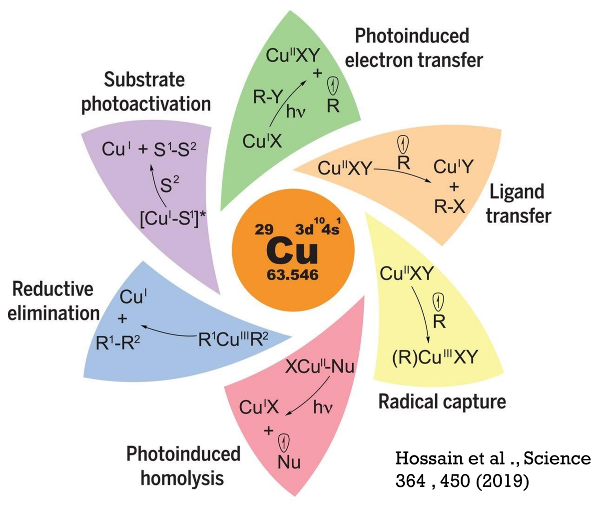
Oxidation of Cu(111) Under h-BN via Intercalation

Motivation

- Cuprous Oxides (Cu_2O) are utilized for numerous catalysis applications:
  - Reforming of MeOH
  - CO oxidation
- Promising photocathode for photoelectrochemical water splitting:

But…unstable in aqueous solutions



Hossain et al., Science 364, 450 (2019)

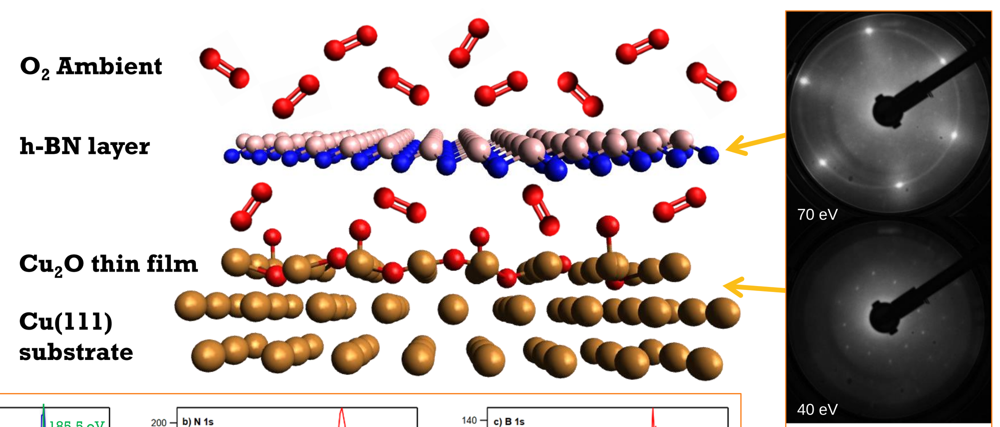
Cover Surface with Hexagonal Boron Nitride (h-BN)

- Excellent thermal and chemical stability
- Can exist in various crystal structures, including hexagonal 2D form
- Enhance transfer of hot electrons to surface

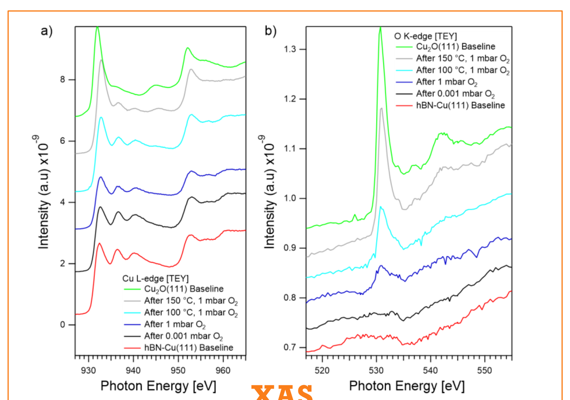
But…difficult to deposit h-BN on metal oxide surfaces

Project Design Objective:

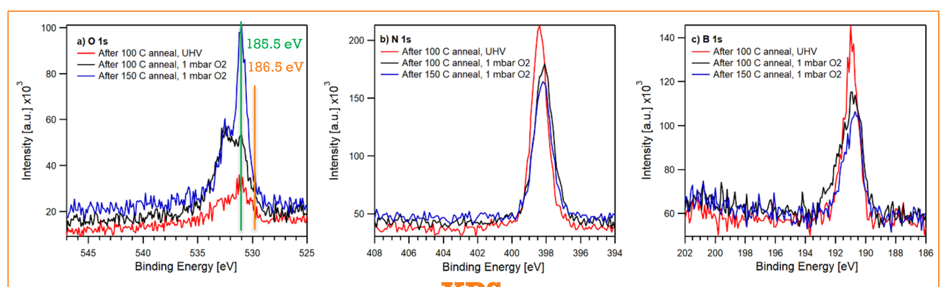
- Prepare well-ordered h-BN monolayer on Cu(111)
- Oxidize Cu(111) via intercalation of O_2 through *h*-BN
- Probe structure, catalytic activity, photoinduced charge carrier dynamics with a range of surface characterization techniques



LEED
Low-Energy Electron Diffraction
Probe lattice structure

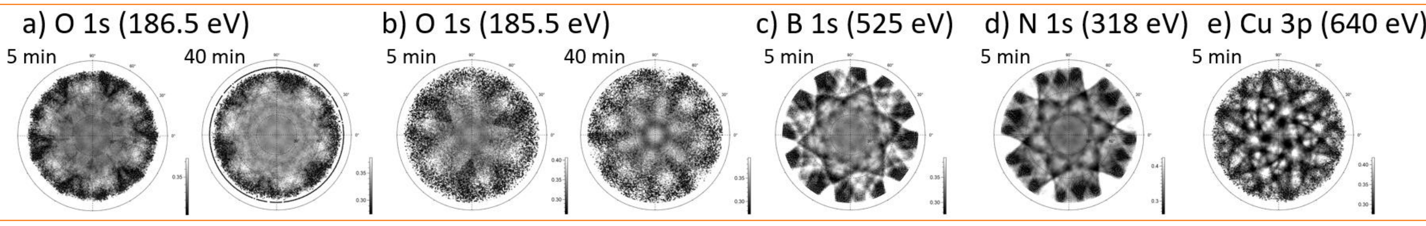


XAS
X-ray Absorption Spectroscopy
Probe electronic structure



XPS
X-ray Photoelectron Spectroscopy
Probe chemical state information

XPD
X-ray Photoelectron Diffraction
Probe atomic structure



The vision is that…

- The h-BN layer can act as a passivation layer
  - Reducing unwanted oxidation or poisoning
  - Enhancing the transfer of hot electrons to the surface oxide.
- Attractive for water splitting, made from cheap materials, and potentially stable at reaction conditions.
- Overall, we improve our understanding of how a weakly interacting 2D monolayer can affect electron transfer in a photocatalyst system.

Trey Diulus, Mert Taşkın, Nicolò Comini, Jan Beckord, Roland Stania

Formation of Ni-Ferrite on Fe_3O_4(001)

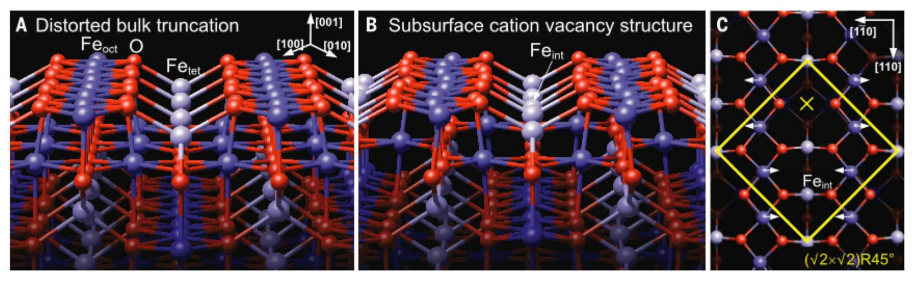
Motivation

Ni-ferrite $NiFe_2O_4$ surfaces have become attractive as a catalyst for photoelectrochemical water splitting due to their:

- Strong activity for water oxidation
- Chemical stability

But…Ni metal is becoming scarce

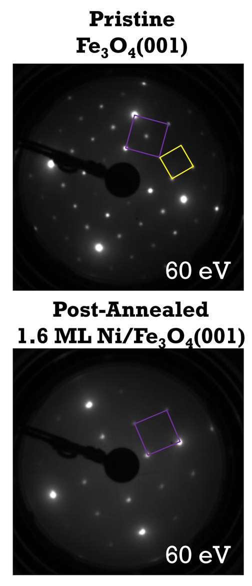
Grow ultrathin films of Ni ferrite on low-cost Fe_3O_4 surfaces



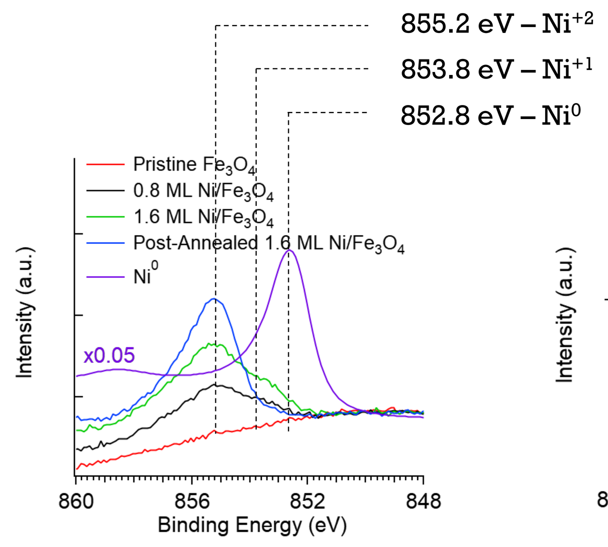
R. Bliem et al., Science, 346,1215 (2014).

Low Coverage

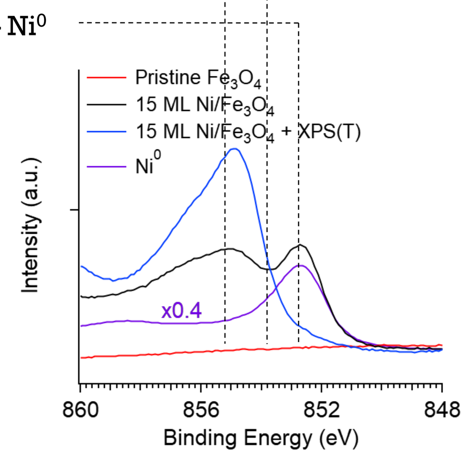
LEED



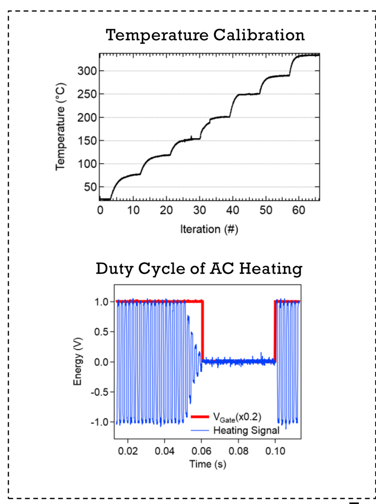
XPS (Mg K_α) - Ni2$p_{3/2}$



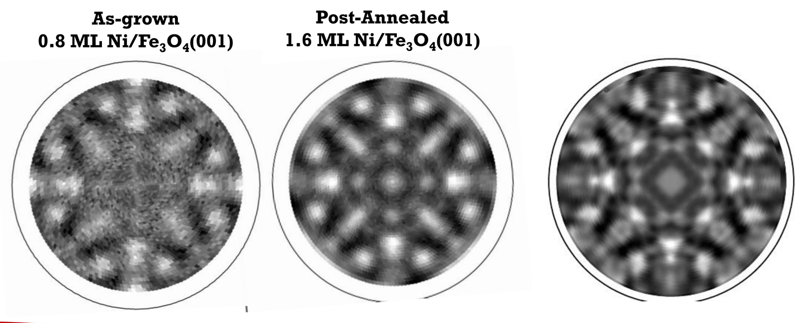
High Coverage

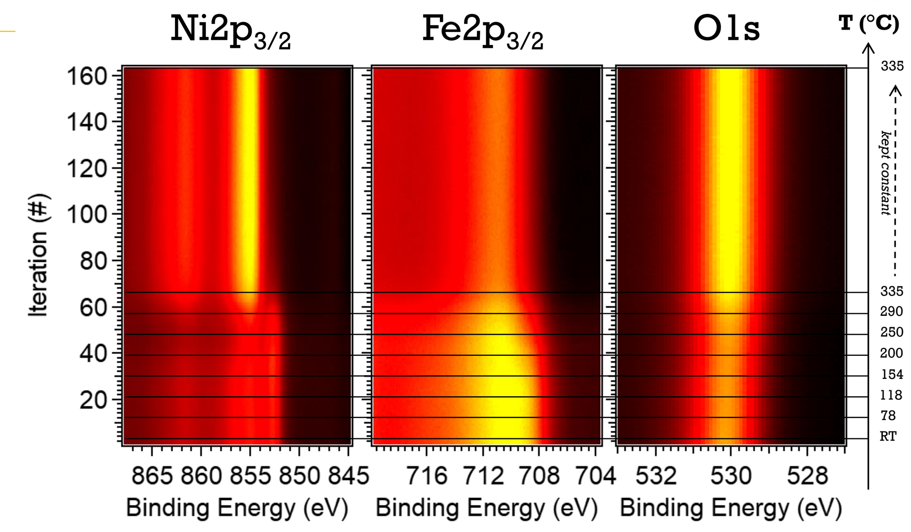


Temperature Dependent XPS (Mg K_α)



XPD (Mg K_α) - NiLMM





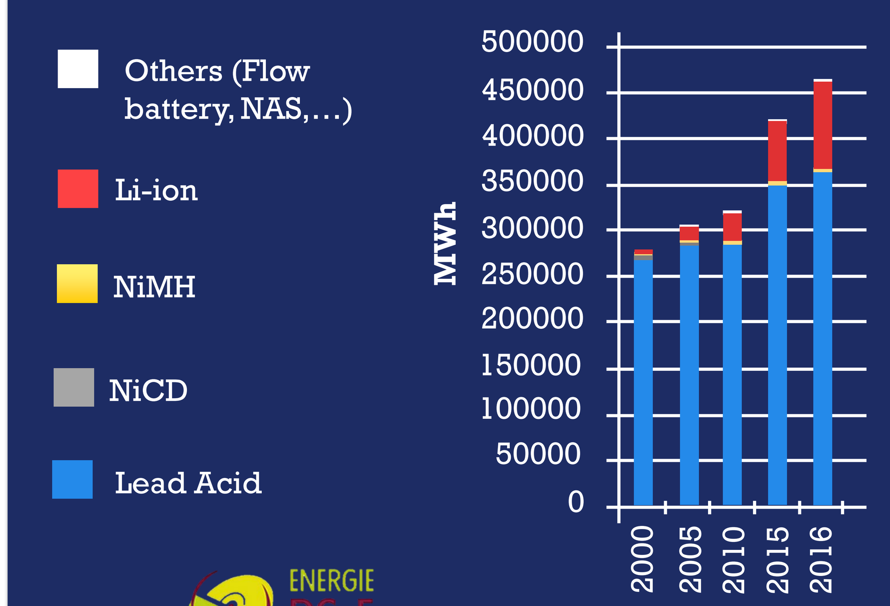
World Energy Issue: Contributions from Surface Science

URPP LightChEC

University of Zurich[UZH]

About energy storage

All batteries in the world (2016):



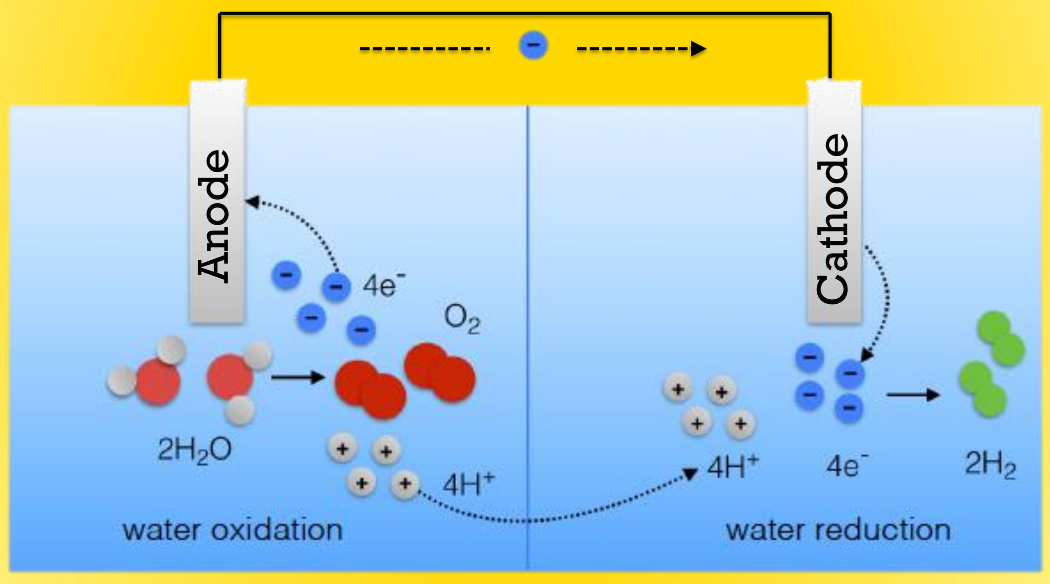
ENERGIE RS2E

Réseau sur le stockage électrochimique de l'énergie

Electricity consumption (2016)

58000 GWh*

*Source: Swiss federal office of energy



Contact us:

Photocatalytic Water Splitting

- ✓ Storage of solar energy into chemical energy
- ✓ Hydrogen as storable energy carrier
- ✓ Oxygen as only side product
- ✓ Non-polluting, cheap, and abundant materials

- **What we do:**

Fundamental research on innovative light absorber materials, catalysts and photosensitizers by means of Surface Science techniques.

- **What we want to know:**

Their electronic and morphological properties, how they interact with light and H_2O.

- **And how:**

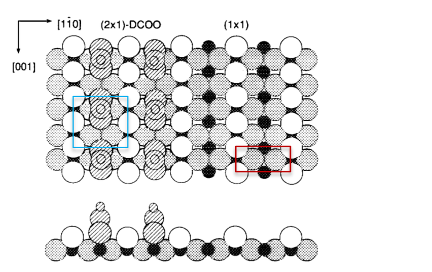
- X-ray photoelectron spectroscopy and diffraction;
- Electron diffraction;
- Atomic force microscopy, scanning tunneling microscopy;
- Time-resolved two-photon photoemission.

Ambient-Pressure experiments at SLS

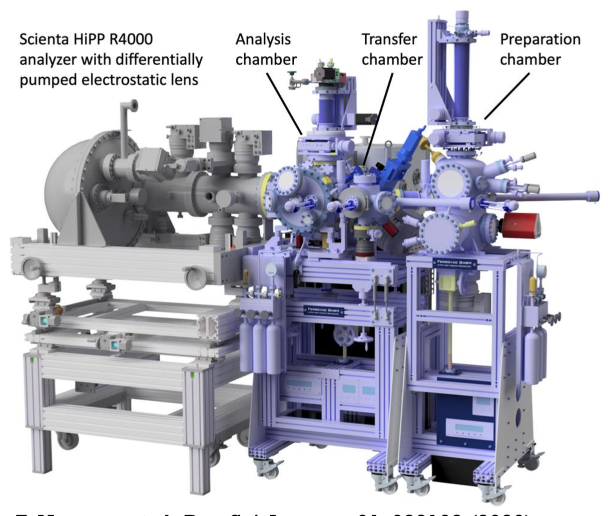
Zbynek Novotny, Matthias Hengsberger, Jürg Osterwalder

Wider experimental opportunities:

- Experimental endstation for high pressure surface science: gas dosing and water exposure possible
- Dip and pull experiments: can study interactions between surface and liquid layer on top
- Possibility to follow electrochemical modification of surfaces: oxidation and reduction *in situ*



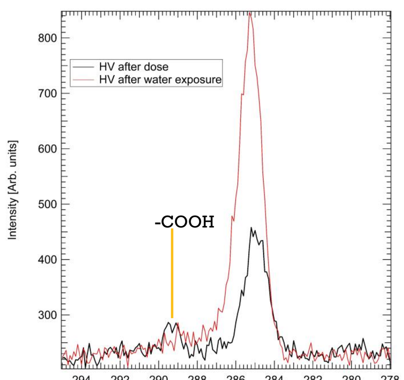
The ordered structure of adsorbed HCOOH on TiO_2(110)
Onishi H. *et al.*, Journal of Catalysis 146, 557-567 (1994)

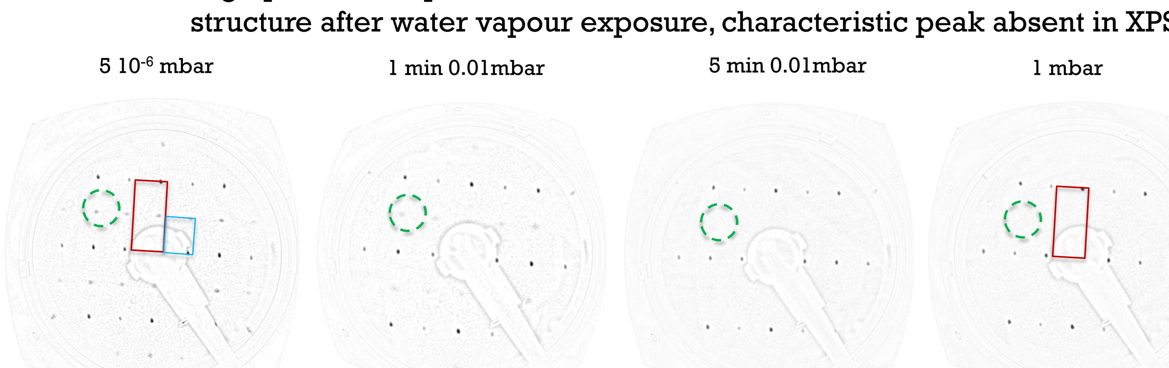


Z. Novotny *et al.*, Rev. Sci. Instrum. 91, 023103 (2020)

Phenomena not observable in high vacuum:

- Adsorption of formic acid (HCOOH) on TiO_2(110): ordered adsorbate layer in vacuum
- Commonly believed to adhere strongly, even in air
- High pressure experiments show otherwise! LEED shows surface structure after water vapour exposure, characteristic peak absent in XPS





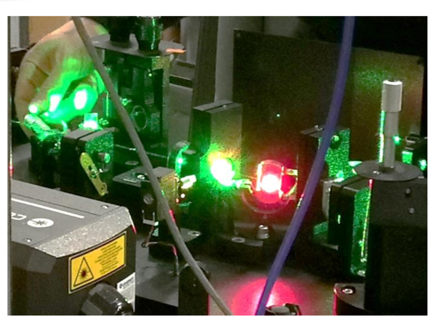
- DFT calculations support newer, high pressure experimental results!

Realistic experimental conditions:

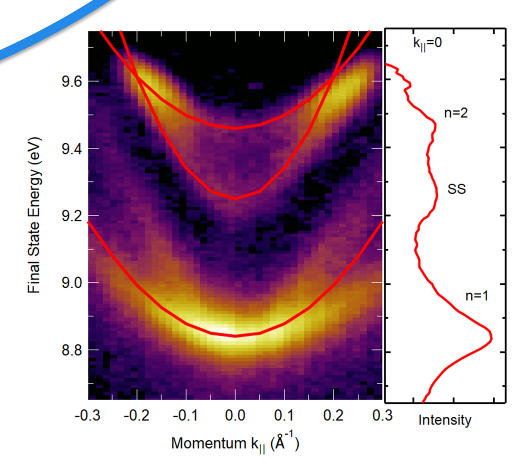
- Studies can approach more practical application conditions
- Important step for photocatalysis applications

The laser lab: Electron dynamics

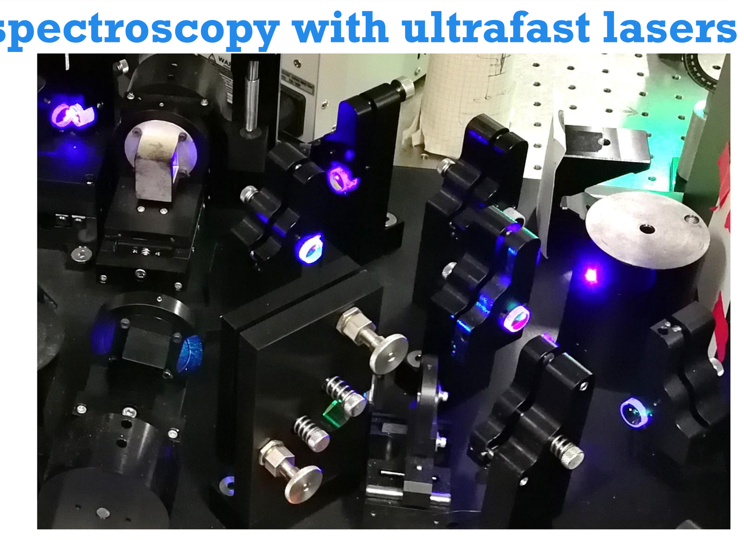
Photoelectron spectroscopy with ultrafast lasers



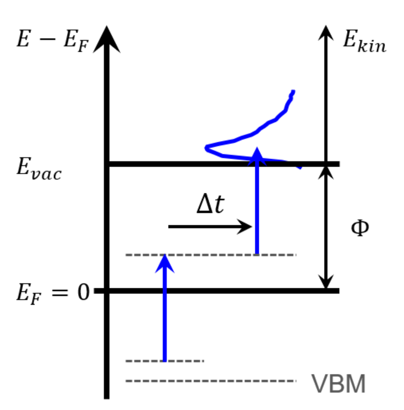
Adjusting the femtosecond laser oscillator

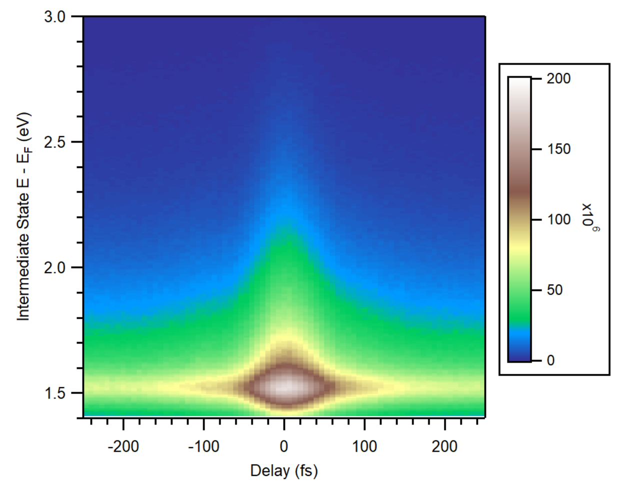


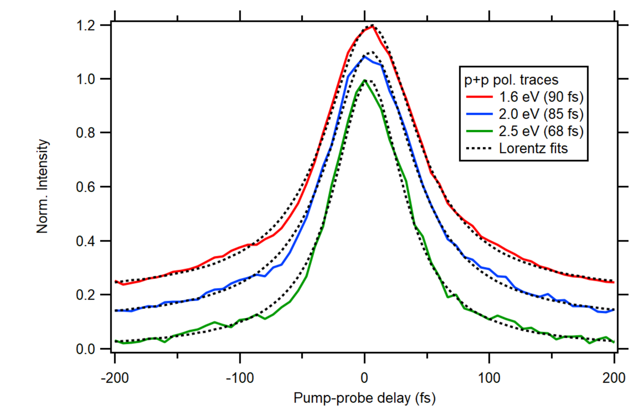
Angle-resolved 2PPE spectrum of image potential states on Cu(111)



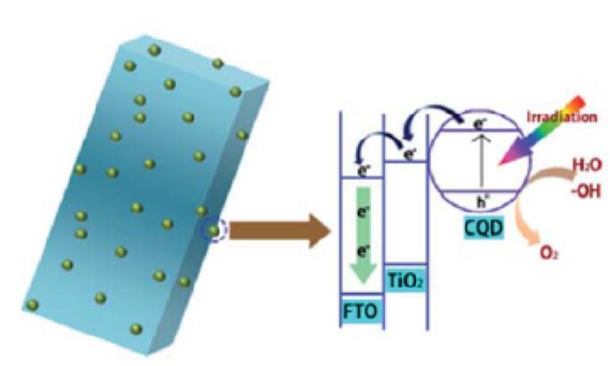
Creating a desired wavelength of laser light with optical parametric amplification (OPA)







- Time-resolved two-photon photoemission (tr-2PPE): Femtosecond pump-probe electron spectroscopy of unoccupied states
- Fitting the time-dependent population curves to obtain information about the decay dynamics of excited states
- Example: studying ultrafast energy relaxation and transfer of photoelectrons from Carbon Dots into the TiO_2(110) substrate
- Ecological, cheap and efficient photocatalyst for solar hydrogen generation and solar fuel generation



S. Xie *et al.*, J. Mater. Chem. A 2, 16365 (2014)

Acknowledgments

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