

High resolution X-ray spectroscopy of electronic and atomic structure of TiO₂ nanostructures and charge transfer processes

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Thessaloniki, May 31st, 2018

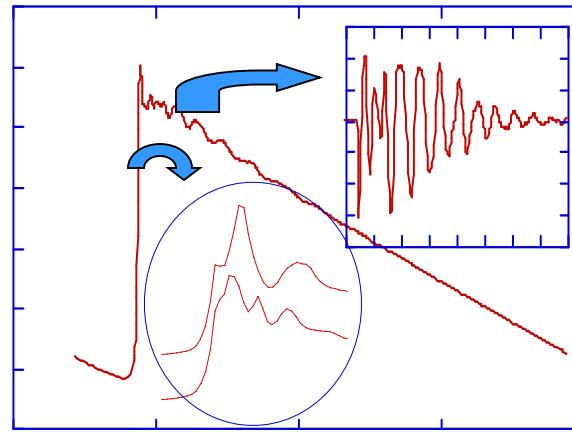
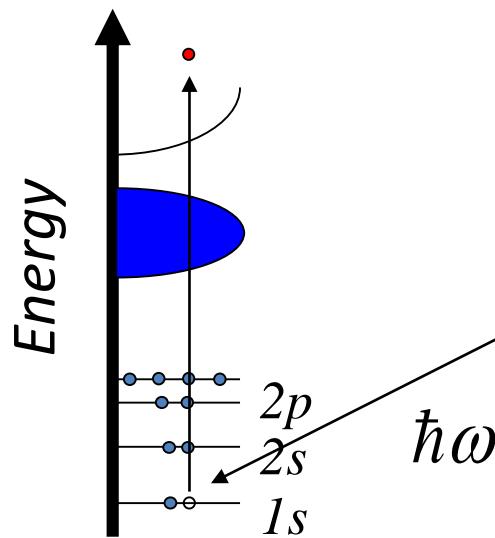


Plan

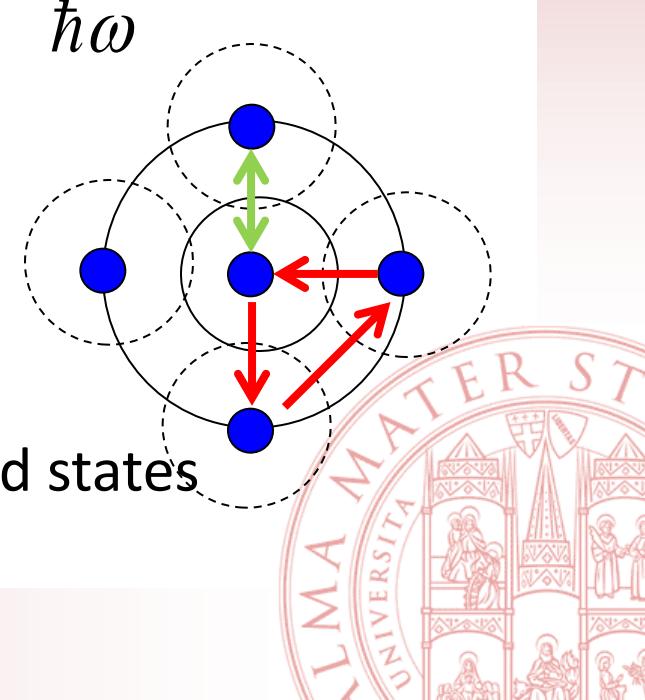
- X-ray Spectroscopies: XAFS, XES & RIXS
- TiO_2 – nanostructures for photocatalysis
 - Au/ TiO_2 : plasmon induced hot electron transfer studied by differential illumination X-ray spectroscopy
 - V-doped TiO_2 dopant matrix electron transfer
 - Ultra fast transient optical spectroscopy
 - Differential illumination X-ray spectroscopy



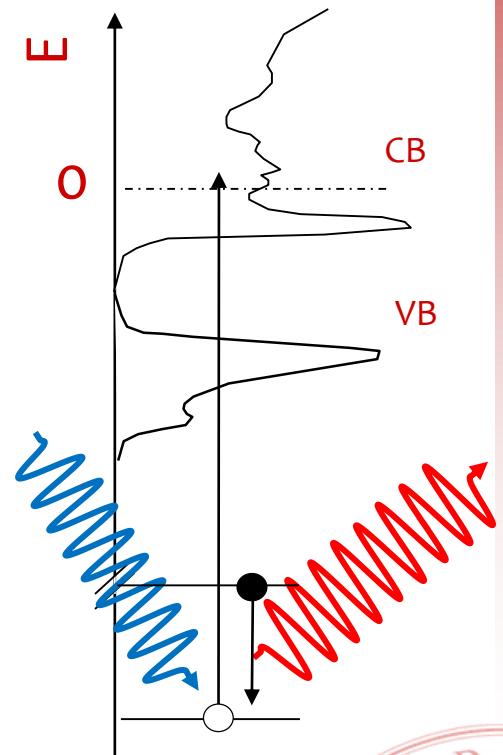
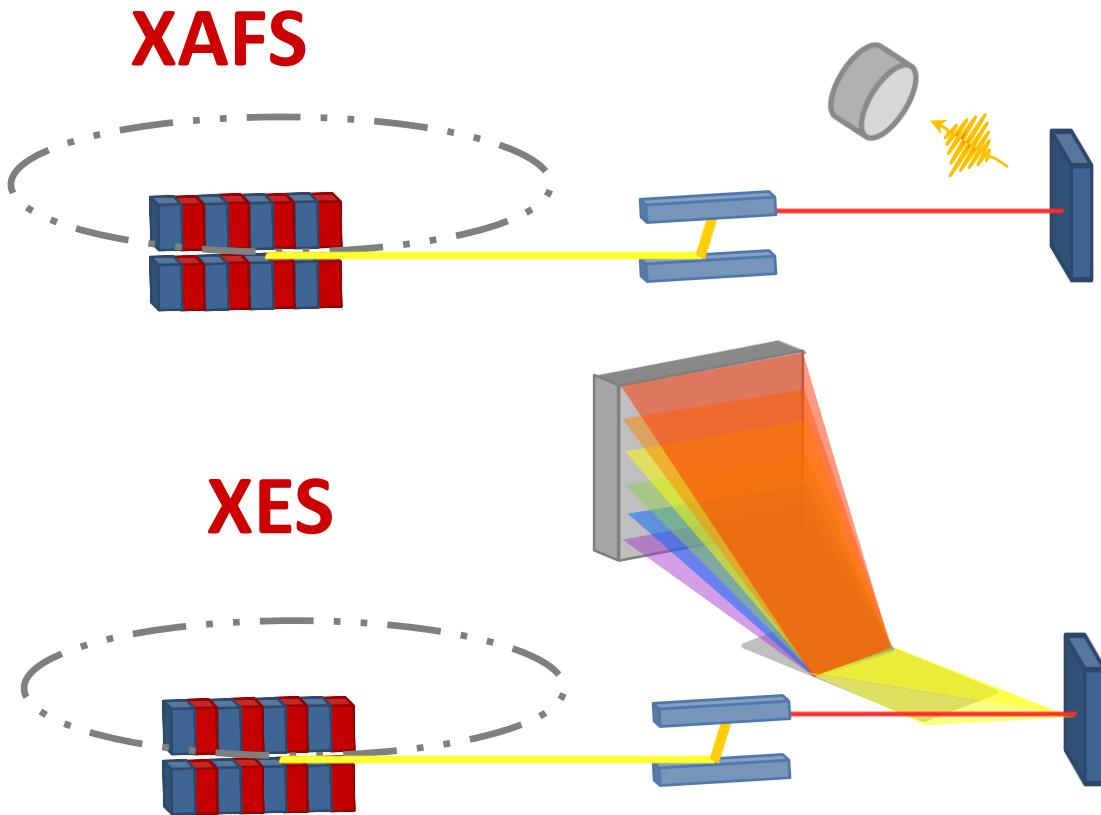
X-Ray Absorption Fine Structure



- “EXAFS”: Coordination numbers
Interatomic distances
Disorder of distances
- “XANES”: Absorber symmetry and
valence/oxidation state
Electronic structure of unoccupied states
Medium range structure

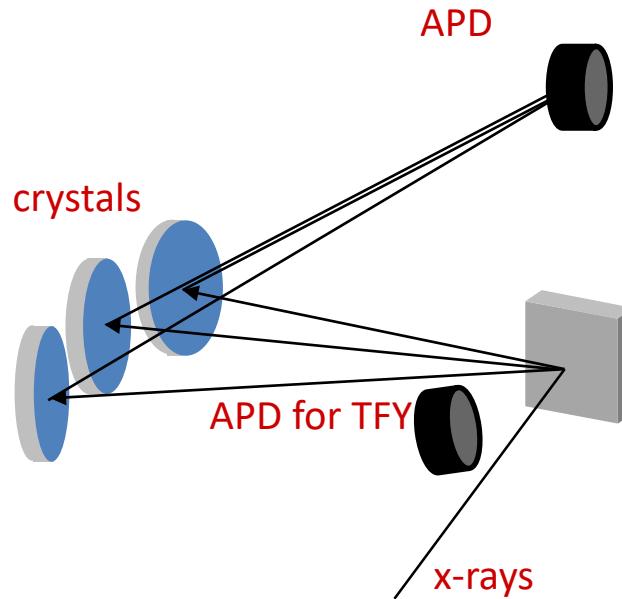
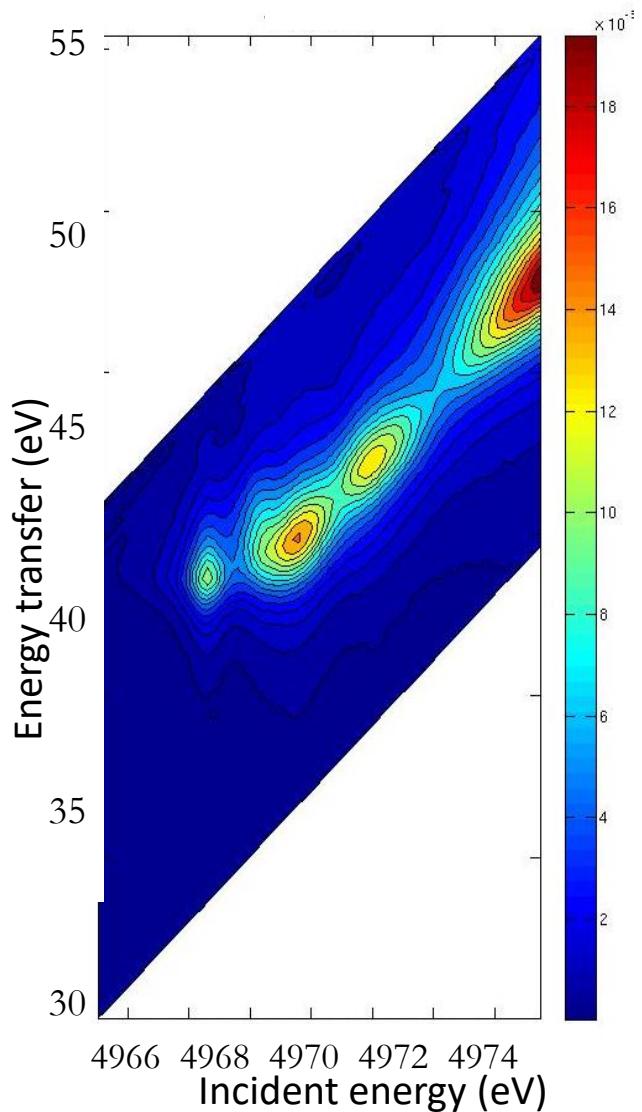


XAFS and X-ray Emission Spectroscopy



Resonant Inelastic X-ray Scattering

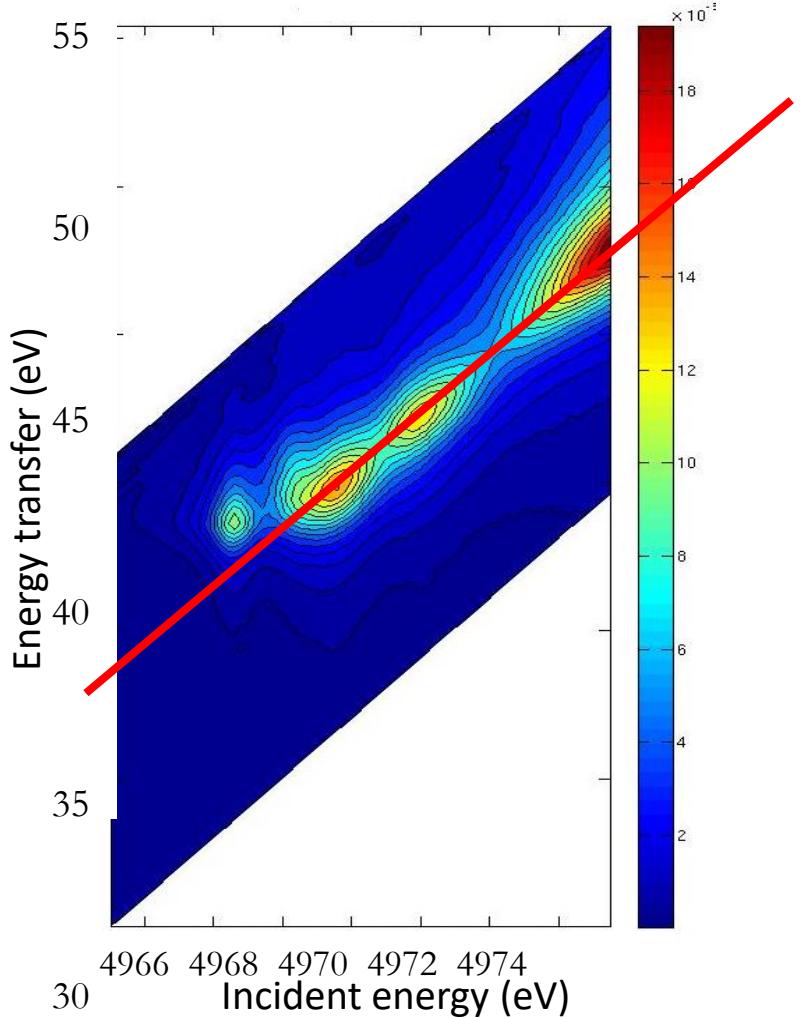
RIXS



Ti K_β (1s3p) RIXS in pre – edge region



RIXS and fluorescence lines



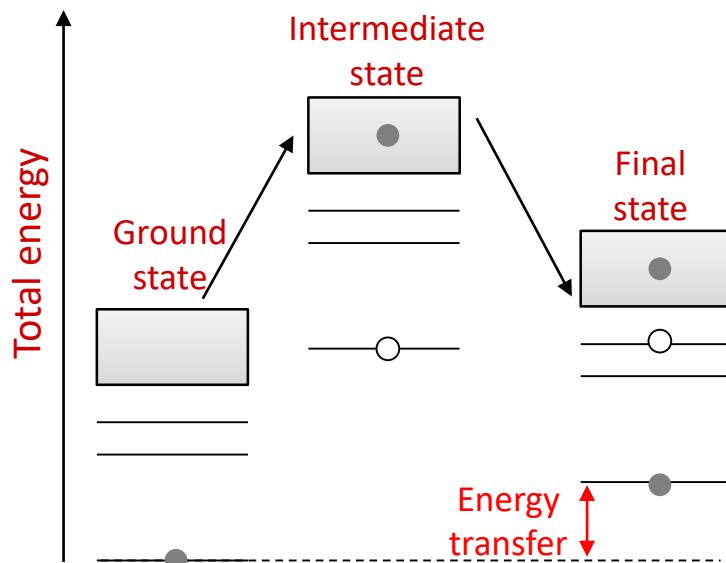
- Above the edge fluorescence lines (e.g. K_{α}, K_{β}) are at fixed energy
- In the RIXS plane fixed energy lines lie on a straight line with slope = 1
- Near the edge the distribution of intensity is more complex



Resonant Inelastic X-ray Scattering

- RIXS is a second order scattering process described by the Kramers – Heisenberg formula

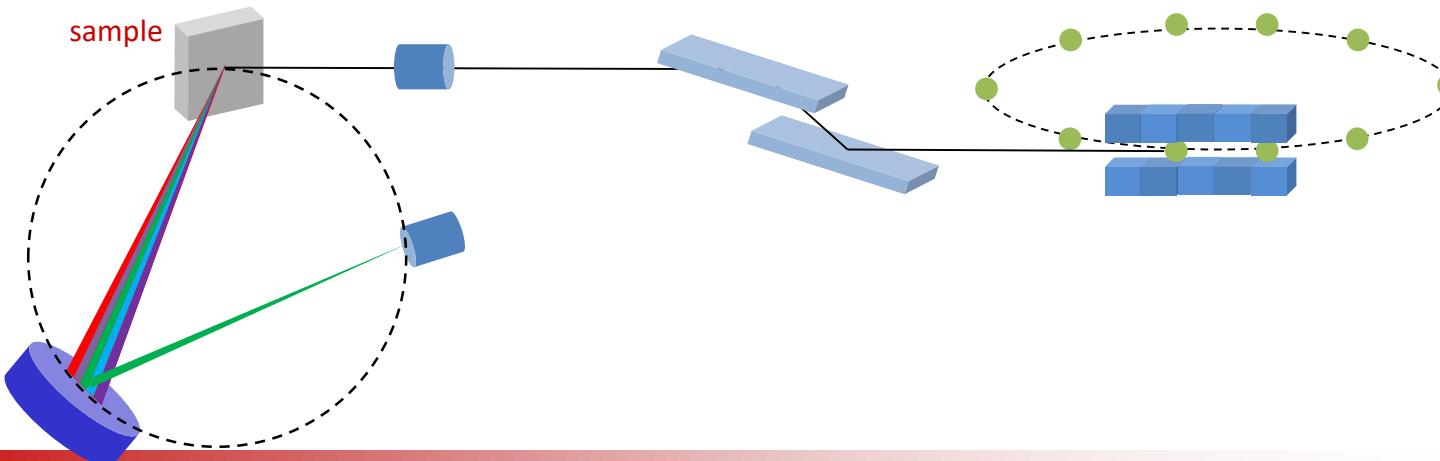
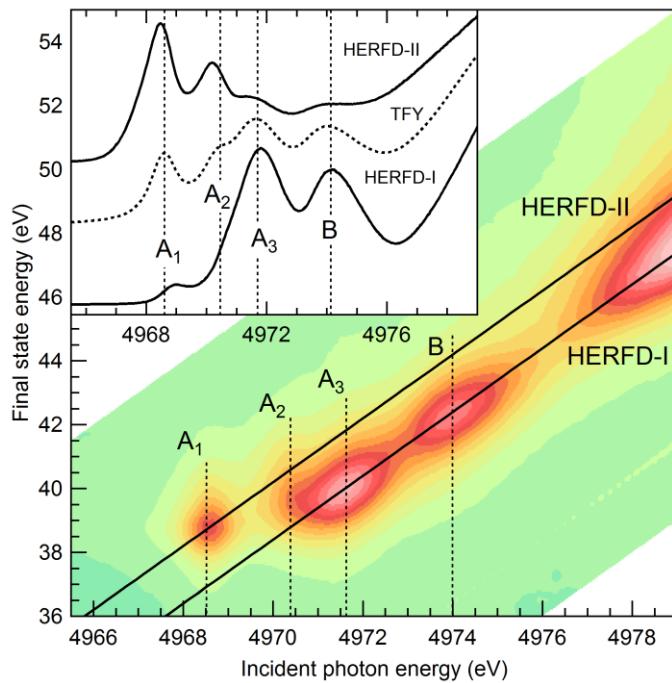
$$\frac{d\sigma}{d\Omega} = r_0^2 \omega \omega'^3 \left| m \sum_n \left[\frac{(\hat{\varepsilon}' \bullet \vec{r}_{bn})(\hat{\varepsilon} \bullet \vec{r}_{na})}{(E_n^0 - E_a^0 - \hbar\omega)} + \frac{(\hat{\varepsilon} \bullet \vec{r}_{bn})(\hat{\varepsilon}' \bullet \vec{r}_{na})}{(E_n^0 - E_a^0 + \hbar\omega')} \right] \right|^2$$



High Energy Resolution Fluorescence Detection

HERFD

- Plot the scattered intensity as a function of incident photon energy for different “cuts” in the RIXS plane
- Obtain “high resolution” XAFS - HERFD



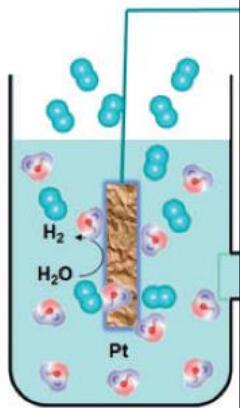
Local structure and charge transfer in doped TiO₂ photocatalysts



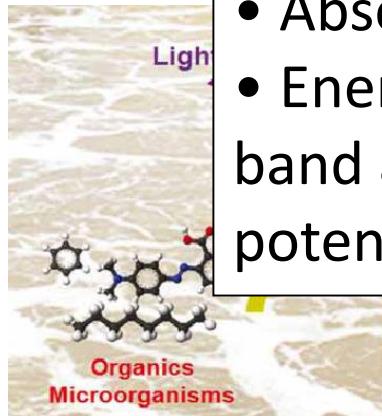
Energy and environmental challenges

- Production of fuels from renewable energies
- Purification of water from toxic pollutants / bacteria

Synthesis of solar fuels and water purification: semiconductor photocatalysts



X. Chen, M. Grätz



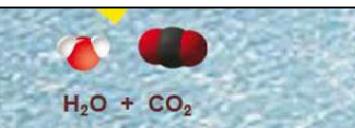
J Mat Chem 20 (2010)

Fundamental steps involved:

- Generation of charge carriers by photo-excitation
 - Separation and migration to trapping sites
 - Interfacial charge transfer

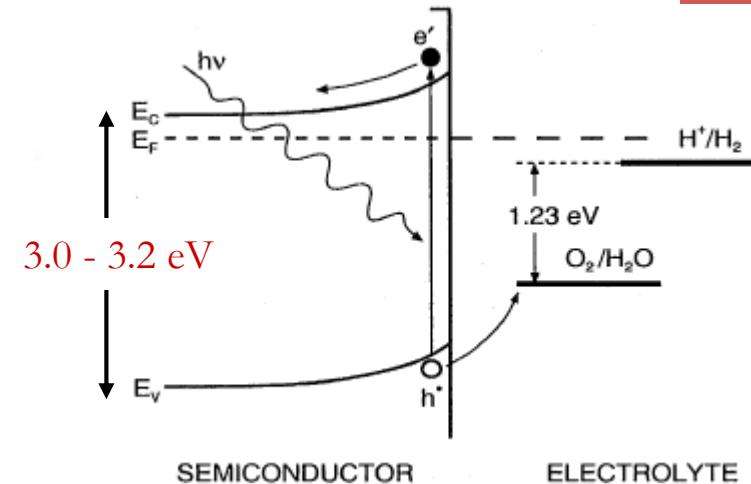
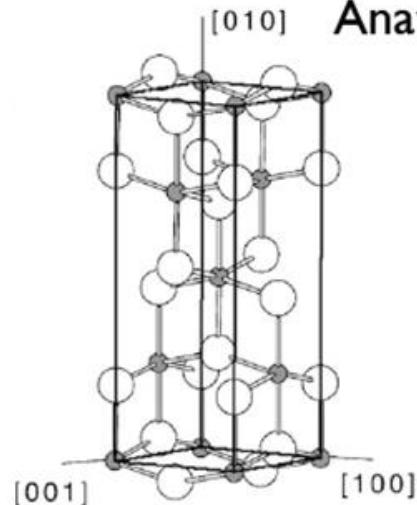
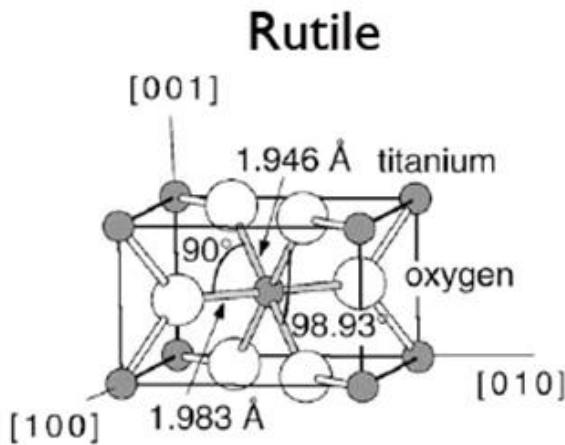
Requirements:

- Absorption in the solar spectral range
 - Energy of conduction band and valence band adapted to the reduction / oxidation potential

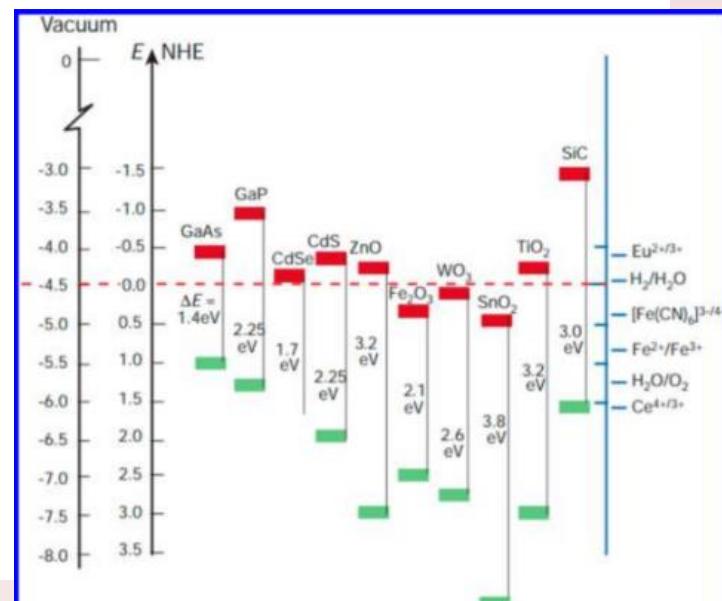


- OH, •O₂⁻, H₂O₂
very active in degradation of
contaminants and inactivation of
microorganisms

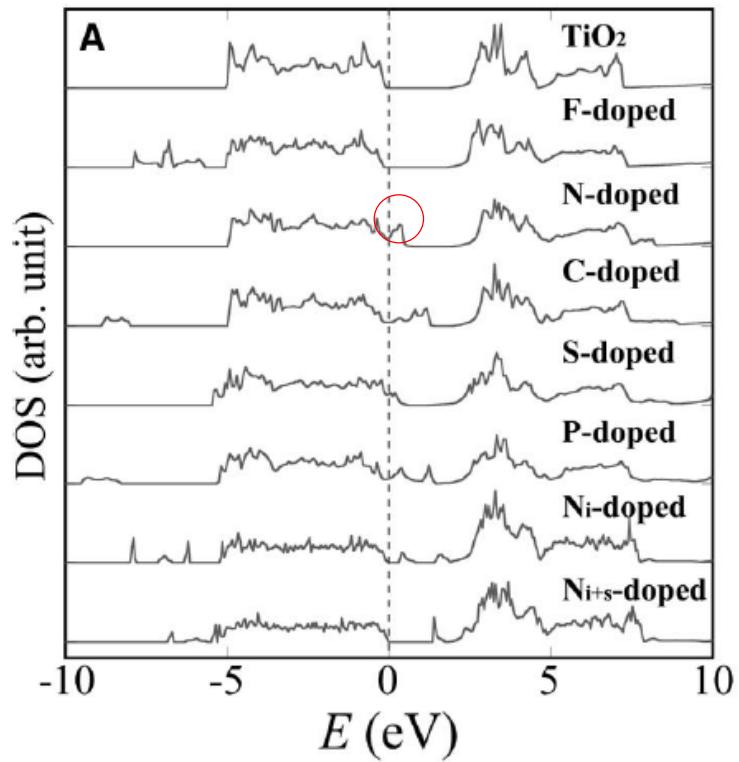
1st generation benchmark: TiO₂



- ☺ long-term photostability and inertness to chemical environments
- ☺ earth abundant material, non-toxic
- ☺ CB / VB energy suitable for water splitting
- ☹ absorbs only a small portion of the solar spectrum



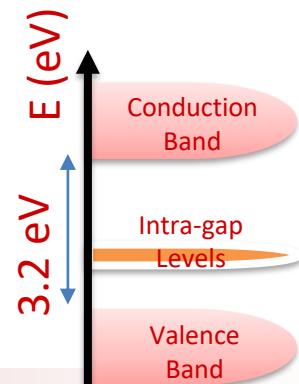
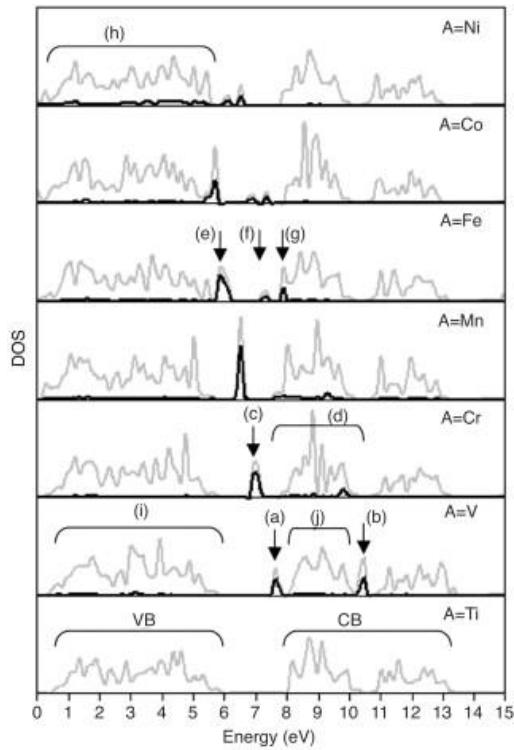
2nd generation photocatalysts: doped TiO₂



13 JULY 2001 VOL 293 SCIENCE REPORTS

Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides

R. Asahi,* T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga



Systems studied

Plasmon enhanced absorption



Au NP:TiO₂

- Plasmon resonance in NP to increase light absorption
- Differential illumination to study charge transfer

Doping



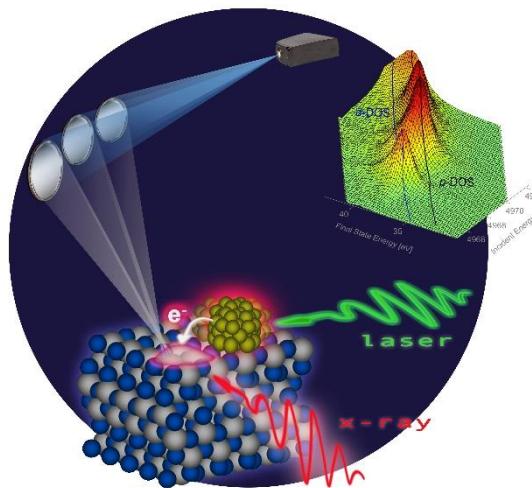
V:TiO₂

- V reduces band gap
- Ultra fast transient absorption spectroscopy
- Location of V
- Differential illumination to study charge transfer

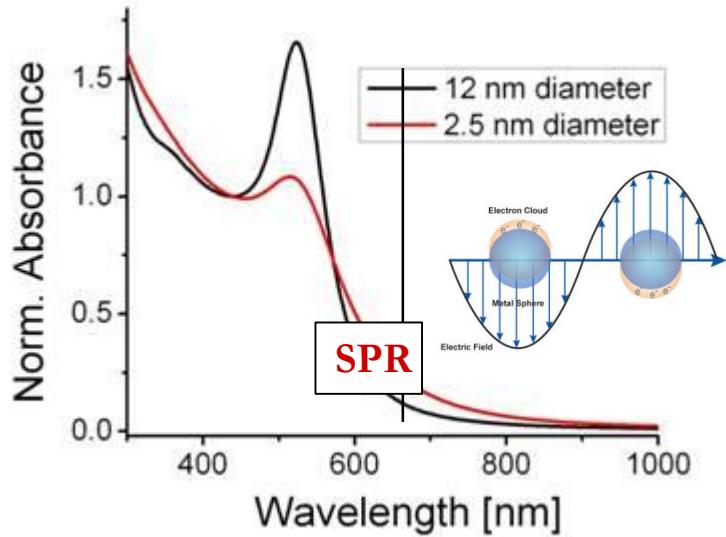
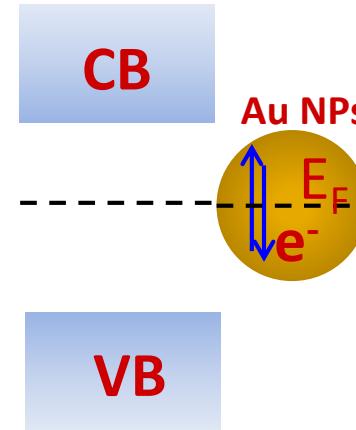
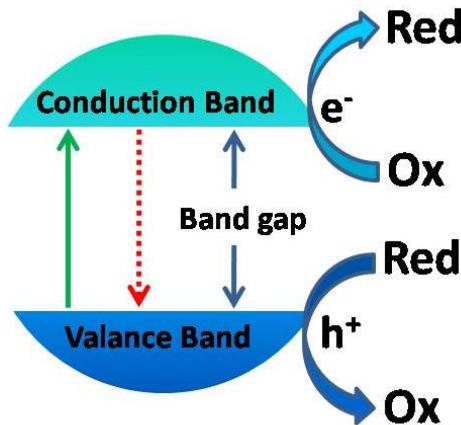
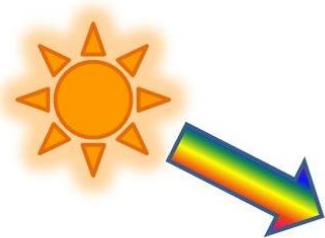


Probing Long-Lived Plasmonic-Generated Charges in TiO_2/Au by High-Resolution X-ray Absorption Spectroscopy**

L. Amidani et al., *Angew. Chem. Int. Ed.* **54**, 5413 (2015)



Surface plasmon resonance in Au NPs

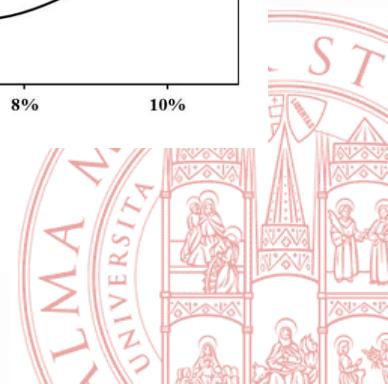
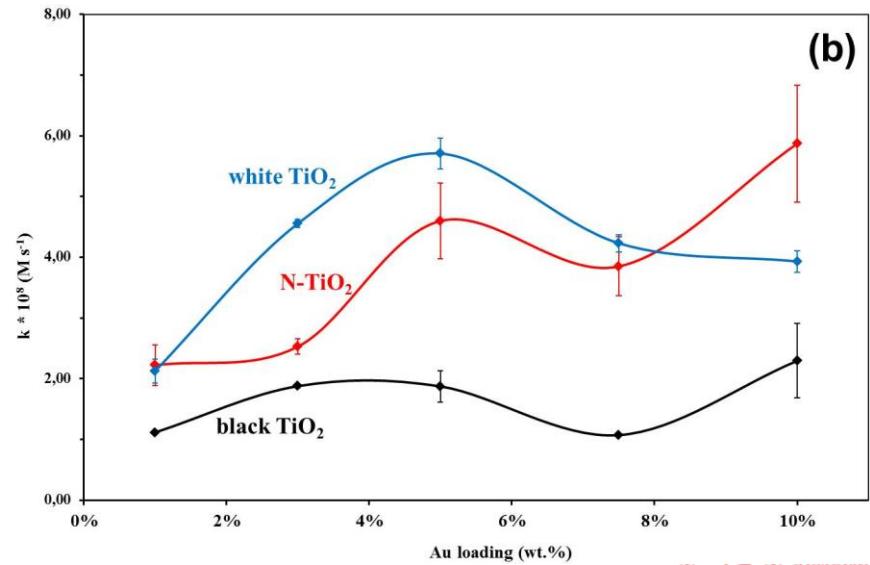
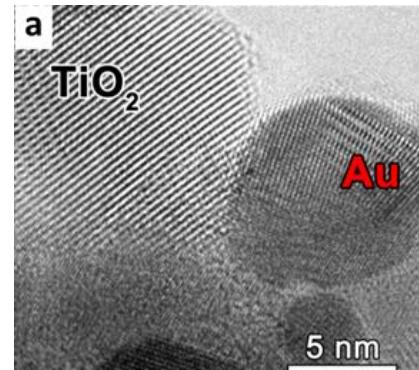


- Sensitize TiO_2 to visible light by coupling TiO_2 with metallic nanoparticles to exploit the **surface plasmon resonance**
- Enhanced photocatalytic activity
- Origin?
 - Energy transfer
 - Hot electron transfer



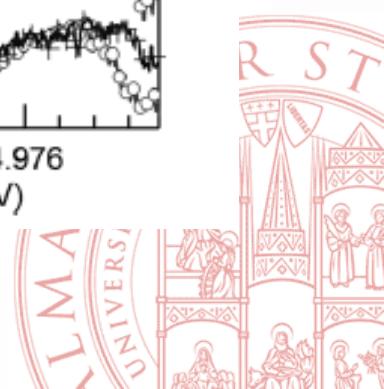
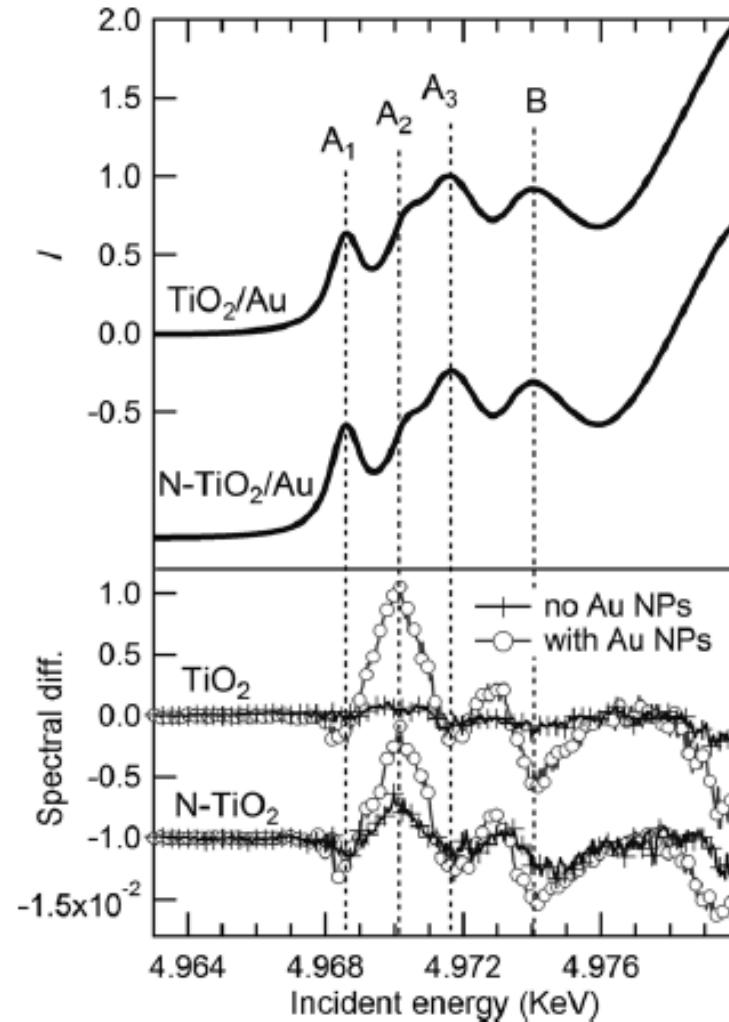
Samples

- TiO_2 NP by sol – gel method
 - Anatase from XRD and XANES
 - «white», «black» (O vacancies) and N – doped samples
- Au NP from HAuCl_4 , 10% in weight
- Au NP: increase rate constant for degradation of formic acid

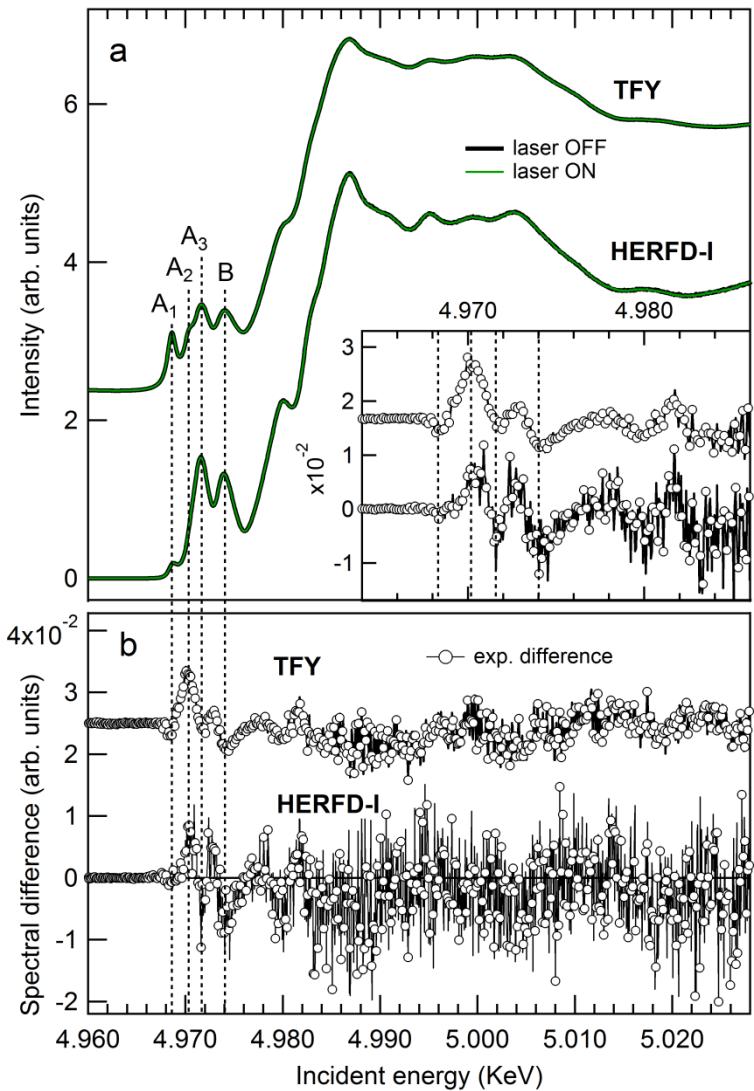


Differential RIXS experiment

- Ti K β RIXS, ID26 ESRF
- Dark / light, $\lambda = 532$ nm, 200 mW in 1 mm spot
- Au NP cause differences in dark – light spectra



Differential Spectra

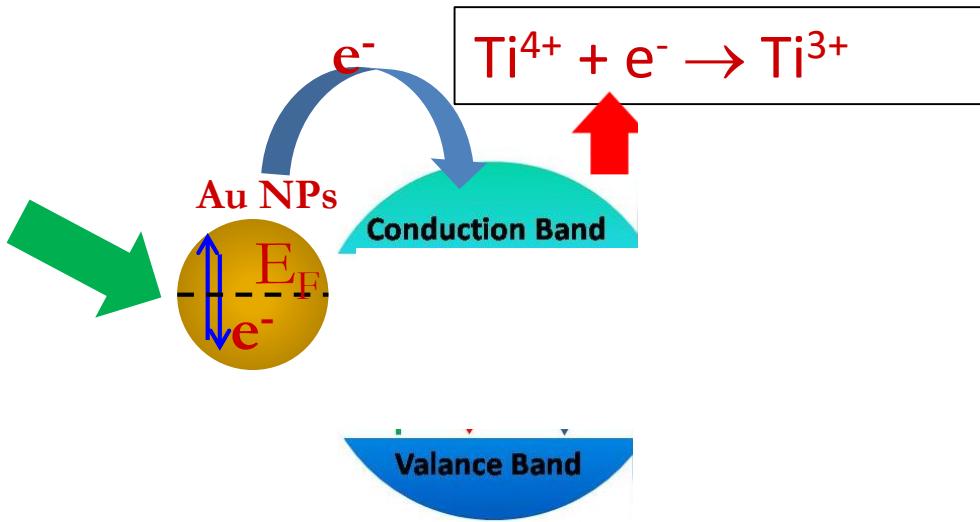


laser on =
laser off =

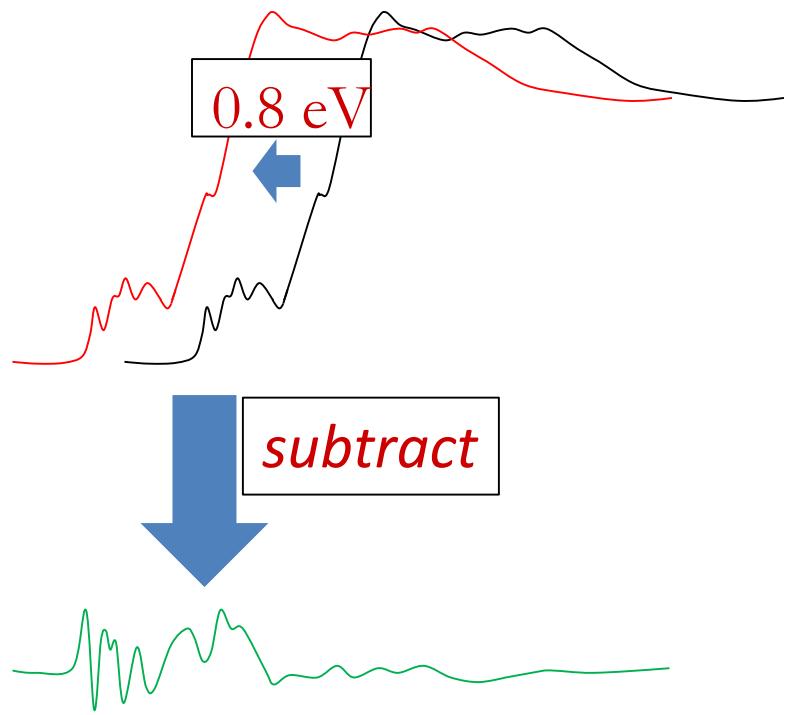
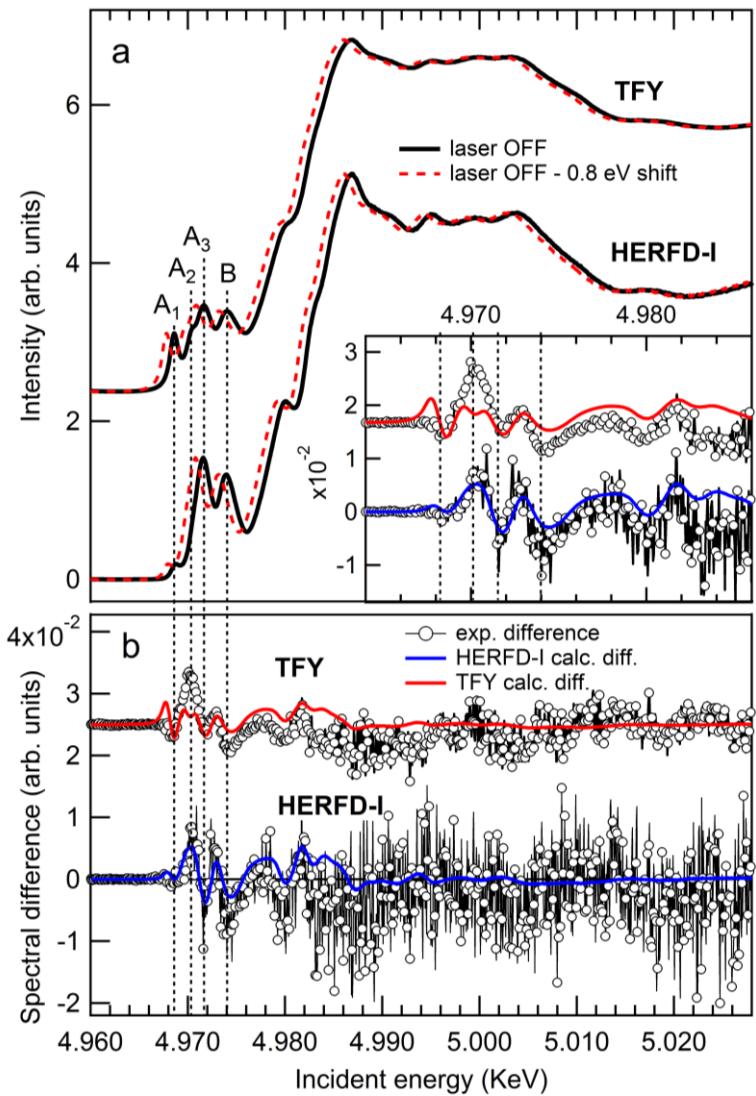
spectral differences for
TFY
HERFD-I



Electron transfer from Au to TiO₂



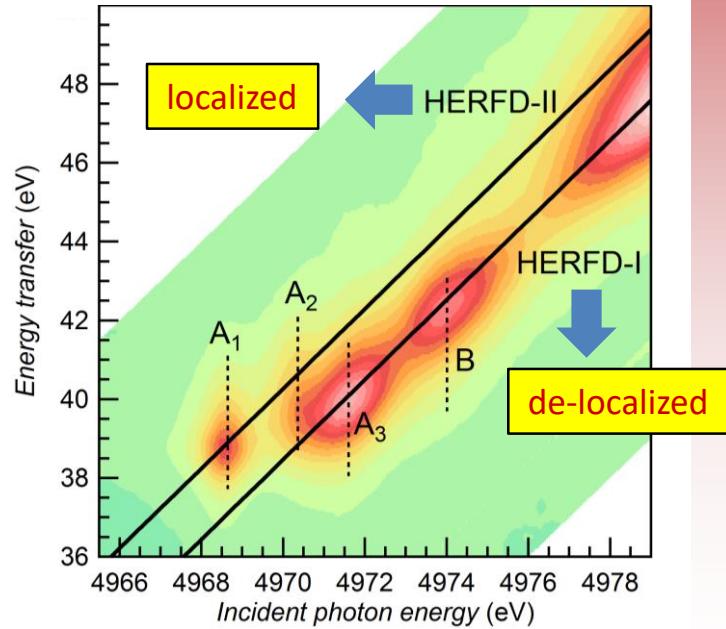
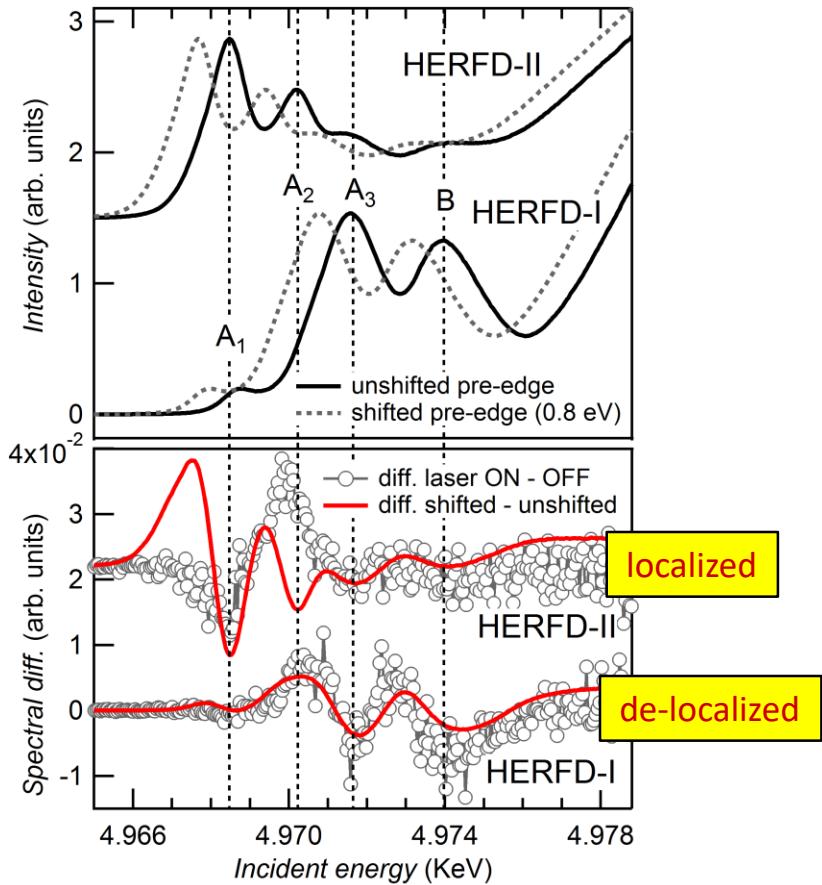
Simulation by edge shift



TFY
HERFD-I

- Assumes same lineshape: no structural rearrangement

One step further: different “cuts” in the RIXS plane

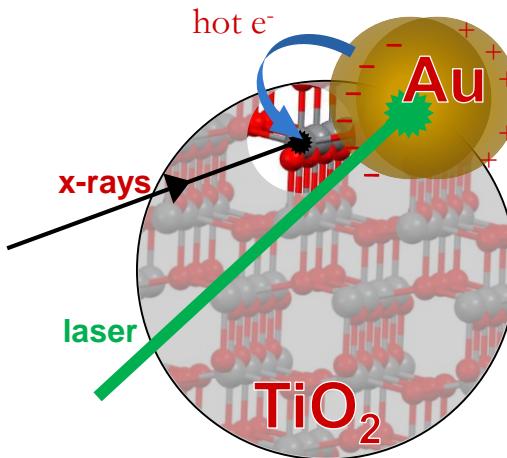
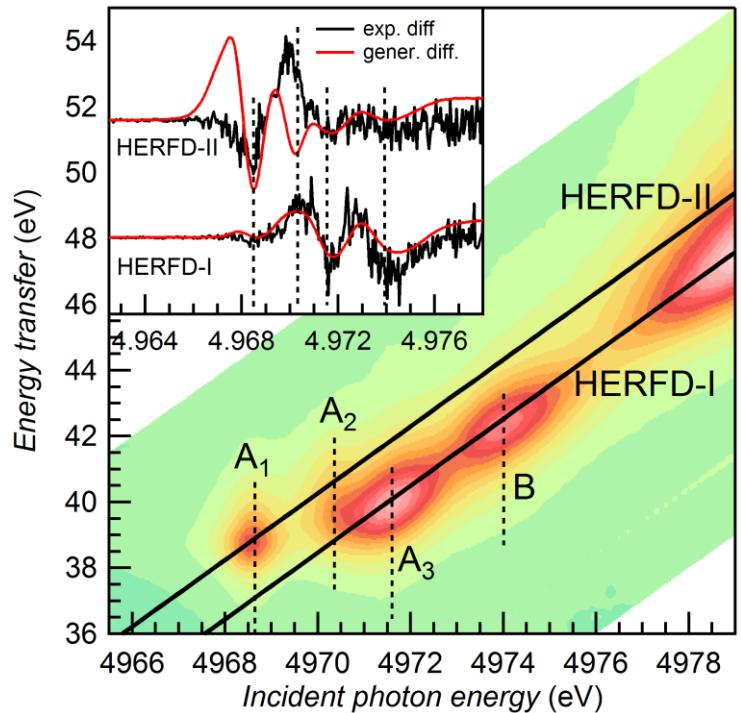


F. de Groot, AIP Conf. Proceed. 2007, 882, 37 – 43

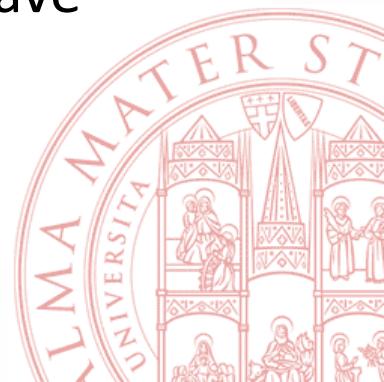
D. Cabaret et al., Phys. Chem. Chem. Phys. 2010, 12, 5619

J. Vanko et al., arXiv:0802.2744, 2008

Interpretation



- Hot electrons generated by SPR in Au are injected to Ti unoccupied orbitals: hot electron transfer
- Injected electrons in localized or de-localized orbitals have different effect
 - De – localized: small structural rearrangement
 - Localized: greater structural rearrangement

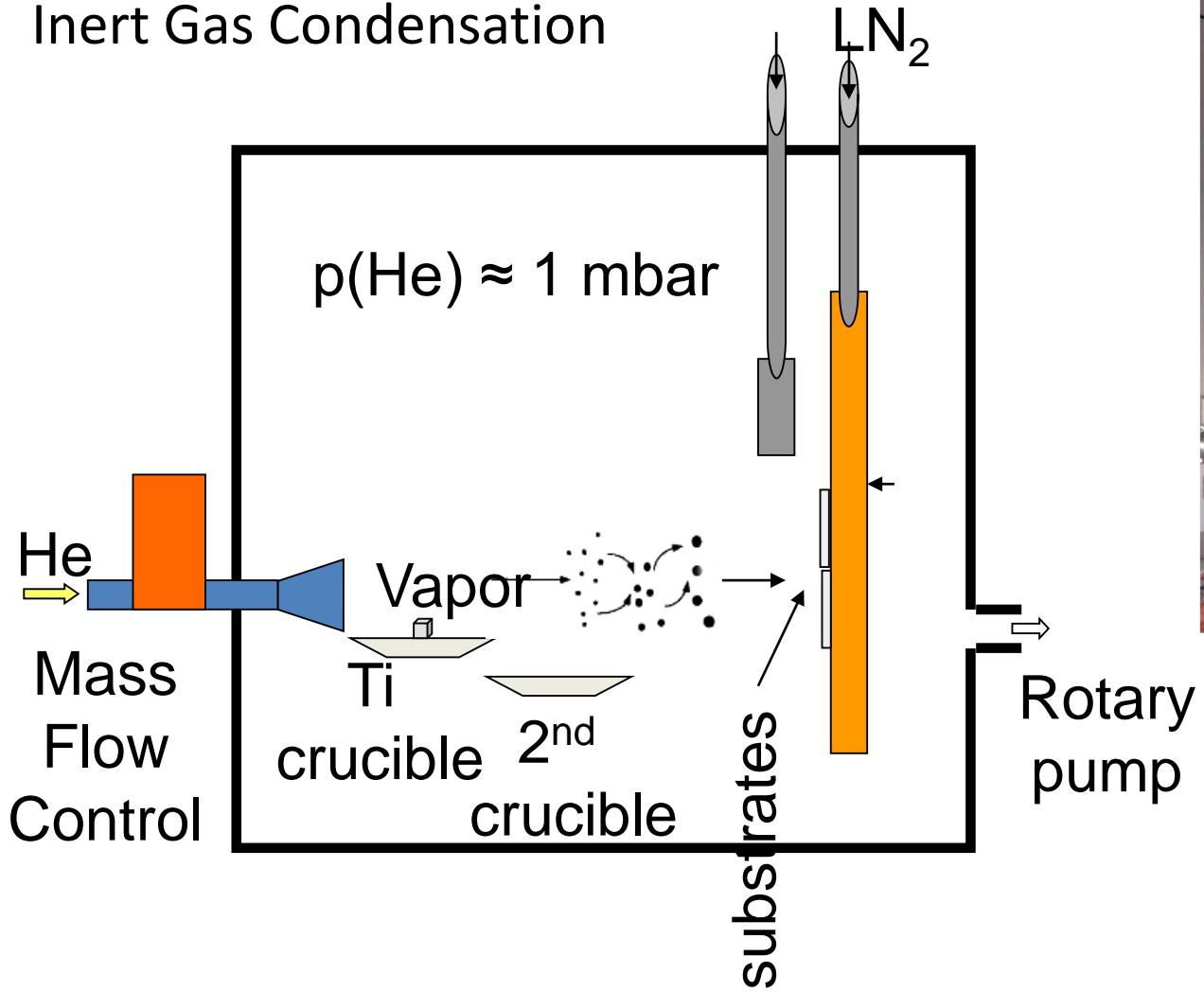


V: TiO₂ nanoparticle assembled films

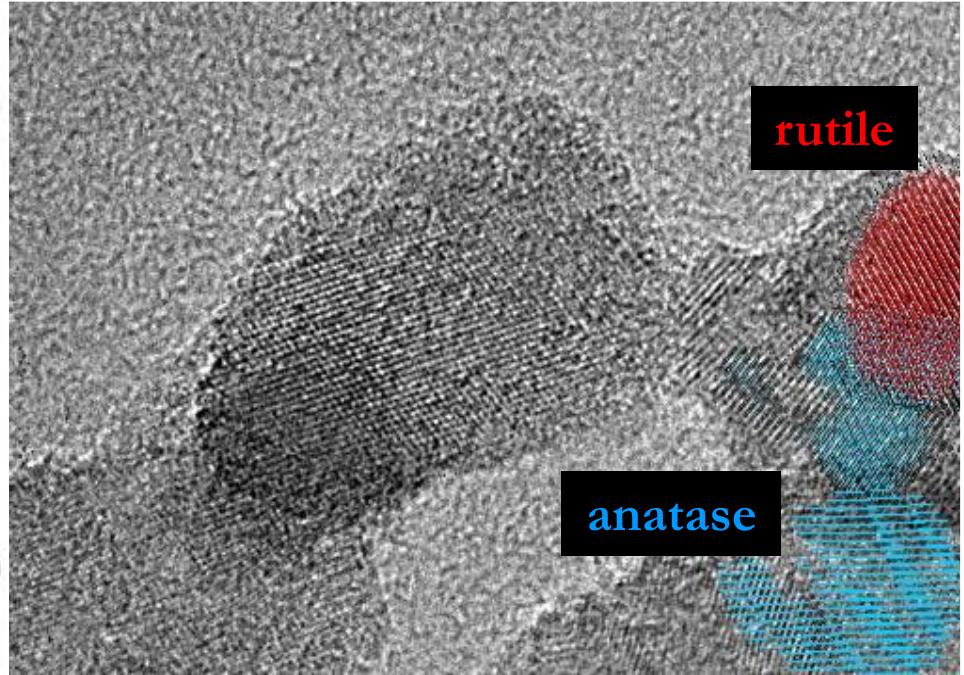
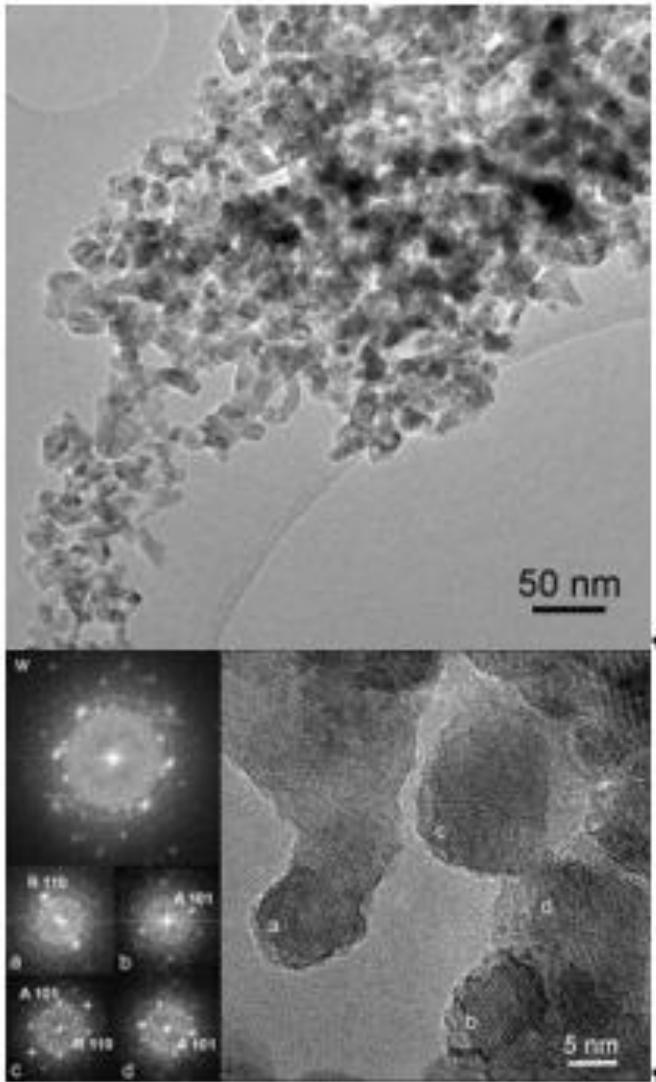


V: TiO_2 nanoparticle assembled films

Inert Gas Condensation



V-doped TiO₂ nanoparticle films

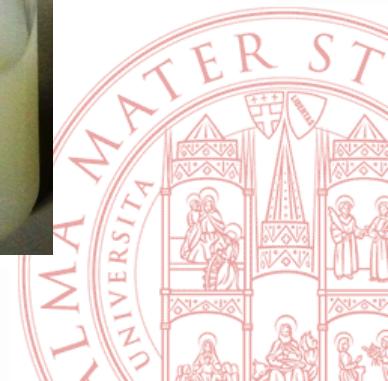
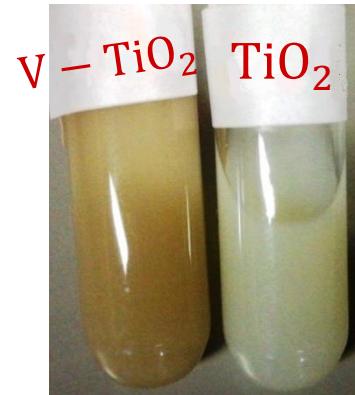
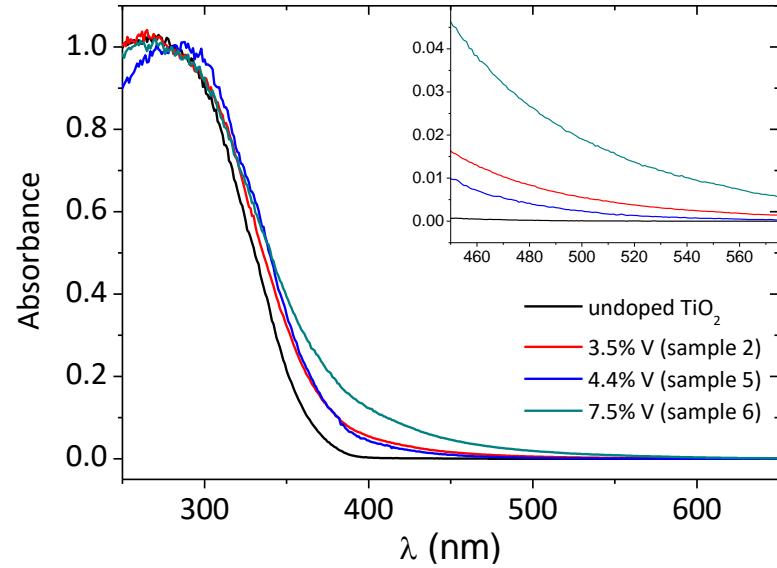


- Particle size 10 – 20 nm
- Mixture of rutile & anatase, depends on deposition rate



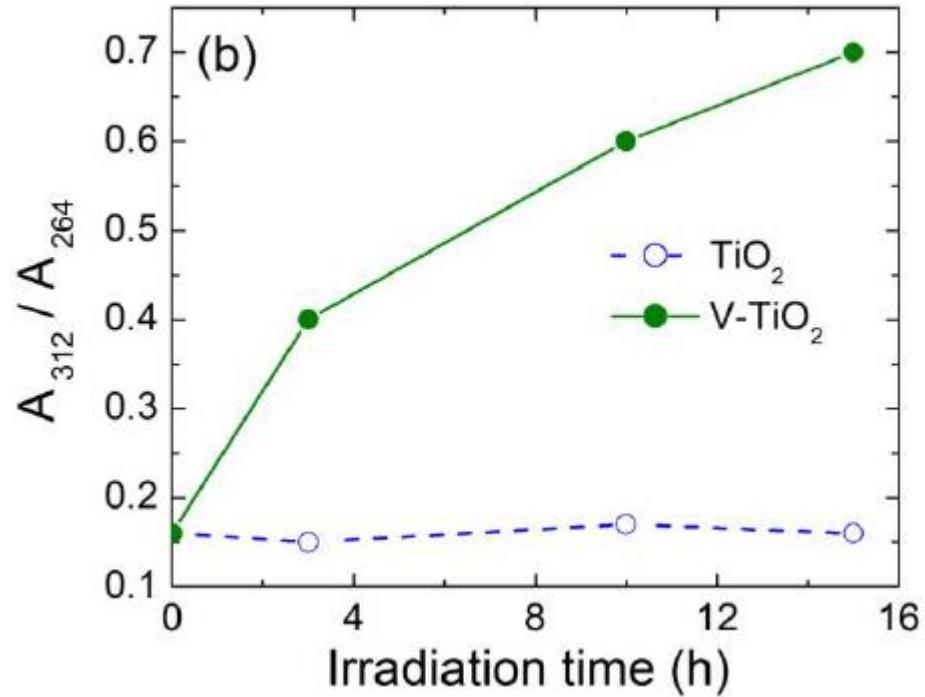
V - TiO_2 Optical Properties

- V-doping: increase of the absorption coefficient in the visible region.
- In particular, the enhancement is localized between 350 and 550 nm



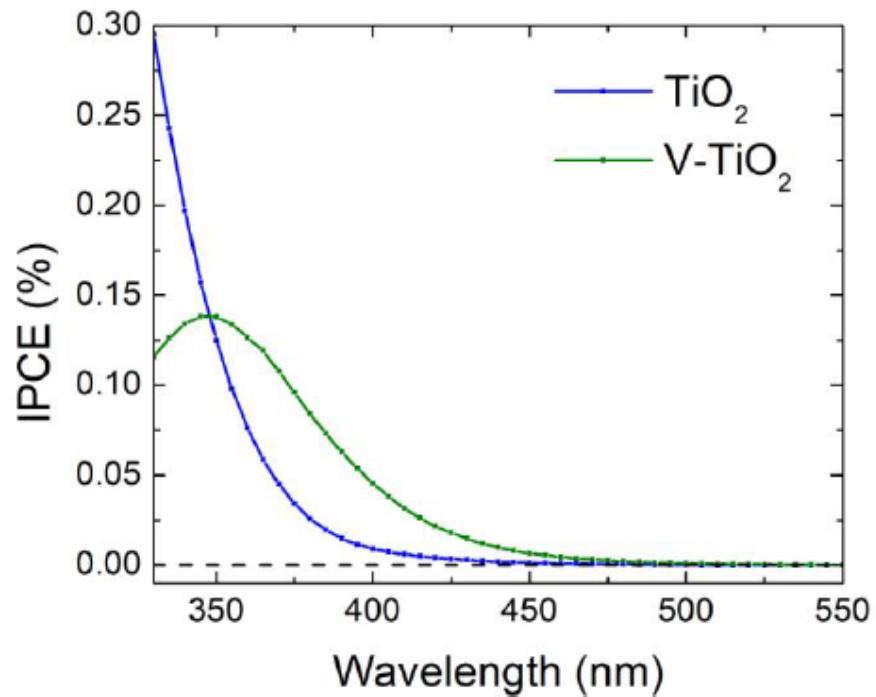
V-TiO₂ photocatalysis

- Reduction of NO₂ group in 4-nitrobenzaldehyde (NO₂-C₂H₄-CHO) to NH₂-C₂H₄-CHO under irradiation with $\lambda > 450$ nm light
 - 9 × 10⁻⁵ M solution of NO₂-C₂H₄-CHO in a CH₃N/C₃H₈O (4/1) mixture



V-TiO₂ water splitting

- TiO₂ and V-TiO₂ NP based photoanodes in a photoelectrochemical cell
 - H₂O/acetylacetone solution
- Photon – current conversion efficiency is enhanced for V-doped NP for $\lambda > 360$ nm

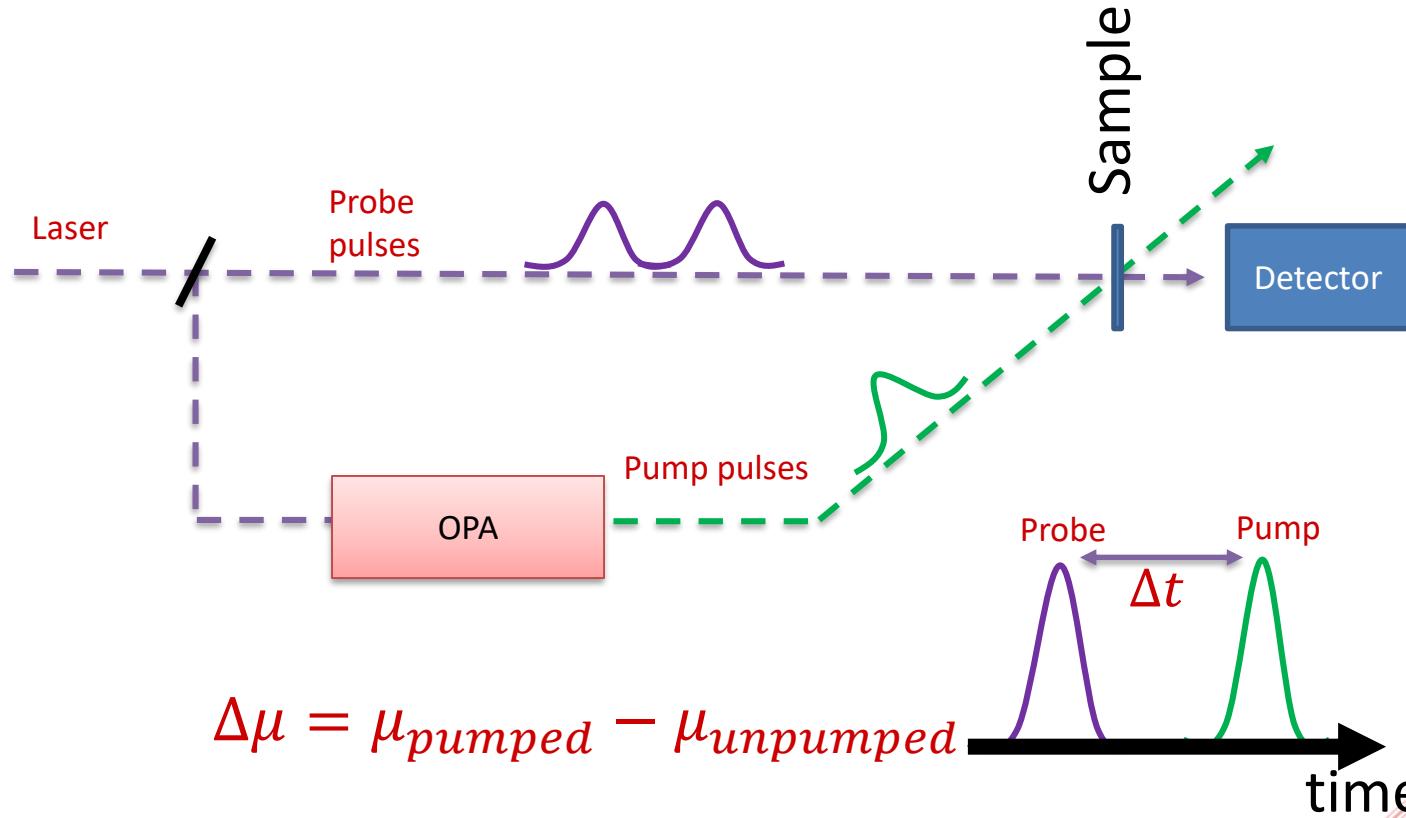


V: TiO₂ nanoparticle assembled films: ultra fast transient optical spectroscopy

Rossi et al., submitted to Appl. Cat. B



Optical Transient Absorption Spectroscopy

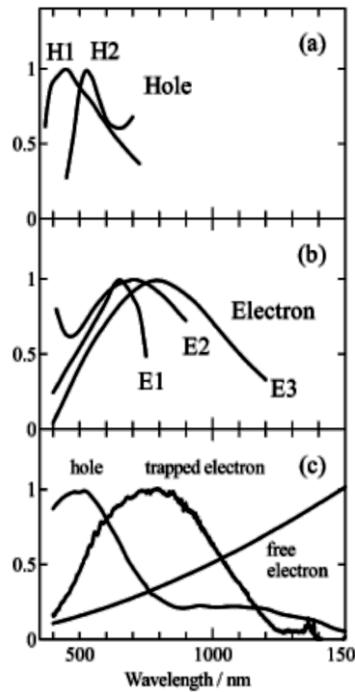


Optical Transient Absorption Spectroscopy

- Above band gap (355 nm) excitation of TiO_2 NPs

Yoshihara et al. J. Phys. Chem. B, Vol. 108, 2004

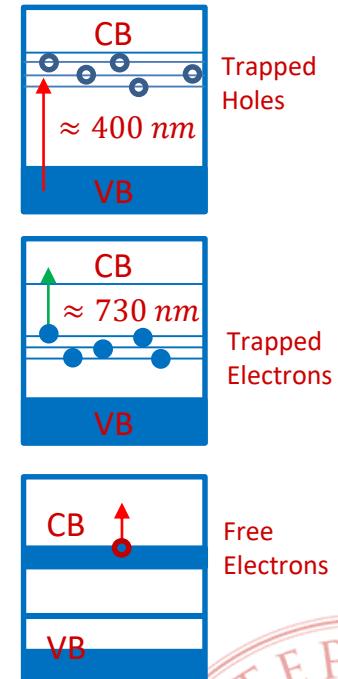
Trapped holes on
NP surface



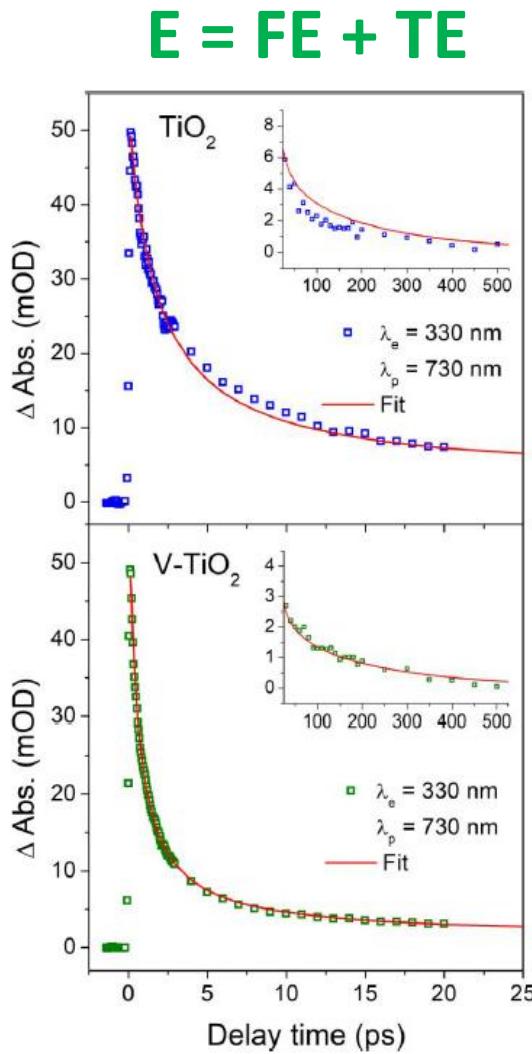
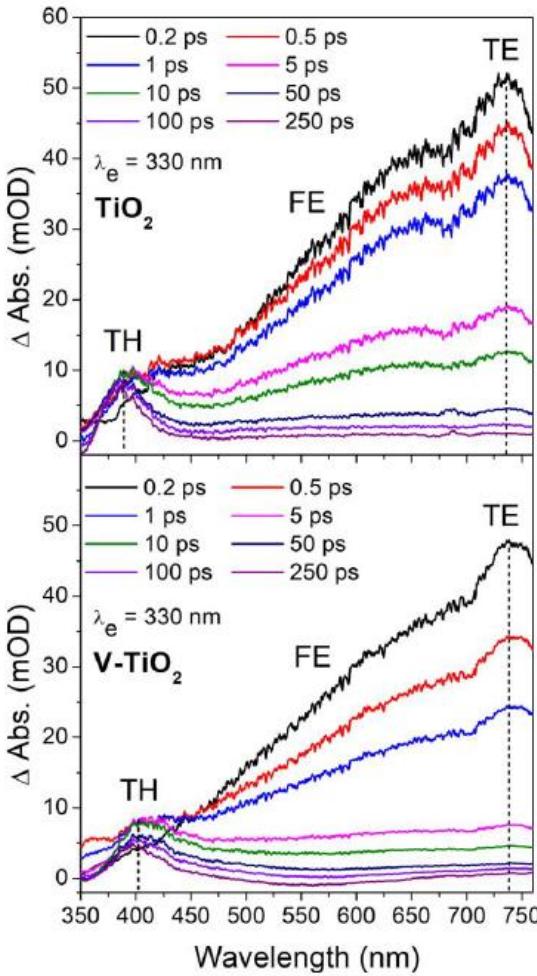
Trapped electrons on
NP surface



Free electrons in
conduction band



Above bandgap excitation (330 nm)



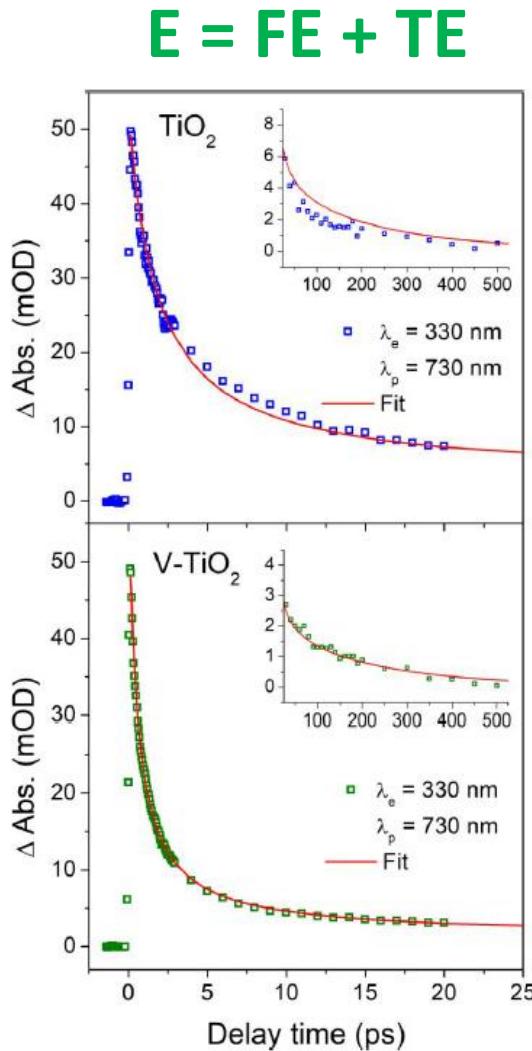
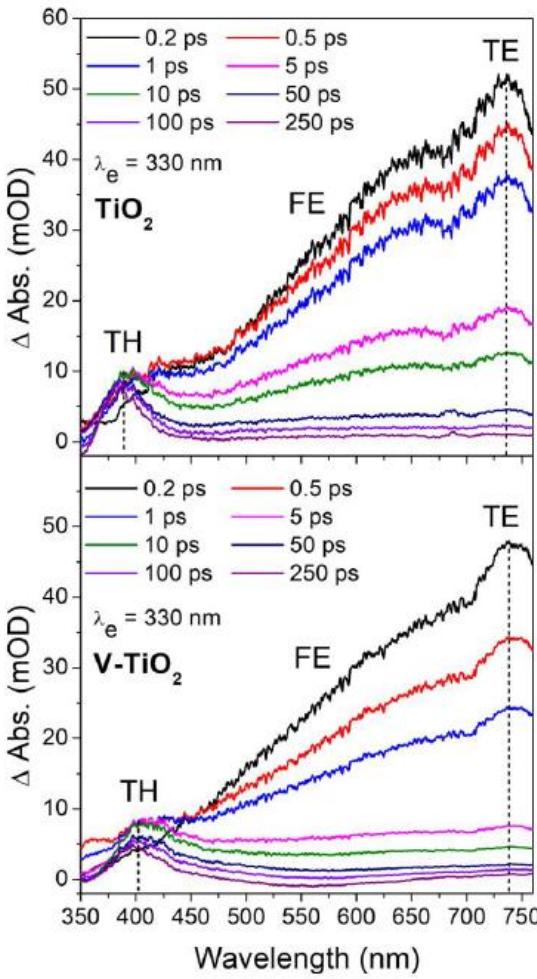
- Rise time of E signal < 80 fs: free electrons
- Fast + slow decay components
 - Fast: 2nd order kinetics, E – H recombination
 - Slow: exp decay, relaxation to deep traps in bulk

Setup Settings

- Pump Wavelength: 330 nm
- Photon per Pulse (Pump): $8.3 \cdot 10^{12}$
- Fluence: $2.1 \cdot 10^{16} \frac{\text{ph}}{\text{mm}^2 \cdot \text{s}}$
- Probe rate: 1 KHz



Above bandgap excitation



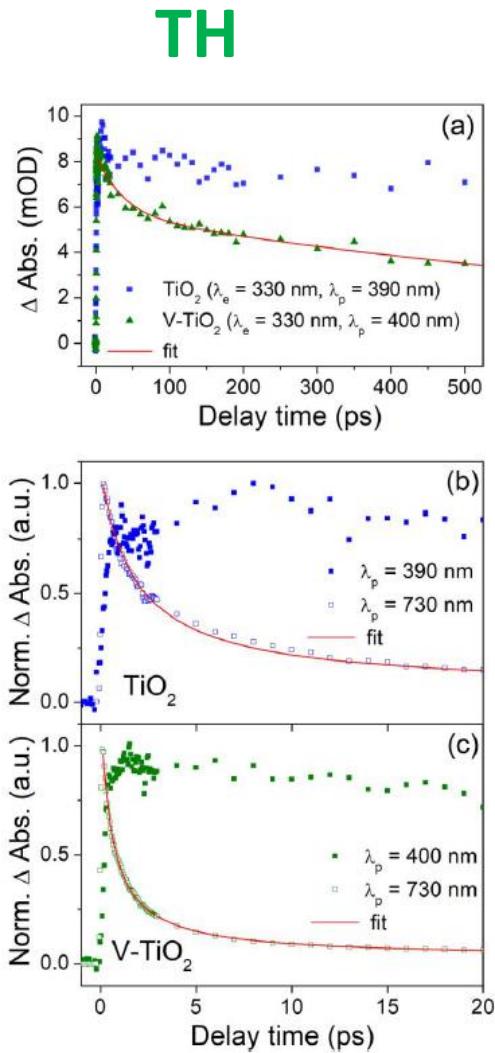
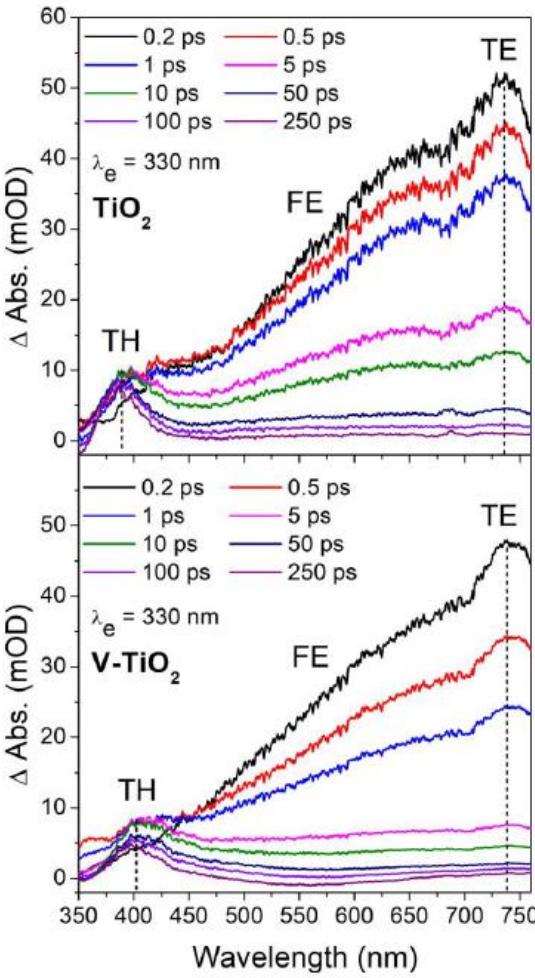
- Doping: speed up of fast decay component
 - Dopant induced traps

Setup Settings

- Pump Wavelength: **330 nm**
- Photon per Pulse (Pump): **$8.3 \cdot 10^{12}$**
- Fluence: **$2.1 \cdot 10^{16} \frac{\text{ph}}{\text{mm}^2 \cdot \text{s}}$**
- Probe rate: **1 kHz**



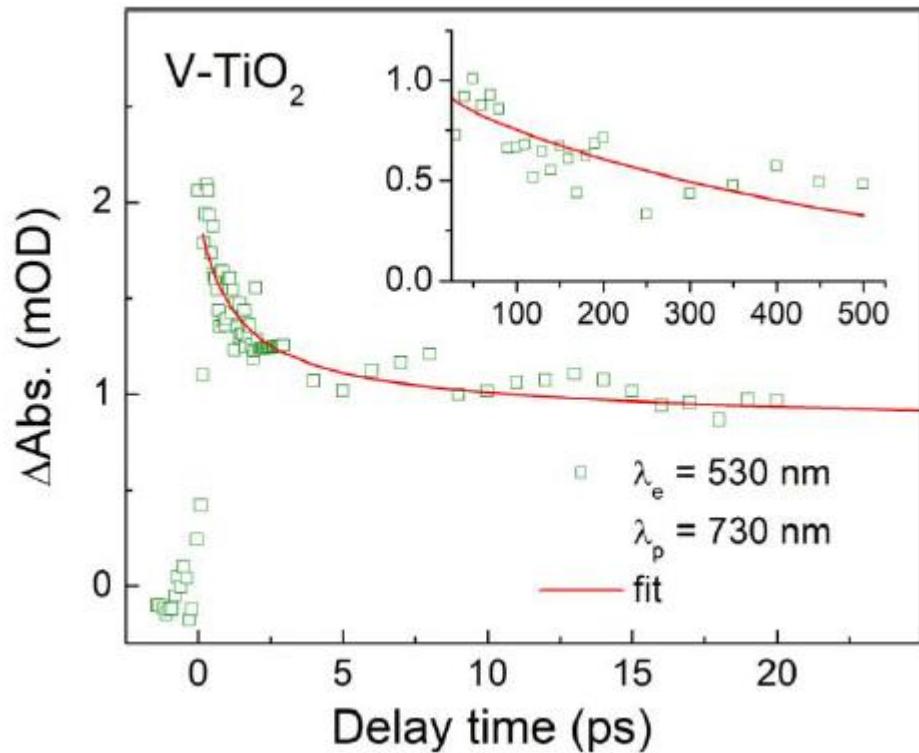
Above bandgap excitation



- TH rise time \sim 200 fs: diffusion from bulk to surface
- TH signal
 - TiO_2 : no decay
 - V-TiO_2 : 50% decay in 300 ps

Below bandgap excitation (530 nm)

E



- Persistent E signal, signature of long lived electrons on NP surface

V: TiO₂ nanoparticle assembled films: site location of V

THE JOURNAL OF
PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Local Structure of V Dopants in TiO₂ Nanoparticles: X-ray Absorption Spectroscopy, Including Ab-Initio and Full Potential Simulations

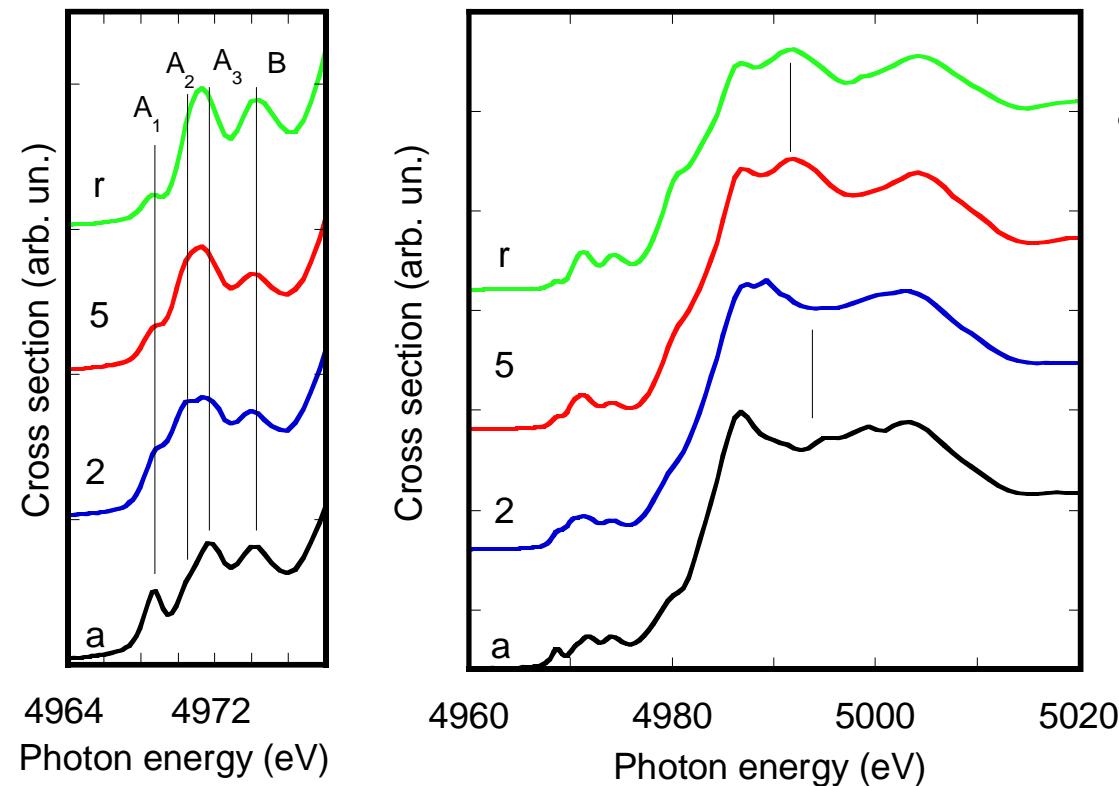
Giacomo Rossi, Marco Calizzi, Valeria Di Cintio, Sotirios Magkos,[†] Lucia Amidani,[‡] Luca Pasquini, and Federico Boscherini*

Rossi et al., J. Phys. Chem. C **120**, 7457–7466 (2016)



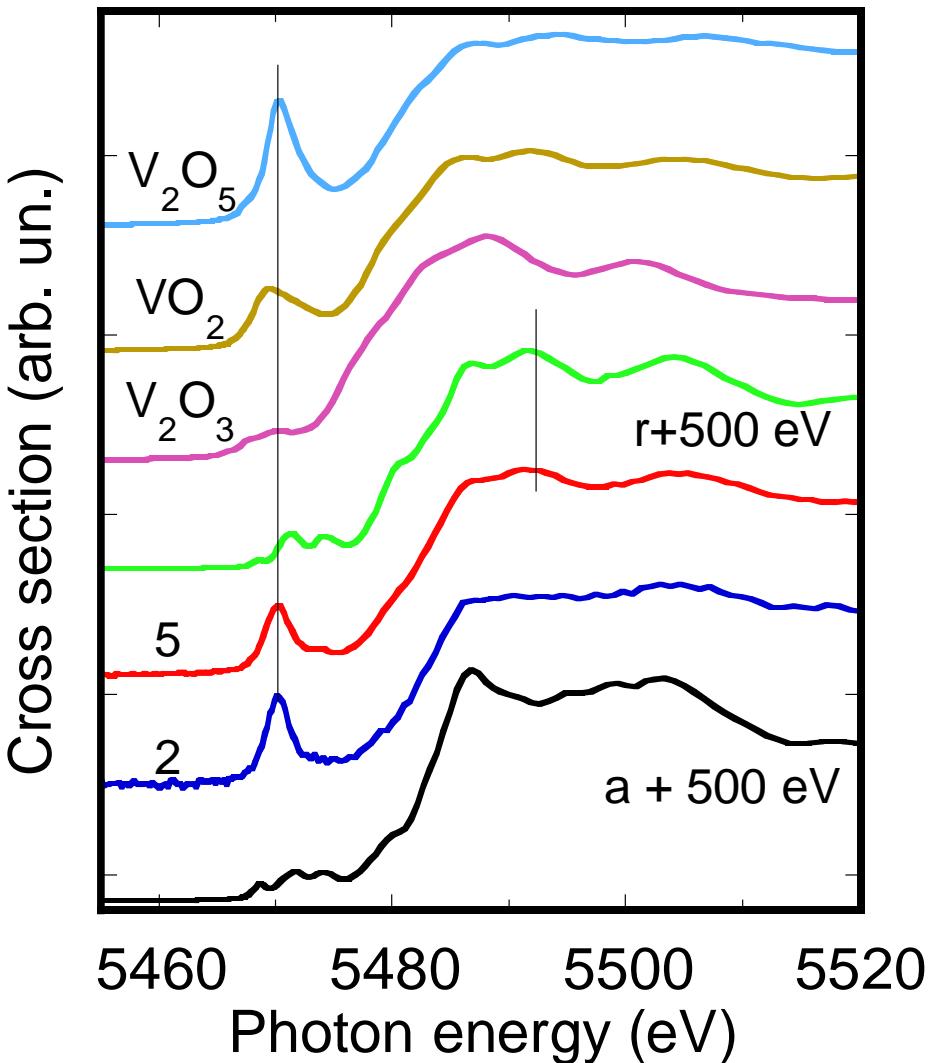
V:TiO₂: Ti K - edge

- BM 23 @ ESRF



- Pre – edge, XANES & EXAFS: local structure is slightly disordered replica of rutile (2) or anatase (5)

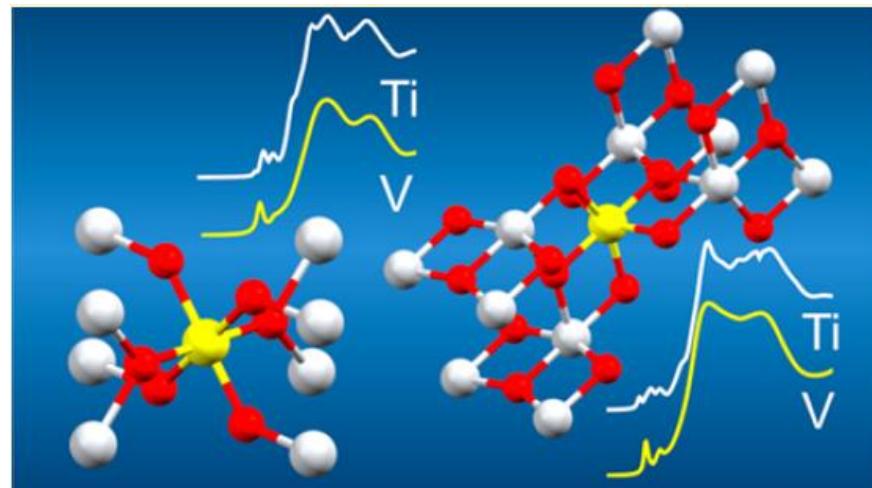
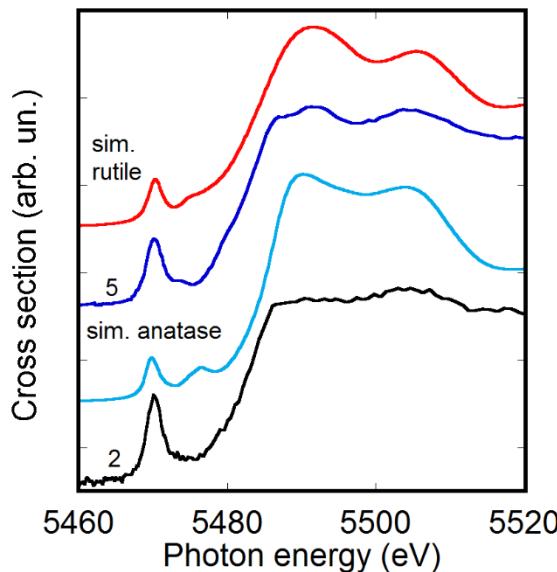
V:TiO₂: V K - edge



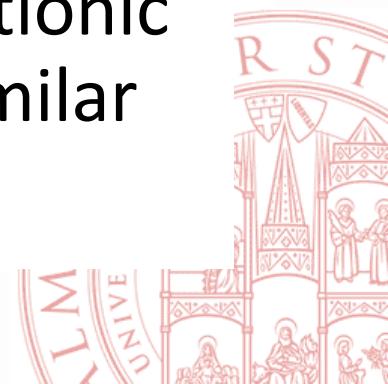
- Main edge: incorporation site is similar to matrix
- Pre-edge: oxidation state of V is mixture of 4+ (bulk) and 5+ (defective, surface sites)



V:TiO₂: V K – edge simulations



- Structural simulations with QUANTUMESPRESSO
- Spectral simulations with FDMNES (no muffin tin)
- Conclusion: V ions occupy substitutional cationic sites in TiO₂, irrespective of whether it is similar to rutile, anatase, or mixed.



V: TiO₂ nanoparticle assembled films: charge transfer by differential RIXS

PHYSICAL REVIEW B 96, 045303 (2017)

Element-specific channels for the photoexcitation of V-doped TiO₂ nanoparticles

Giacomo Rossi,¹ Marco Calizzi,¹ Lucia Amidani,² Andrea Migliori,³ Federico Boscherini,^{1,4,*} and Luca Pasquini¹

¹*Department of Physics and Astronomy and CNISM, University of Bologna, Viale C. Berti Pichat 6/2, 40127, Bologna, Italy*

²*ESRF – The European Synchrotron, CS40220, 38043 Grenoble, France*

³*Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e i Microsistemi, Bologna, Italy*

⁴*Consiglio Nazionale delle Ricerche, Istituto Officina dei Materiali, Strada Statale 14, Km. 163.5 in AREA Science Park, 34149 Basovizza, Trieste, Italy*

(Received 20 February 2017; revised manuscript received 1 June 2017; published 7 July 2017)

Rossi et al., Phys. Rev. B 96, 045303 (2017)

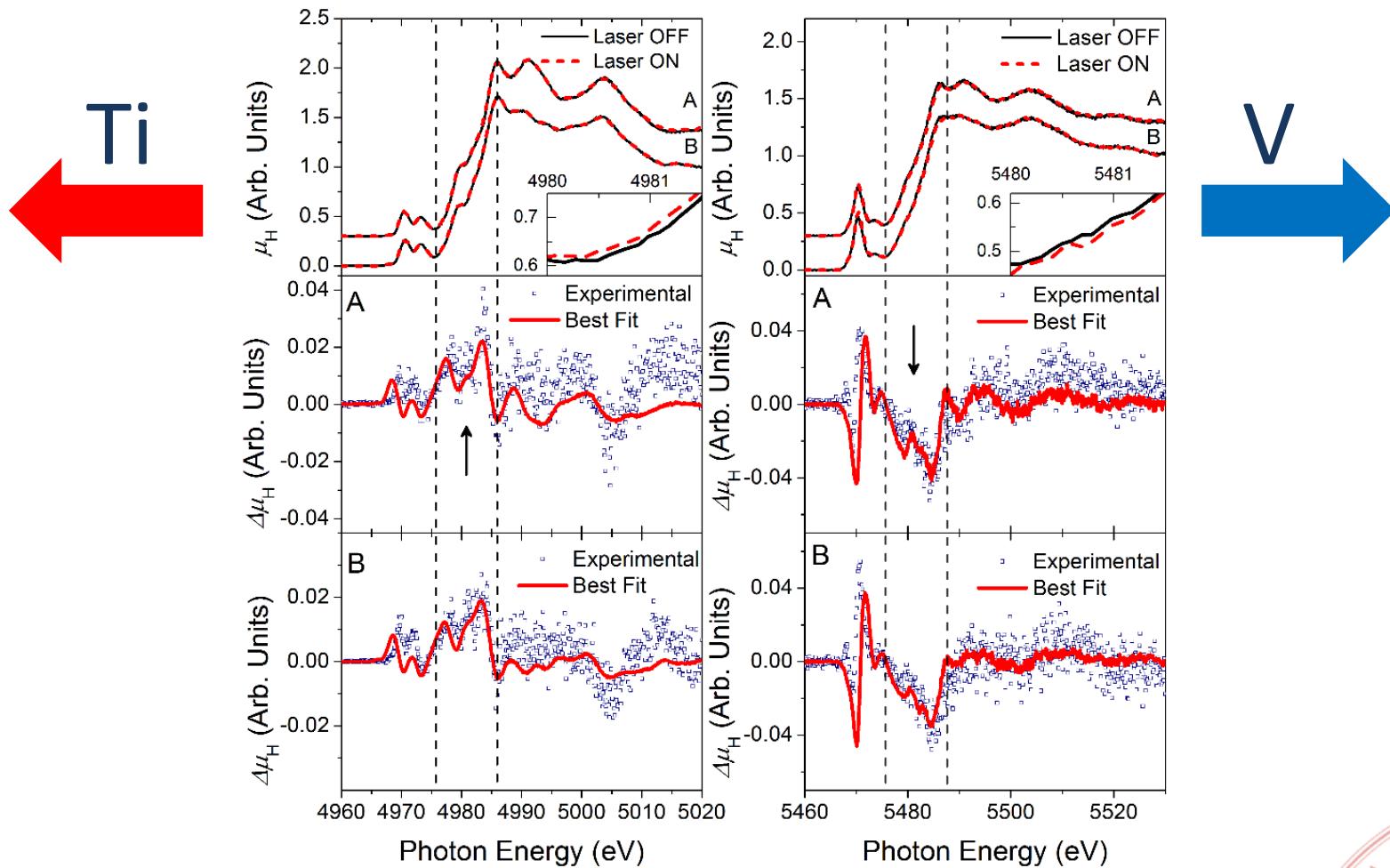


Differential RIXS on V:TiO₂

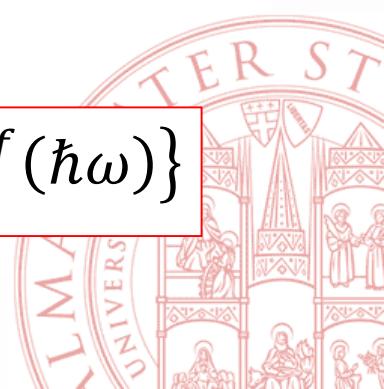
- Differential RIXS experiment, ID 26 @ ESRF
- Laser diode on/off, $\lambda = 532$ nm
- Ti and V edges



Differential RIXS on V:TiO₂

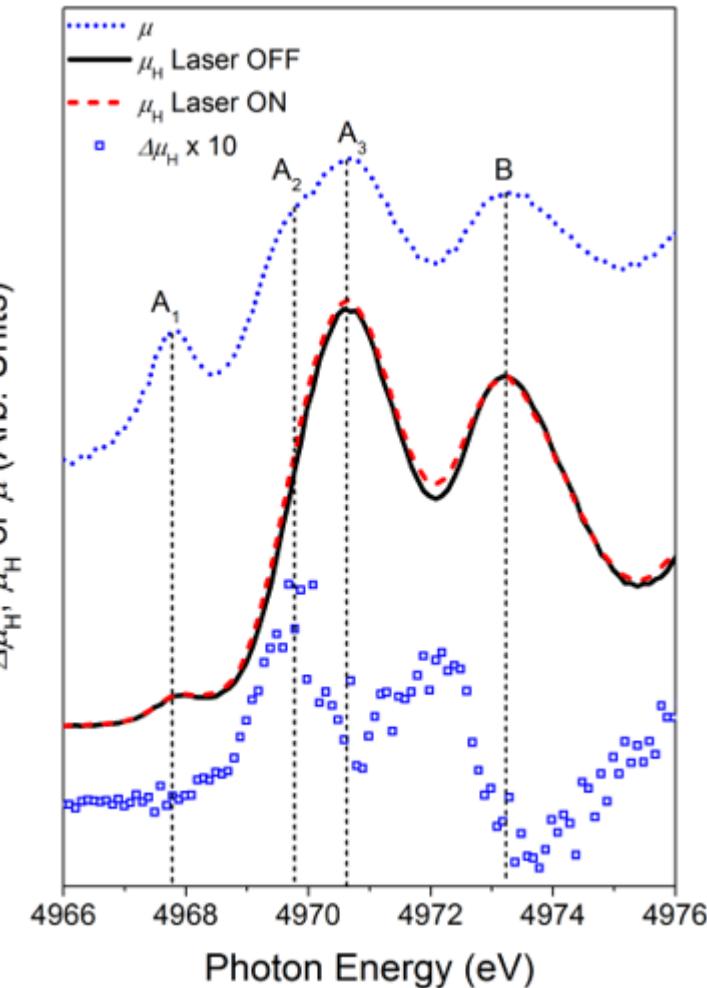


$$\text{Fit with } \Delta\mu_H(\hbar\omega) = \xi \{ \mu_H^{off}(\hbar\omega - \Delta E) - \mu_H^{off}(\hbar\omega) \}$$

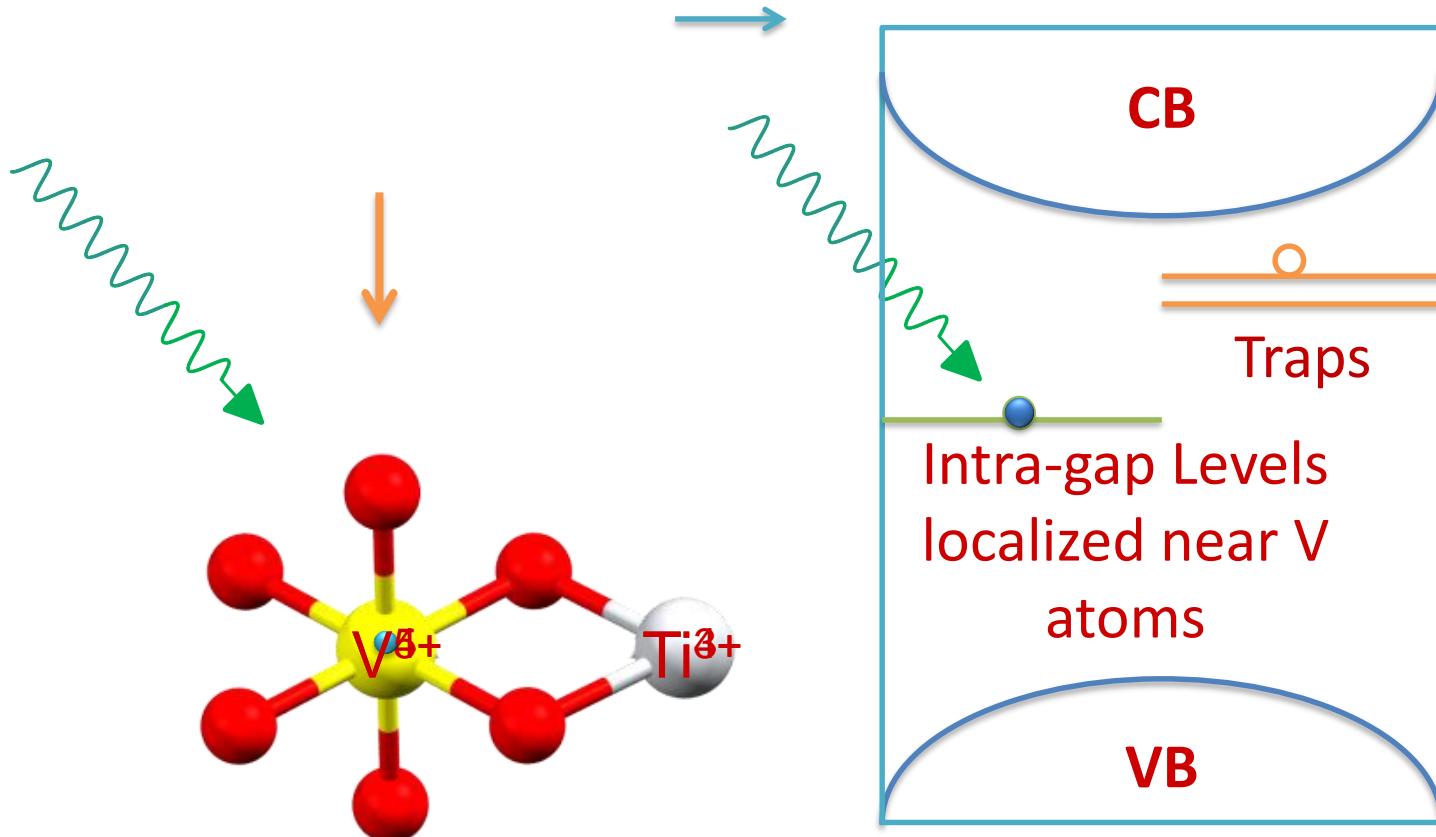


Differential RIXS on V:TiO₂

- Ti and V edges shift in opposite directions!
- Evidence for simultaneous light induced oxidation of V / reduction of Ti (defective sites)



Physical Mechanism

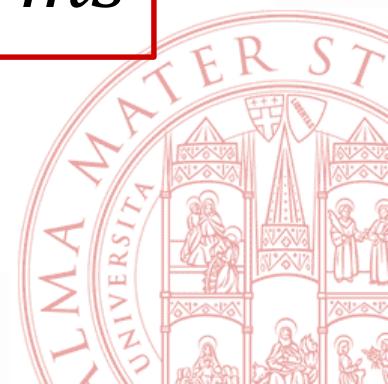


Two level steady state model

- The excited state fraction n_e obeys

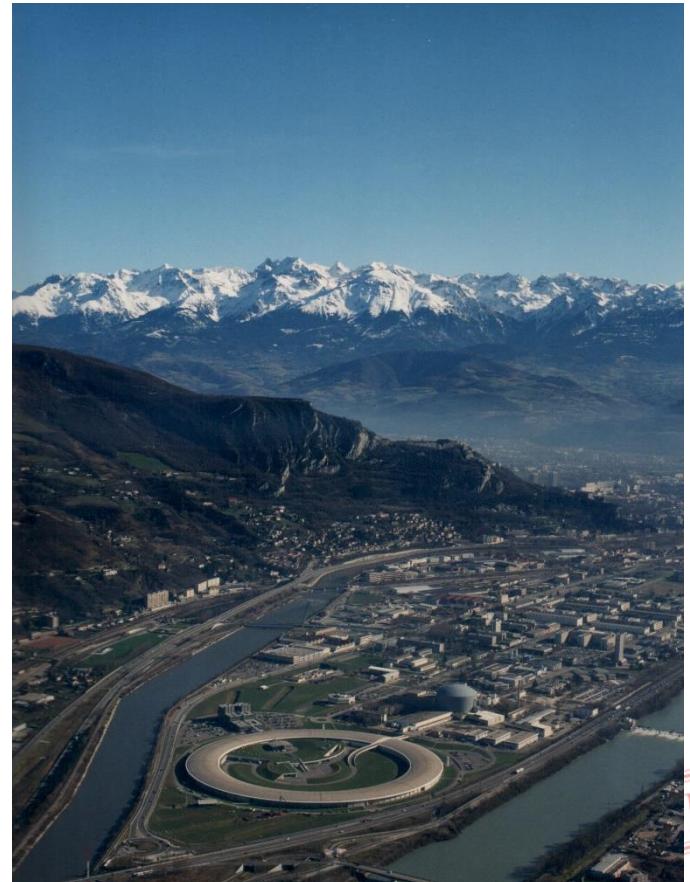
$$\frac{dn_e}{dt} = \frac{(1-n_e)}{\tau_{ge}} - \frac{n_e}{\tau_{eg}}$$

- In the steady state $\tau_{eg} = \frac{n_e}{(1-n_e)} \tau_{ge}$
- Differential HERFD – XANES, $n_e \approx 0.2$
- τ_{ge} from optical attenuation and laser fluence
- Lifetime of the trapped state $\tau_{eg} \approx 0.8 \text{ ms}$



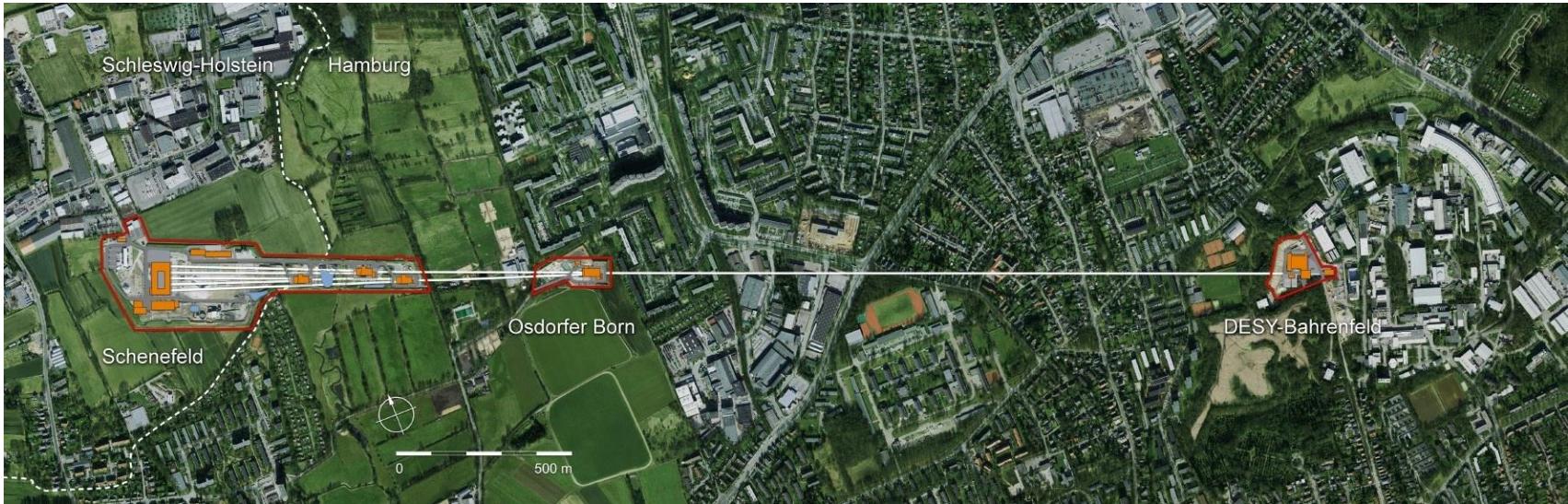
Perspectives

- Time resolved x-ray spectroscopy
 - 100 ps time resolution with SR storage ring, European Synchrotron Radiation Facility, Grenoble



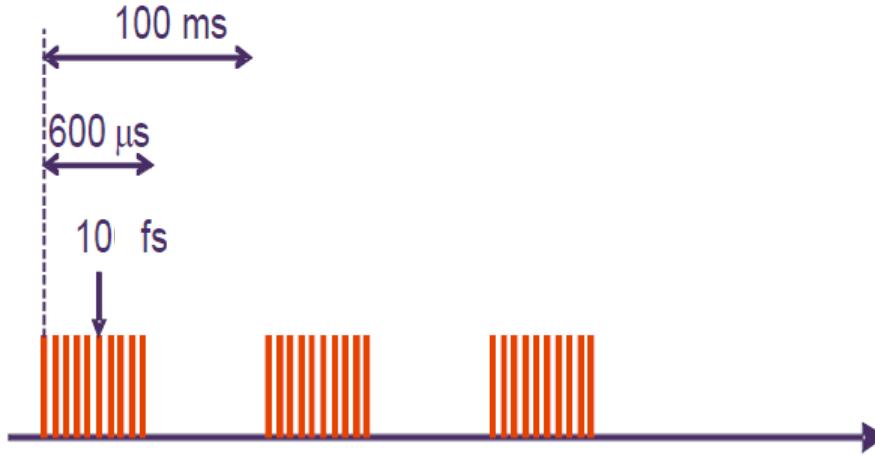
Perspectives

- Time resolved x-ray spectroscopy
 - 100 fs time resolution possible at European X-ray Free Electron Laser, Hamburg



EU-XFEL time structure

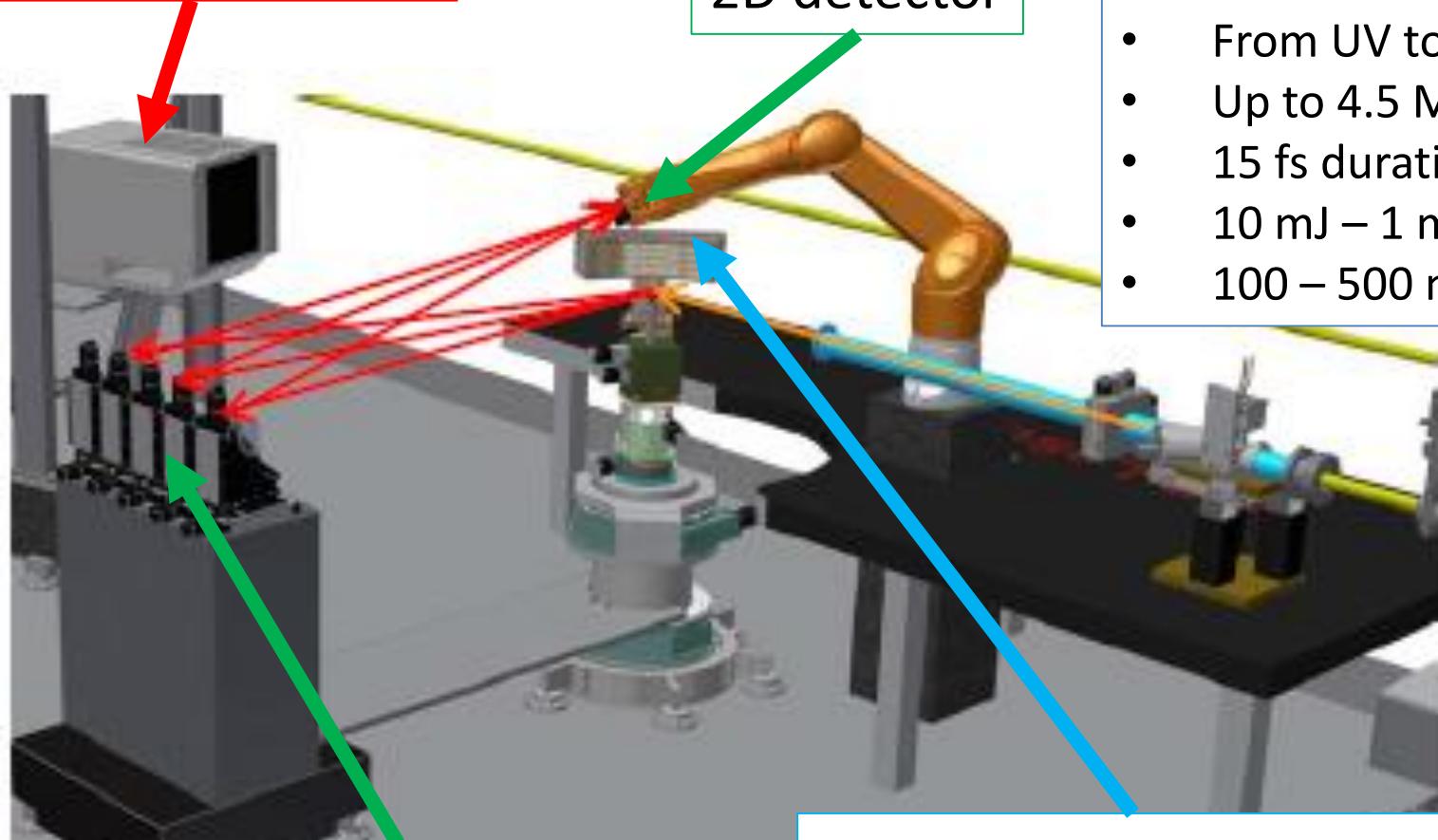
- Full burst mode
 - 2700 pulses/600 μ s every 100 ms, time between pulses = 222 ns, frequency = 4.5 MHz
- Intermediate case
 - 120 pulses/600 μ s,
time between pulses = 5 μ s,
frequency = 200 kHz
- Single pulse mode
 - 1 pulse every 100 ms,
frequency = 10 Hz.



The FXE Instrument (5 – 20 keV)

Large Pixel Detector

2D detector



Laser

- From UV to THz
- Up to 4.5 MHz
- 15 fs duration (min)
- 10 mJ – 1 mJ
- 100 – 500 mm

Johann scanning spectrometer

Von Hamos spectrometer



Collaborators, funding

- Collaborators
 - Bologna: Luca Pasquini, Giacomo Rossi, Marco Calizzi, Nicola Patelli, Alberto Piccioni
 - Stefano Caramori, Serena Berardi (Univ. Ferrara)
 - Alberto Naldoni (CNR Milano), Marco Malvestuto (Elettra)
 - Lucia Amidani, Pieter Glatzel (ESRF)
- Funding: PIK «EX-PRO-REL», PRIN 2015 «NEWLI»





The end

