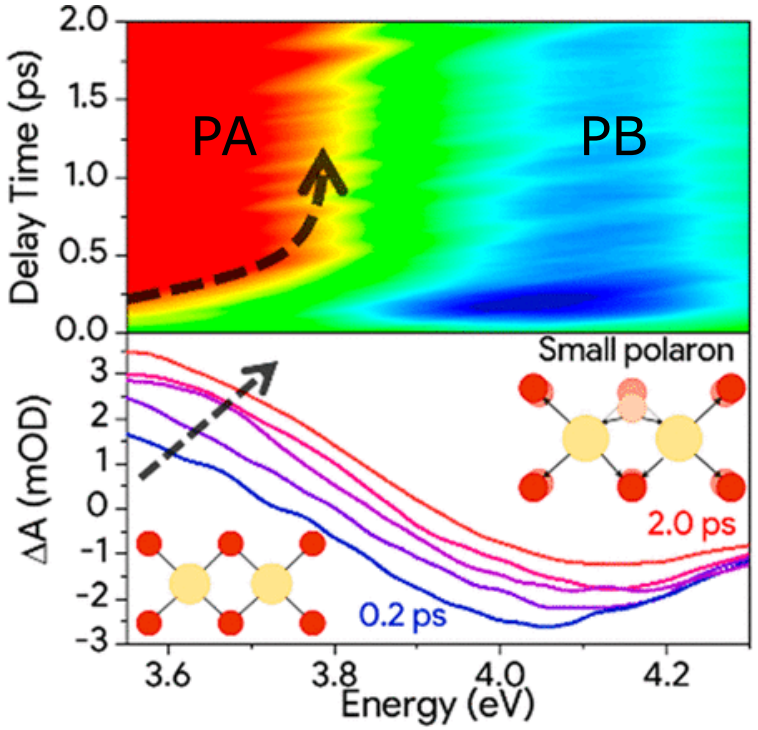
P. O'Keeffe, D. Catone

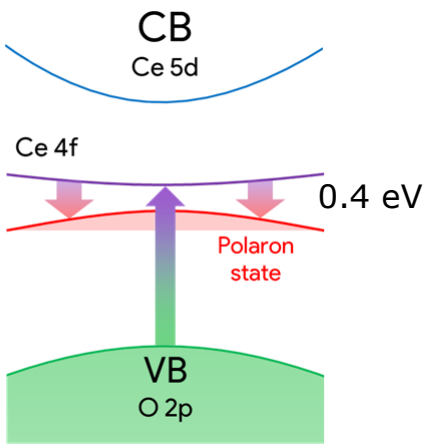
pump 275 nm

$\Delta A(t,\lambda) = A_{pump} - A_{no\text{-}pump}$



excited-state lifetime > 500 ps



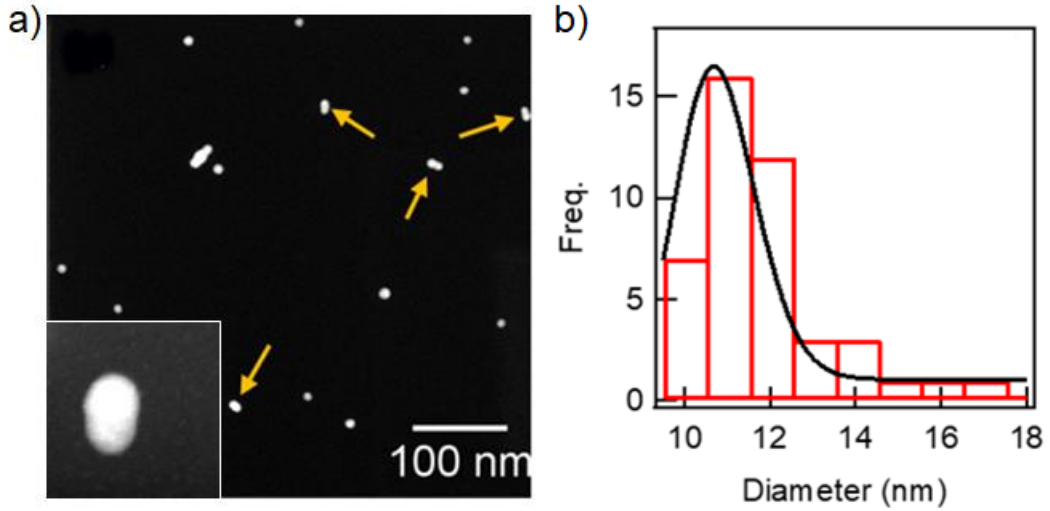


ultrafast (t<330 fs) formation of small polarons

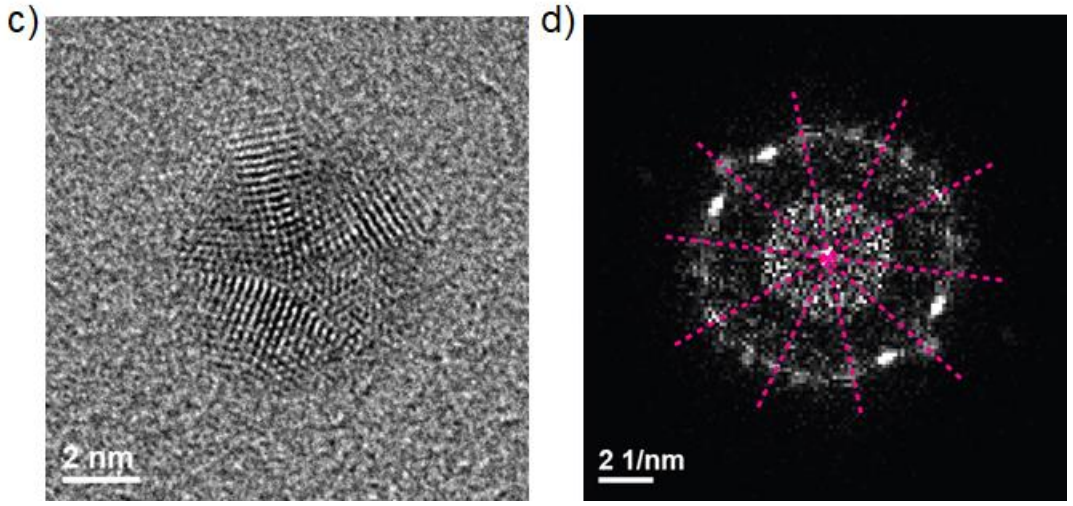
$E_{polaron}$ = 0.4 eV **transient increase of reducibility**

J. S. Pelli Cresi et al. J. Phys. Chem. Lett. 11, 5686 (2020).

Sensitization of CeO_2 to visible light → Ag NPs



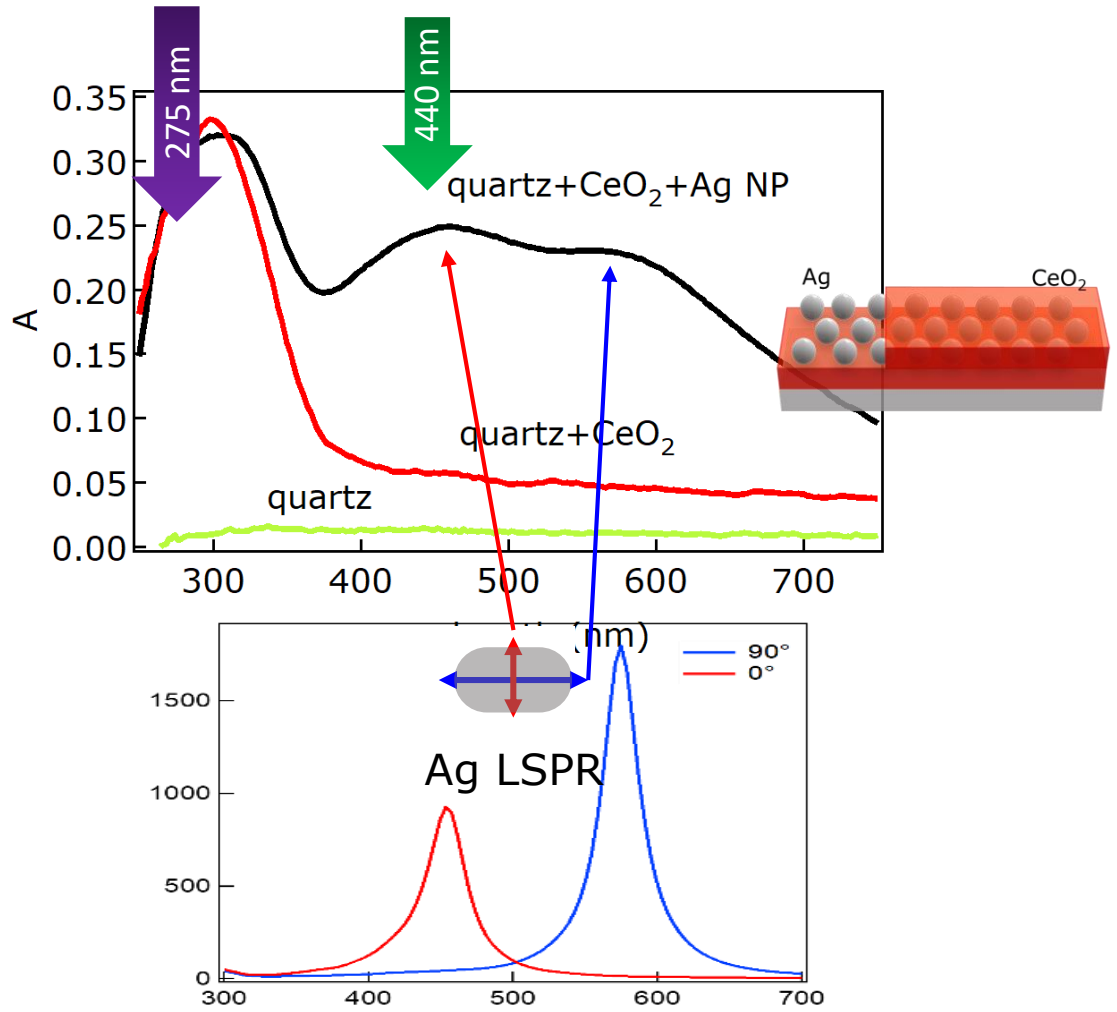
- partial agglomeration - NP diameter ~ 10 nm



- polyhedral shape - multi-twinned structure

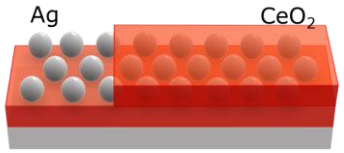
UV pump
VB → Ce 4f

VIS pump
LSPR

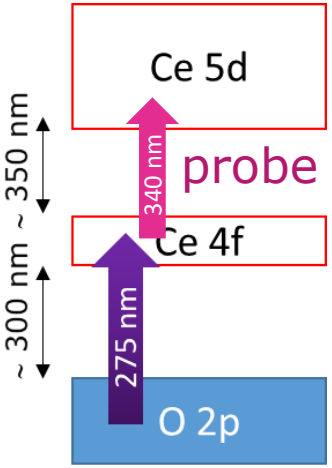


J. S. Pelli Cresi et al. Nanoscale 11, 10282 (2019).

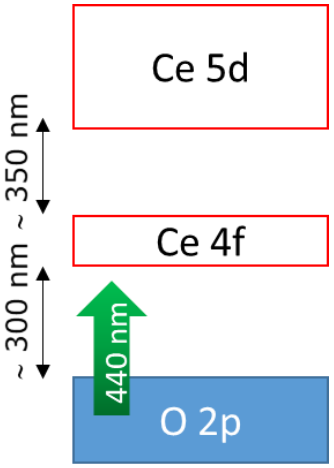
Dynamics of excited states in CeO_2 + Ag NPs



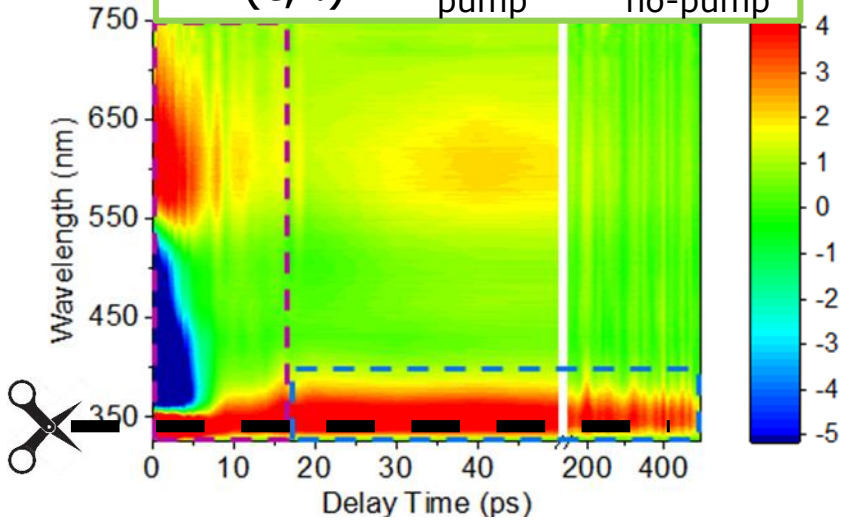
UV pump
275 nm
above BG

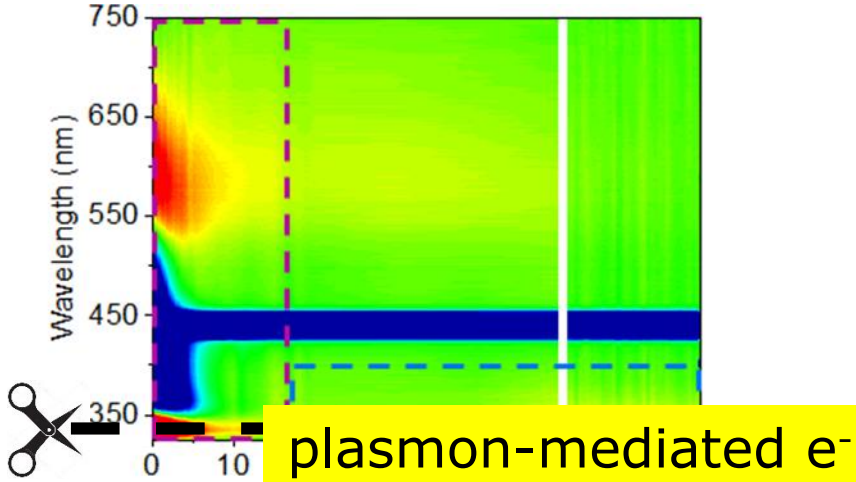


VIS pump
below BG
@LSPR

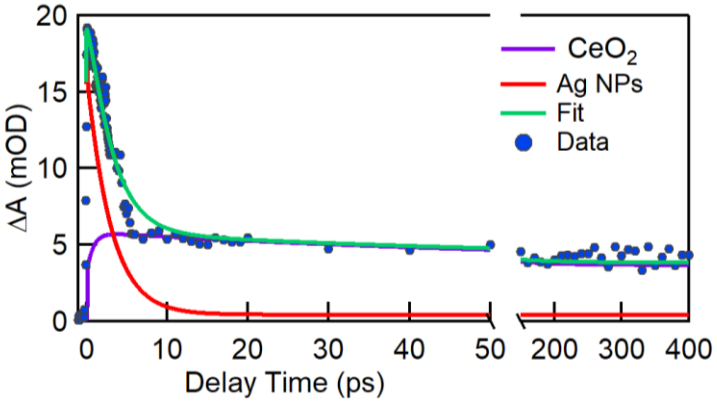


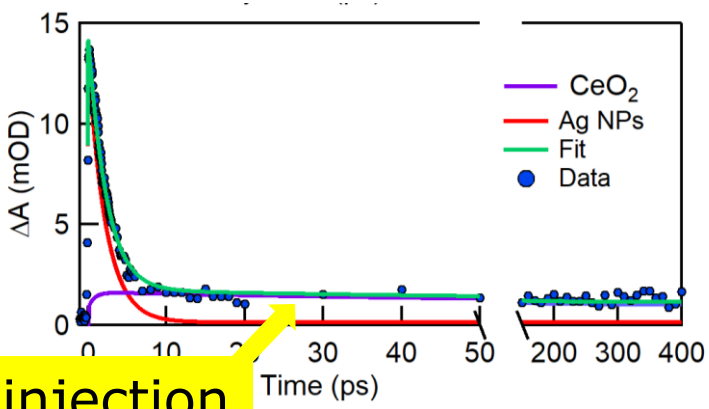
$\Delta A(t,\lambda) = A_{pump} - A_{no\text{-}pump}$





time cuts @ 340 nm

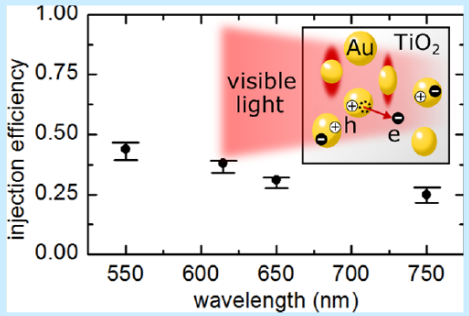




plasmon-mediated e^- injection from Ag NP to CeO_2

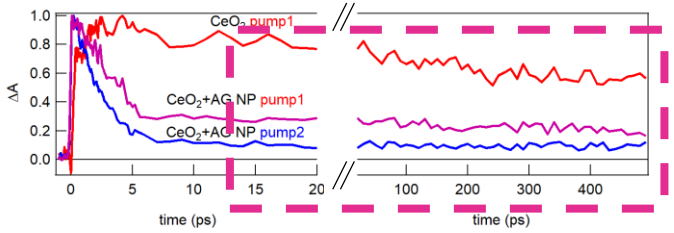
J. S. Pelli Cresi et al. Nanoscale 11, 10282 (2019).

Electron injection efficiency in CeO_2 + Ag NPs

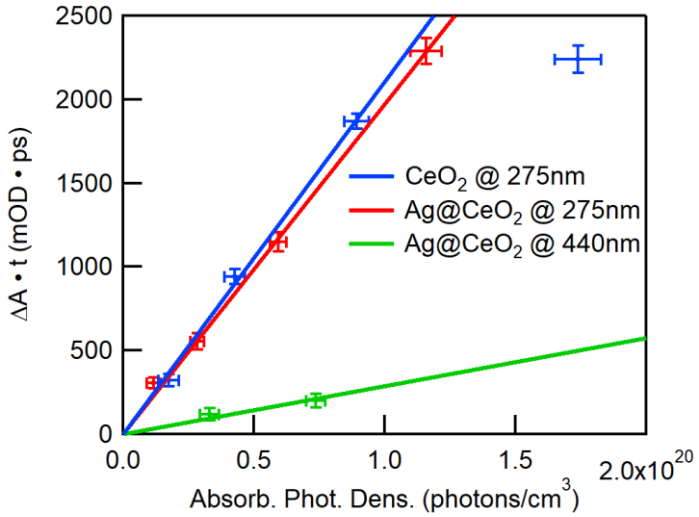


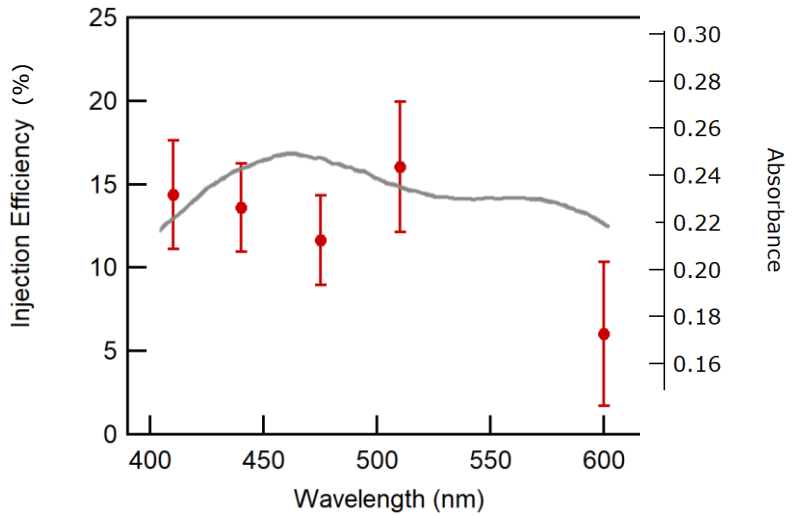
D. Ratchford et al., Nanoletters 17, 6047 (2017).

injection efficiency → number of electrons injected by LSPR in CeO_2 per absorbed photon



ΔA at different pump energies and fluences





$$n_{ph} = \frac{A(\lambda_{pump}) \cdot F}{D \cdot E_{pump}}$$

$$\eta = \frac{k_{Ag@CeO2}}{k_{CeO2}}$$

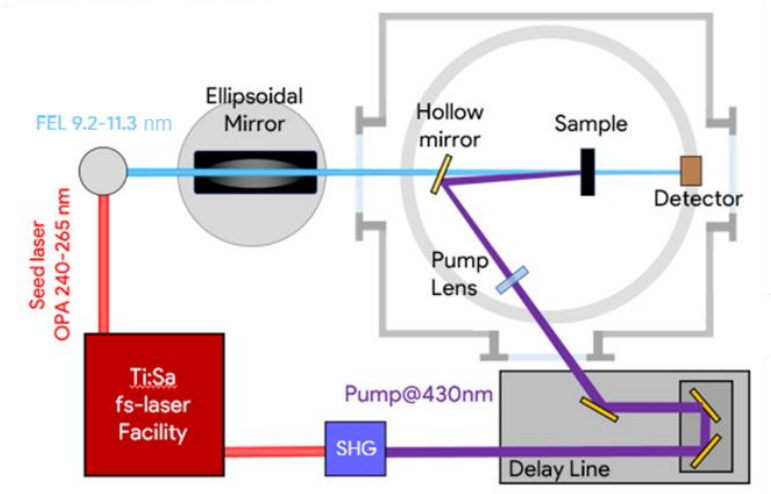
J. S. Pelli Cresi et al. Nanoscale 11, 10282 (2019).

high injection efficiency

Combining time resolution and chemical sensitivity

Fermi@ELETTRA

Elettra Sincrotrone Trieste



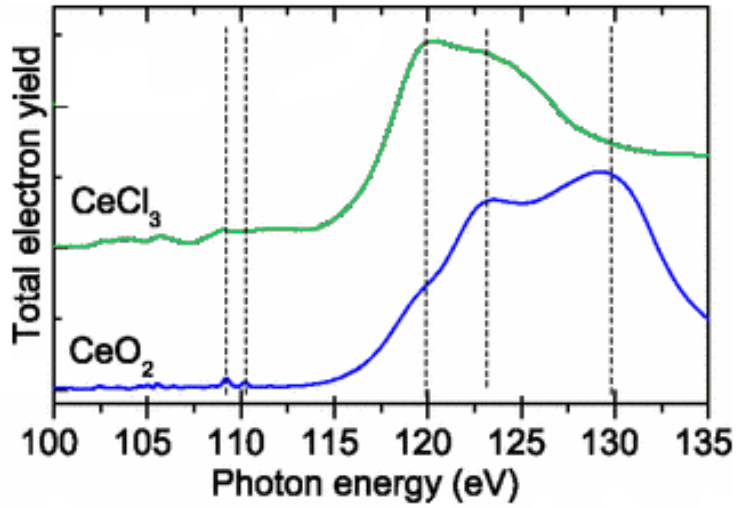
FEL2
single shot operation mode

CeO_2 and $Ag@CeO_2$ films on parylene-N membranes (100 nm)

EIS-TIMEX
Pump-probe X-ray Absorption Spectroscopy

Coll. : E. Principi, J. S. Pelli Cresi

Ce N_{45}-edge



S. O. Kucheyev et al., Phys. Rev. B **76**, 235420 (2007)

pump → 410 nm LSPR ($<E_{BG}$)

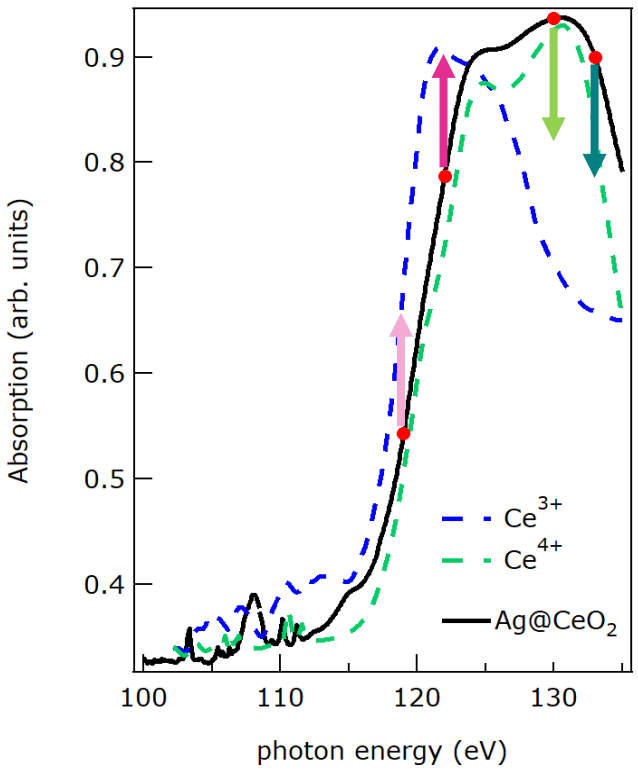
FEL probe → Ce N_{45} edge = 100-135 eV

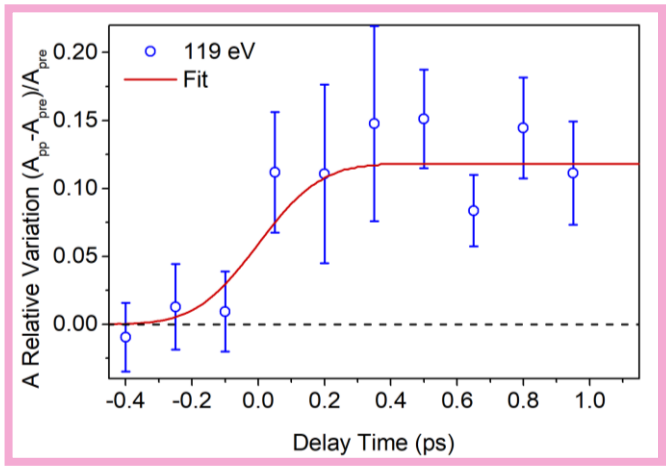
pump-probe Ce N_{45} XAS on CeO_2 + Ag NPs

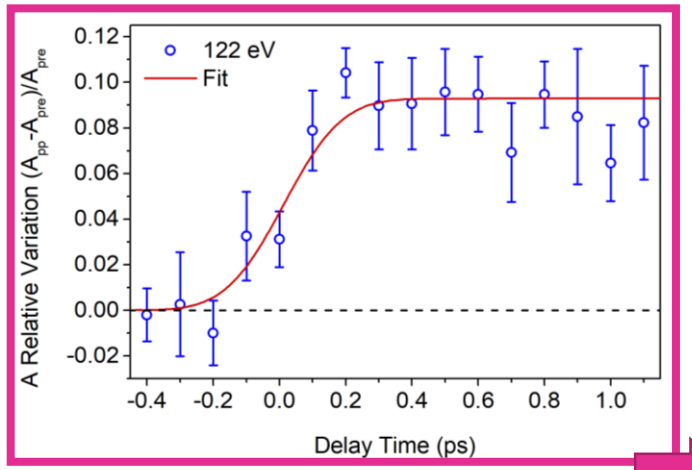
pump → Ag LSPR = 410 nm (<E_{BG})

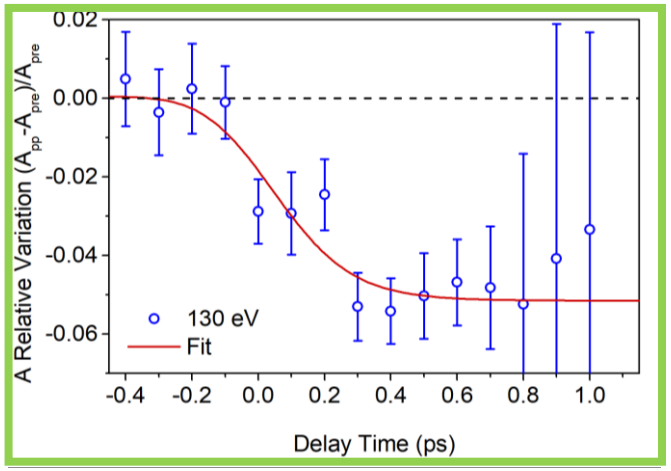
probe → Ce N_{45} edge = 100-140 eV (8.8–12.4 nm)

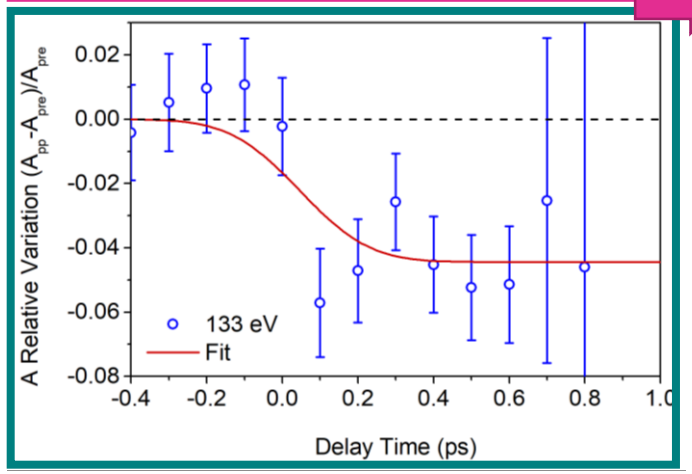
BEAR – ELETTRA
Ce $N_{4,5}$ edge XAS











increase of TA

Ce^{4+} → Ce^{3+}

LSPR-mediated charge transfer

t < 200 fs

decrease of TA

J. S. Pelli Cresi et al. Nano Letters 21, 1729 (2021).

Au and Cu plasmonic NPs

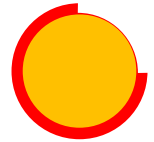
Au Cu NPs → LSPR in the visible range

- **Au**: + very stable → different oxide/NP architectures

  sharp interfaces

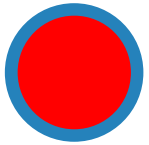
  - expensive

ultrathin shells

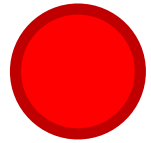


discontinuous shells

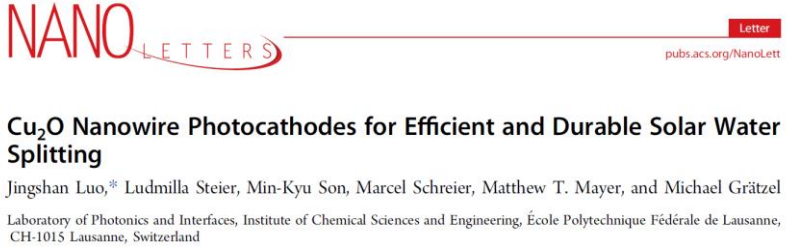
- **Cu**: + cheap and abundant
  - easily oxidized
  + protective oxide shells
  + interesting catalytic properties of Cu_xO



oxide shells



Cu_xO shells



NANO LETTERS

Letter

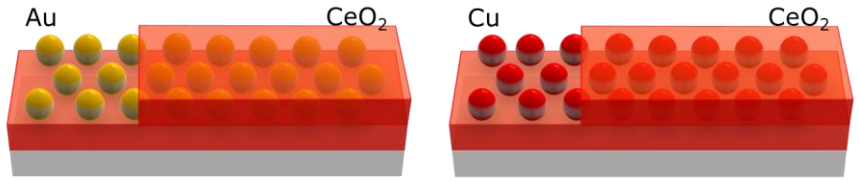
pubs.acs.org/NanoLett

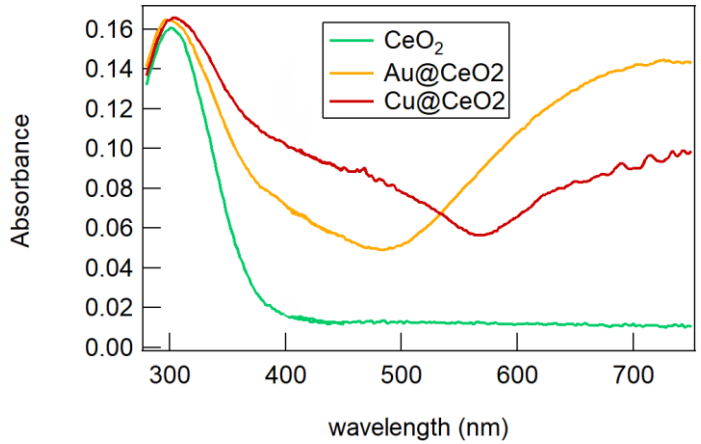
Cu_2O Nanowire Photocathodes for Efficient and Durable Solar Water Splitting

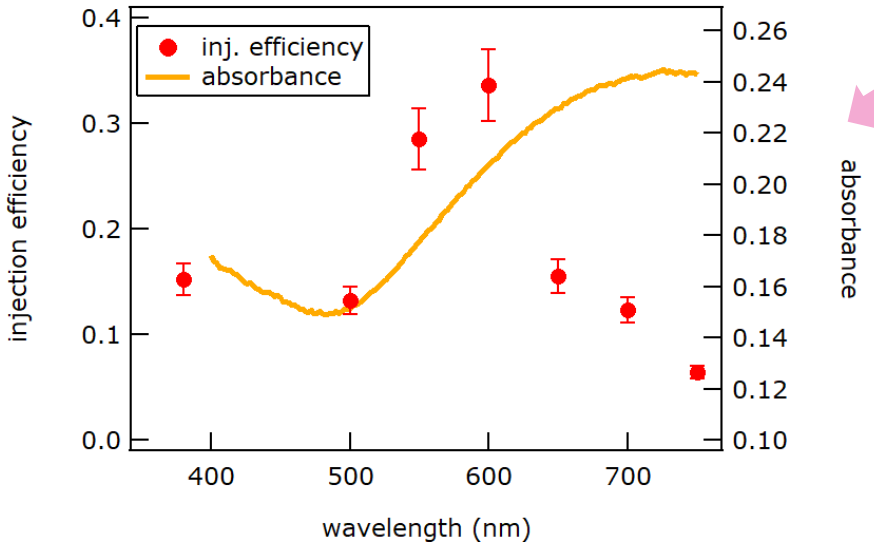
Jingshan Luo,* Ludmilla Steier, Min-Kyu Son, Marcel Schreier, Matthew T. Mayer, and Michael Grätzel

Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

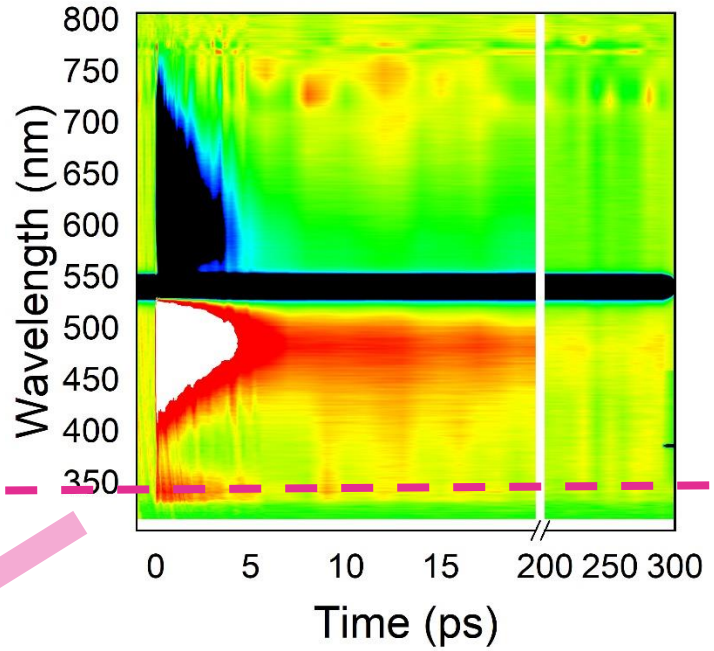
Dynamics of excited states in CeO_2 + Au and Cu NPs



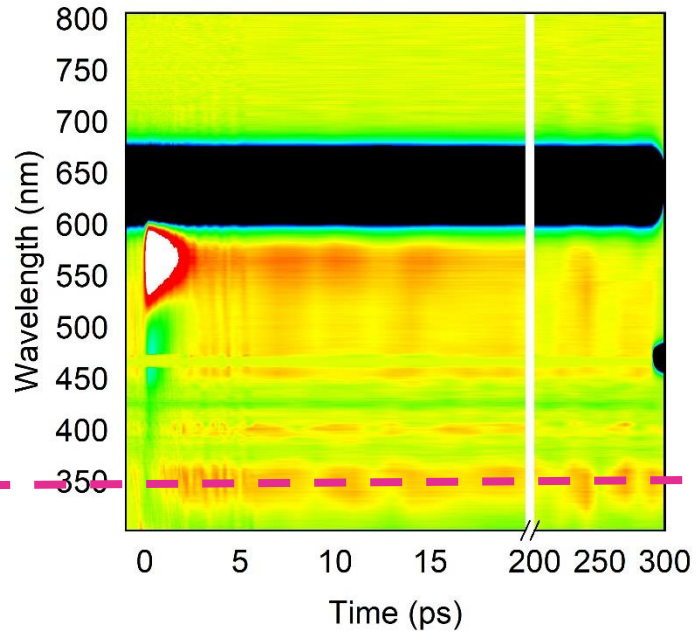




$Au@CeO_2$
pump @ LSPR (650 nm)



$Cu@CeO_2$
pump @ LSPR (650 nm)

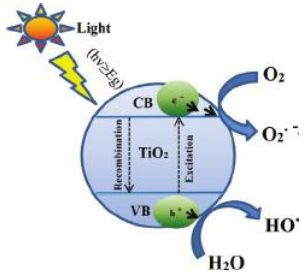


LSPR - induced charge transfer

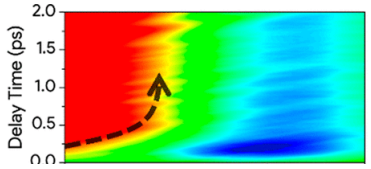
$Au \rightarrow CeO_2$ high injection efficiency

See presentation by **Eleonora Spurio** for more detail

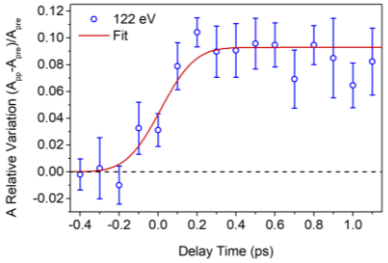
Conclusions



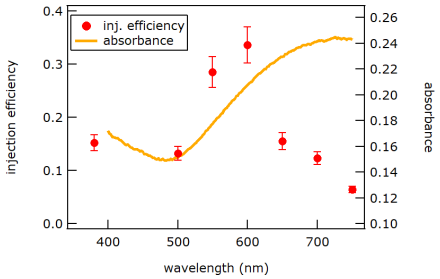
Ultrafast methods provide information on charge excitations and charge transfer, relevant to understand the functionality of oxide-based materials



→ formation of a small-polaron state after BG excitation of CeO_2



→ efficient and persistent LSPR-induced charge transfer from Ag NPs to CeO_2



→ Au NPs in CeO_2 are promising in view of investigating ultrashort time scales

→ Also Cu NPs in CeO_2 maintain LSPR and charge transfer

Acknowledgements

Members


Stefania Benedetti


Sergio D'Addato


Alessandro di Bona


Sergio Valeri

PhD students


Eleonora Spurio


Avinash Viakatakavi


Riccardo Magrin Maffei

Samuele Pelatti

Collaborators

- Federico Boscherini
  University of Bologna

- Daniele Catone, Patrick O'Keeffe
  + ESFL Flash.it CNR-ISM staff

- E. Principi, J. S. Pelli Cresi
  + EIS-TIMEX FERMI staff

- Stefano Nannarone
  + BEAR beamline staff

MIUR PRIN Project 2015CL3APH
2017-2019