

Vanadium local structure and photoinduced charge transfer in V-TiO₂ by X-ray absorption spectroscopy

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Outline

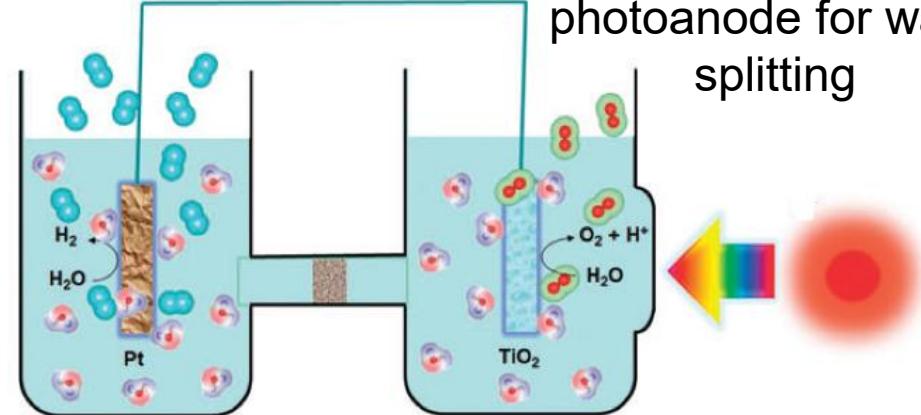
- Intro: TiO₂-based photocatalysts, 1st and 2nd generation
- Deposition and structure of V-TiO₂ thin films
- X-ray Absorption Spectroscopy: results and simulations
- Laser on / off differential RIXS: V→Ti charge transfer
- Conclusions



Semiconductor photocatalysts

Photo-electrochemical cell (PEC) with oxide photoanode for water splitting

e^-



X. Chen, M. Grätzel et al., Chem Soc Rev (2012)

Habisreutinger et al., Angew. Chem (2013)

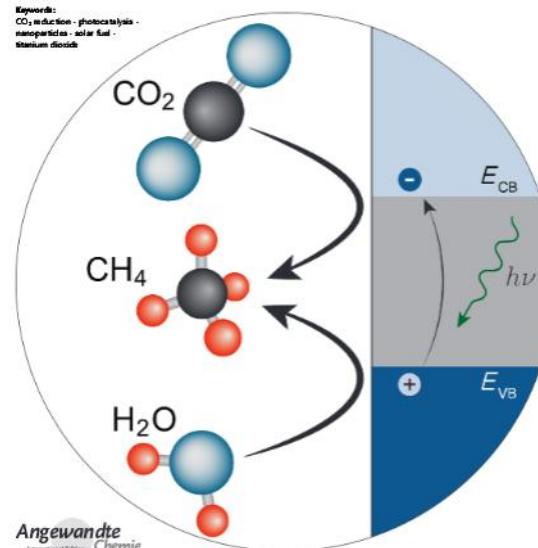
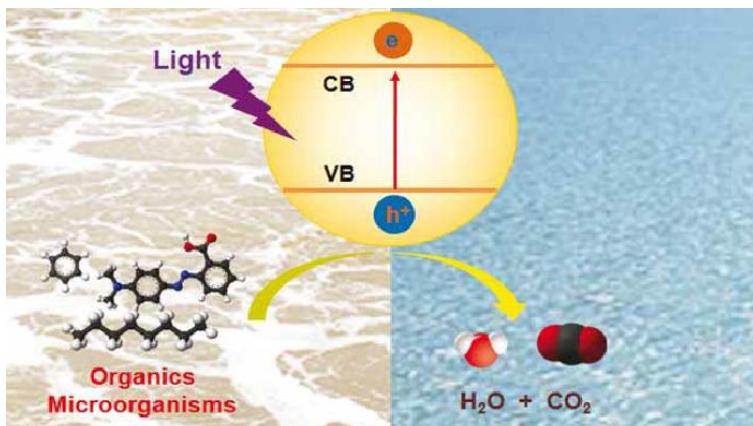


Photo-catalytic CO₂ reduction

Photo-generated •OH,
•O₂⁻, H₂O₂
→mineralization of
organic contaminants /
inactivation of
microorganisms

J Mat Chem 20 (2010)



TiO₂ – based photocatalysts



Semiconductor photocatalysts

Habisreutinger et al., Angew. Chem (2013)

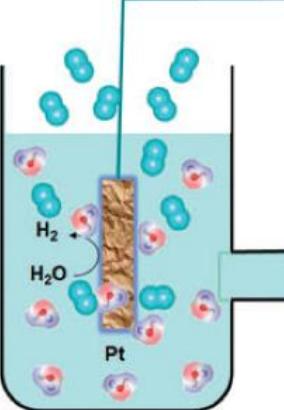
Photo-electrochemical
cell (PEC) with oxide

Keywords:
CO₂ reduction - photocatalysis -
nanoparticles - solar fuel -
titanium dioxide

e

Fundamental steps involved:

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



X. Chen, M. C.

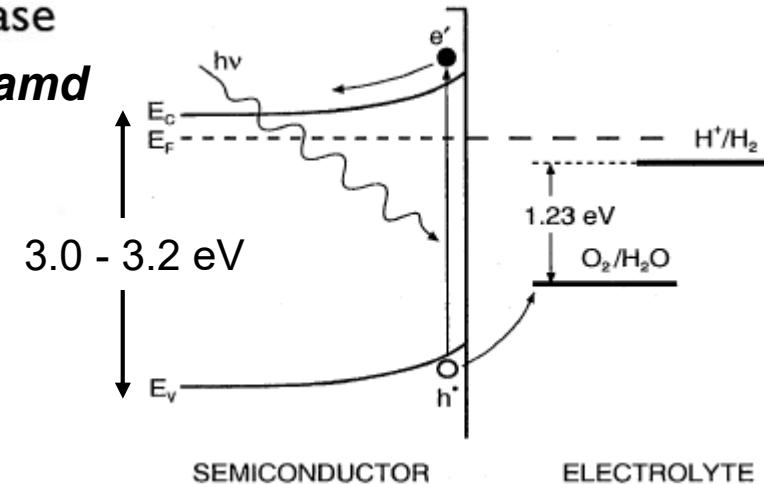
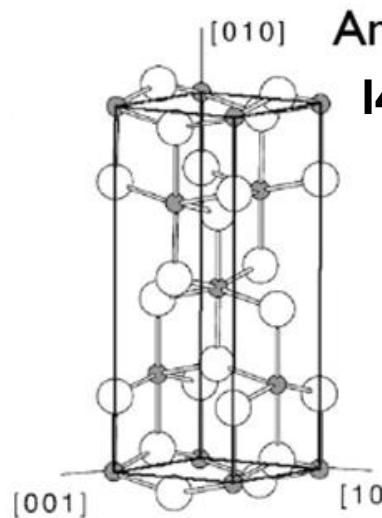
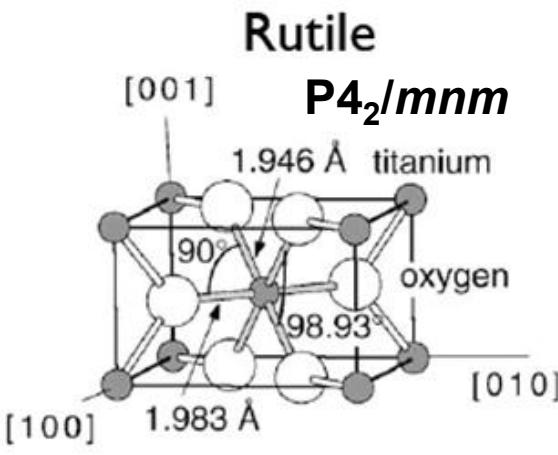
Photo-gener
• O₂⁻, H⁺
→minerali
organic cont
inactivat
microorganism

J Mat Chem 20 (2010)

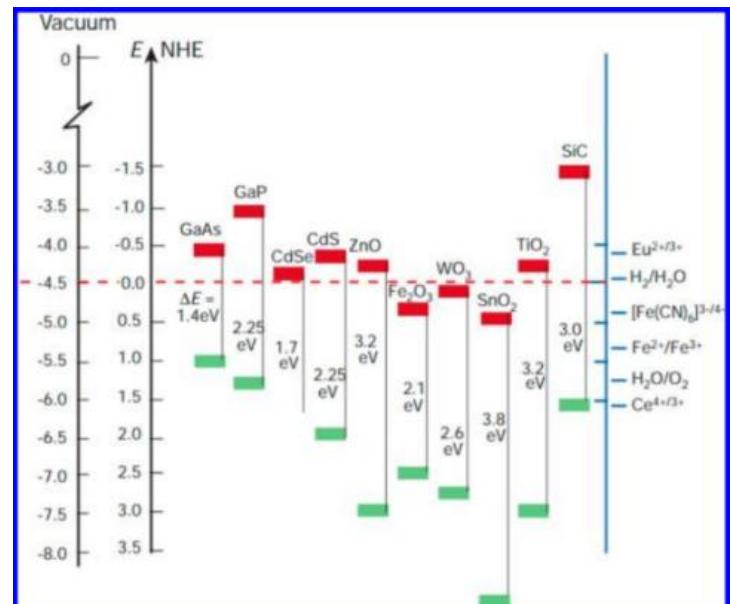


TiO₂ – based photocatalysts

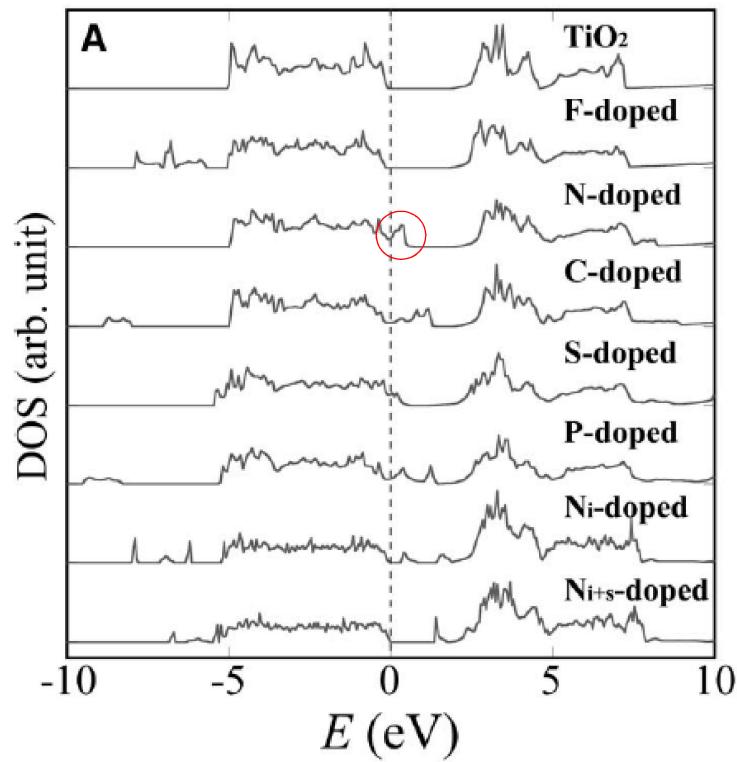
1st generation benchmark: TiO₂



- ☺ 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

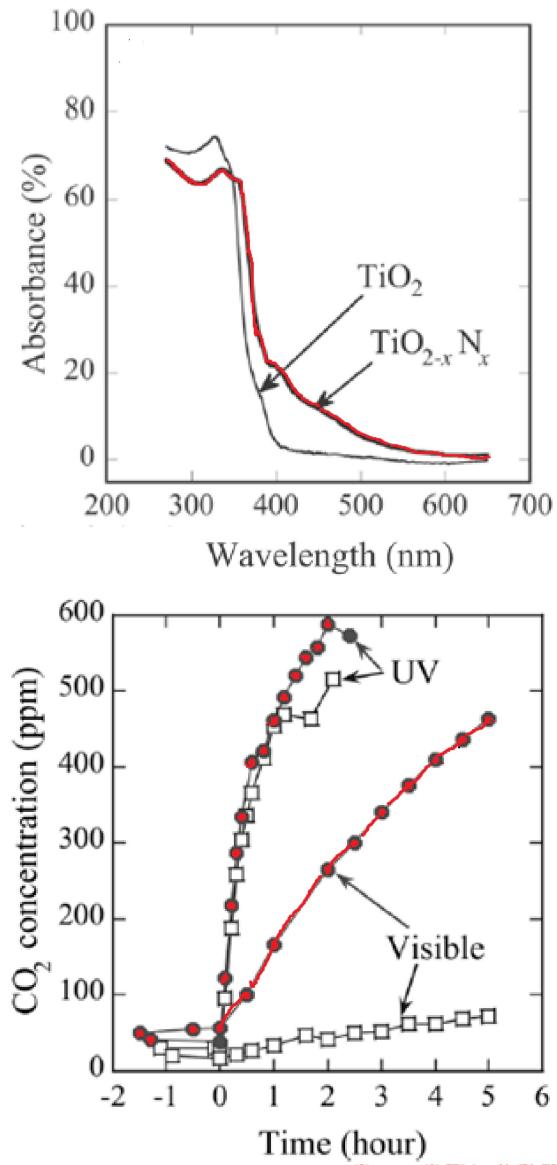


13 JULY 2001 VOL 293 SCIENCE REPORTS

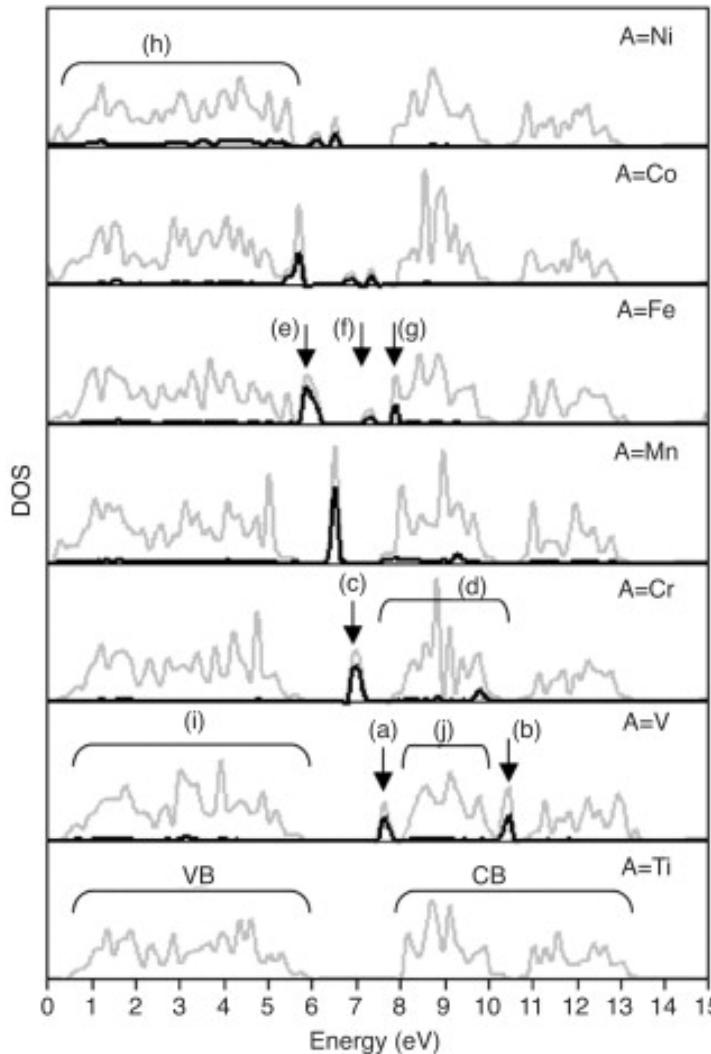
Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides

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

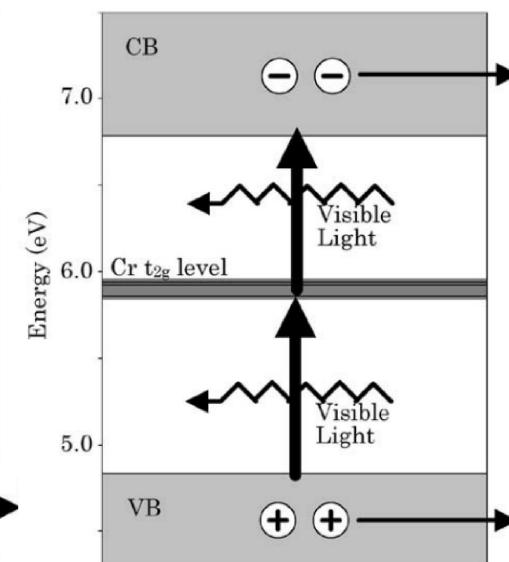
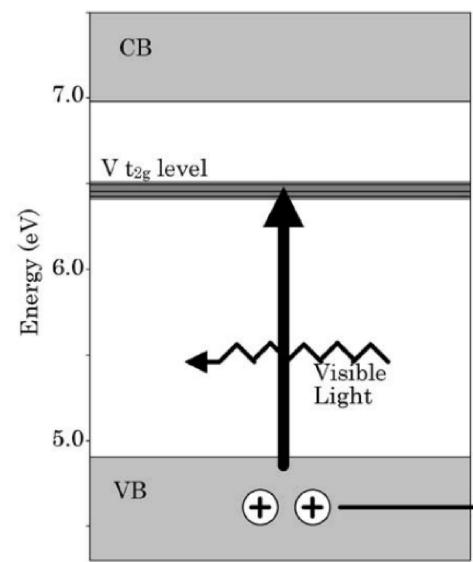
TiO₂ -based photocatalysts



Electronic structure of metal-ion doped TiO₂



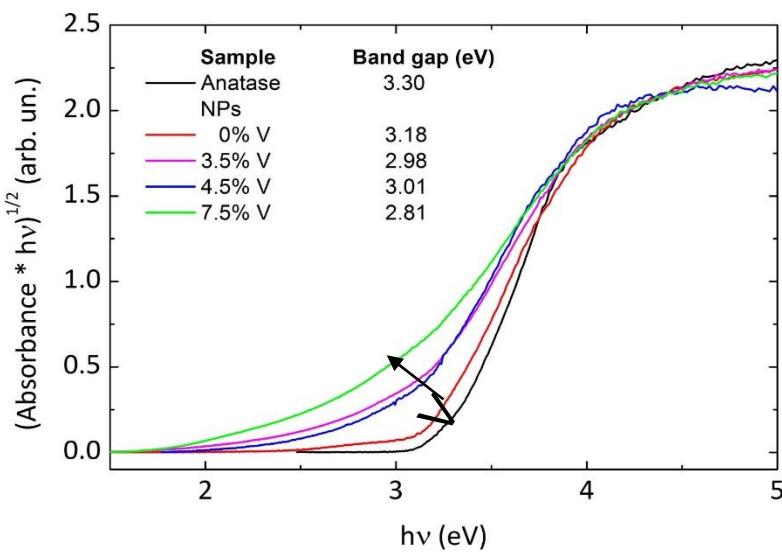
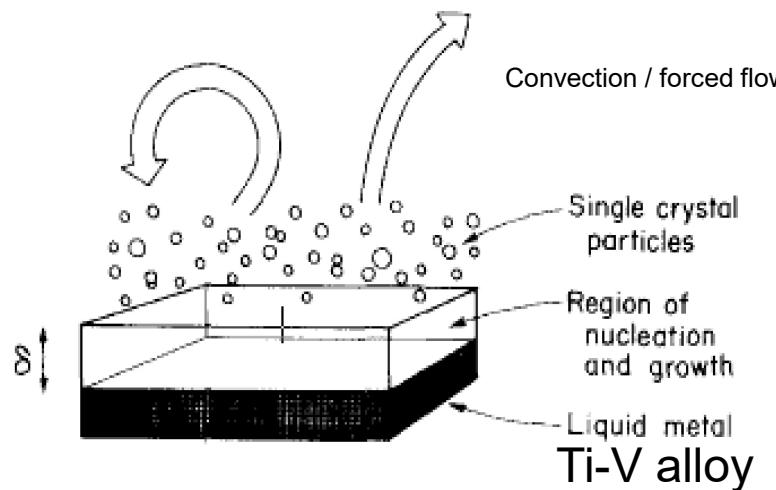
the position of the dopant's t_{2g} state in the octahedral field determine which optical transitions occur: from the dopant into TiO₂ states or from TiO₂ states into the dopant. While both types of transitions may occur using visible light, both do not have the same potential for redox



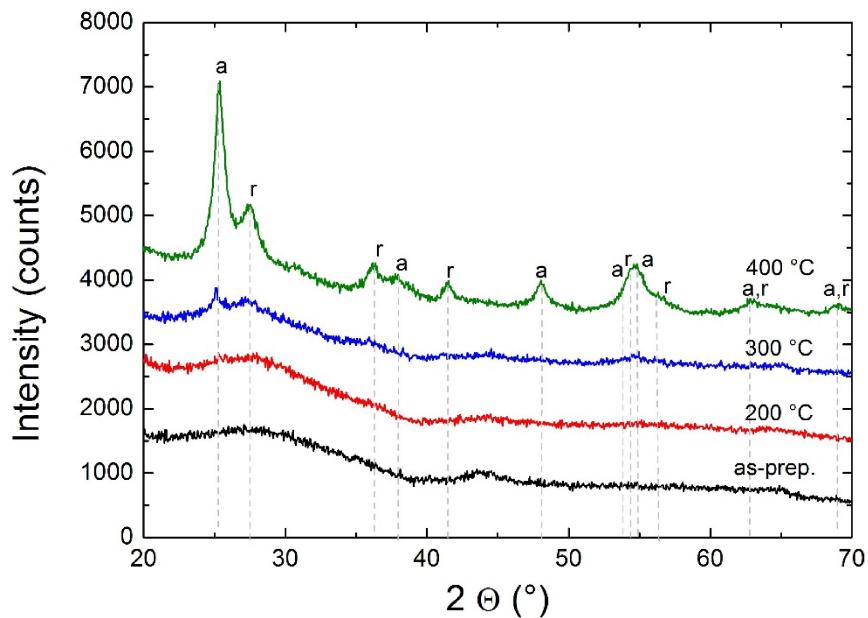
T. Umebayashi et al, J Phys Chem Sol (2002)

Deposition of NPs and NPs-assembled V-TiO₂ films

Gas-phase condensation @ DIFA, UniBO



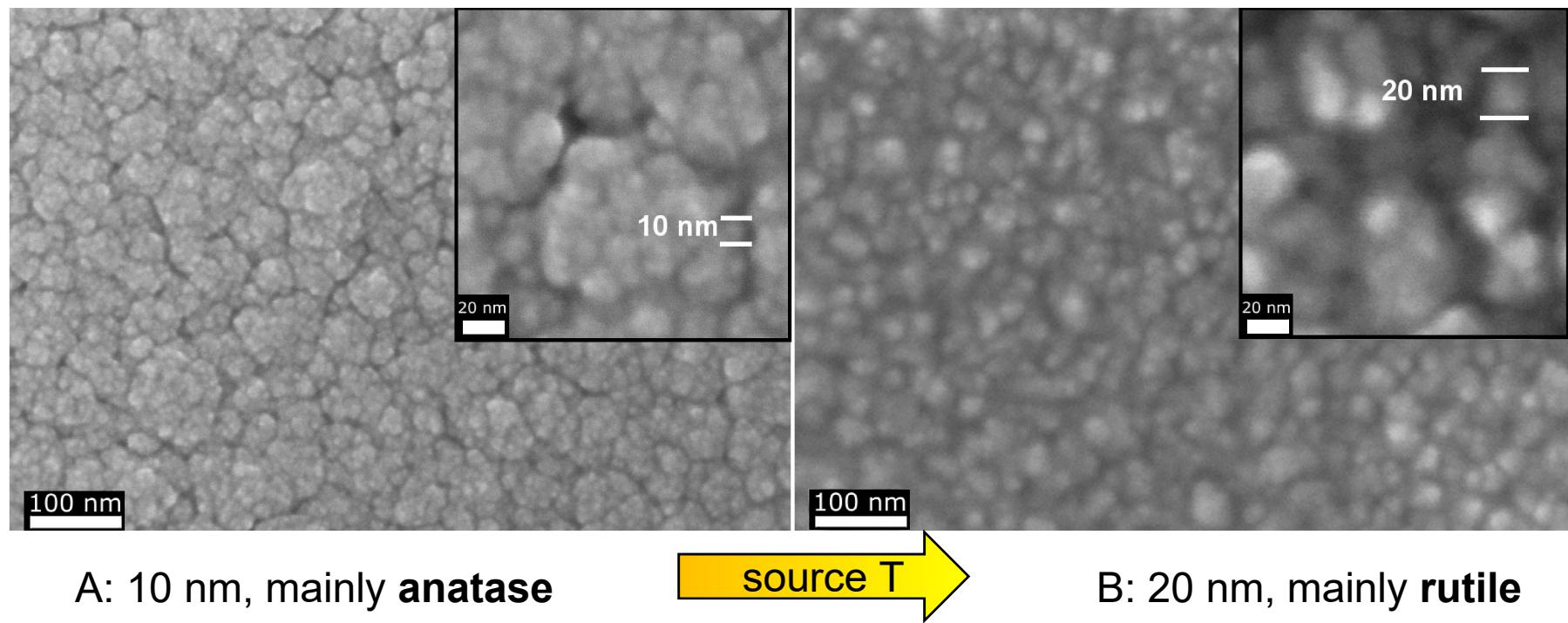
+ annealing in air



- V / T ratio: from 3 to 8 at.%
- Anatase / rutile mixture
- Visible-light absorption \uparrow and B.G. \downarrow decreases with V \uparrow

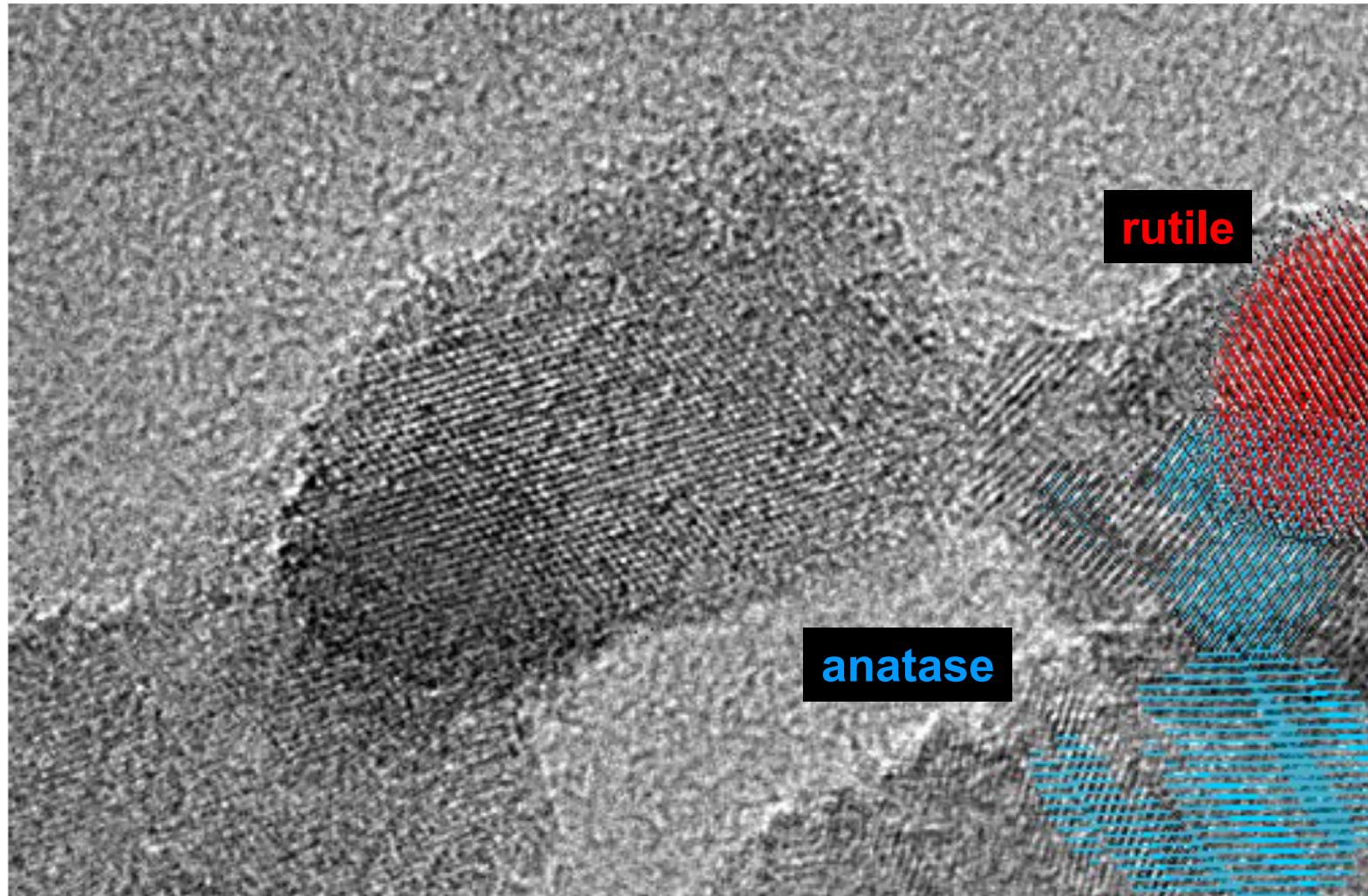
G. Rossi et al, *J. Phys. Chem. C* **120** (2016)

Structure of NPs and NPs-assembled V-TiO₂ films



G. Rossi et al, *J. Phys. Chem. C* **120** (2016)

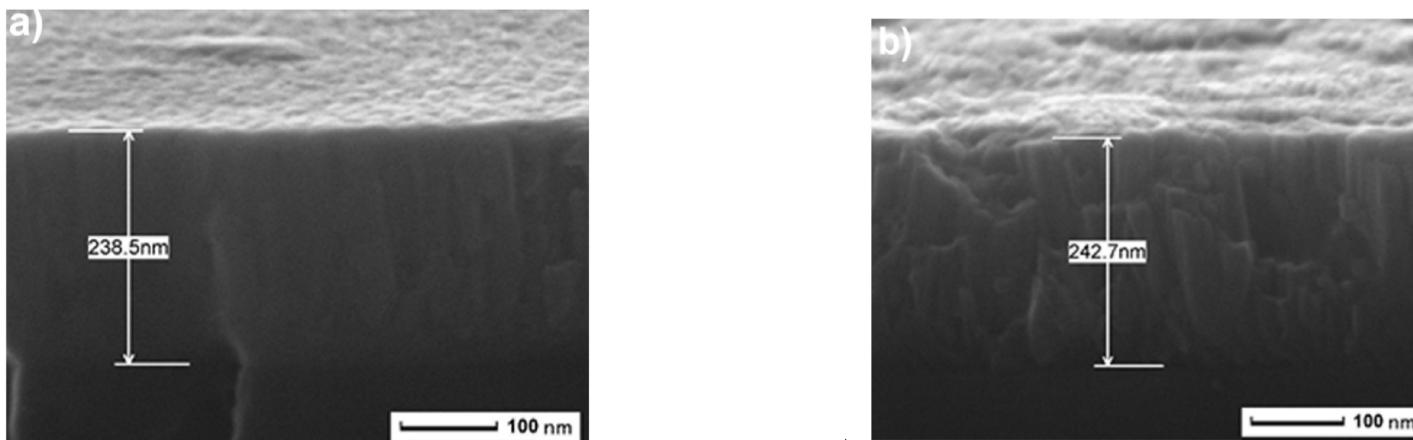
Structure of NPs and NPs-assembled V-TiO₂ films



HRTEM of V-TiO₂ NPs - courtesy of A. Migliori, IMM CNR BO

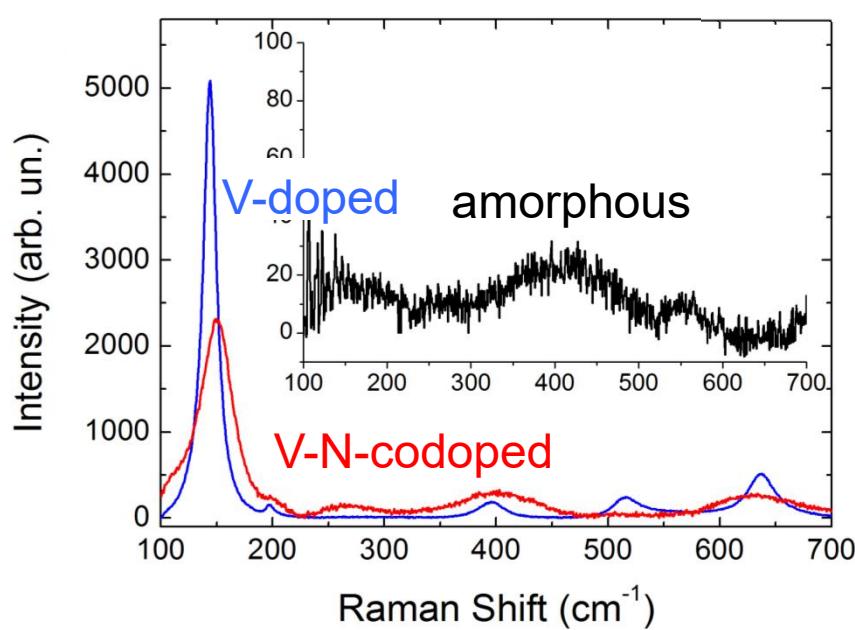
Deposition of V-(N)-TiO₂ compact thin films

RF magnetron sputtering of a composite TiO₂ / V target @ Dept. Physics, UniTN



50 °C: amorphous

350 °C: anatase



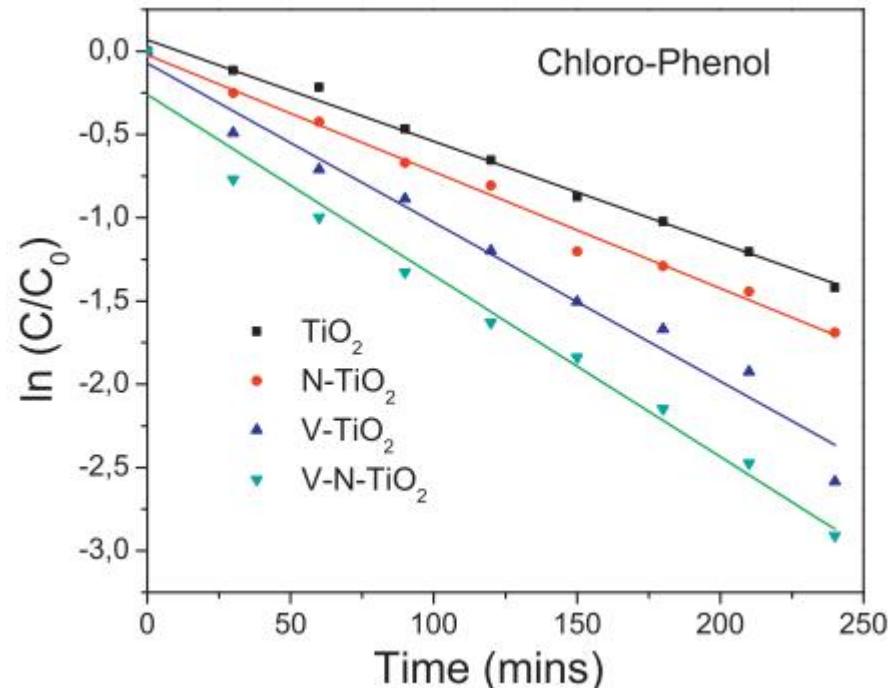
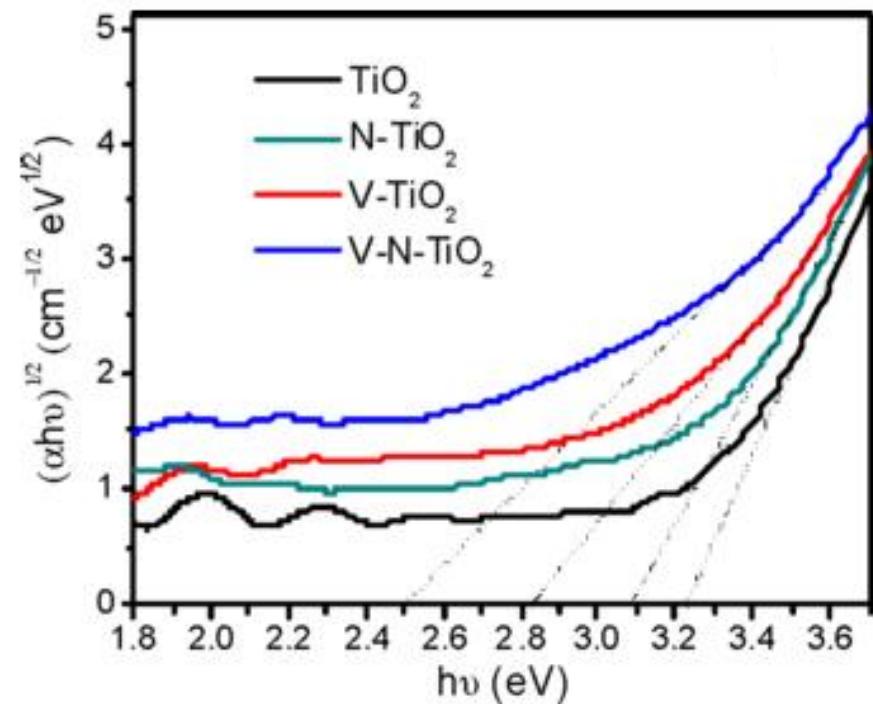
- V / T ratio: from 2.5 to 4.5 at. %
- N codoping by reactive sputtering with Ar/N₂ mixture (N/O ~ 4 at. %)

Ei Koura et al, *Int. J. Nanotechnol.* 11 (2014)



Deposition of V-(N)-TiO₂ compact thin films

Enhanced visible-light absorption and photo-catalytic activity by V and V-N doping

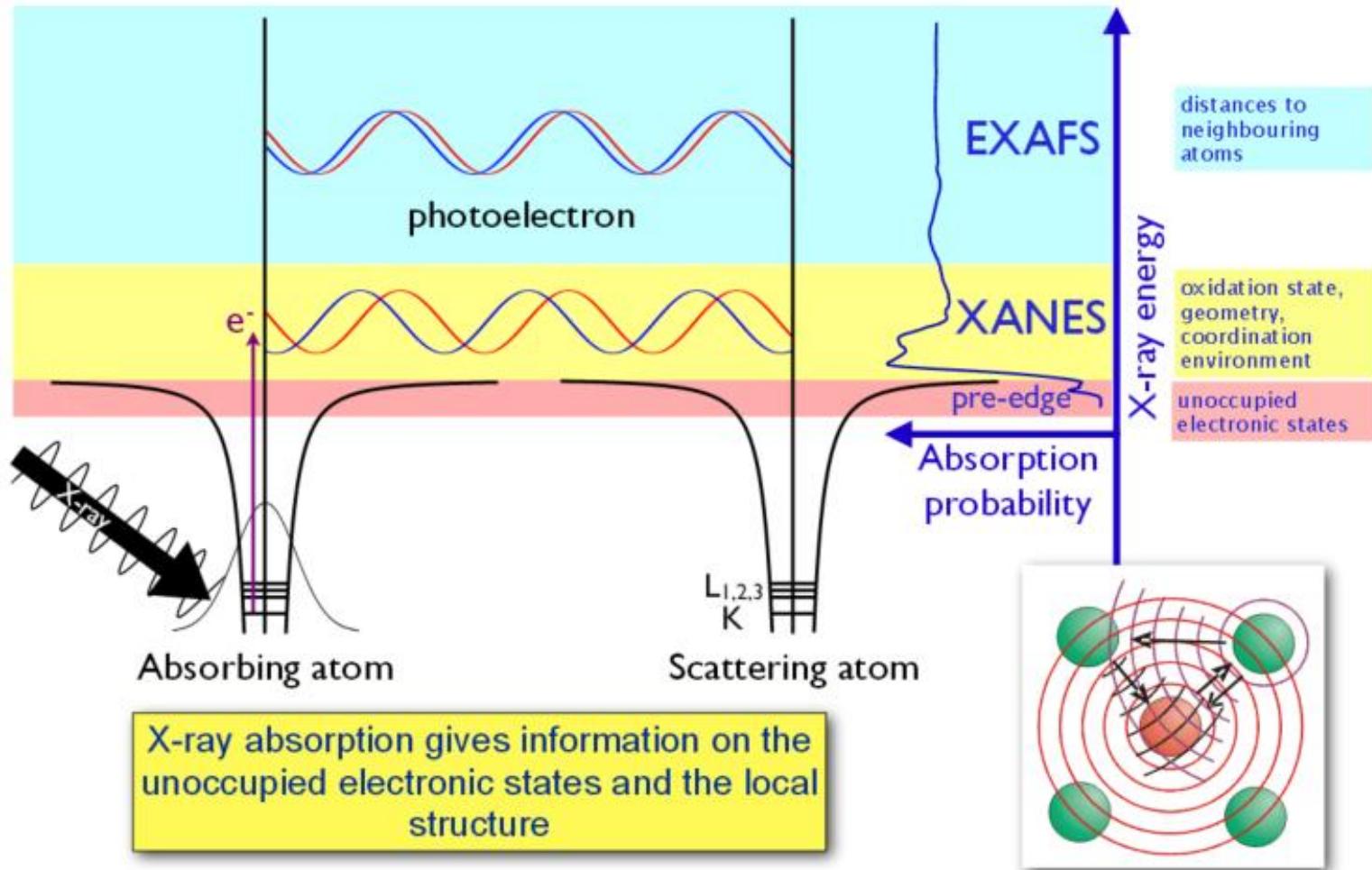


Z. El Koura et al, *Int. J. Nanotechnol.* 11 (2014)

N. Patel et al, *Appl. Catal. B* 150-151 (2014)

Aim: characterize the local structure and oxidation state of V with “bulk” sensitivity

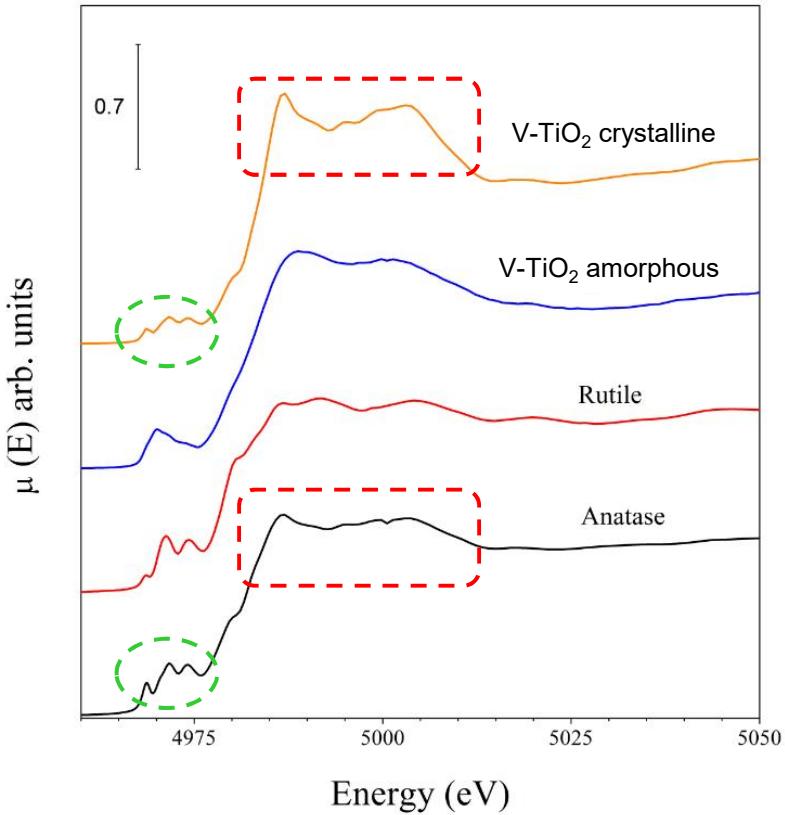
X-ray Absorption Fine Structure (XAFS)



From C. Milne, SwissFEL Conceptual Design Report (2013)

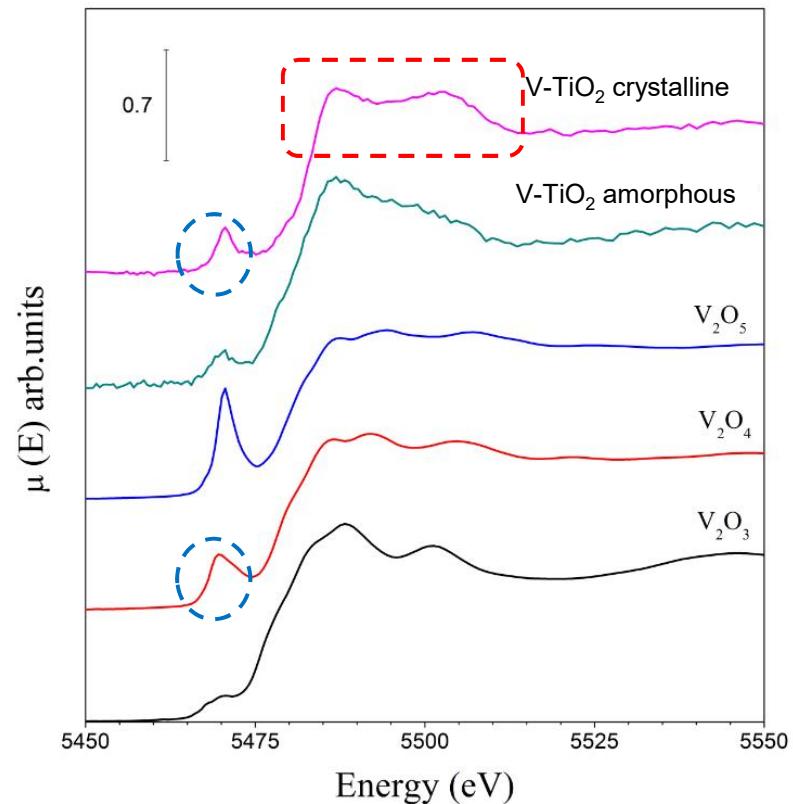
XAS on V-TiO₂ compact films

Ti K-edge



BM23 @ ESRF

V K-edge

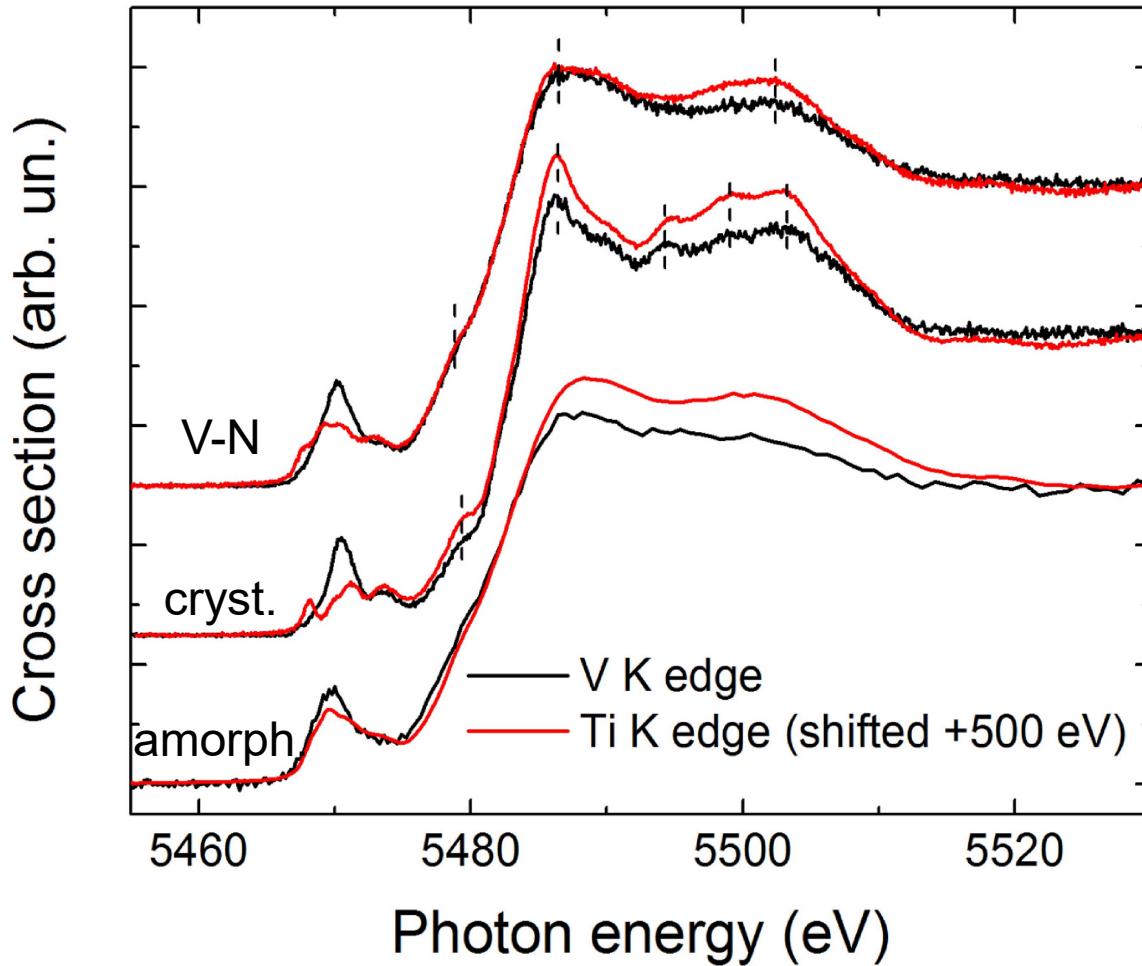


Main edge: V similar to shifted Ti (anatase)

V pre-edge: similar to VO₂

Z. El Koura et al, *submitted*

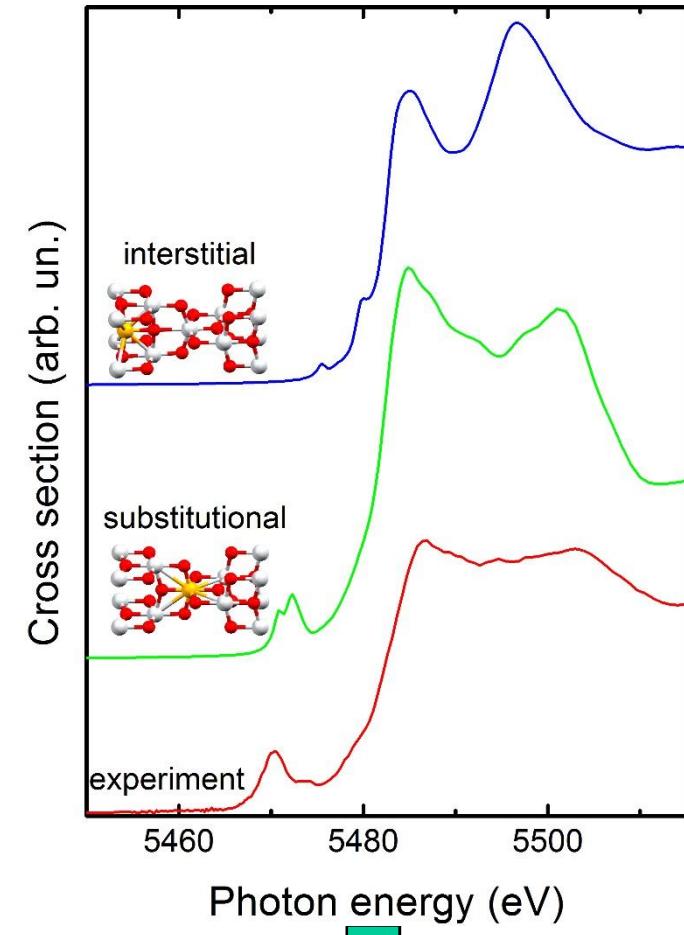
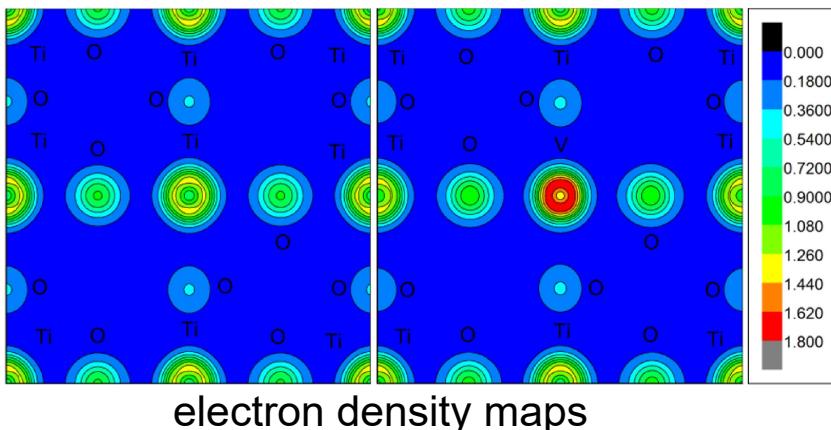
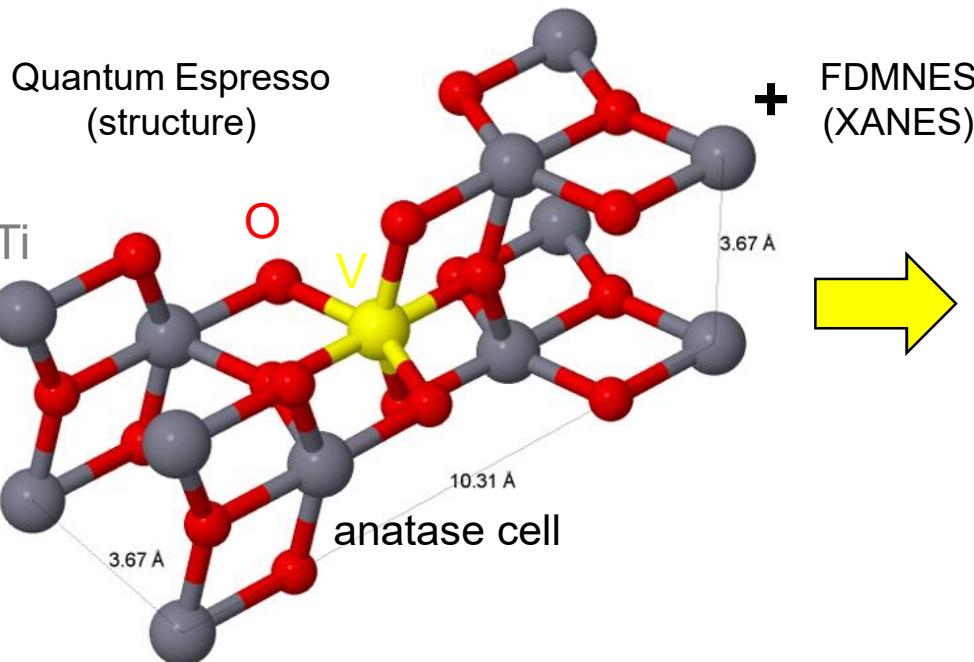
XAS on V-TiO₂ compact films



The strong similarity between V and Ti (shifted) K main edges holds for all samples

Z. El Koura et al, *submitted*

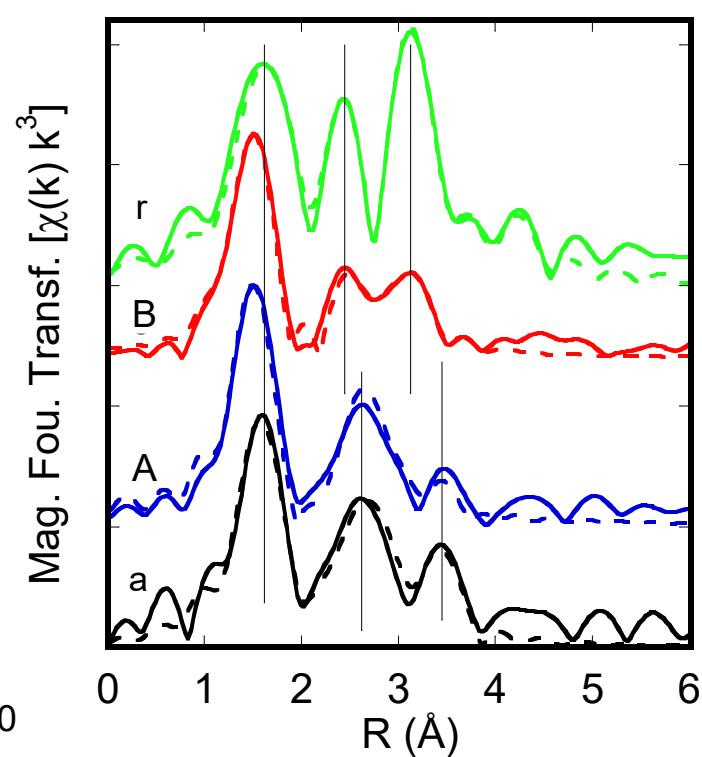
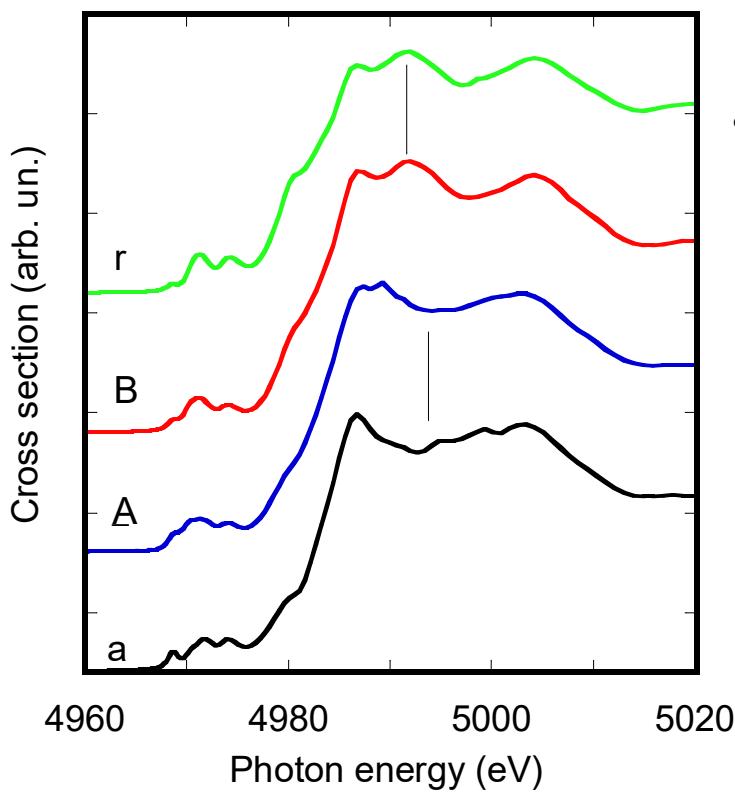
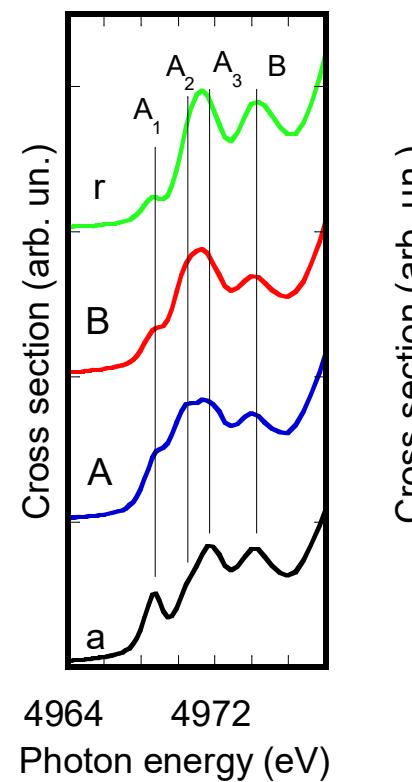
V site: experiment vs *ab initio* DFT calculations



• substitutional cation
• 4+ oxidation state

XAS on V-TiO₂ NPs-assembled films

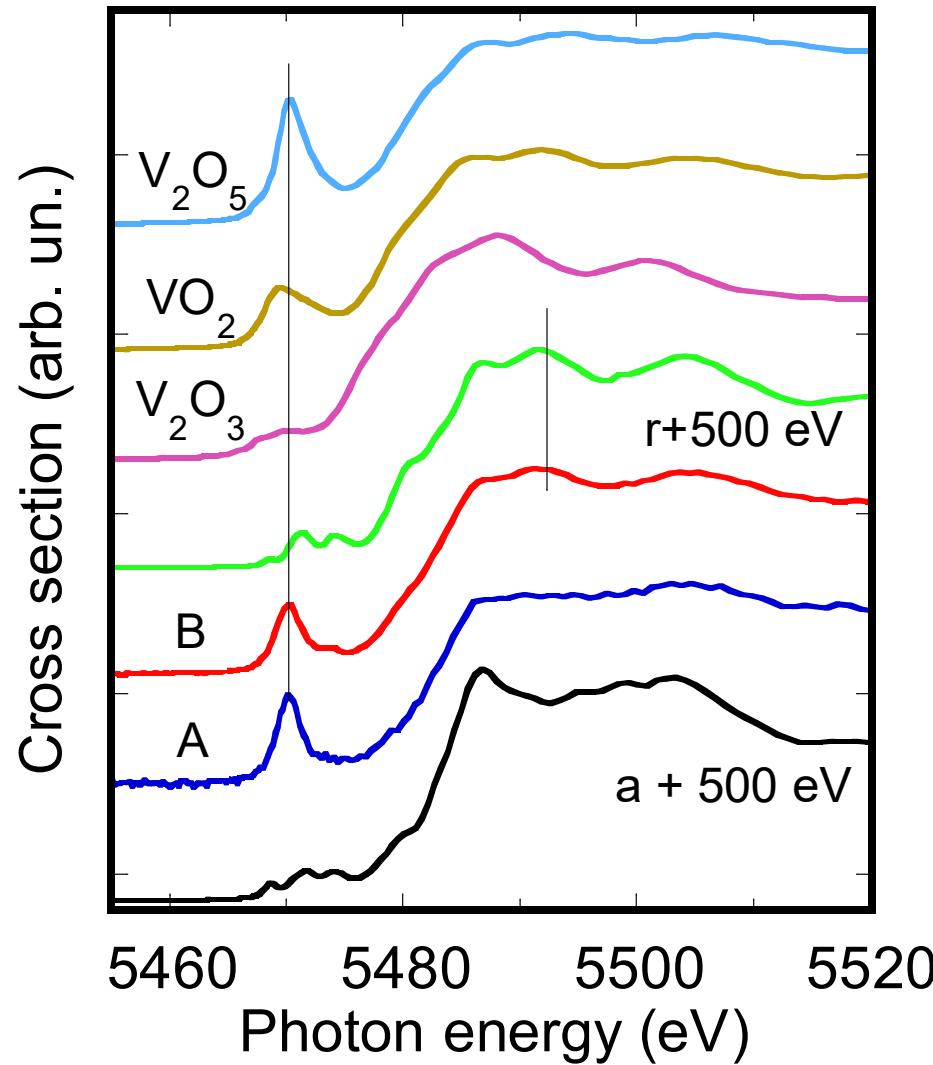
BM23 @ ESRF: Ti K-edge XANES and EXAFS



G. Rossi et al, *J. Phys. Chem. C* **120** (2016)

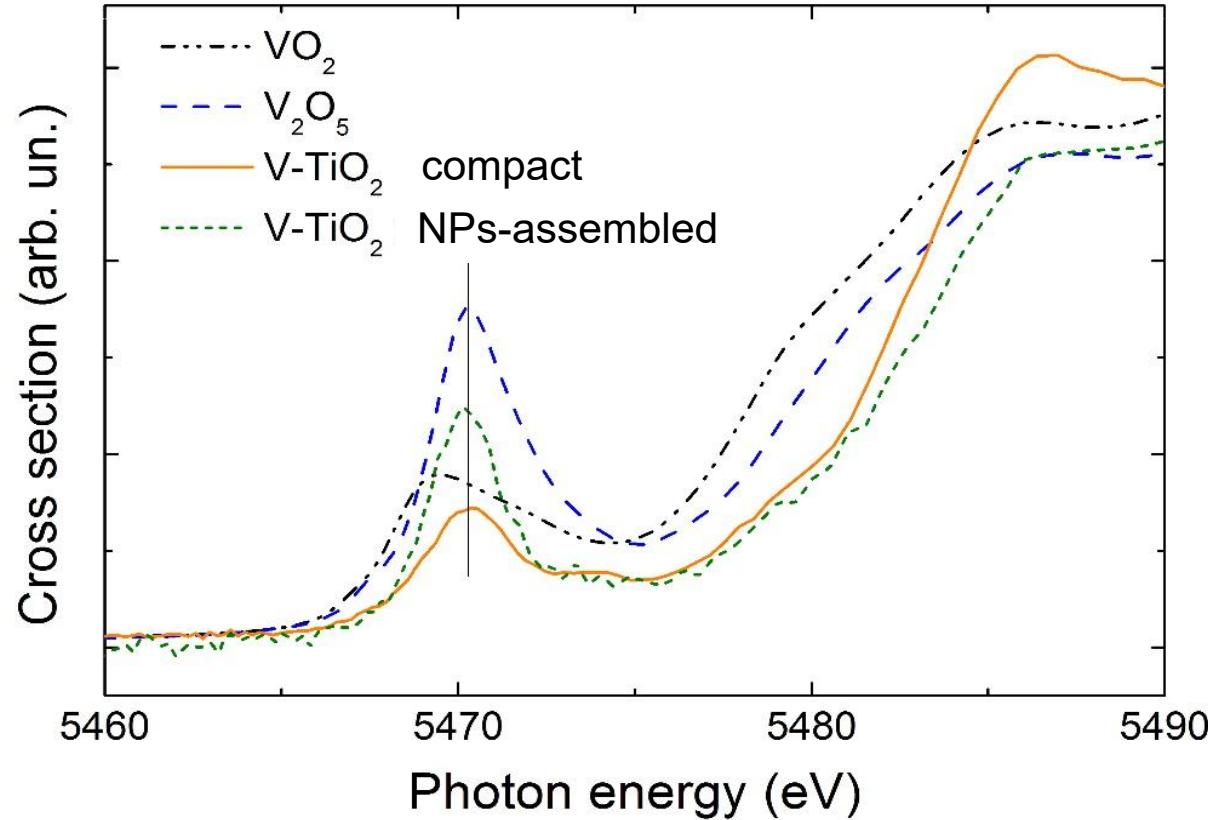
XAS on V-TiO₂ NPs-assembled films

BM23 @ ESRF: V K-edge XANES



G. Rossi et al, *J. Phys. Chem. C* **120** (2016)

V oxidation state: NPs-assembled vs compact films



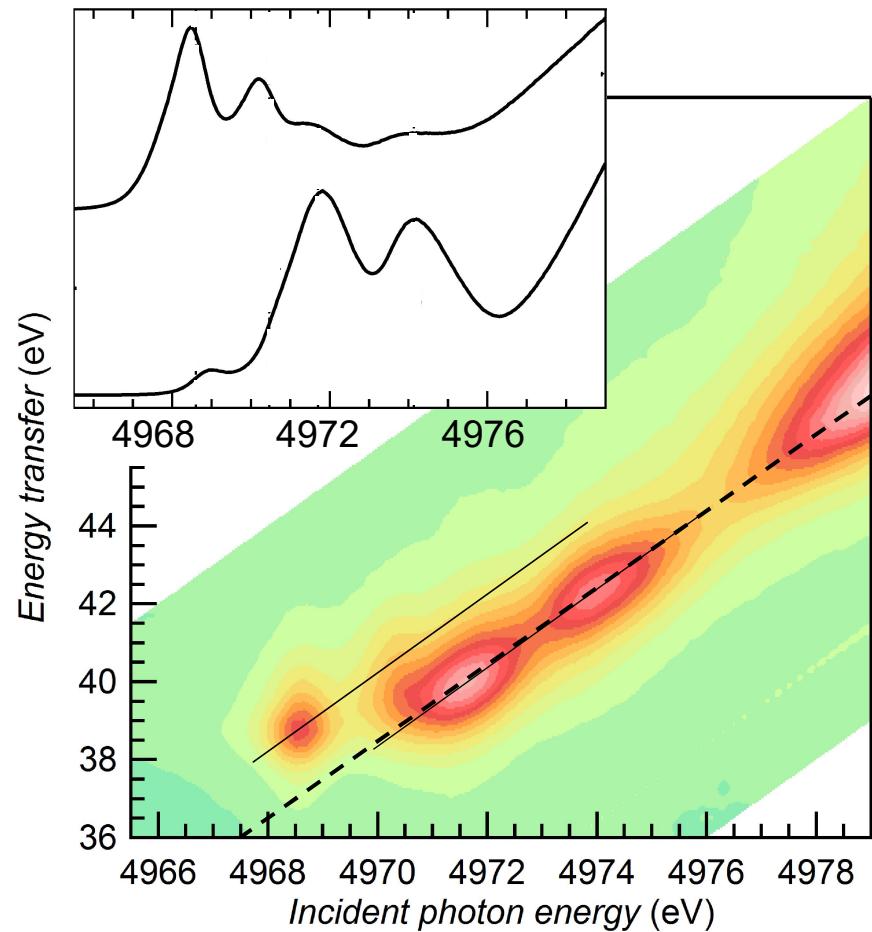
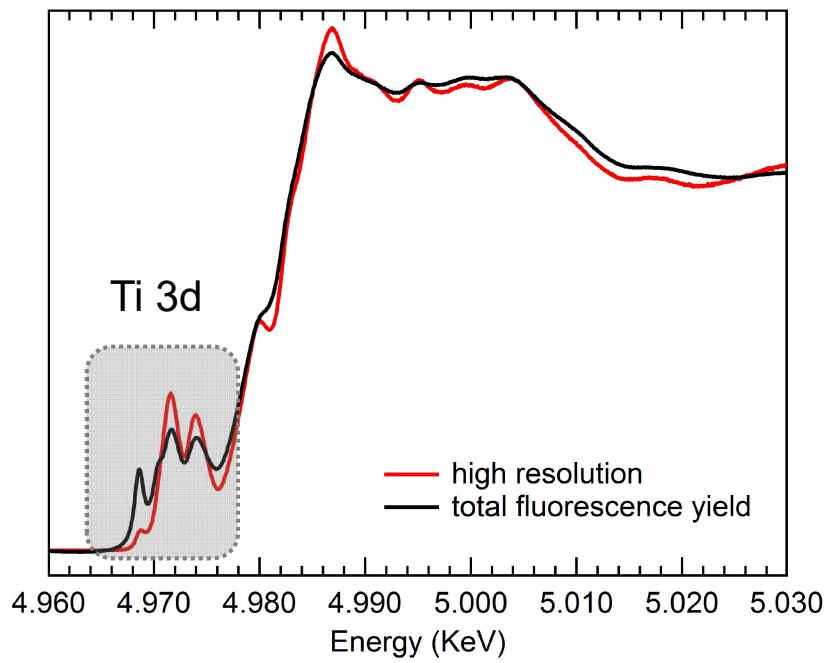
In NPs-assembled films, both V^{4+} and V^{5+} cations, the latter likely located at near-surface sites, contribute to the pre-edge peak

Combining X-ray Absorption and Emission: RIXS

what do we gain combining XAS & XES?

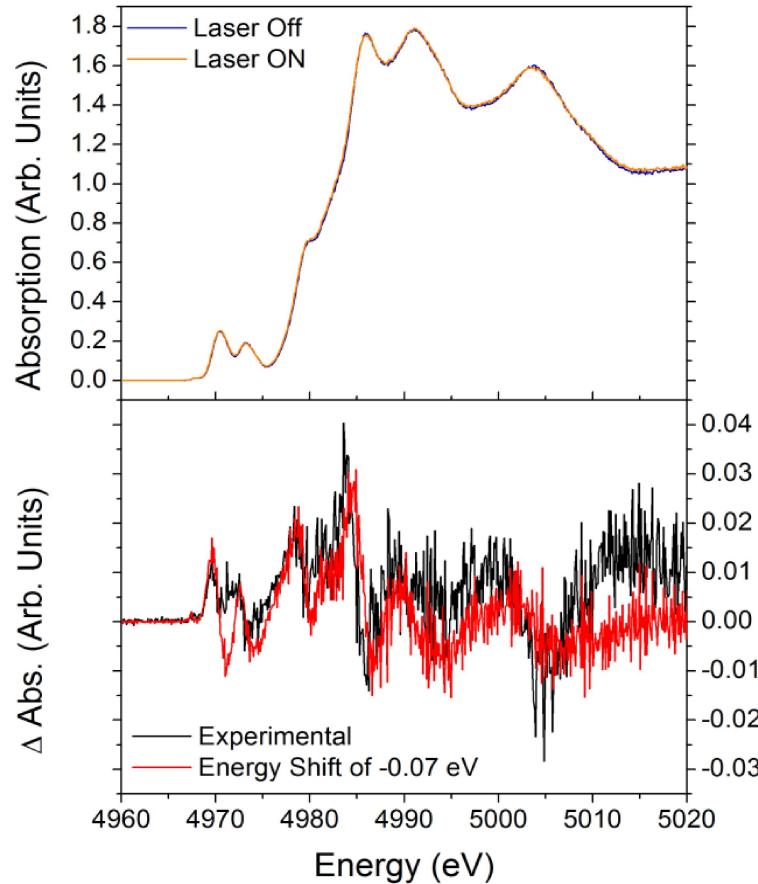
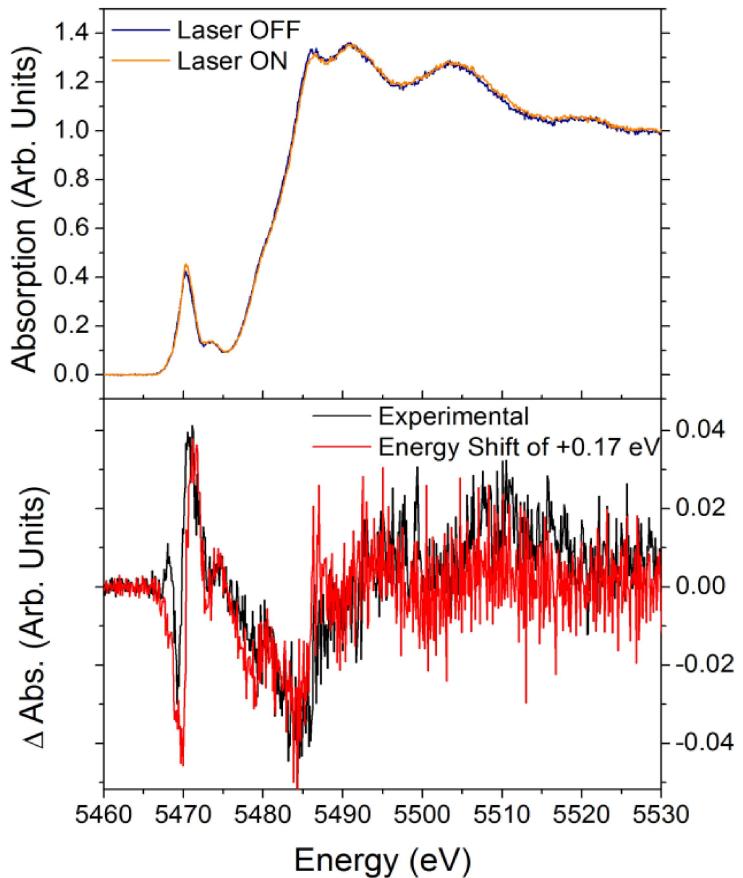
1. high resolution diagonal cut of RIXS plane

2. in TiO_2 special sensitivity to
localization of final states



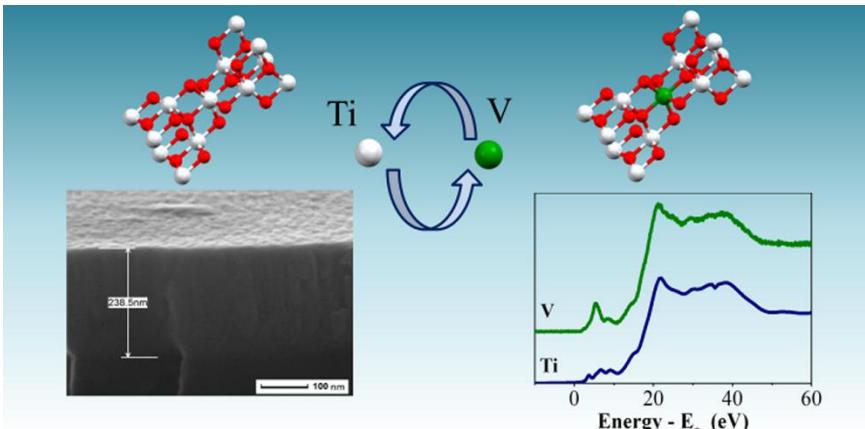
Laser On/Off differential RIXS

Experiment @ ID26, ESRF

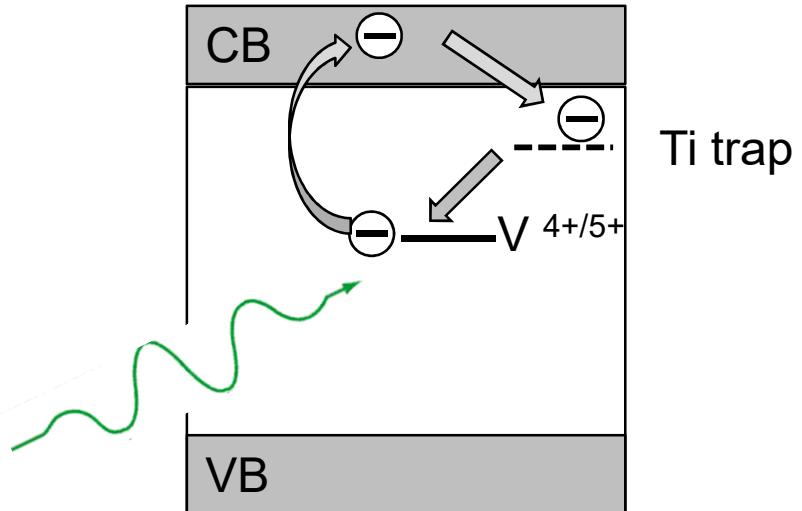


- Ti and V edges shift in opposite directions!
- Evidence for charge transfer: oxidation of V / reduction of Ti
- The effect is clearly visible in NPs but quite weak in compact films

Conclusions and Outlook



Substitutional V
 V^{5+} at the surface, V^{4+} in bulk



$V \rightarrow Ti$ e⁻ transfer
Long-lived (μs) e⁻ trapping in Ti sites

Future activities:
N K-edge XANES with soft X-rays
Time resolved pump/probe experiments

Thanks for your kind attention