Combined Study of Ionic Processes on Surfaces: Photoelectric and Photocatalytic Effects

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Introduction

Challenge:

- molecular reaction pathways in photocatalytic and photoelectric processes remain unclear
- previously published mechanisms seem to explain only individual cases under certain selected conditions
- reaction mechanisms are required
- determination of the presence and the role of reagent ions, like as for example O_2^-, is necessary
- differentiation between surface bound and gas phase ions and reactions, respectively
- investigation of possible molecular level connections between photoemissive and photocatalytic electron processes

Approach:

- combination of two well evaluated reaction systems
  - capillary Atmospheric Pressure Electron Capture Ionization (cAPECI) [1]
  - heterogenous conversion of NO on commercial photocatalytic dispersion paint [2]
- system conditions are simplified
  - use of inert gases
  - vacuum conditions
  - monochromatic light excitation
  - monocrystaline oxides

Application:

- environmental chemistry
- negative ion atmospheric pressure mass spectrometry
- heterogeneous catalysis

Methods

Experimental Setup:

MS	Esquire 6000 QIT, Bruker Daltonic
Photoreactor	custom designed flow tube type reactor (Fig. 2))
Photoemissive materials	Sto PhotosanNOX (TiO_2); monocrystaline ZnO; Cu; Al
Radiation sources	ATL Atlex KrF*- excimer laser (248nm); NUV-Diode (390 nm); low pressure mercury lamp (PenRay) (185/254 nm)
Measurement chamber	custom designed chamber with detector and target plate (Fig. 3))
Ion Current measurements	Keithley 602 electrometer; Textronix oscilloscope
NO_x monitor	NO_2 LOPAP instrument
Pump	Pfeiffer Vakuum TurboDrag Pump

Background

cAPECI

- use of the photoelectric effect at atmospheric pressure
- UV-light interaction with metal surfaces yields low energy electrons
- electron capture forms negative ions
- superoxide, O_2^-, represents main reagent ion when oxygen is present

Photocatalysis

Photoexcitation (< 390 nm) of TiO_2 leads to the formation of e^- in conduction band and h^+ in valence band.

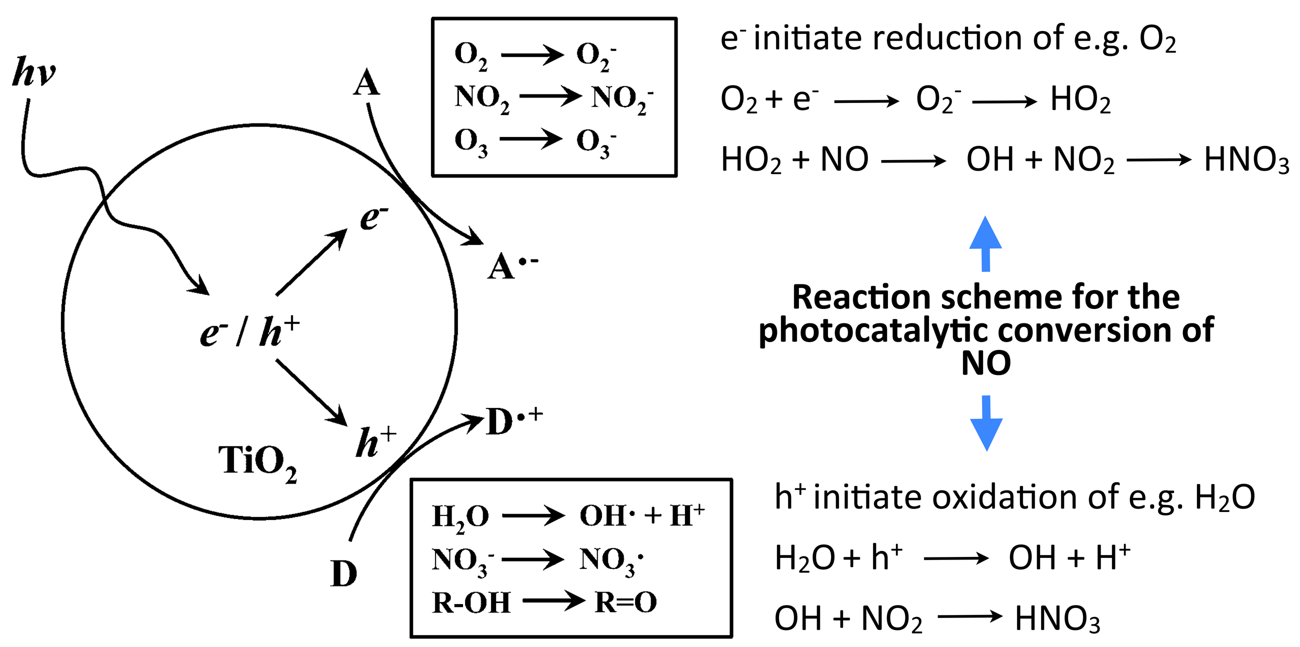


Figure 1) Proposed mechanism for photocatalysis on TiO_2 surfaces [3]

Experimental Setup

Photoemissive measurements:

- radiation is directed through a quartz window onto the sample material
- adjustable acceleration voltage is applied to the probe plate
- distance between probe and detector plate is variable
- detector plate is connected to the electrometer to measure ion/photo current
- chamber background pressure is adjustable down to 10^{-5} mbar
- chamber is pressurized with N_2 or synthetic air to vary gas phase conditions

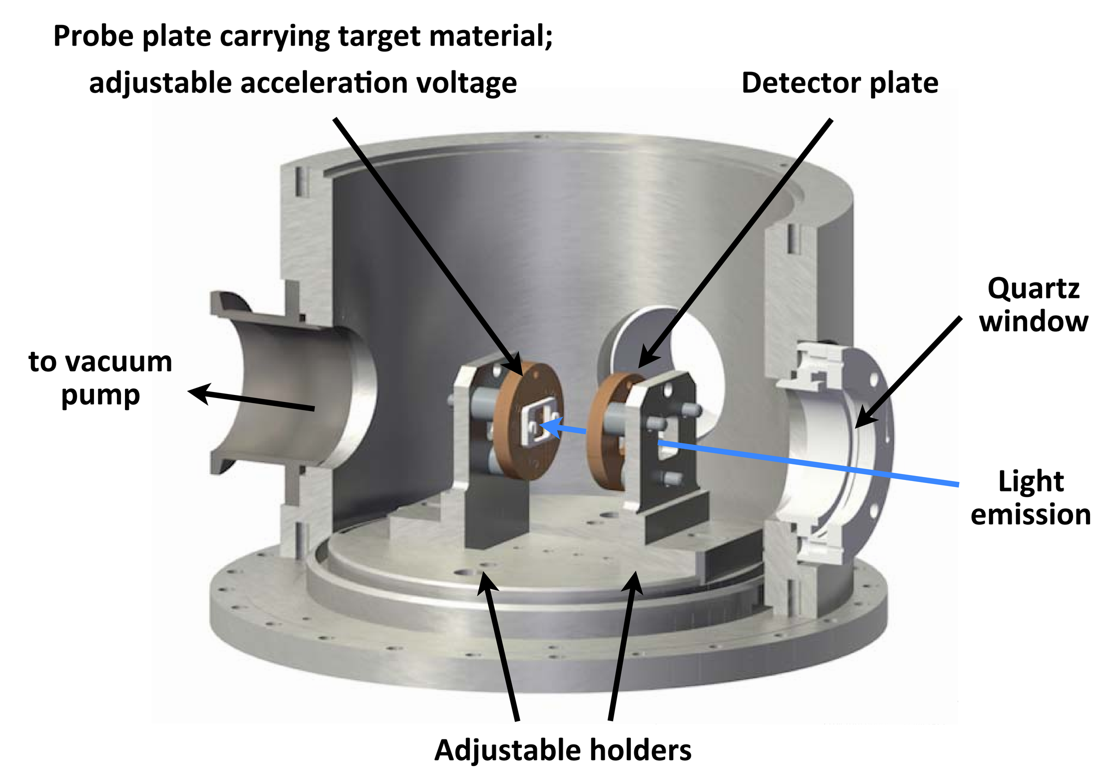


Figure 3) Custom designed measurement chamber

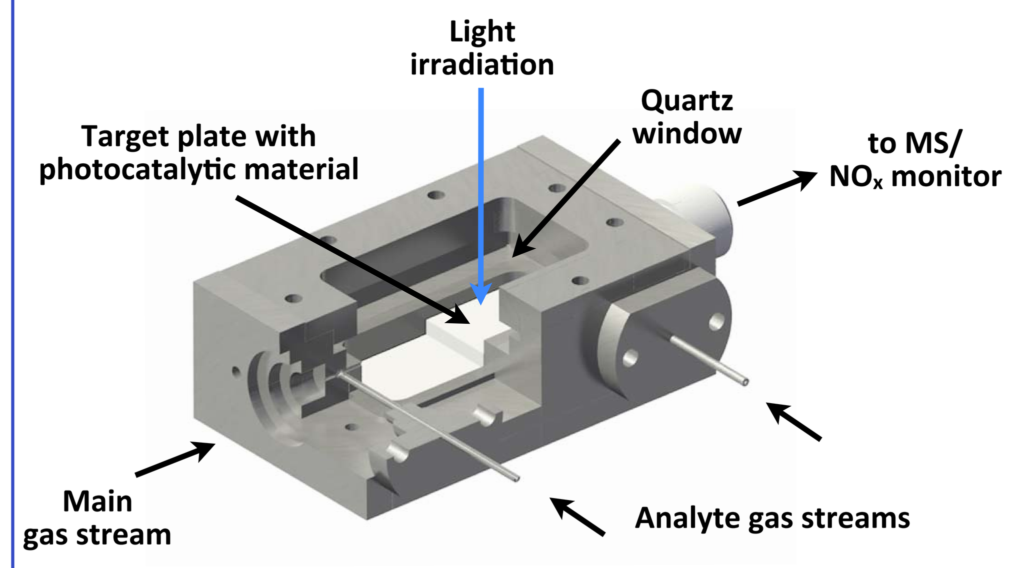


Figure 2) Custom designed flow tube type photoreactor based on cAPECI source design [2]

Photocatalytic measurements:

- radiation source is mounted on top of the quartz window
- target plate is adjustable in height, photocatalytic material is exchangeable
- analyte or other compounds are added to the main gas stream up or downstream of the irradiated volume
- coupling to NO_x monitor to investigate photocatalytic activity
- coupling to MS to check for generated gas phase ions and to determine gas phase composition (post ionisation)

Dependencies of the Photoelectric Yield

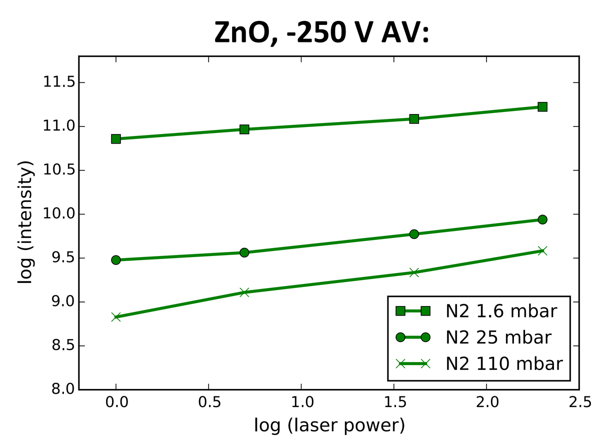
Laser power

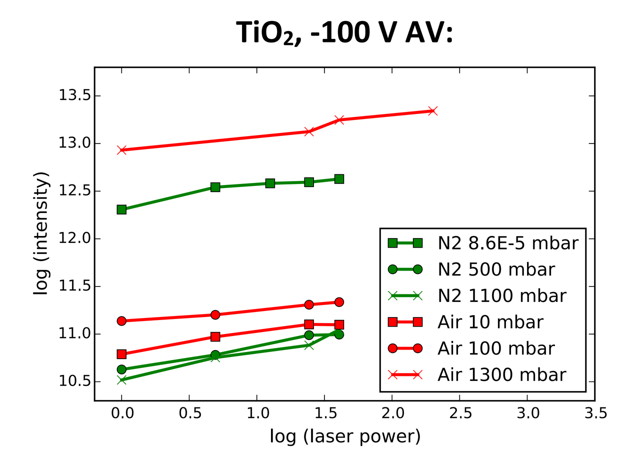
Ion intensities $I(M^+)$ vary with laser power P_{Laser} to the power of the number of photons required to generate photo electrons provided the corresponding transitions are not saturated:

$$I(M^+) = c\ P_{Laser}^{\ n}$$

It follows:

$$\log I(M^+) = n \log P_{Laser} + c$$

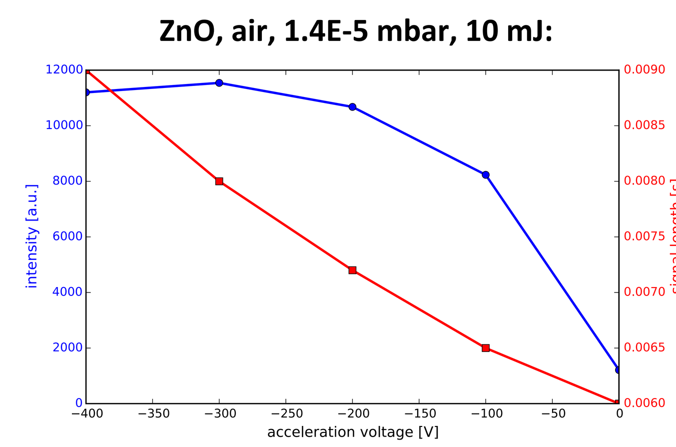


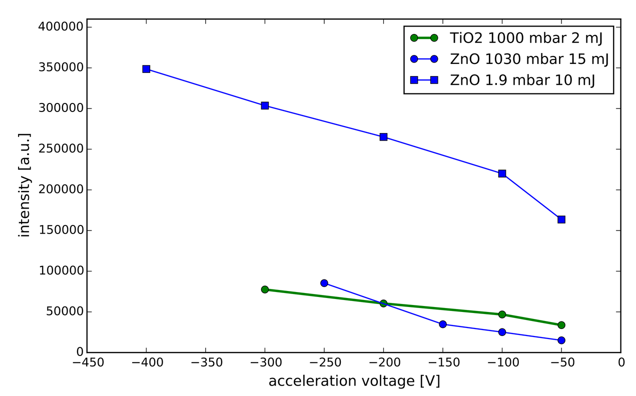


above and left: Variation of the laser intensity between 1 and 10 mJ results in ion currents which correspond to a range of n between 0.1 and 0.3. We explain this observation by saturation of the transitions leading to generation of photo electrons due to the high laser power and the relatively small irradiated area. A variation of pressure, acceleration voltage, laser frequency or gas has no influence on the proportionality slope.

Acceleration voltage (AV)

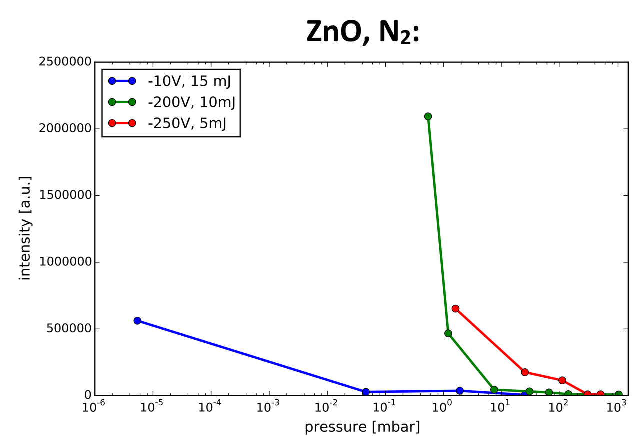
right: A negative acceleration voltage is applied to the probe plate. The signal intensity (integral area of the time-resolved photo current signal) increases with increasing acceleration. Additionally, the peak shape varies with the acceleration voltage. The signal length increases with rising field strength. This effect is especially pronounced at low pressures and high acceleration voltages.





left: At elevated pressures a minimum value of acceleration voltage is necessary to yield a measurable ion current. The different measurements are not comparable with respect to the absolute signal intensity because of changing experimental conditions (gas phase, electrode distance and laser power).

Pressure



left: The signal intensity strongly depends on the pressure. The photoelectric yield increases with decreasing pressure. Additionally, the signals become narrower.

Gas

Surprisingly, the photoemissive measurements do not show any significant differences between air or nitrogen being present in the chamber. Previous investigations revealed a strong dependency on the oxygen ratio for photoemissive as well as photocatalytic effects. For cAPECI-MS the presence of oxygen is necessary. In contrast, the used commercial photocatalytic dispersion paint (TiO_2) shows photocatalytic activity even in an oxygen-free atmosphere, which is traced back to the fact that water and/or oxygen is adsorbed on the surface (see figure 1)).

Conclusions

Photocatalytic measurements:

- VUV irradiation (185 nm) leads to generation of gas phase negative ions when aluminum as well as TiO_2 dispersion paint is used as photoemissive material
- measured ion distributions are consistent with previous cAPECI-MS measurements
- photocatalytic conversion of NO is observable using the TiO_2 dispersion paint at 390 nm
- NUV irradiation (390 nm) does not generate any gas phase ions detectable by the MS

Photoemissive measurements:

- dependencies of the photoelectric yield on the acceleration voltage and the pressure are as expected
- at elevated pressures no photoelectric yield without applying acceleration voltage
- variation of laser power shows a surprisingly low dependency of the photo current
- no significant difference between air or nitrogen, most probably caused by gas impurities
- used materials do not show significant differences in their photoemissive properties

Outlook:

- presented results are pre-examinations, further MS-experiments will follow
- use of light source which is tunable in energy and power (e.g. OPOs)
- further investigations on gas phase dependencies (water vapor, noble gases, compounds with high electron affinities e.g. SF_6)
- differentiation between photo and ion currents

Literature

[1] V. Derpmann; *Development and characterization of capillary Atmospheric Pressure Electron Capture Ionization (cAPECI)*; Dissertation; Bergische Universität Wuppertal; 2014

[2] S. Laufs, G. Burgeth, W. Duttlinger, R. Kurtenbach, R. Maban, C. Thomas, P. Wiesen, J. Kleffman; *Conversion of nitrogen oxides on commercial photocatalytic dispersion paints;* Atmospheric Environment; 44(19); 2341-2349; 2010

[3] C. Haihan, C. E. Nanayakkara, V. H. Grassian; *Titanium dioxide photocatalysis in atmospheric chemistry;* Chemical Reviews; 112(11); 5919-5948; 2012

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