Deep into the Coating – Novel Features of MSS-Coatings

Progress of the INTERREG V A-project AutoProtect

Surfaces with self-protective properties for the maintenance of chemical and microbial cleanliness

Webinar#4
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wfk – Cleaning Technology Institute e. V.

The Scope of AutoProtect – Functional Coatings

What is a coating?

The fundamental function of coatings is to build a functional barrier between material and environment:

- protect the surface mechanically → scratches, dents, punches
- protect the surface chemically → corrosion, decomposition of soiling
- ease the cleaning of surfaces → repellant, easy to clean, non-wetable, lotus effect
- yield antimicrobial activity → inactivation, decomposition
- yield electrical properties → conductivity

Geometric diversity

- thin vs. thick layers (< 1 µm or µm-mm)
- unilayered vs. multilayered
- uniform vs. internally structured

Chemical diversity

- metals and/or glasses
- crystallite materials (coarse, powdery)
- polymers (+ dielectric coatings)
- semiconductors
- type of deposition

Diverse application methods

- gaseous (physical vapor deposition, sputtering)
- liquid (spin & dip coating, (spray) painting)
- solid (powder & plasma coating, electro spraying)

The Scope of AutoProtect – Functional Coatings

What is hygiene?

- is derived from Hygiéia, Greek Goddess of Health
- is the whole range of measures taken to prevent disease and illness
- is aiming to maintain health of humans and the environment
- is a prophylactic measure but not a cure

What are catalytic Multi-Stimulus-Systems coatings (MSS)?

- coatings with a set of catalytic properties → additive effect
- harvest diverse environmental stimuli to activate/excite the catalysts
- higher catalytic activity and higher efficiency
- suitable for multi-purpose applications
  - achieve high antimicrobial activity
  - enhance decomposition of organic soilings
  - ease the cleaning of surfaces
  - protect the surface
- reduce/avoid the use of conventional biocides

Antimicrobial coatings that release soluble agents
- silver, copper, other metals
- antimicrobial peptides
- antibiotics
- ROS-producing catalysts

[1] Report of the Robert-Koch-Institut, Berlin // [2] (JP Burke. Infection control – a problem for patient safety. N Engl J Med. 2003;348:651–656) // [3] (Postnote, Parliamentary Office of Science and Technology, June 2005) // [4] (ECDC, Annual Epidemiological Report 2012)

The Scope of AutoProtect – Use of Functional Coatings

Objectives of AutoProtect and targeted economic sectors

principles of action

sustainable and self-protective MSS-coatings on surfaces

inactivation of microorganisms and disinfection

degradation / decomposition of chemical residues and soils

hygiene aspects of microbial (re-)contamination

maintenance and longevity of products / surfaces

cleanliness in production processes

fields of application & problems

- pathogen transmission
- nosocomial infections (NI) are acquired in hospitals and other health care facilities
- causing severe life-threatening infections
- causing high costs to healthcare systems

- accumulation of pollutants, soilings over time
- microbial growth leads to
  - biofilm formation
  - biocorrosion
  - biofouling
- compromise function, efficacy, reliability, safety

- processes and products compromised by means of function, quality, safety
- high tech facilities require high levels of cleanliness
- products for human consumption require high standards of hygiene

The Scope of AutoProtect – Use of Functional Coatings

Objectives of AutoProtect and targeted economic sectors

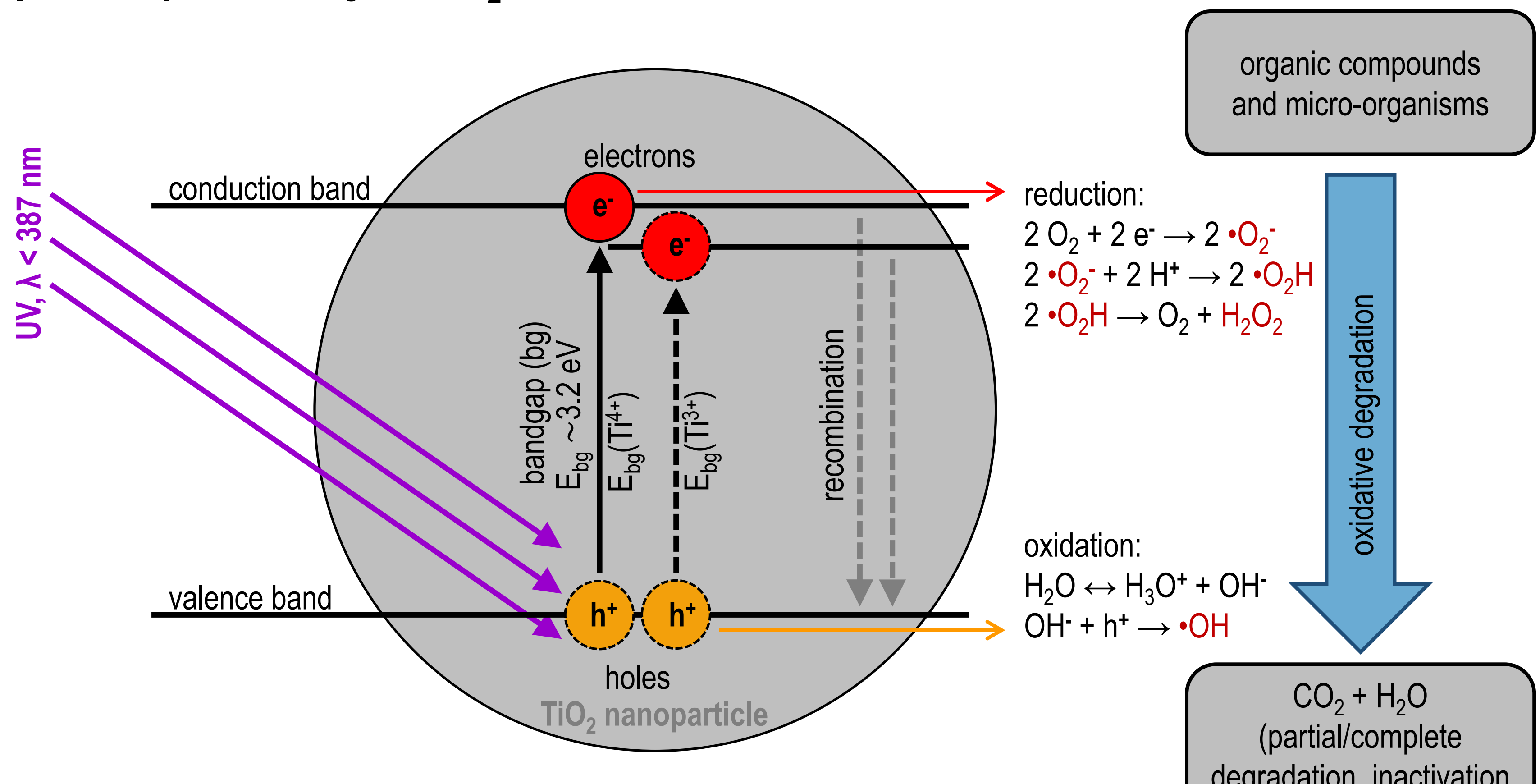
primary beneficiaries

medical and health care sector	maintenance, facility management sector	production and manufacturing sector
Economic burden of NI is estimated to be **9 billion €/year** in GER	Volume of cleaning services is estimated to be **50-80 billion €/year** in GER	Volume of soiling-related product failure estimated to be **50-100 € billion/year** in GER

sec. beneficiaries

medical and health care sector	maintenance, facility management sector	production and manufacturing sector
medical technology	food processing	mech. engineering
pharmaceuticals	restaurants / catering	metal working
analytics	cosmetics	paint / lacquer / varnish
public health	sports facilities	construction
public welfare	wellness/spa/hotel	vehicle operators
renewable energies	wind / solar power plants	vehicle manufacturers

Mechanisms of catalytic Multi-Stimulus-Systems (MSS)
Example: the photocatalysts TiO_2



- UV elevates e^- to the conduction band and forms electron-holes h^+ in the valence band.
- e^- and h^+ can produce ROS which degrade organic compounds and inactivate micro-organisms.

The Scope of AutoProtect – The MSS Approach

Mechanisms of catalytic Multi-Stimulus-Systems (MSS)
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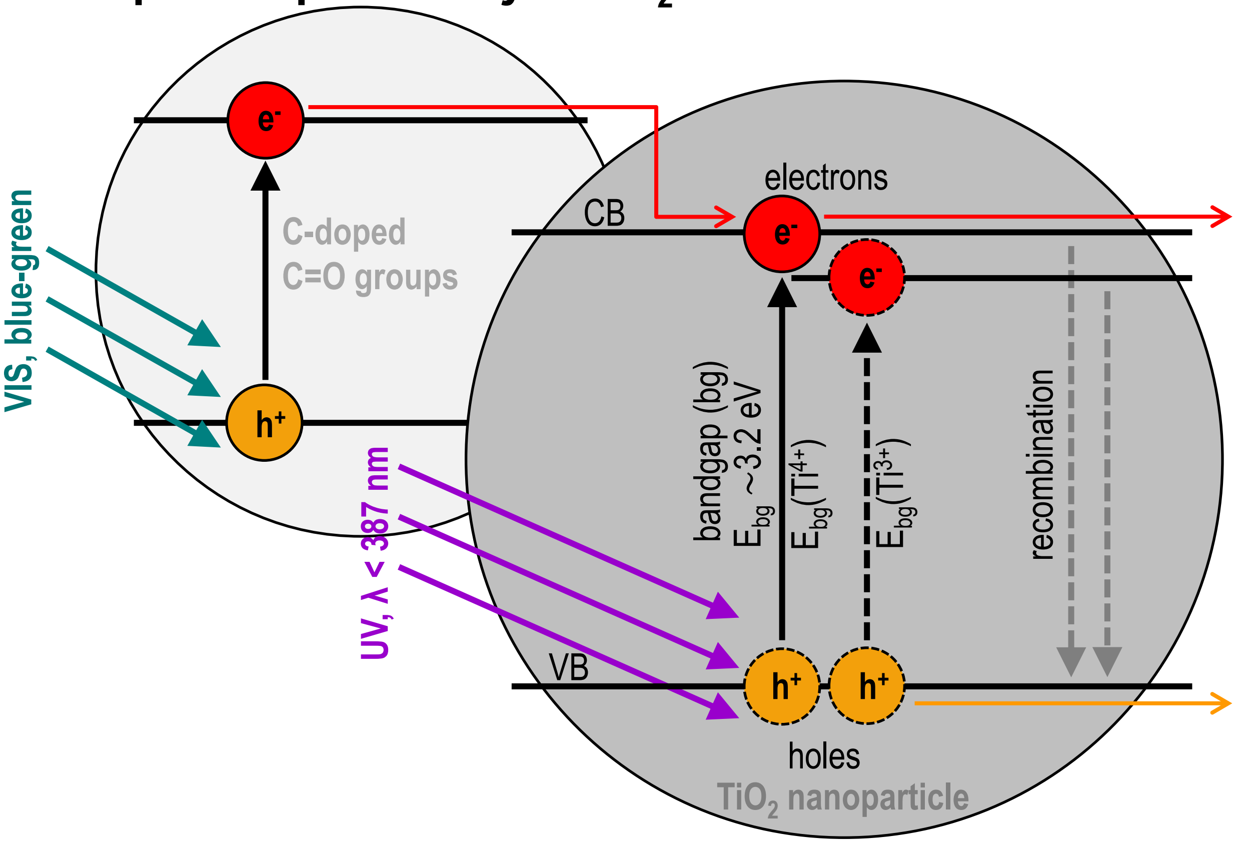
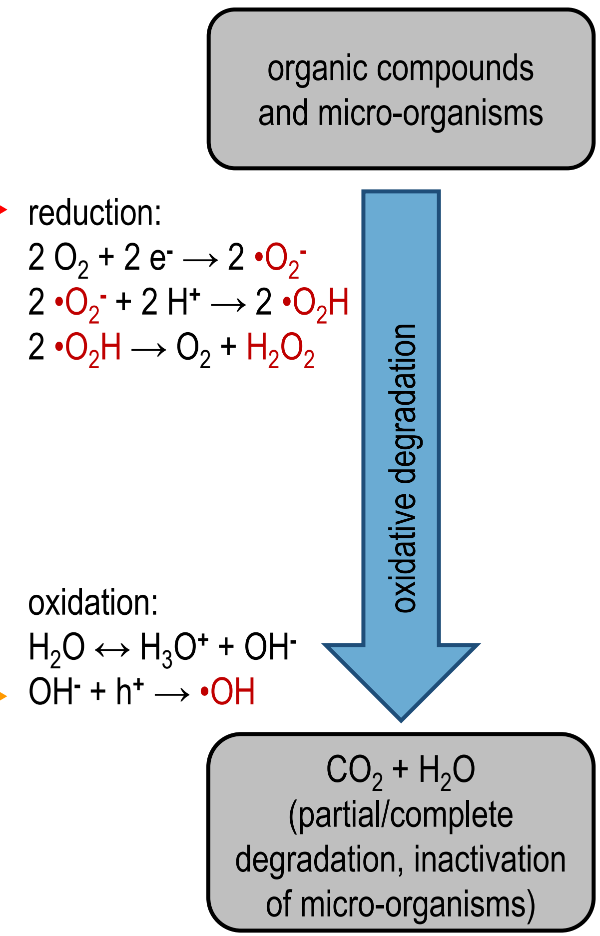


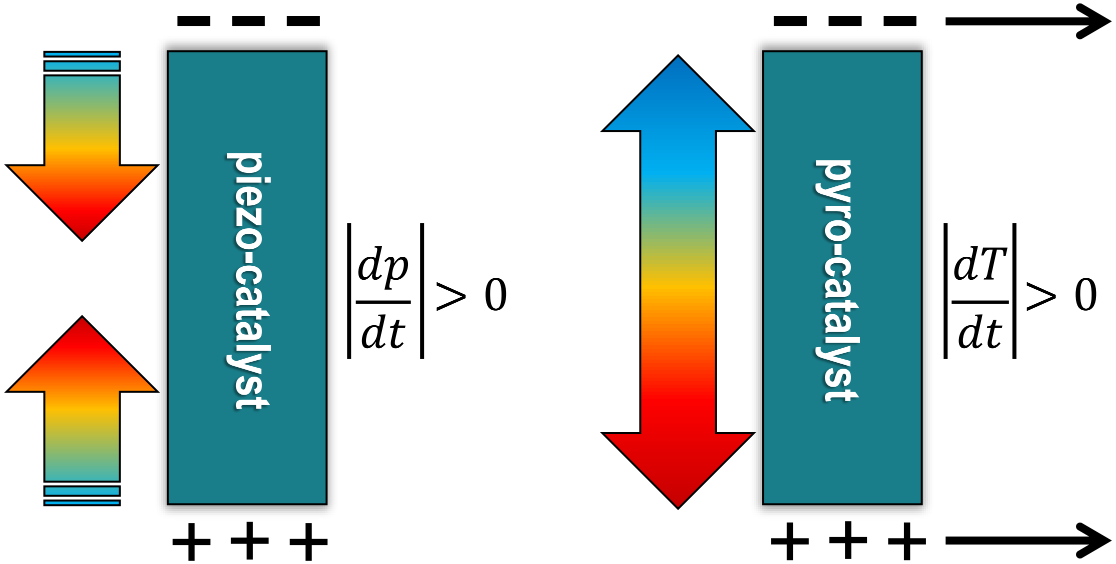


- carbon modification during TiO_2 curing extends the activating light to blue and green
- blue/green may light boost the degradation of (in)organic compounds enormously

The Scope of AutoProtect – The MSS Approach

Mechanisms of Catalytic Multi-Stimulus-Systems (MSS)

Piezocatalysts **Pyrocatalysts**



reduction:

$e^- + O_2 \rightarrow \bullet O_2^-$

$2\ \bullet O_2^- + 2\ H_2O \rightarrow H_2O_2 + 2\ OH^- + O_2$

$H_2O_2 \rightarrow 2\ \bullet O_2^-$

oxidation:

$h^+ + H_2O \rightarrow H^+ + \bullet OH$

$2\ h^+ + 2\ H_2O \rightarrow 2\ H^+ + H_2O_2$

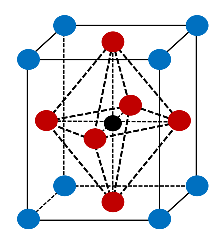
$H_2O_2 \rightarrow 2\ \bullet OH$

Piezoelectric effect

- change in electrical polarization when subjected to mechanical load and relaxation

Pyroelectric effect

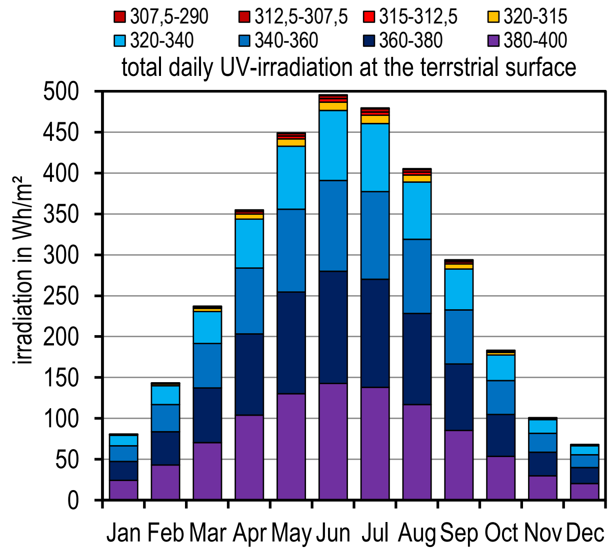
- temperature fluctuations generate an electric potential across the material
- all pyroelectric materials are also piezoelectric

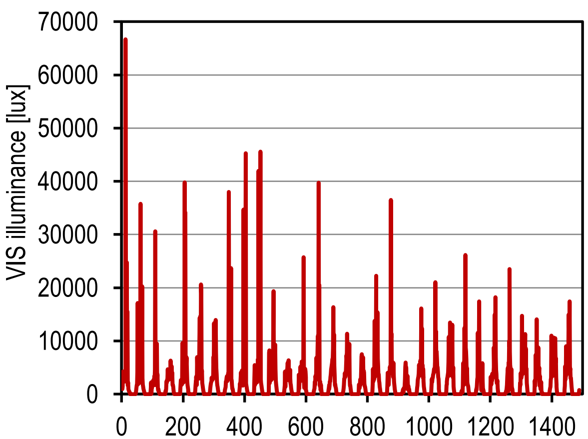


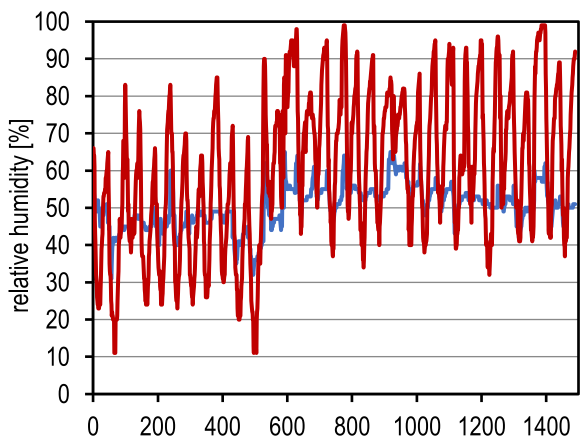
The Scope of AutoProtect – The MSS Approach

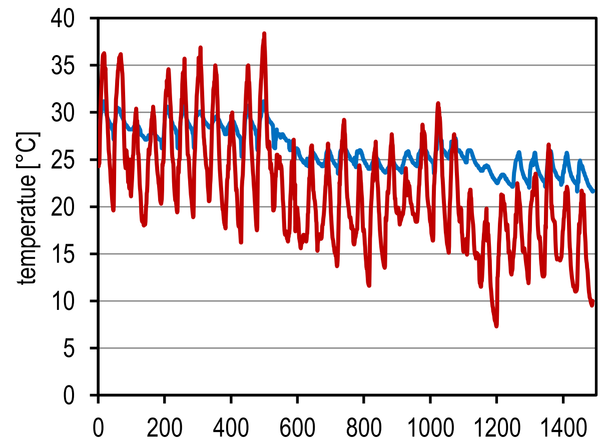
Stimuli for Catalytic Multi-Stimulus-Systems (MSS)

stimulus	outdoor conditions	indoor conditions
temperature cycling (ΔT)	daily and high T cycles (>10°C, up to 60°C)	daily but low (<3°C) T cycles, even when not mediated (i.e. AC)
irradiation / insolation / illumination	sufficient insolation 6.500-100.000 lx 80-90% >1.000 lx 10-30% >10.000 lx 70-495 Wh/m² UV per month	insufficient illumination/irradiation 300-2.000 lx at desk height 50-200 lx in w/o windows UV via sunlight is scarce glass filters UV
water availability	sufficient supply of water high precipitation (rain, fog, dew) high air humidity (73-83% rel.H.)	insufficient supply of water no precipitation (rain, fog, dew) low air humidity (30-55% rel.H.)
pressure changes (Δp)	low, mostly very local incidence, mainly vibrational, insufficient data	very low, mostly very local incidence, mainly vibrational, insufficient data









The Scope of the present Webinar Talk

The scope of this talk is to focus on photocatalysts and oligodynamic effects!

oligodynamic effect	photocatalysis	pyrocatalysis	piezocatalysis
Biocidal effect of metals, especially heavy metals (such as copper and silver) that occurs even in low concentrations	photocatalytic activity	pyroelectric effect	piezoelectric effect
	irradiation ↓	heating/cooling (ΔT) ↓	mechanical stress (Δp) ↓
	electron / hole pairs ↓	electric charge ↓	electric charge ↓
	free radicals ↓	free radicals ↓	free radicals ↓

secondary reactions with organic matter

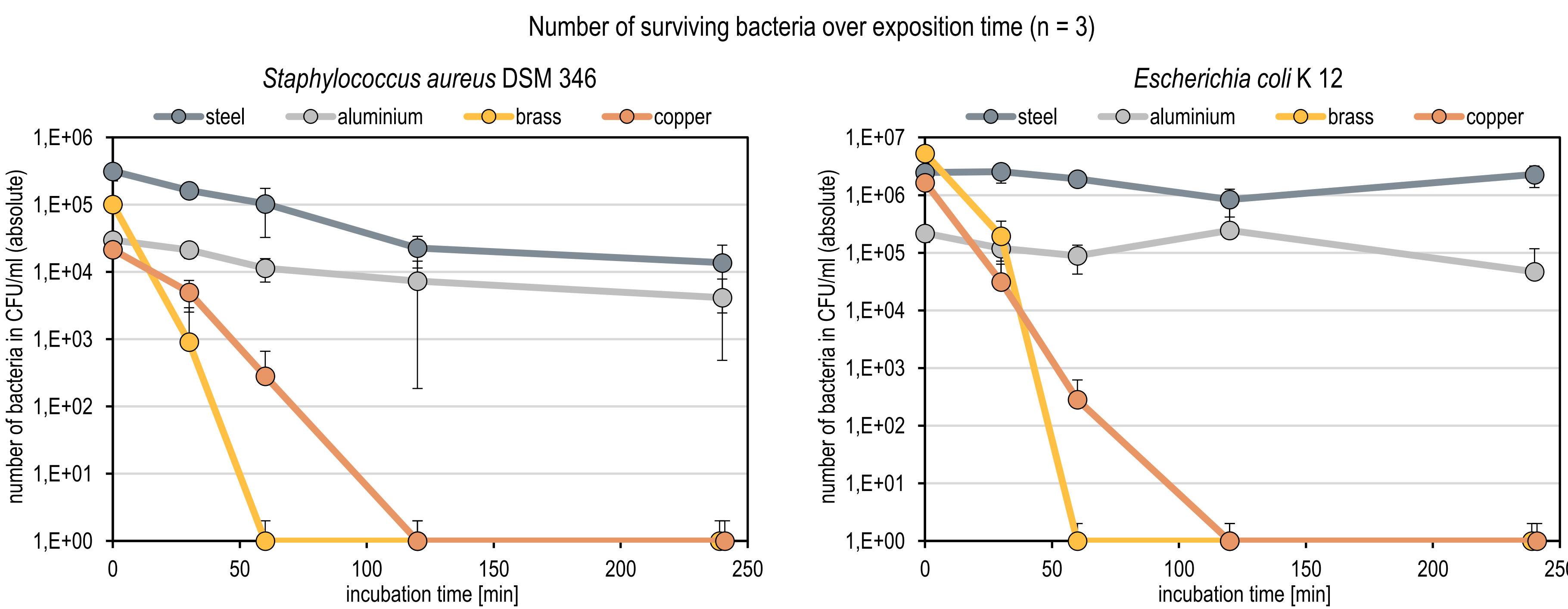
↓

decomposition of organic soilings, inactivation of viruses and microbes

The Results – Testing the Oligodynamic Effect

Comparing the effect of metal surfaces with Generation 1 Coatings (metal powder/polymer)

- coatings are an already standing product of an AutoProtect partner
- potential antimicrobial activity is utterly interesting
- tests performed according to ISO 22196:2011-08
- “Measurement of antibacterial activity on plastics and other non-porous surfaces”



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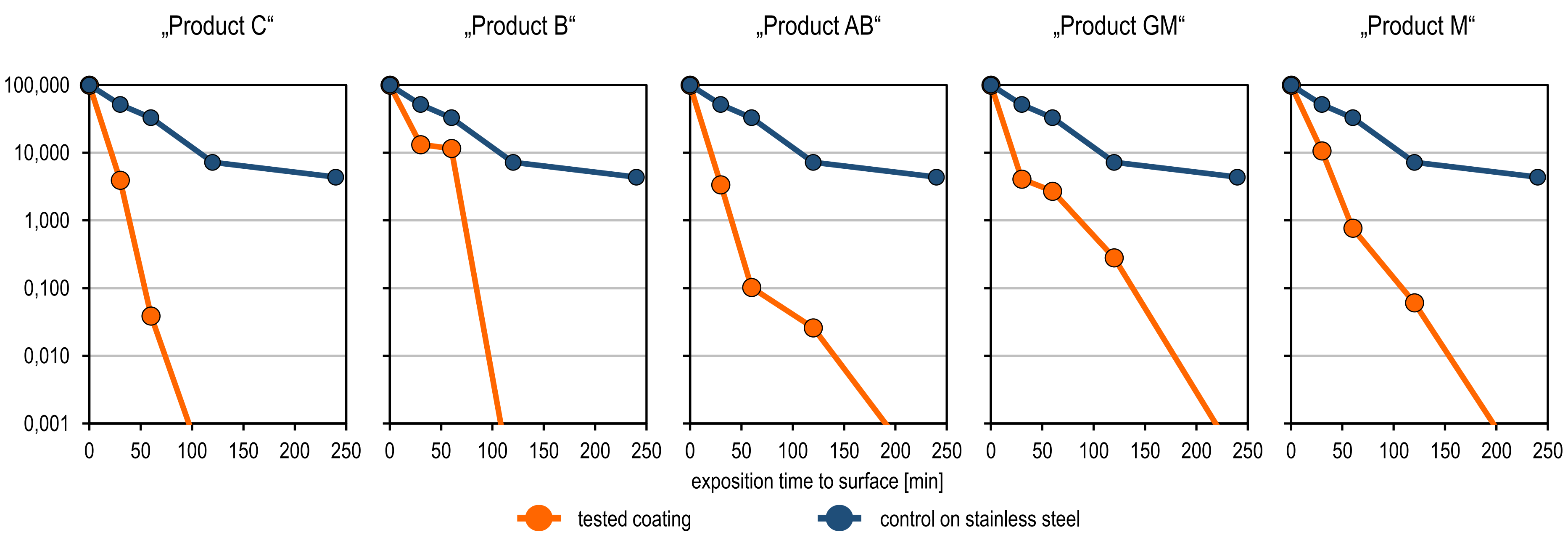
Percentage of surviving bacteria over exposition time (*S. aureus* DSM 346, n = 6)



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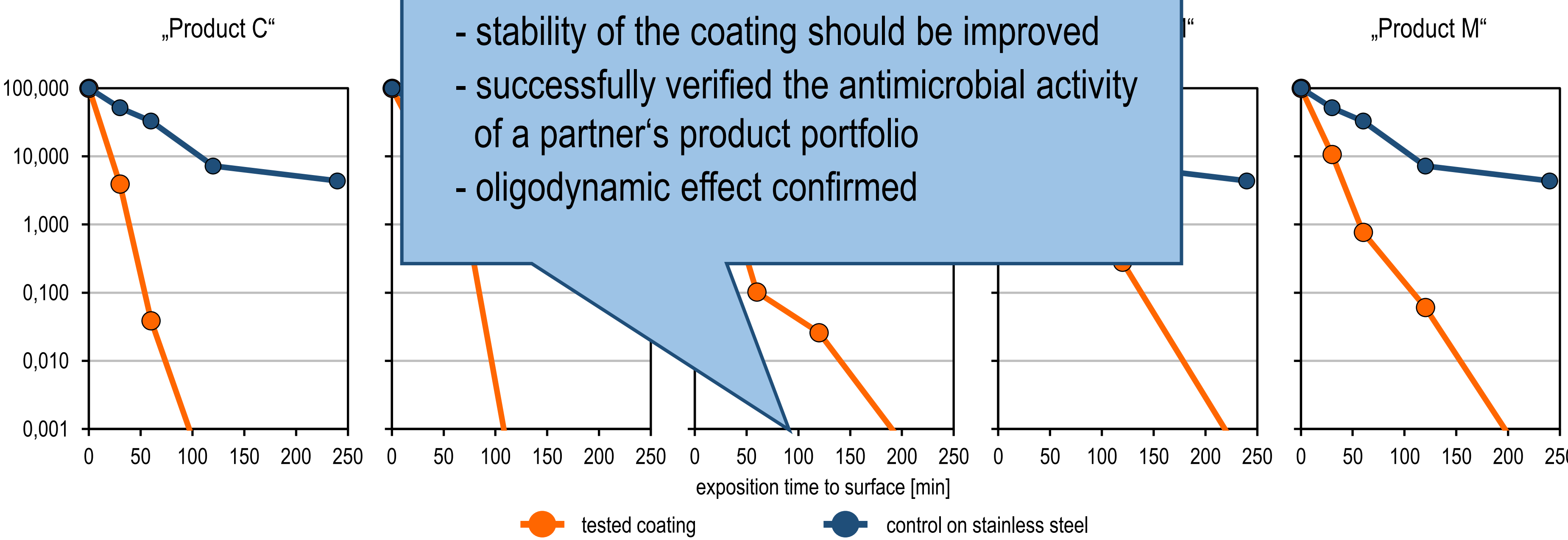
Comparing the effect of metal surfaces with Generation 1 Coatings (metal powder/polymer)

- coatings are an already standing product of an AutoProtect partner
- potential antimicrobia
- tests performed acco
- “Measurement of ant ... rfaces”

Conclusions

- all coatings show good antimicrobial activity
- reduction of 4 $\log_{10}$ in less than 4 hours
- overall result are consistent
- stability of the coating should be improved
- successfully verified the antimicrobial activity of a partner‘s product portfolio
- oligodynamic effect confirmed

= 6)

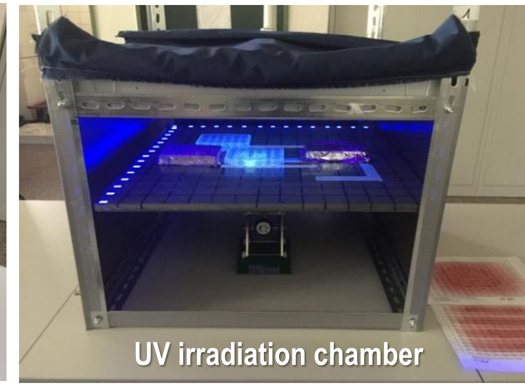


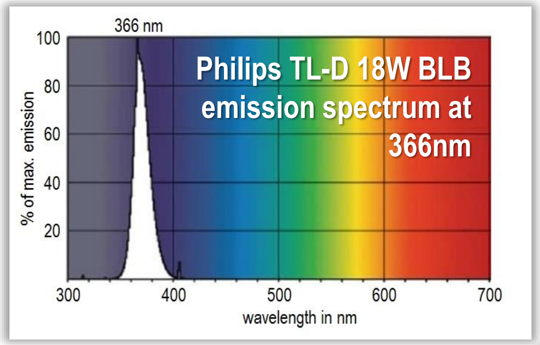
The Results – Characterizing and Testing Potential Photocatalysts

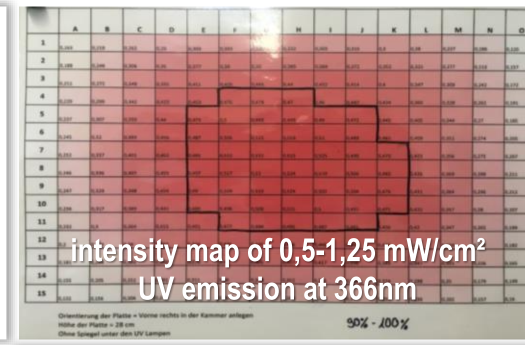
Establishing irradiation procedures

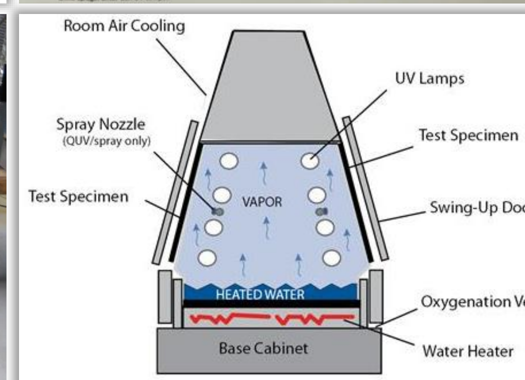
- three self-made UV-irradiation chambers build
- UV-B irradiation with narrow spectrum around 366 nm
- height-adjustable stage for variable regulation of the UV dose
- 2 modes of operation:
  no mirrors: diffuse but uniform, up to 0,52 mW/cm²
  with mirrors: highly focussed, up to 1,25 mW/cm²
- refurbishable for daylight simulation

- QUV accelerated weathering tester
- UV at 351 nm, up to 45 mW/cm²
- saturation with water vapor possible





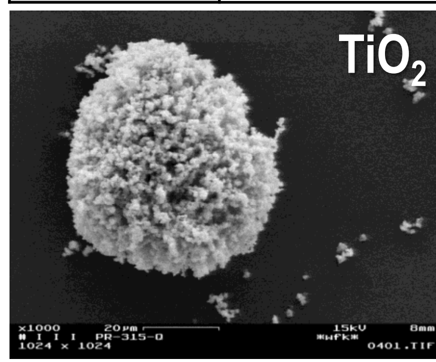


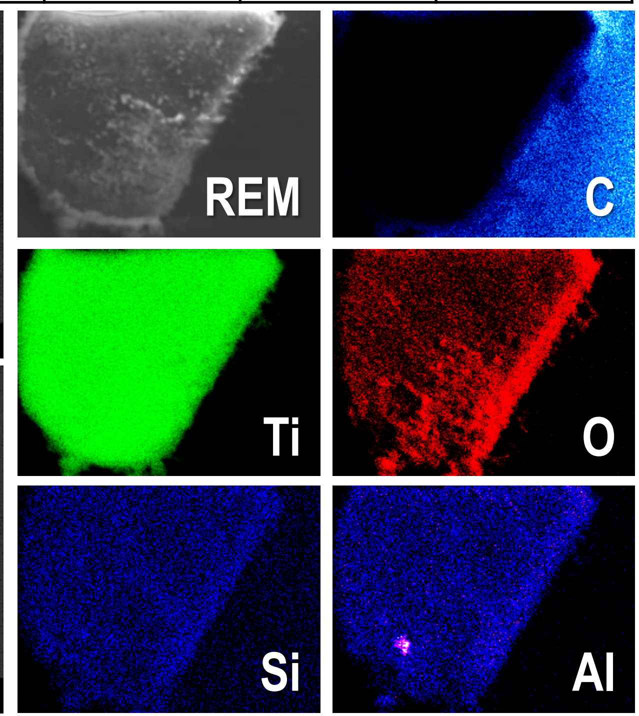


Commercial photocatalysts

- 13 commercial products tested
- 5 manufacturers
- 11 TiO_2 and 2 ZnO
- 4 rutile-type, 7 anatase-type TiO_2
- 4 UV+VIS active TiO_2 tested
- 7 merely UV active TiO_2 tested
- characterization by
  - particle size (REM)
    - TiO_2: 0,5-2,0 µm
    - ZnO: <0,5 µm
  - aggregation type (REM)
    - mostly massive
  - shape (REM)
    - mostly irregular
  - elementary composition (EDX)
    - Si, Al, et al.

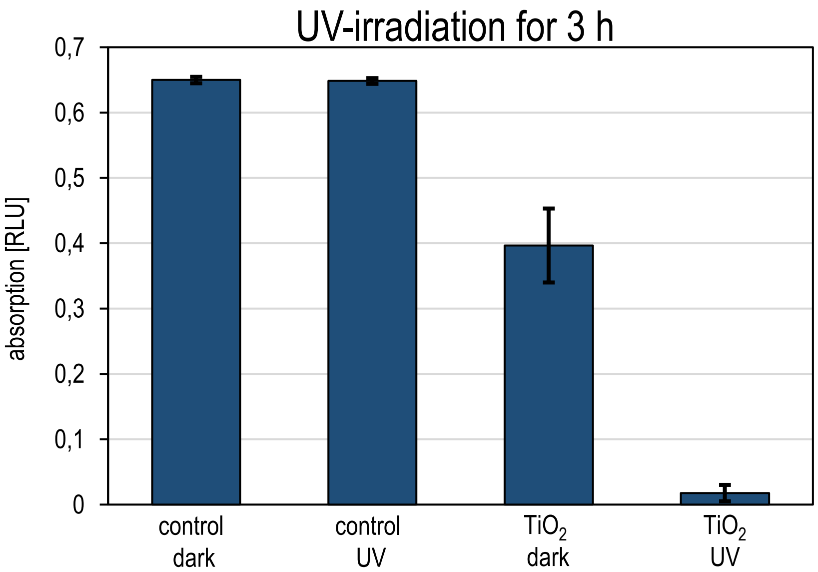
photocatalys	manufacturer	rutile	anatase	VIS activity
TiO_2	Kronos	1	5	2
TiO_2	Sigma	1	-	-
TiO_2	Evonik	-	1	1
TiO_2	Titan Dix	1	-	-
TiO_2	HW Nanomaterials	1	1	1
ZnO	Sigma	n. a.	n. a.	n. a.
ZnO	HW Nanomaterials	n. a.	n. a.	n. a.

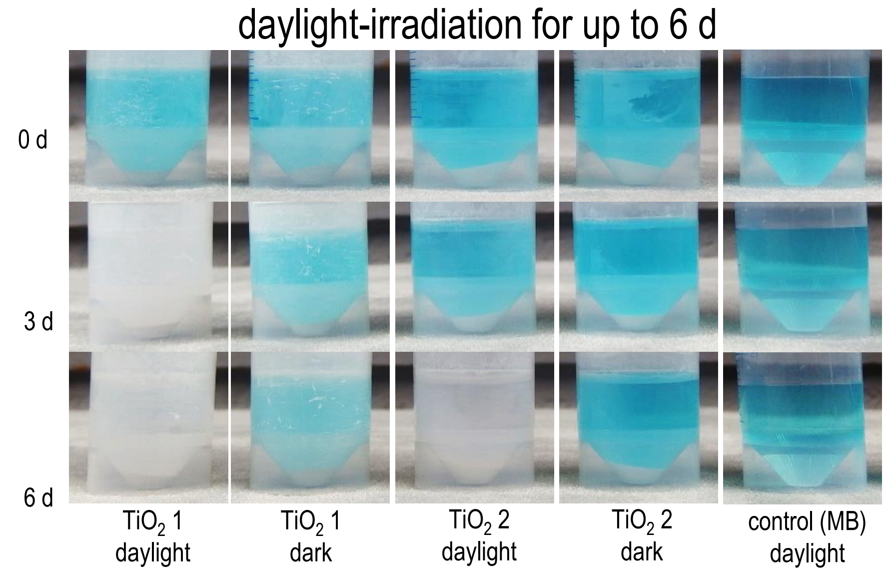


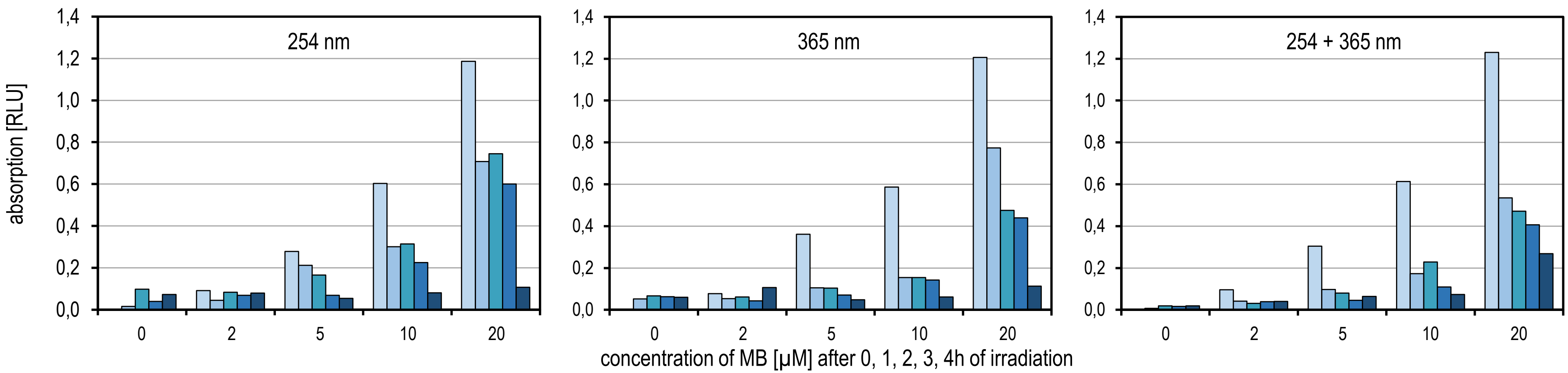


The Results – Characterizing and Testing Potential Photocatalysts

Testing radical formation at TiO_2 with methylene blue (MB) according to DIN 52980







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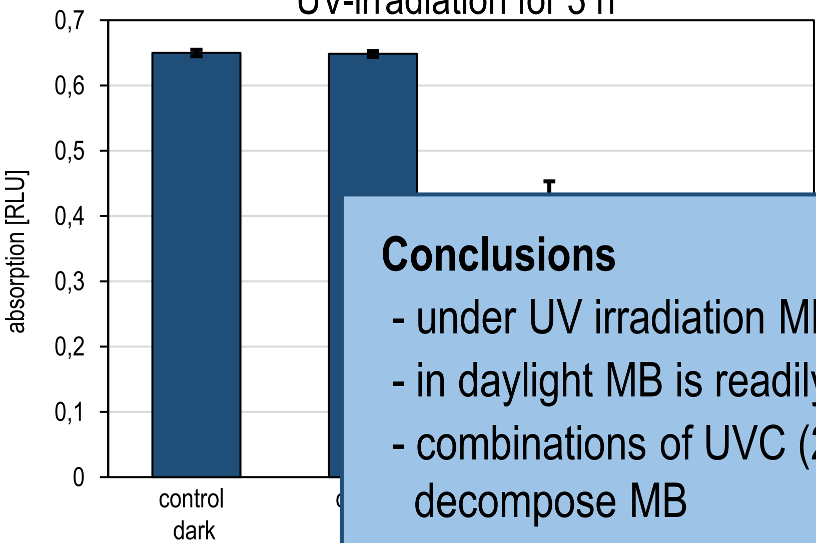
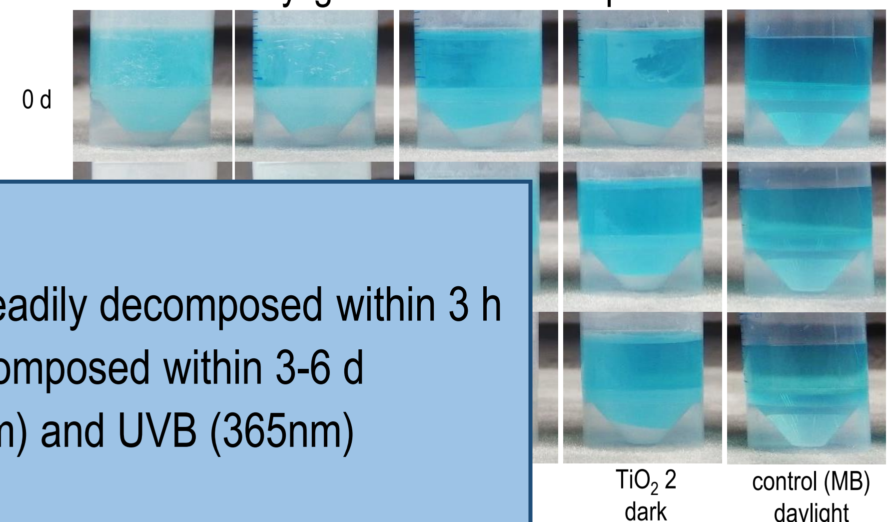
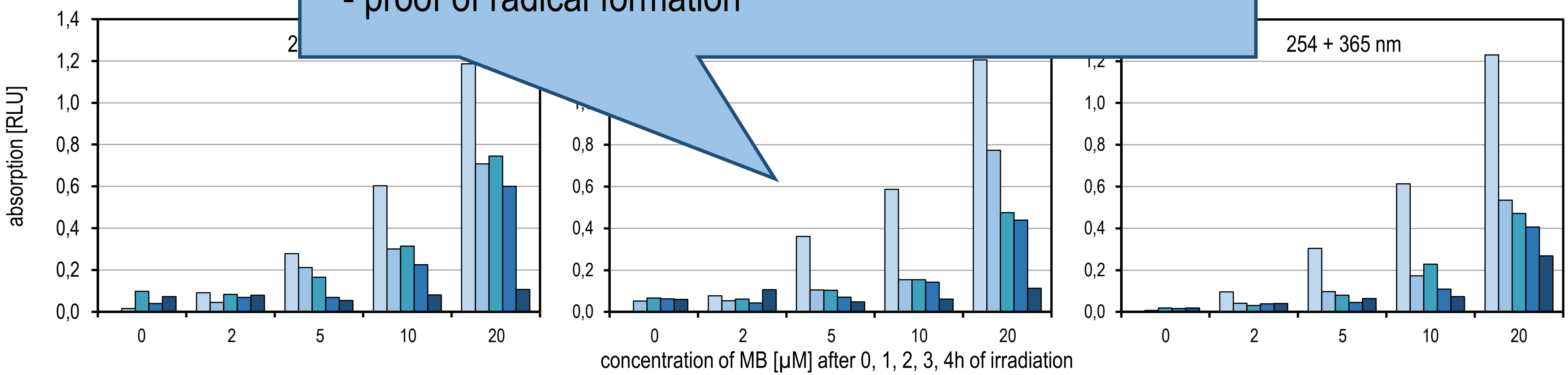




Conclusions

- under UV irradiation MB is readily decomposed within 3 h
- in daylight MB is readily decomposed within 3-6 d
- combinations of UVC (254nm) and UVB (365nm) decompose MB
- proof of radical formation



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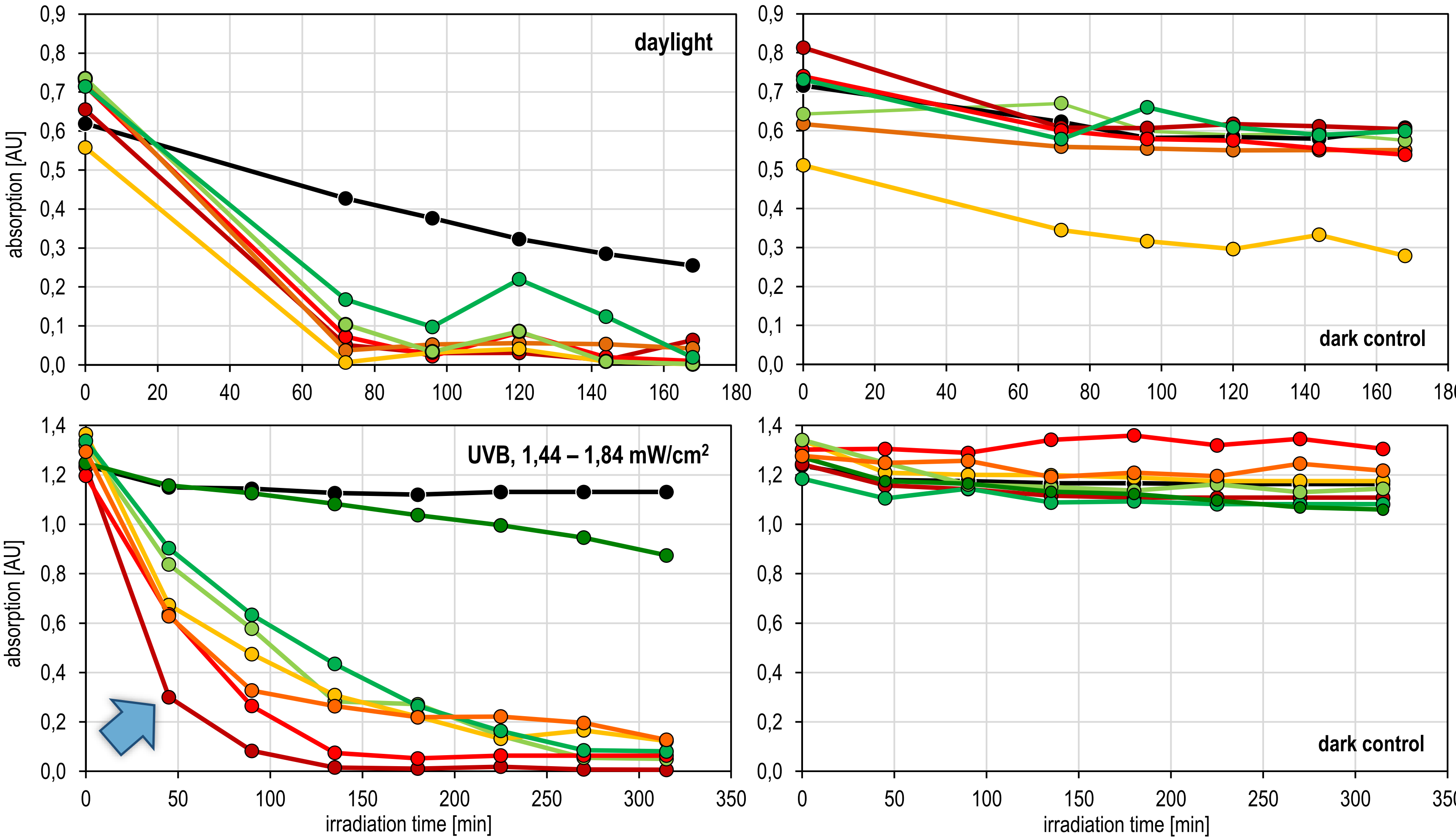
daylight

UV irradiation



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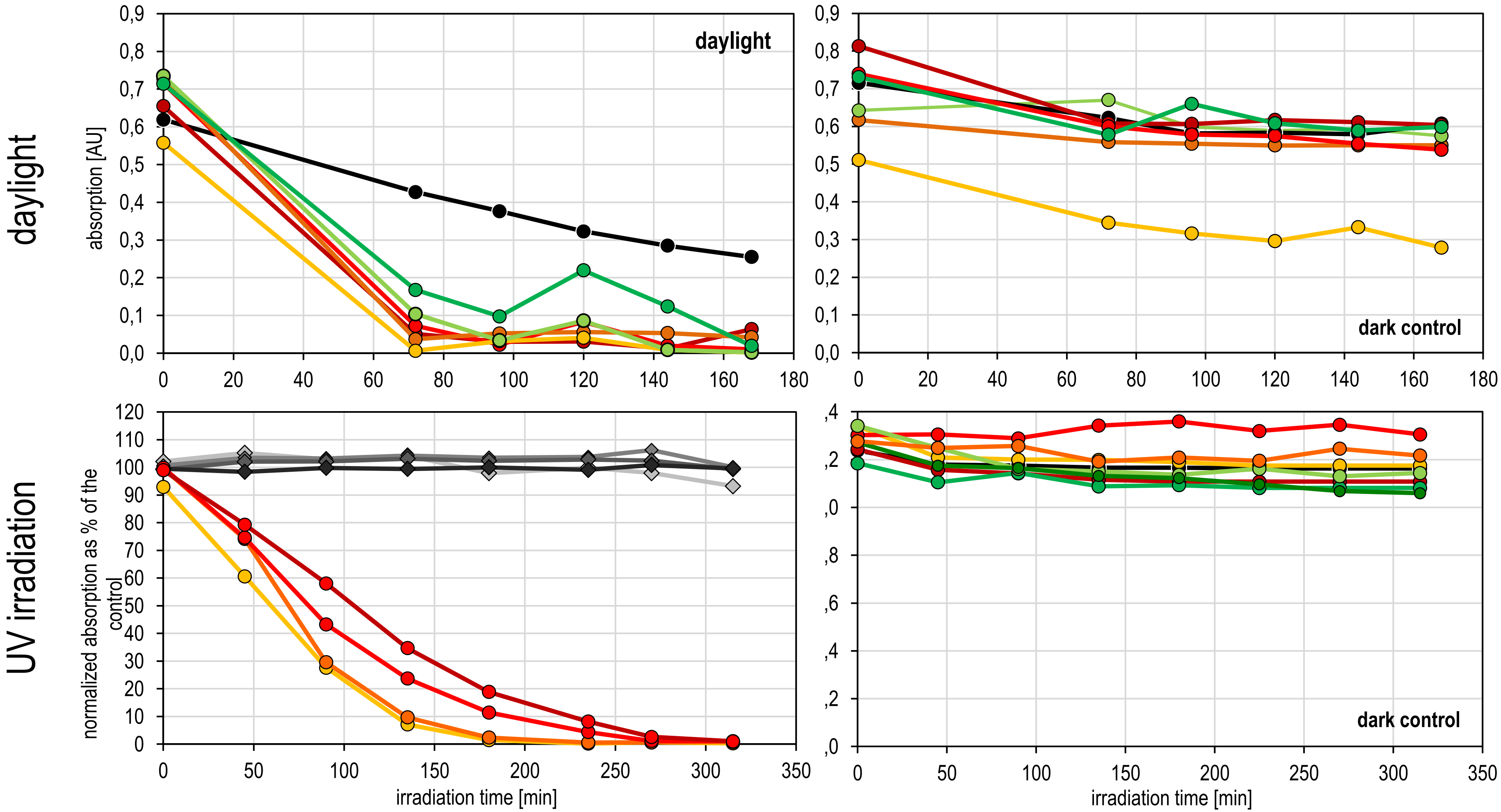

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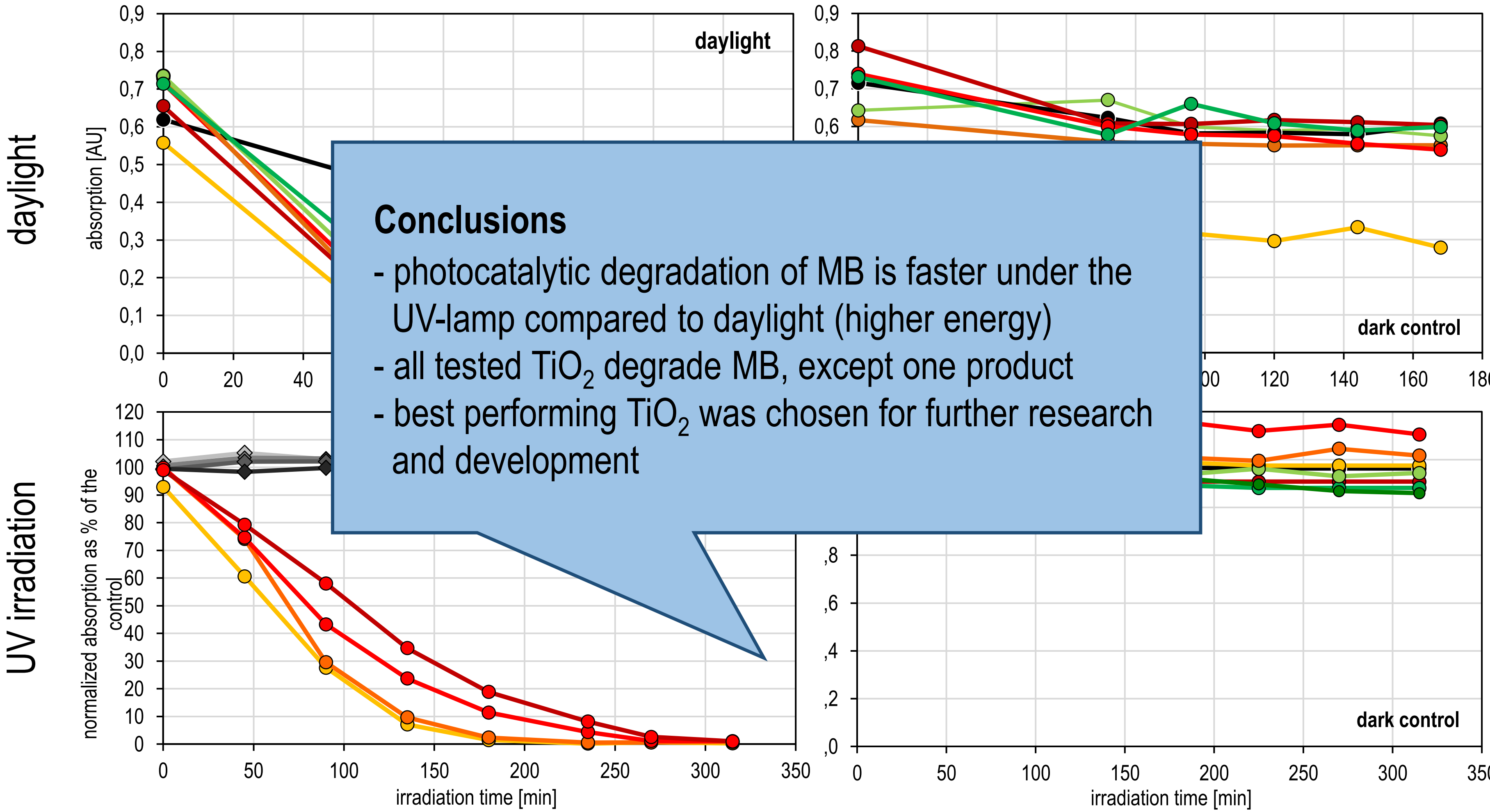


Conclusions

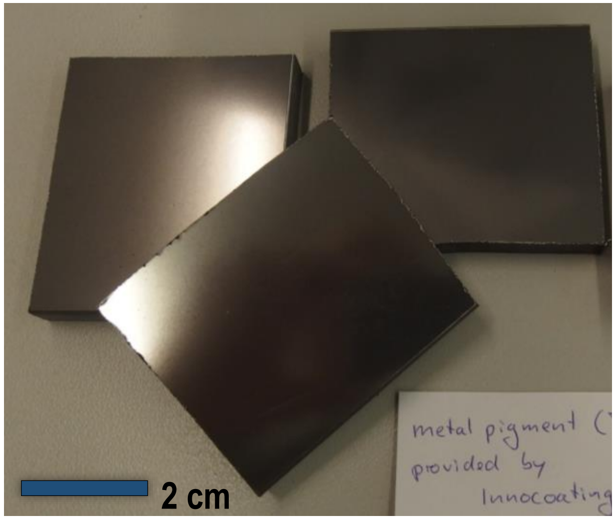
- photocatalytic degradation of MB is faster under the UV-lamp compared to daylight (higher energy)
- all tested TiO_2 degrade MB, except one product
- best performing TiO_2 was chosen for further research and development

The Results – Testing the bifunctional Generation 2 Coating

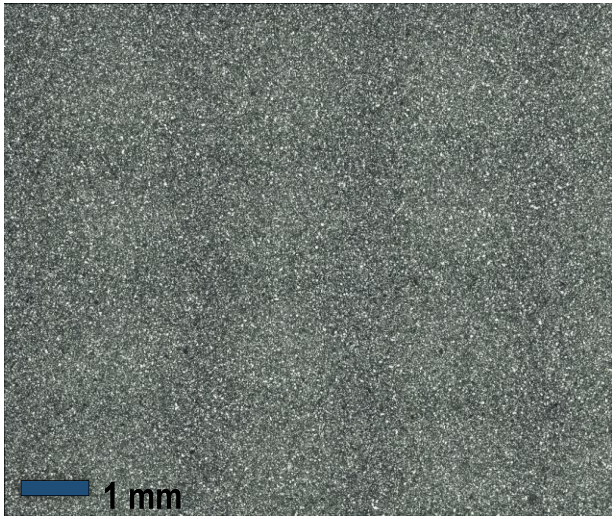
Performance testing of the generation 2 coatings developed with an AutoProtect partner

- TiO_2 as a photocatalytic additive with degrading and antimicrobial activity
- copper-containing metal pigments with an oligodynamic effect

metal pigment coating supplemented with the best performing TiO_2 produced & provided by an AutoProtect partner



even dispersion of white TiO_2 particles within in the darkish coating

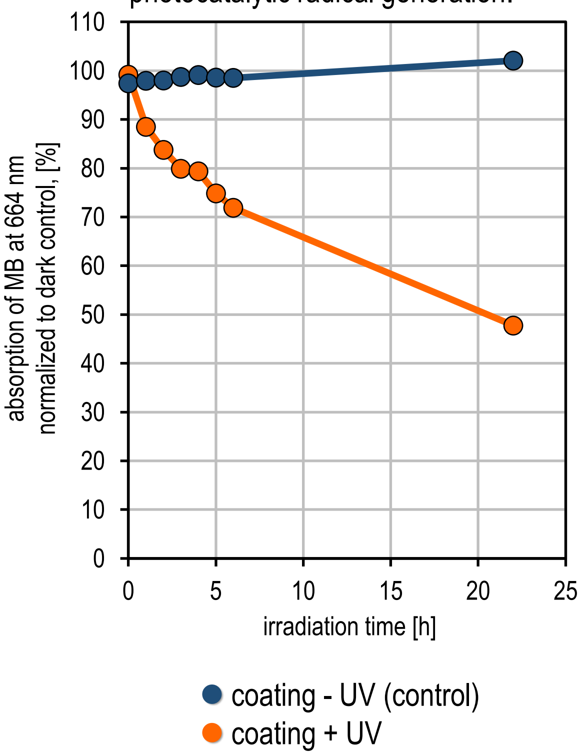


copper-coloured metallic inclusion in the coating → metal pigment with additional oligodynamic effect

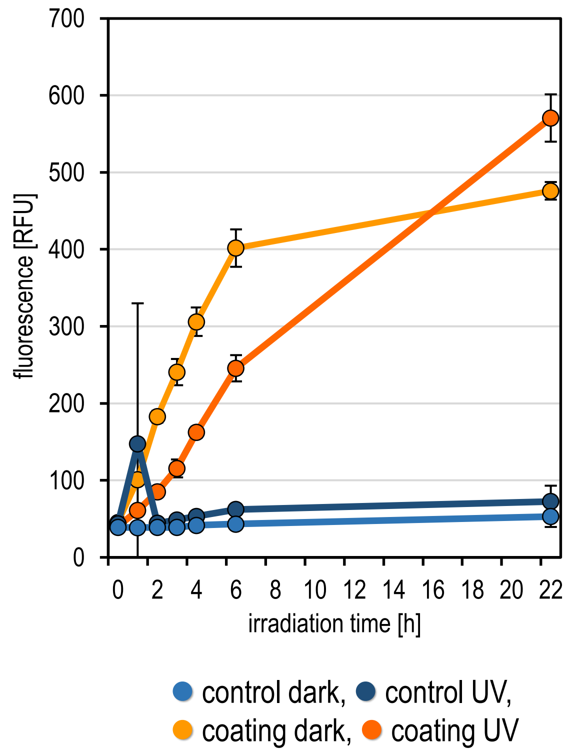
Testing the bifunctional Generation 2 Coating

- testing radical formation with the methylene blue and the coumarin assays
- testing the antimicrobial activity with the ISO 22196 assay

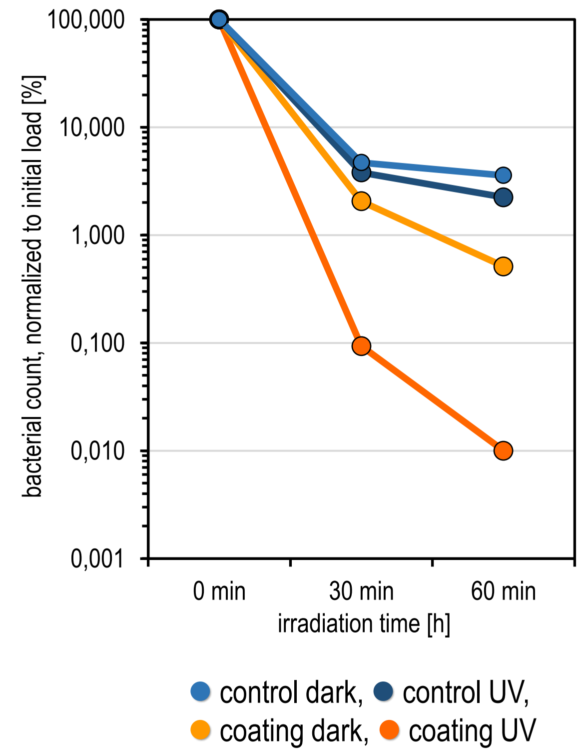
reduction of absorption of methylene blue at 664 nm as a measure of photocatalytic radical generation.



increase of fluorescence (λ_{ex} 360nm / λ_{em} 455nm) of 1 mM coumarin after UV-irradiation at 365nm at 1mW/cm^2



the effect of photocatalytic radical generation on the reduction of bacteria with *E. coli* DSM 1578



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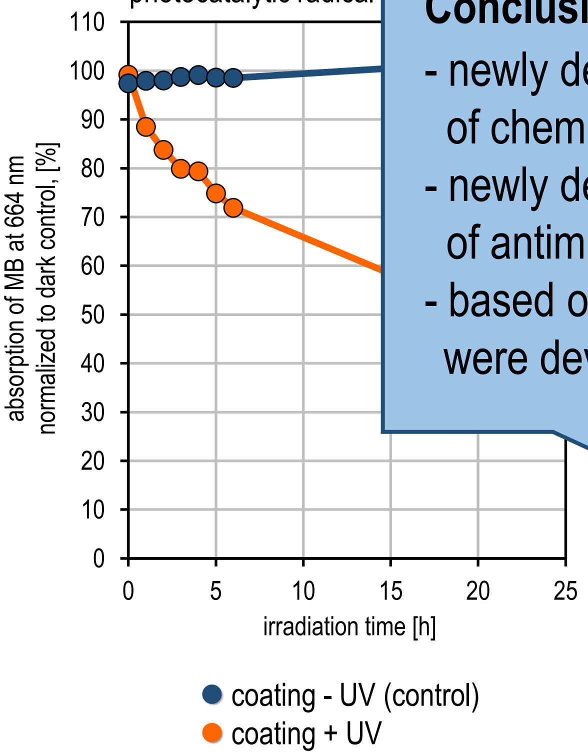
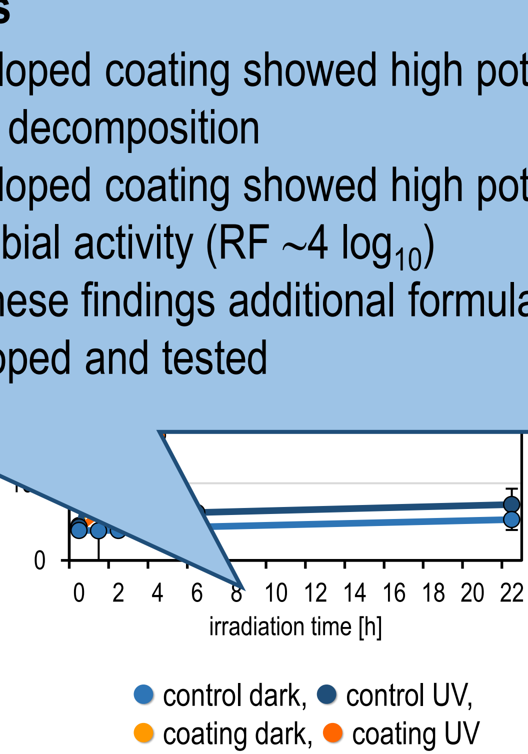
reduction of absorption of methylene blue at 664 nm a… photocatalytic radical …



increase of fluorescence (λ_{ex} 360nm / …



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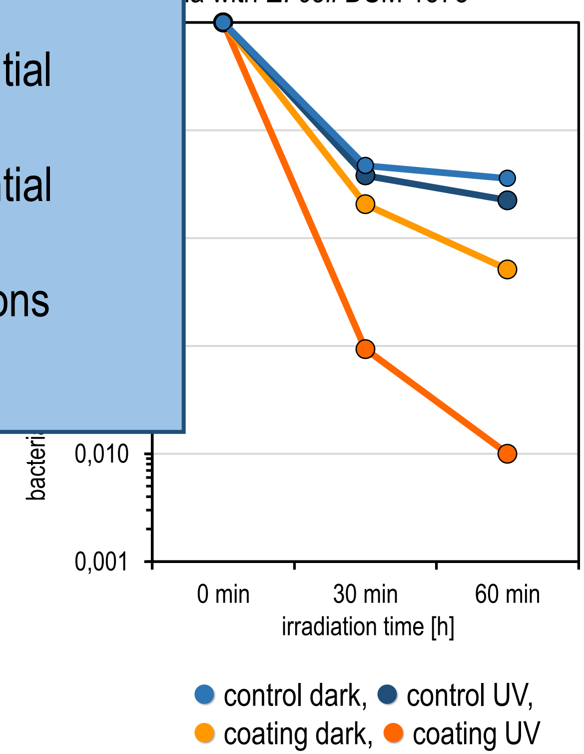
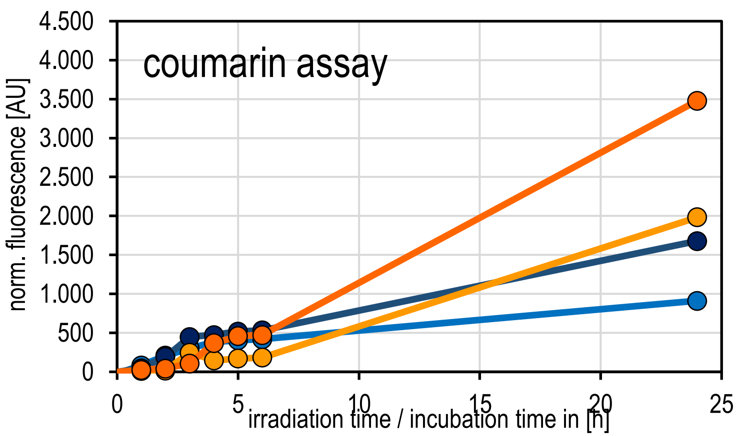


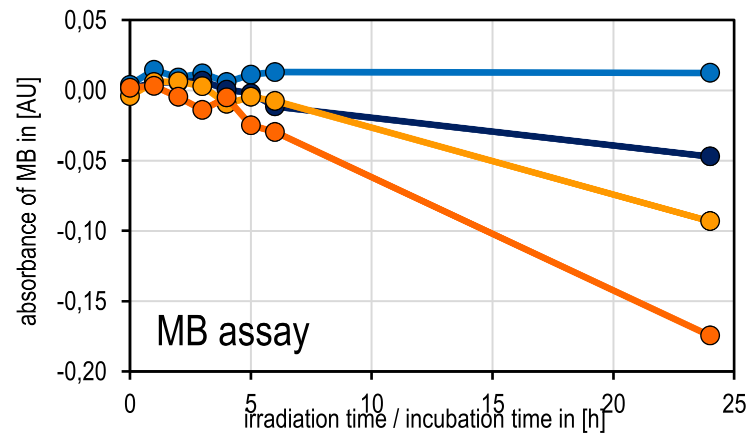
Conclusions

- newly developed coating showed high potential of chemical decomposition
- newly developed coating showed high potential of antimicrobial activity (RF ~4 log_{10})
- based on these findings additional formulations were developed and tested

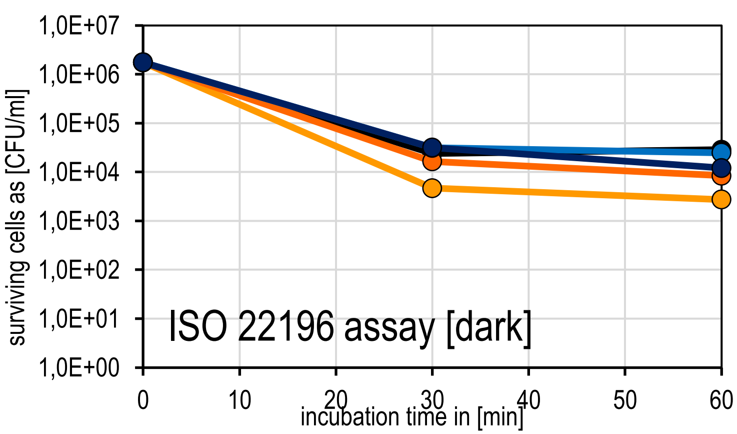
Performance testing of the generation 2 coatings developed with an AutoProtect partner

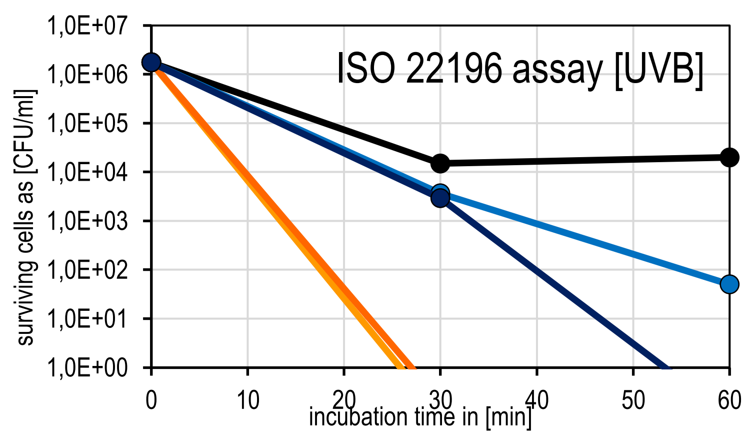
Coating containing metallic particles and a supplement of TiO_2 in two concentrations (● **A2%,** ● **A5%**)





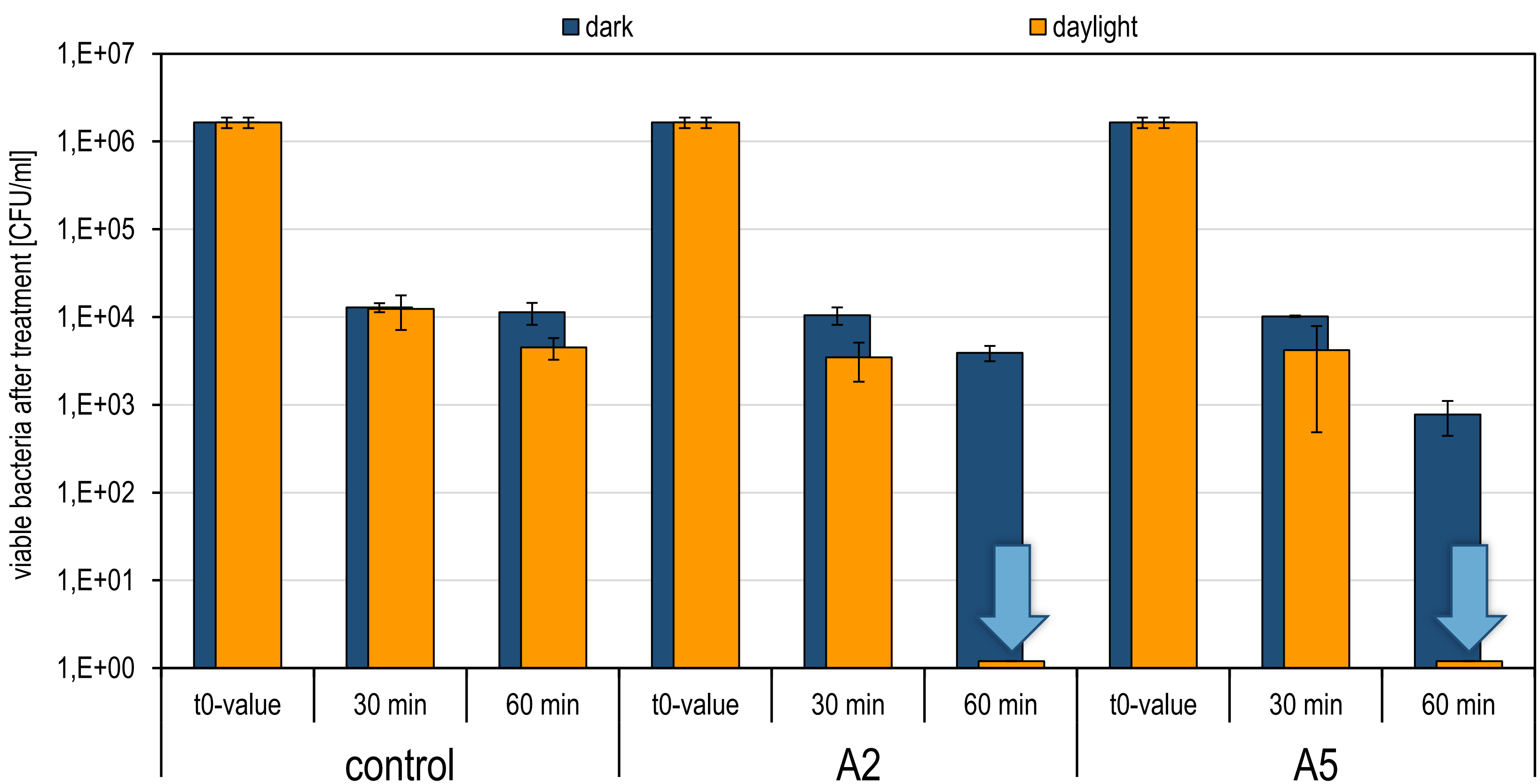
Coating without metallic particles but with a supple-ment of TiO_2 in two concentrations (● **B2%,** ● **B5%**)





Performance testing of the generation 2 coatings developed with an AutoProtect partner

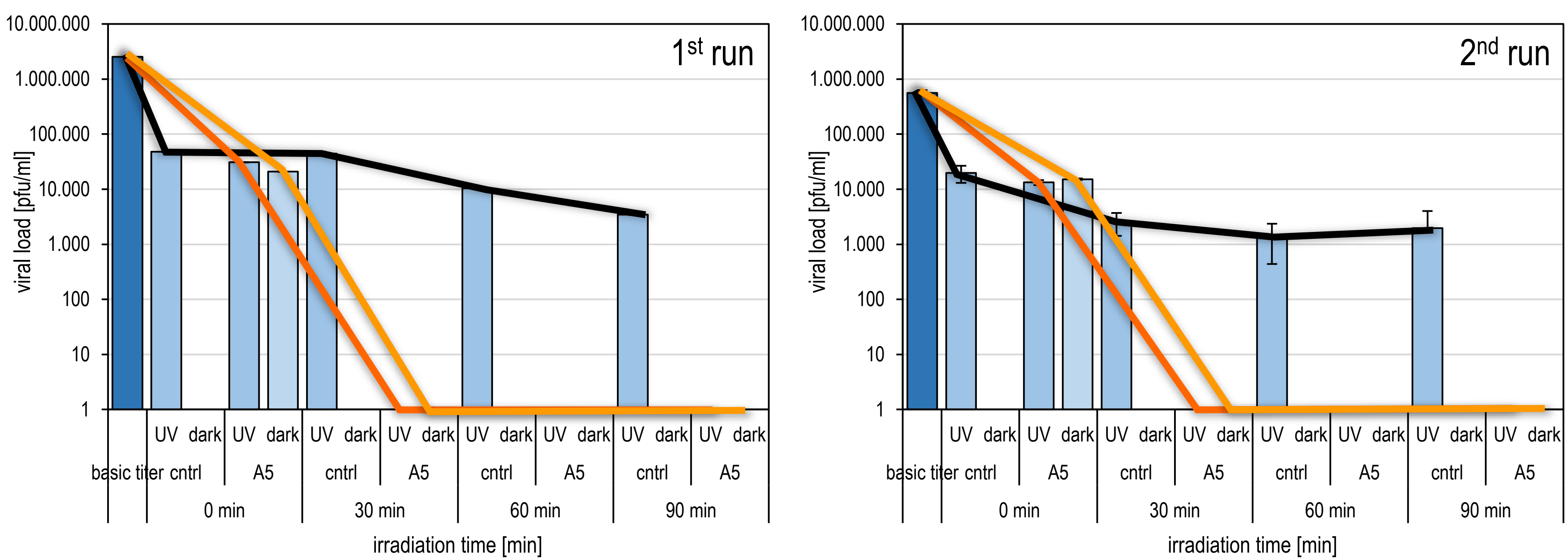
inactivation of *E. coli* on coating A2 and A5 after illumination with daylight neon tubes
at 222-246 mJ/cm² (30 min) and 444-491 mJ/cm² (60 min)



The Results – Testing the bifunctional Generation 2 Coating

Performance testing of the generation 2 coatings developed with an AutoProtect partner

- testing the antiviral capacity in accordance to ISO 22196 towards the bacteriophage Phi 6
- traits of Phi 6 resemble those of SARS-CoV-2 → lipid envelope, +ssRNA, 75nm
- testing under wet conditions, drying may lead to viral inactivation by its own
- complete inactivation of Phi 6 in the dark and under UV after exposure periods of >30min



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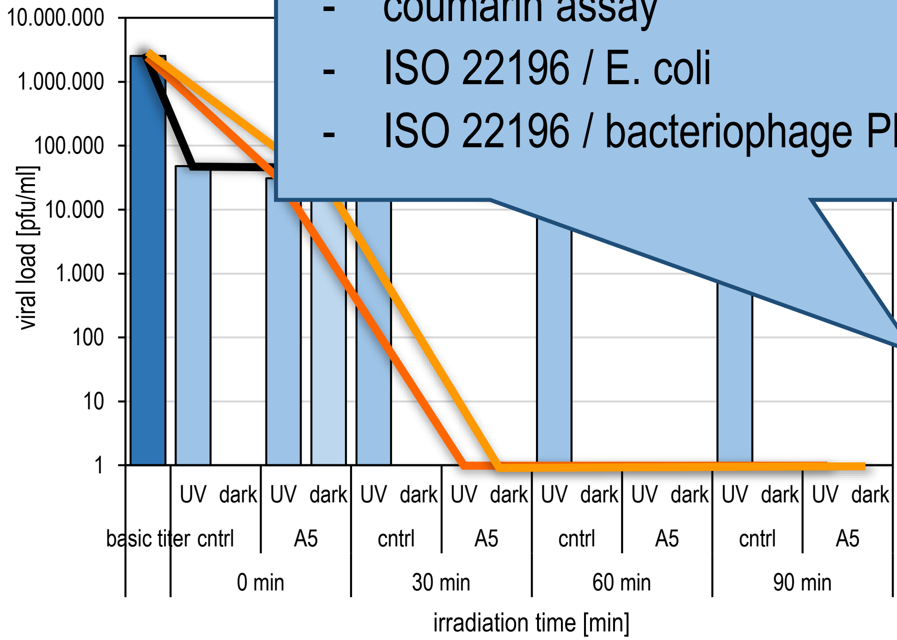
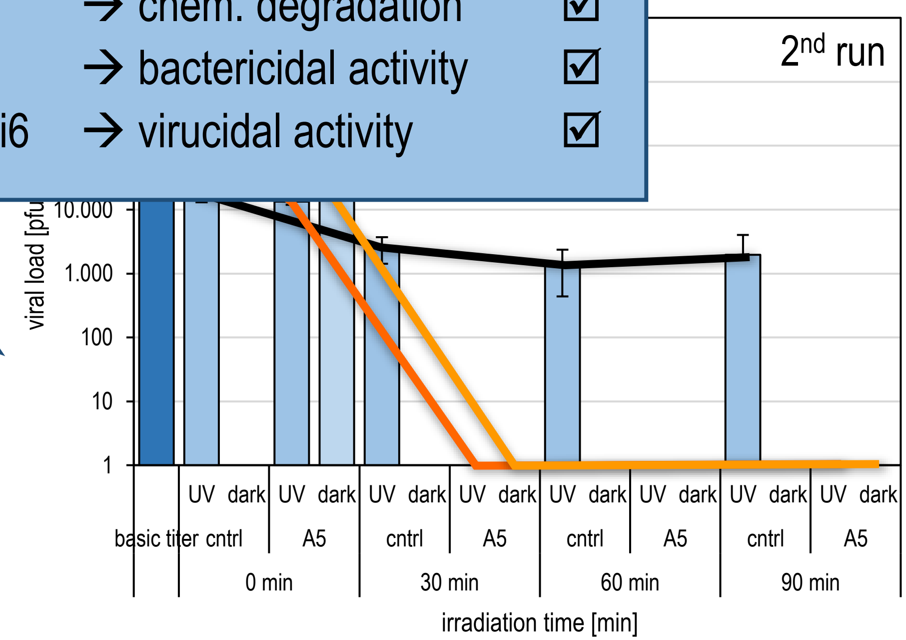
- testing under wet conditions, drying may lead to viral inactivation by its own
- complete i … 0min

Conclusions on bifunctional coatings:

- methylene blue assay → chem. degradation ☑
- coumarin assay → chem. degradation ☑
- ISO 22196 / E. coli → bactericidal activity ☑
- ISO 22196 / bacteriophage Phi6 → virucidal activity ☑





The Results – In-house Synthesis of Photocatalytic ZnS Particles

Synthesis of zinc sulfide nanoporous nanoparticles

Experiment

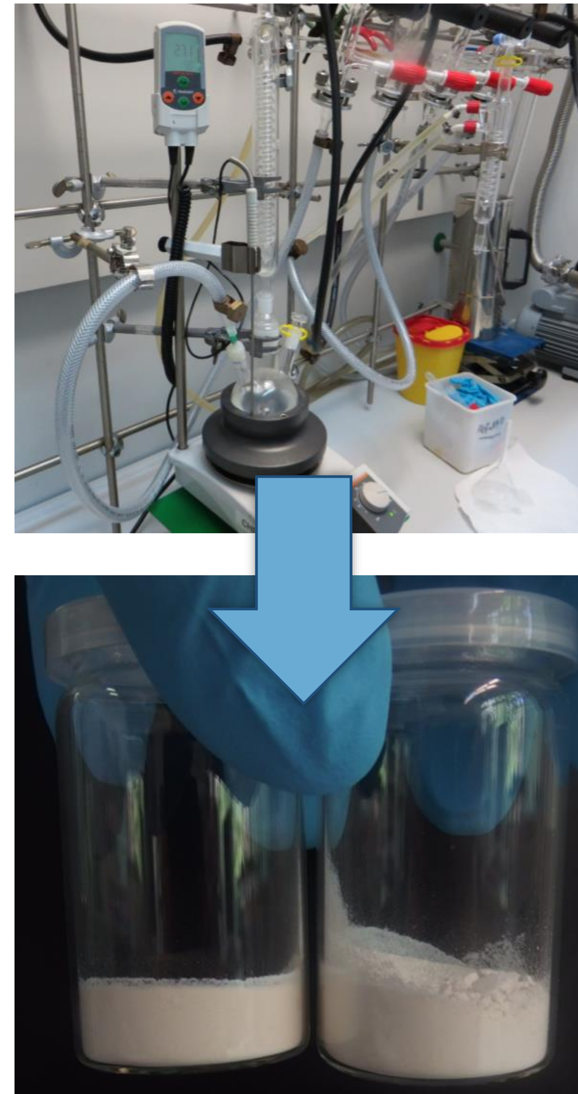
- synthesis of zinc sulfide nanoporous nanoparticles (ZnS-NPNPs)
- synthesis according to Hu et al. 2005
- synthesis under Argon at Schlenk's line
- compared to commercial ZnS
- testing with MB and coumarin assays

Results

- photocatalytic effect with both, commercial ZnS and ZnS-NPNPs
- self-made ZnS-NPNPs are slightly more efficient photocatalysts
- results resemble those of mediocre commercial TiO_2

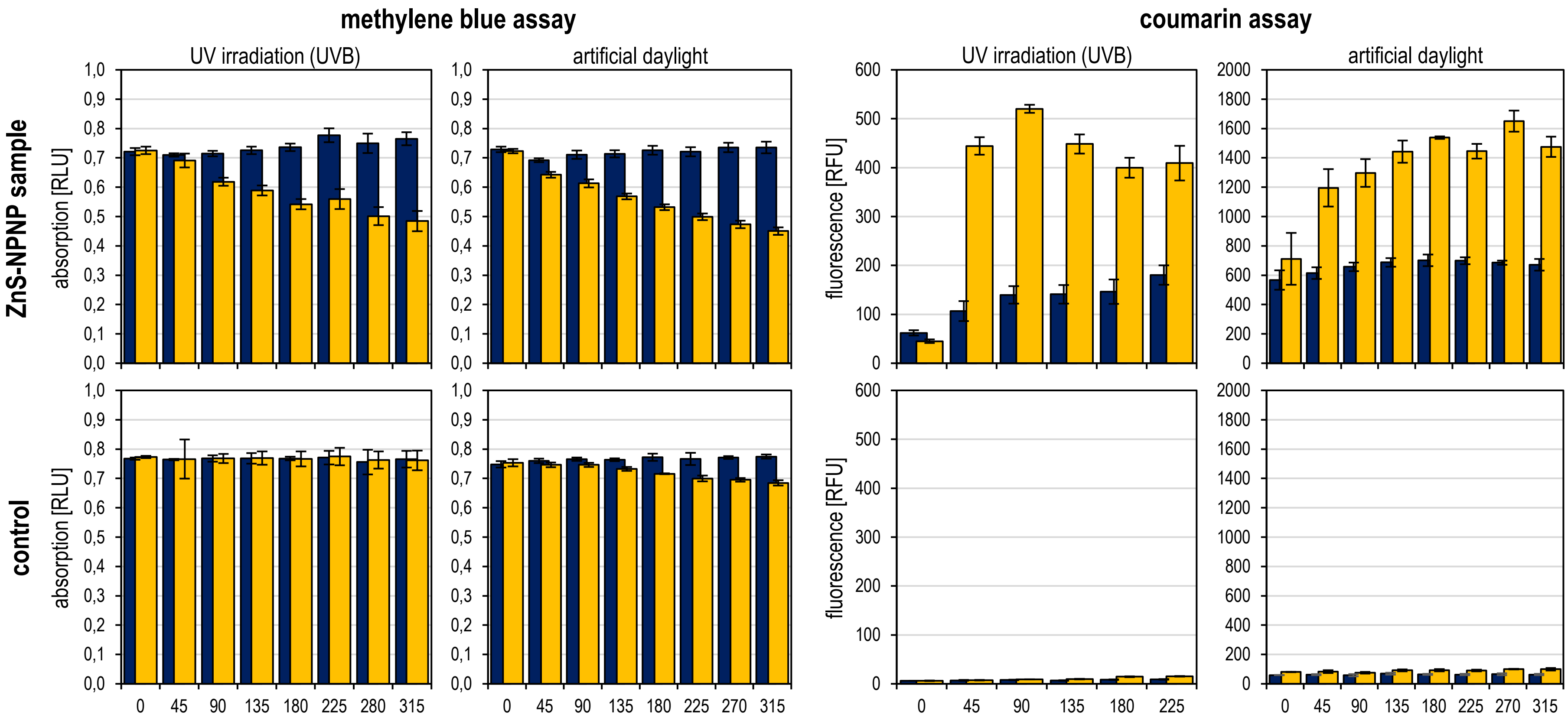
Achievement

- first successful in-house synthesis of a new photocatalyst class



Synthesis of zinc sulfide nanoporous nanoparticles

- Photocatalytic effect with both, commercial ZnS and ZnS-NPNPs
- self-made ZnS-NPNPs are more efficient than commercial ZnS
- but results resemble those of mediocre commercial TiO_2

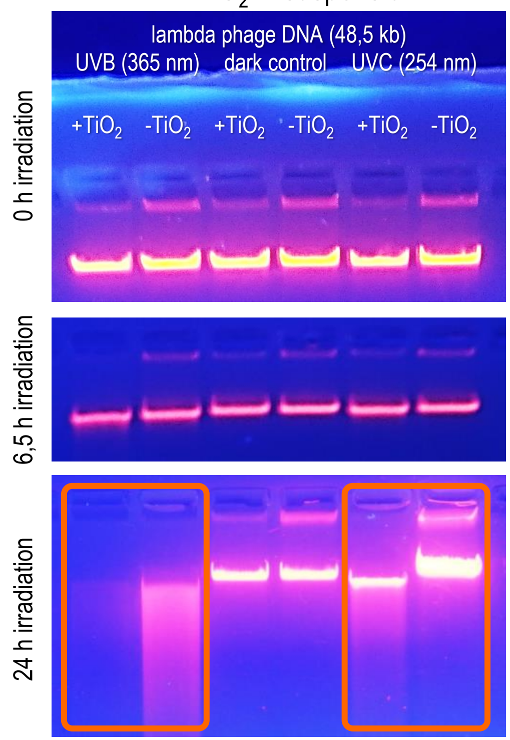


The Results – Degradation of organic compounds for self-cleaning

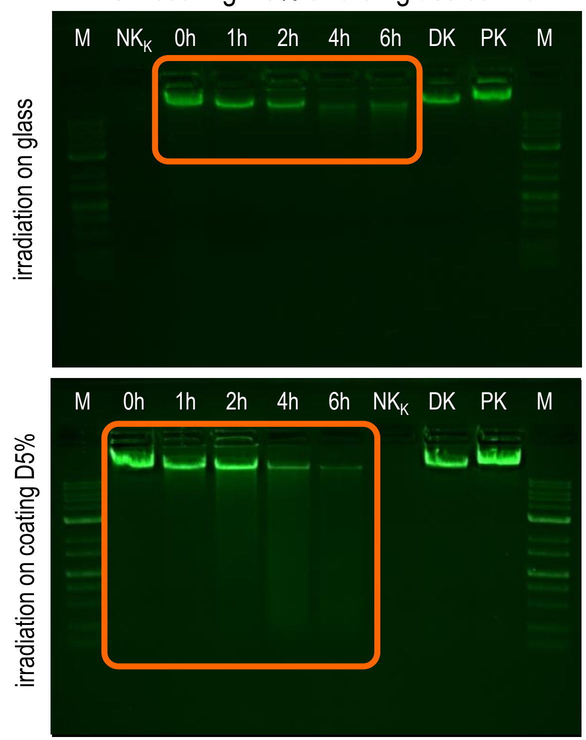
Degradation of organic compounds – DNA as a substitute for nucleic acid

- besides radical formation, antibacterial and antiviral activity (self-disinfection), MSS-coatings should degrade organic soilings on surfaces (**self-cleaning**, **easy-to-clean properties**)
- typical biological soilings include macromolecules as nucleic acids, proteins, carbohydrates, lipids

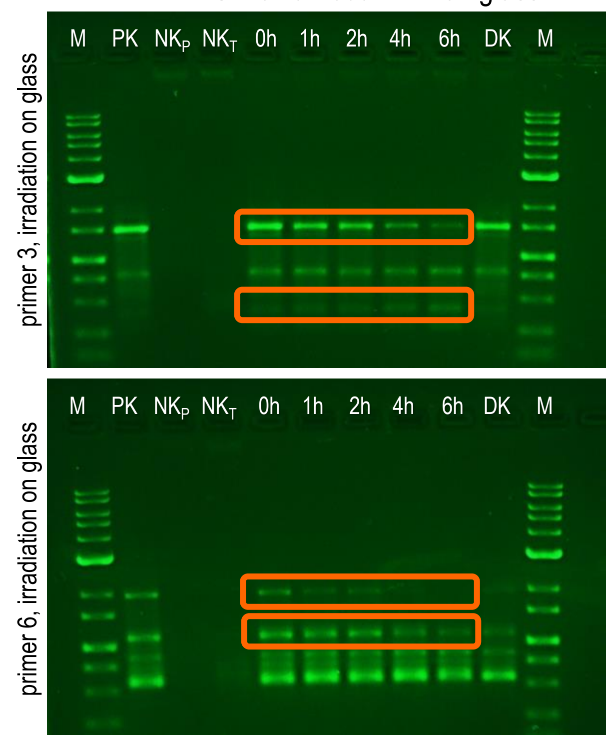
UV-B/C irradiation of lambda DNA with TiO_2 in suspension



351nm irradiation (QUV) of lambda DNA on TiO2-coating D5% and on glass control



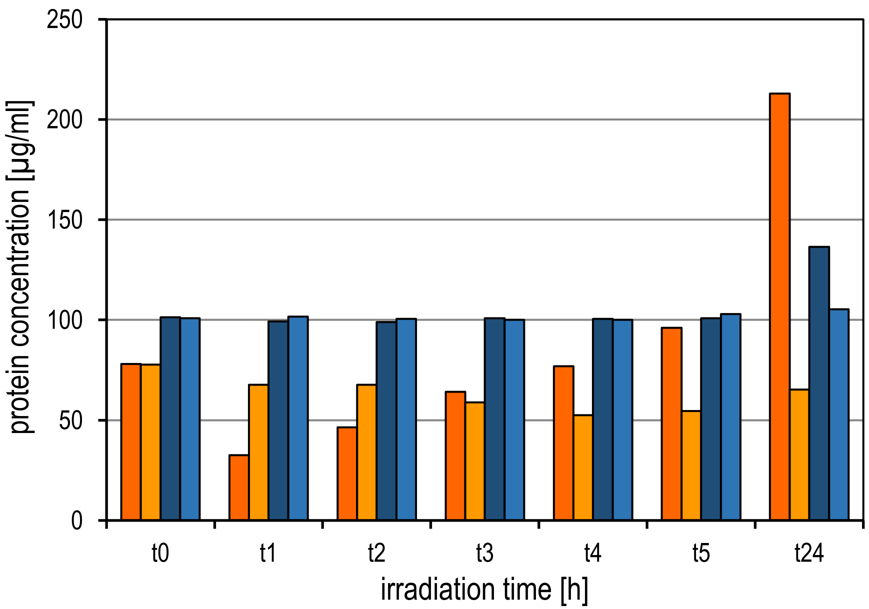
351nm irradiation (QUV) and susequent RAPD-PCR of lambda DNA on glass

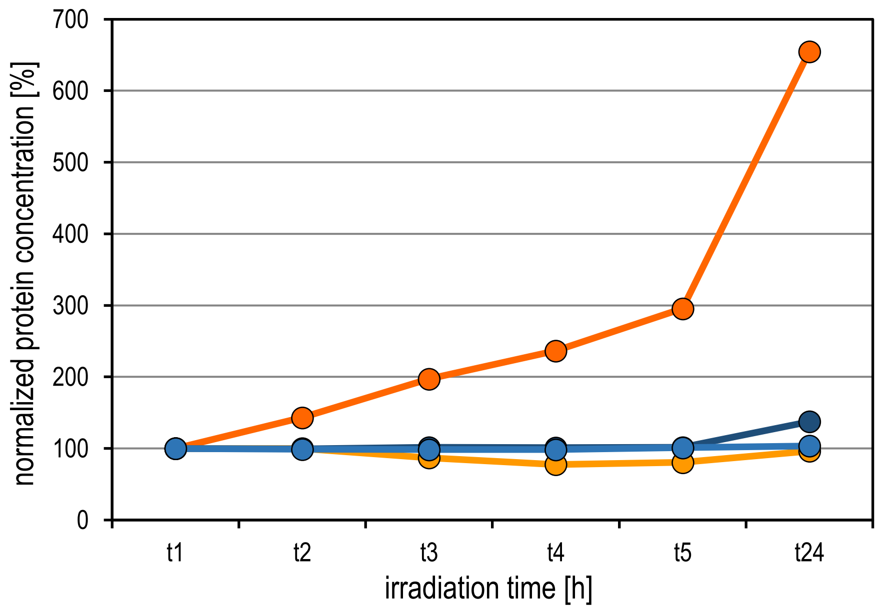


The Results – Degradation of organic compounds for self-cleaning

Degradation of organic compounds → bovine serum albumin (BSA) as a common protein

- proteins are extremely critical soilings
- testing with **BSA**: photocatalytic activity breaks up BSA into smaller fragments
  measured protein concentration <u>increases</u> when measured by OPA method



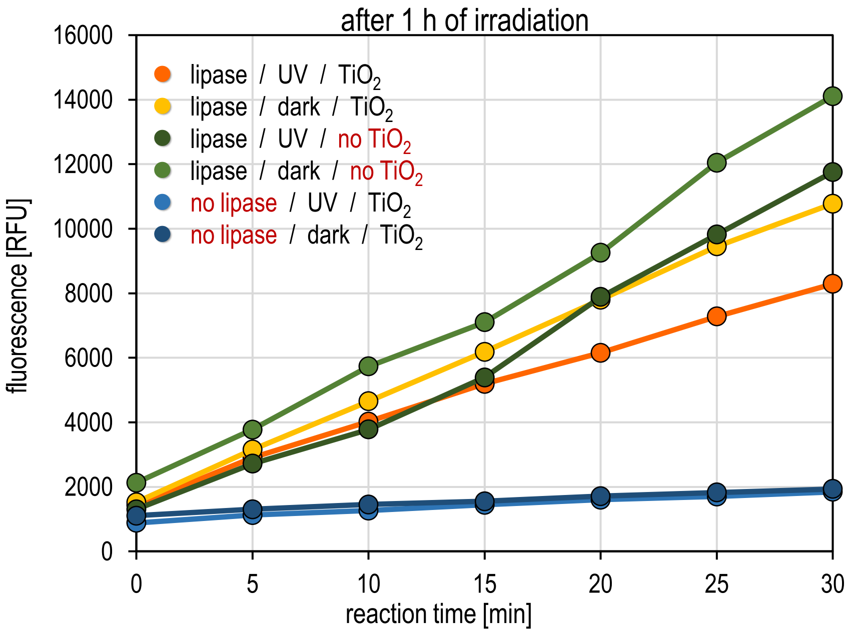


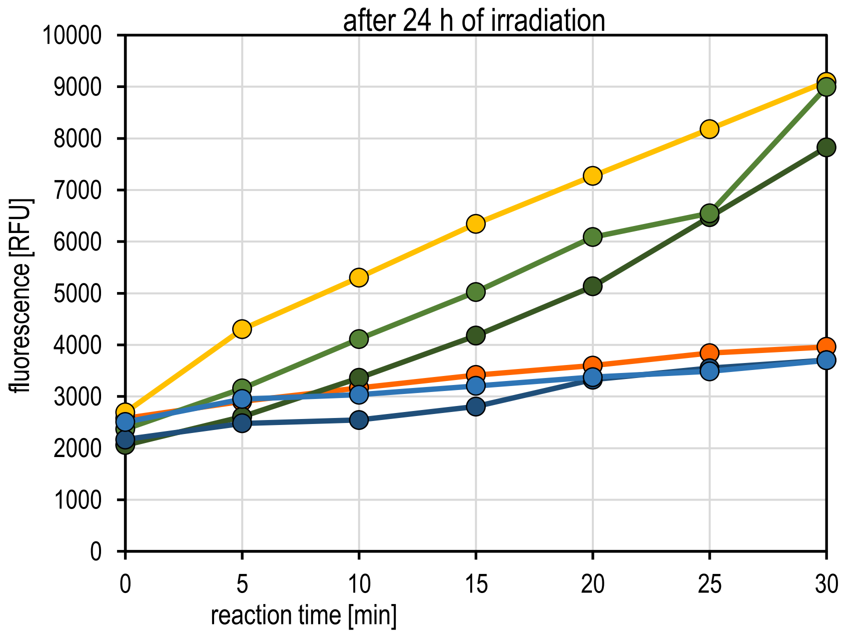
The Results – Degradation of organic compounds for self-cleaning

Degradation of organic compounds → lipase from *C. viscosum* as an enzyme

- proteins are extremely critical soilings
- testing with **enzymes**: photocatalytic activity inactivates the enzymes

  enzyme activity <u>decreases</u> when measured in appropriate assay





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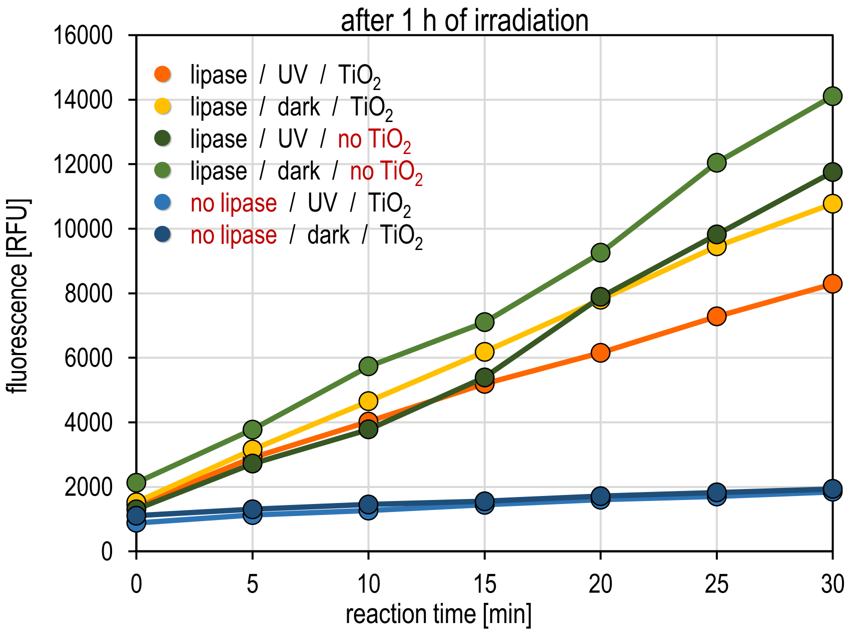

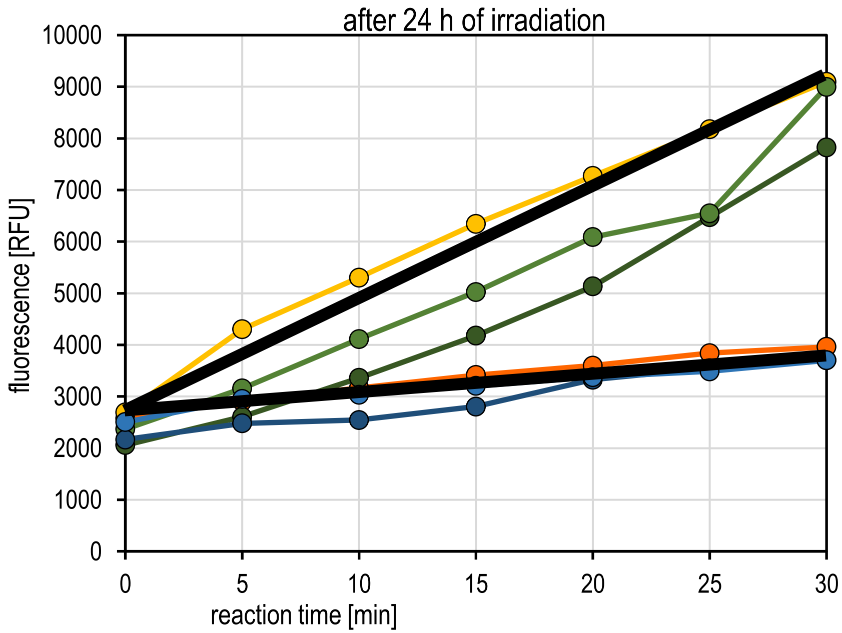

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