

PHOTOCATALYSIS

Detlef Bahnemann

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Callinstraße 3, 30167 Hannover*

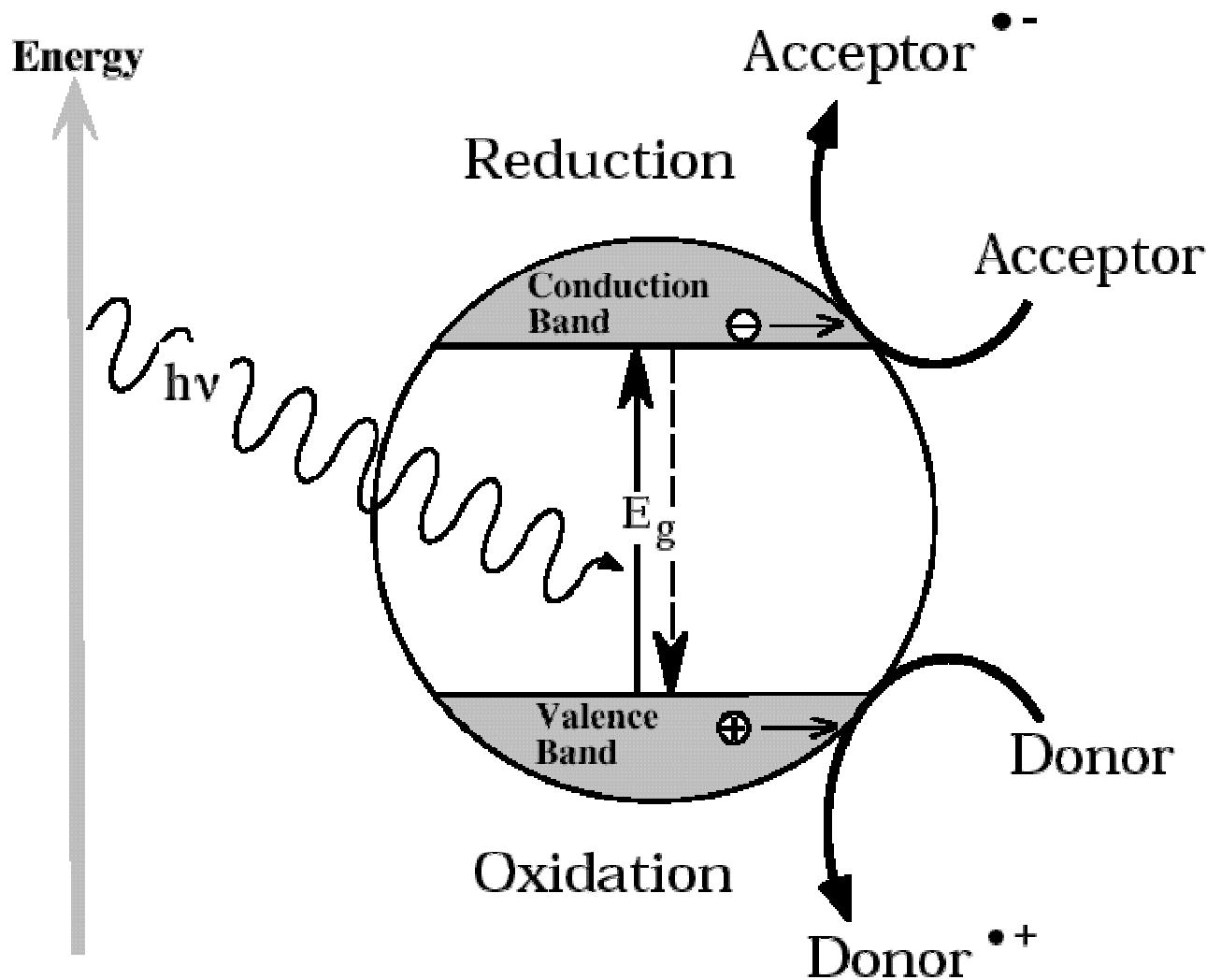


Outline

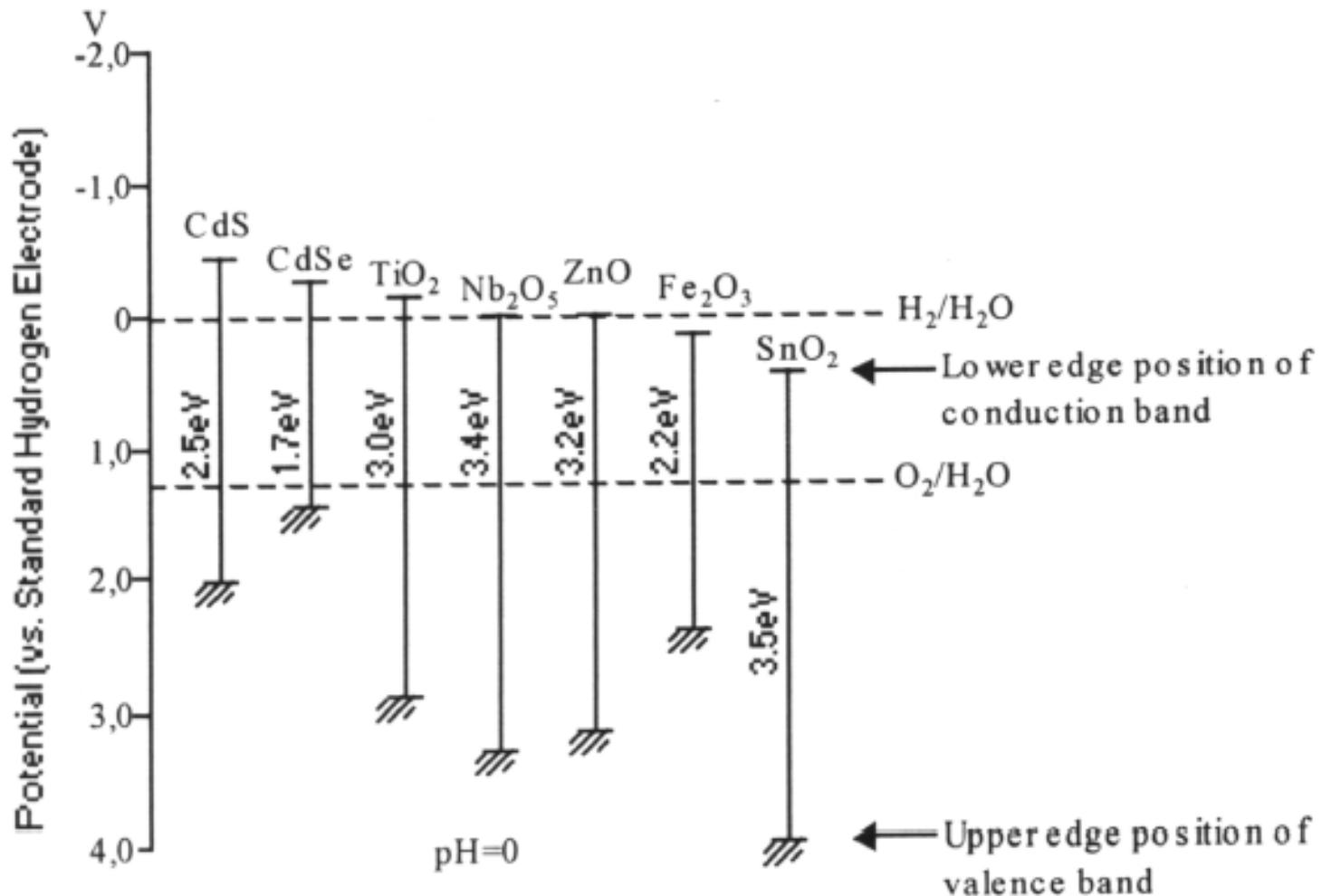
- Mechanistic Investigations
 - Time-Resolved Laser Flash Photolysis
 - Antenna & Deaggregation Mechanism
- Solar Water Treatment
 - Reactor Engineering & Pilot Plants
- Self-Cleaning Surfaces
 - Preparation & Properties
- Determination of Photocatalytic Activity
 - Standardization & Commercial Products



The Principle of Photocatalysis

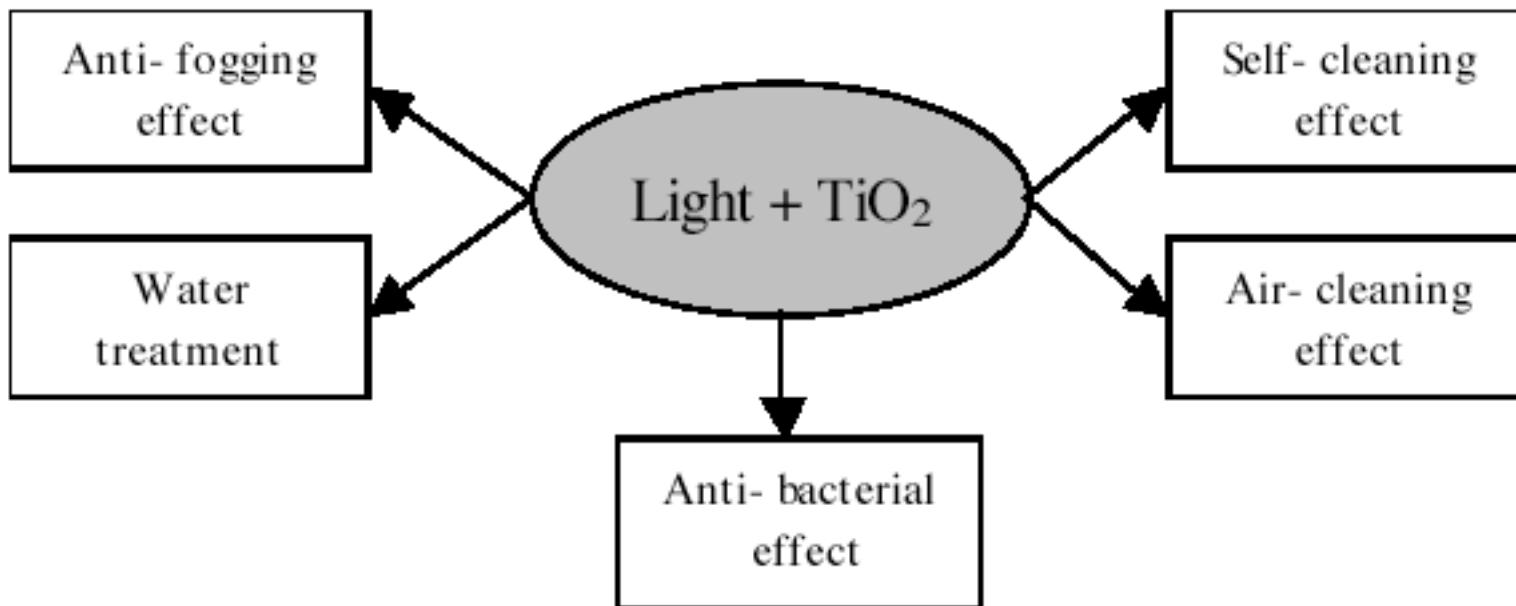


Photocatalytic Materials: Bandgap Energies



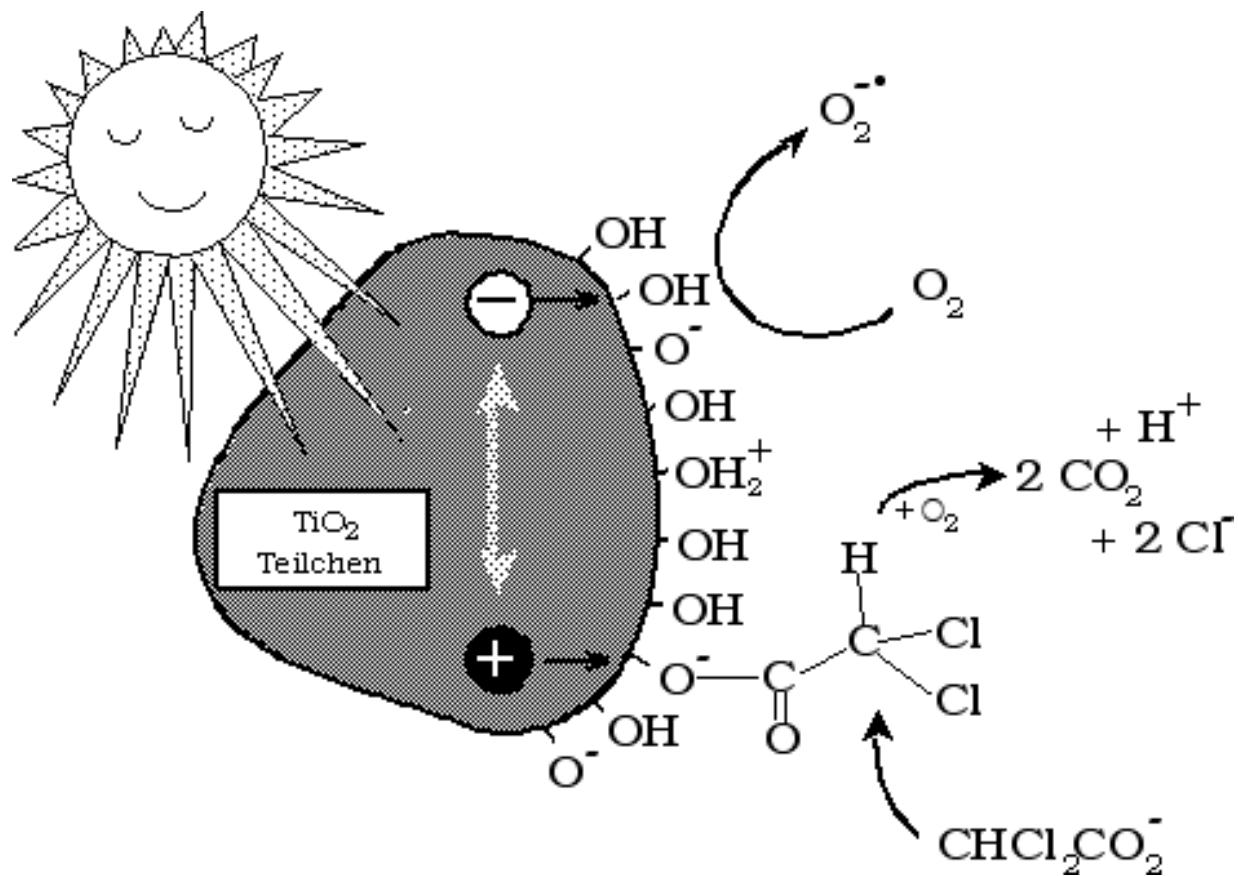
Photocatalysis:

Fields of Applications



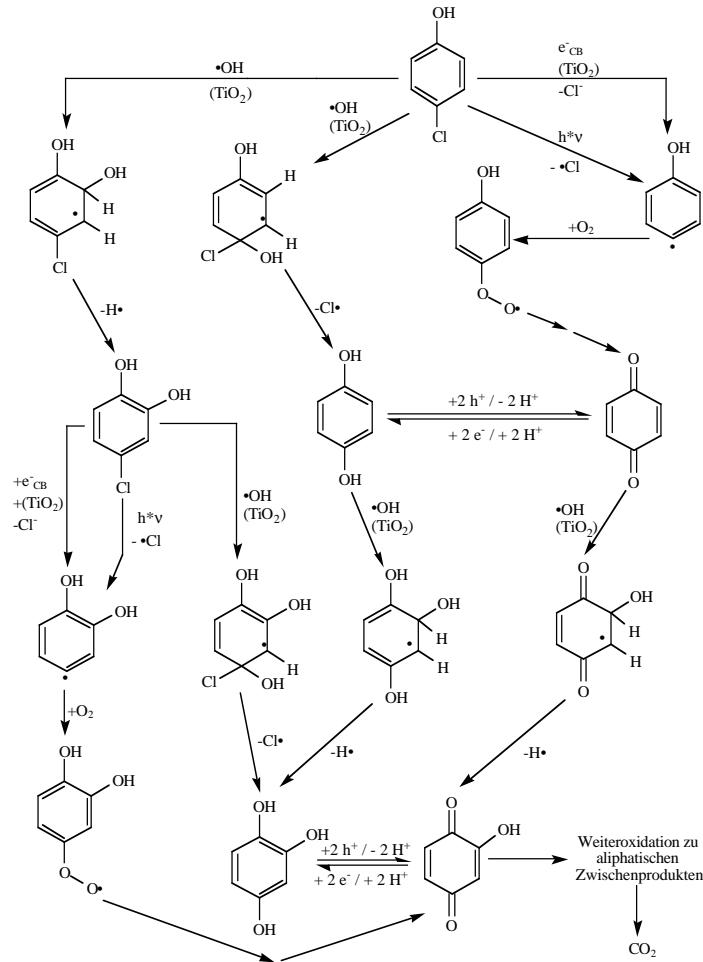
Mechanistic Details in Photocatalysis

Dichloroacetate (DCA) Degradation

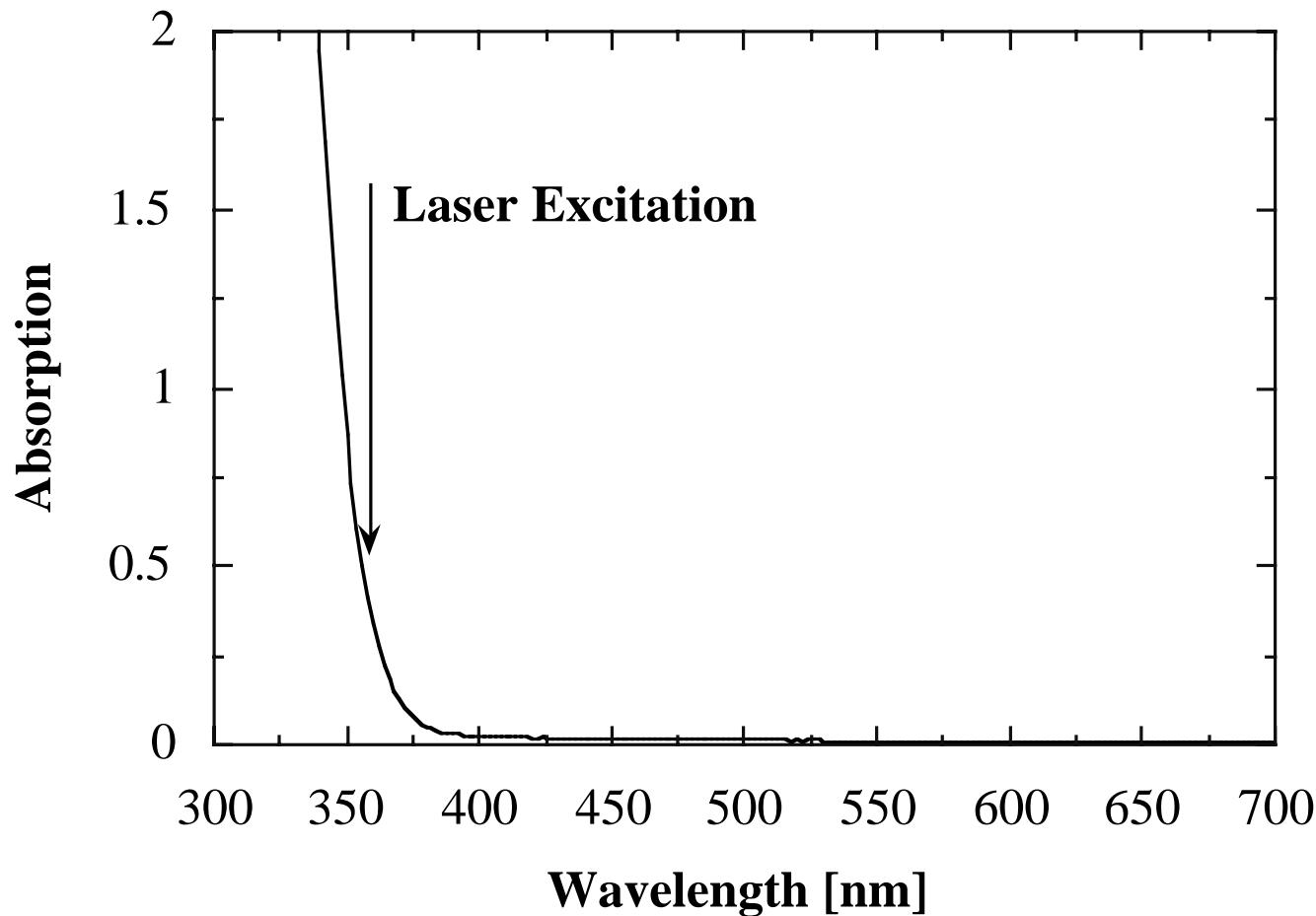


Mechanistic Details in Photocatalysis

4-Chlorophenol (4-CP) Degradation



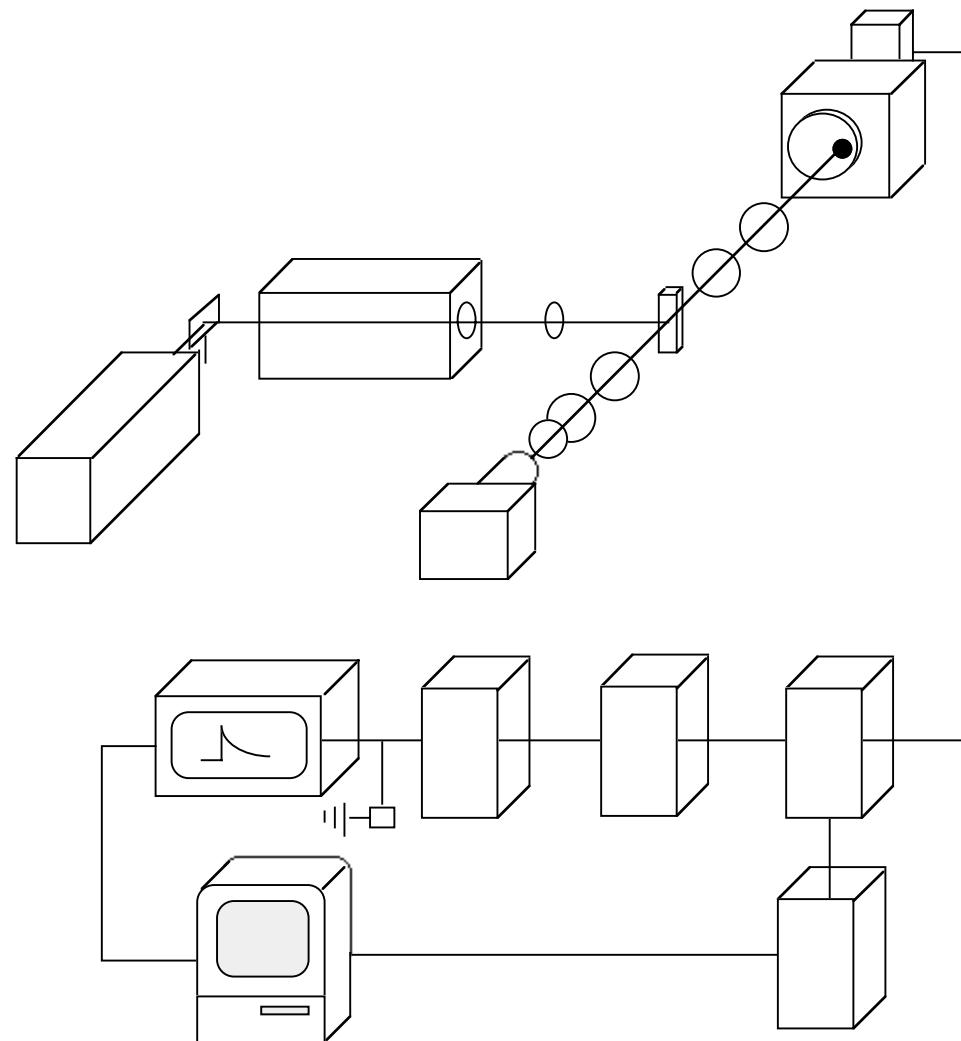
TiO₂-Colloids used for Laser Flash Photolysis



UV/Vis Absorption Spectrum of an aqueous colloidal Suspension containing
2g/l TiO₂, pH 2.3, Particle Diameter 2.5 nm.



Experimental Set-up



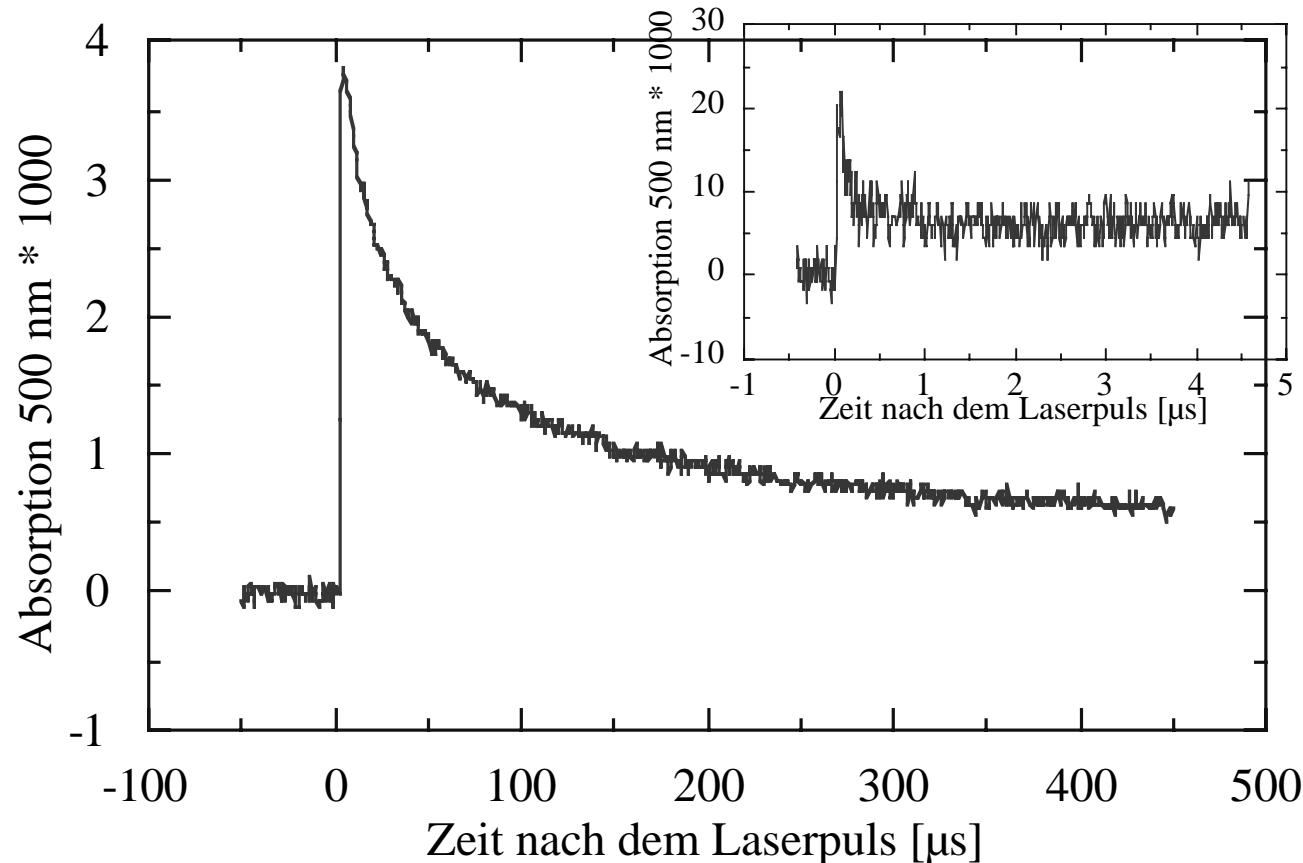
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Laser Flash Photolysis: TiO_2/Pt -Colloids

Transient Absorption/Time-Signals

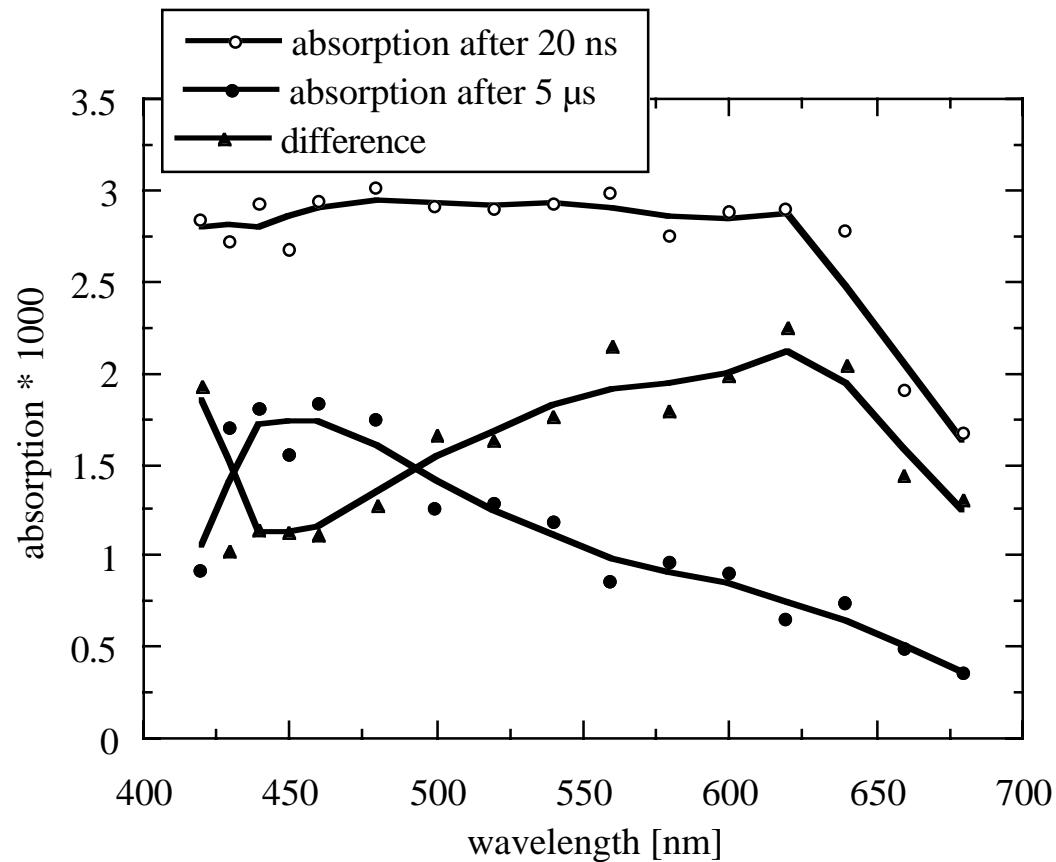


Transient Absorption-/Time-Signals at $\lambda_{\text{obs}} = 500\text{nm}$ following a 25 ns laser pulse
($\lambda_{\text{ex}} = 355\text{nm}$, 16 μM hv/pulse), 2g/L TiO_2/Pt -colloid (1% Pt), pH 2.5, air-sat.



Laser Flash Photolysis: TiO₂/Pt-Colloids

Transient Absorption Spectra

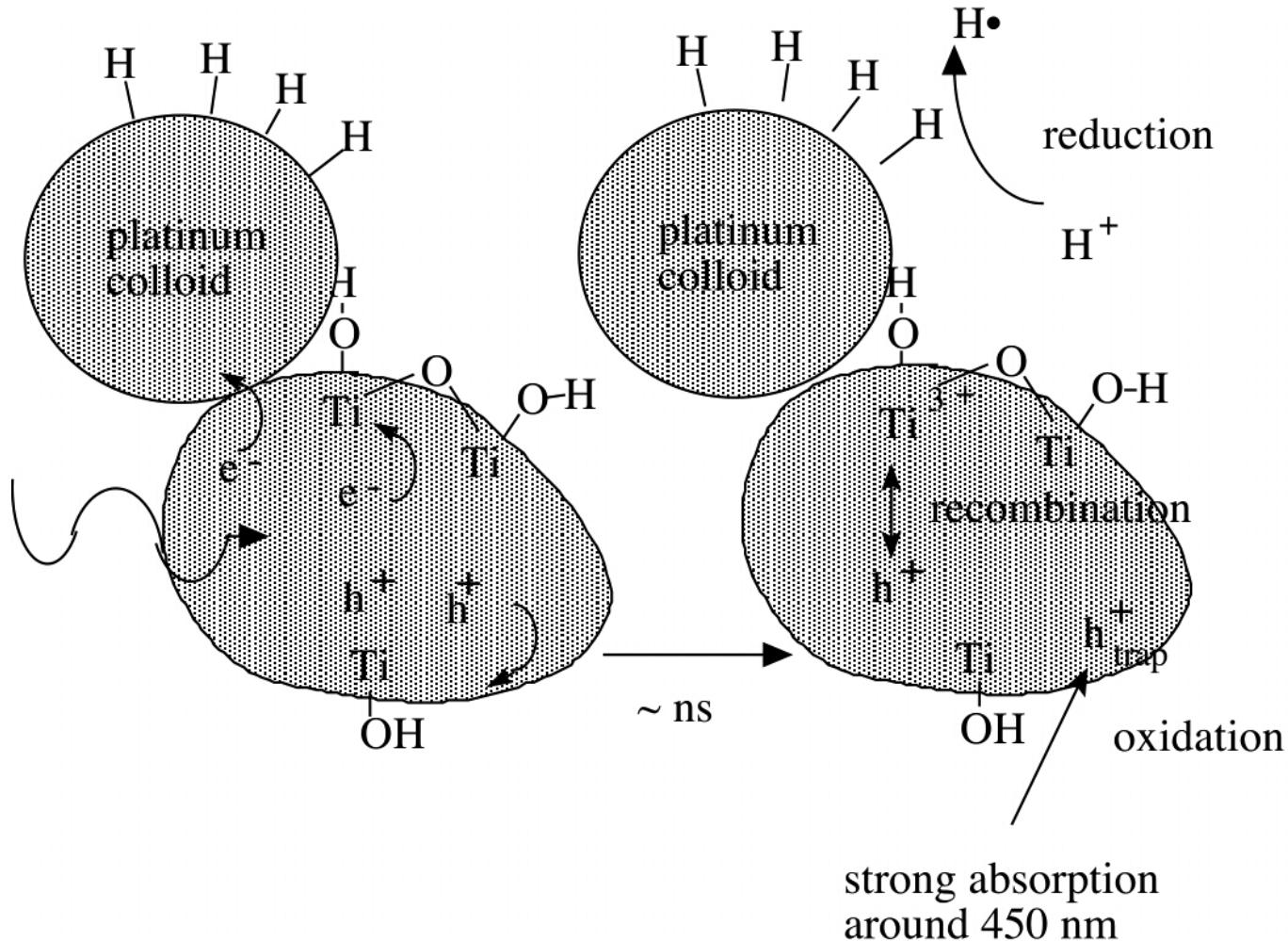


Transient Absorption spectra taken at various times following a 25 ns laser pulse ($\lambda_{\text{ex}} = 355\text{nm}$, 16 μM $h\nu/\text{pulse}$), 2g/L TiO₂/Pt-colloid (1% Pt), pH 2.5, air-sat.

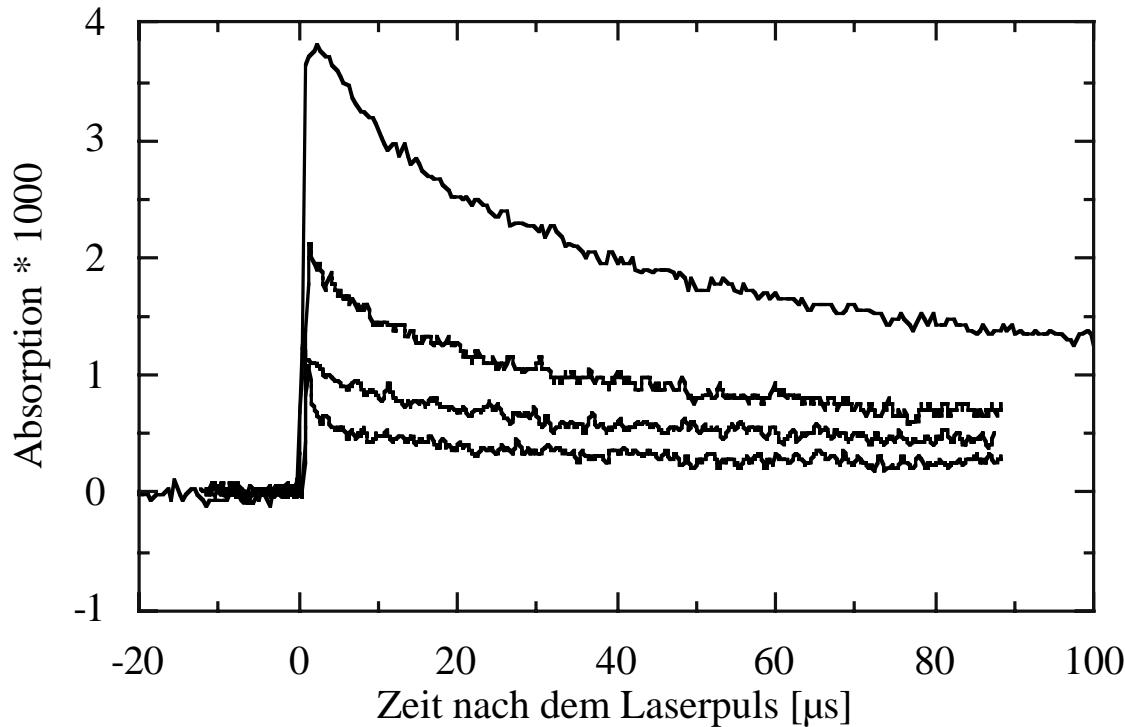


Laser Flash Photolysis: TiO_2/Pt -Colloids

Proposed Reaction Mechanism



Laser Flash Photolysis: TiO₂/Pt-Colloids Reaction with Dichloroacetate (DCA)

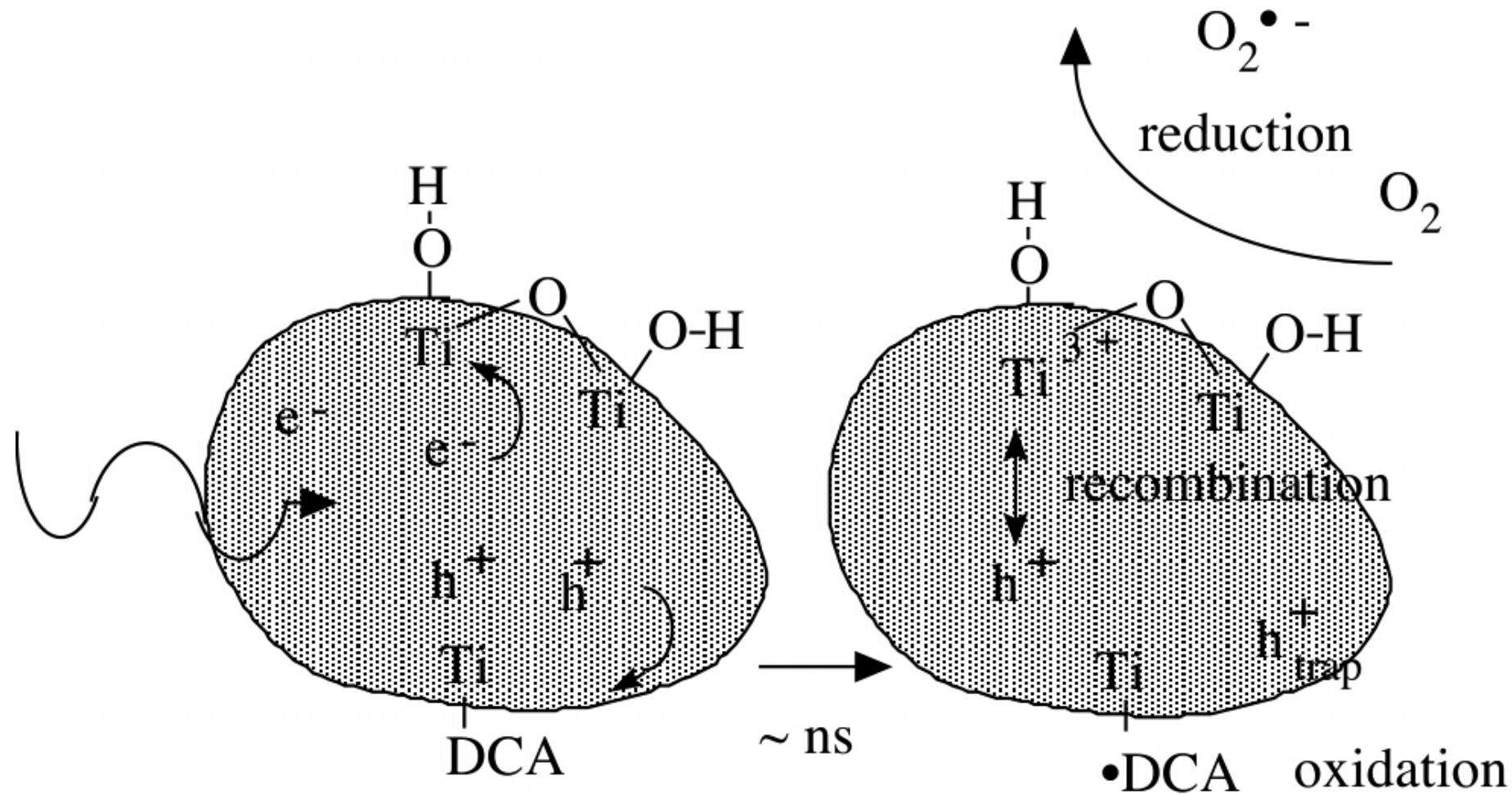


Transient Absorption-/Time-Signals at $\lambda_{\text{obs}} = 500\text{nm}$ following a 25 ns laser pulse ($\lambda_{\text{ex}} = 355\text{nm}$, 16 μM hν/pulse), 2g/L TiO₂/Pt-colloid (1% Pt), pH 2.5, air-sat., various DCA concentrations (0, 40, 80, 200 mM).



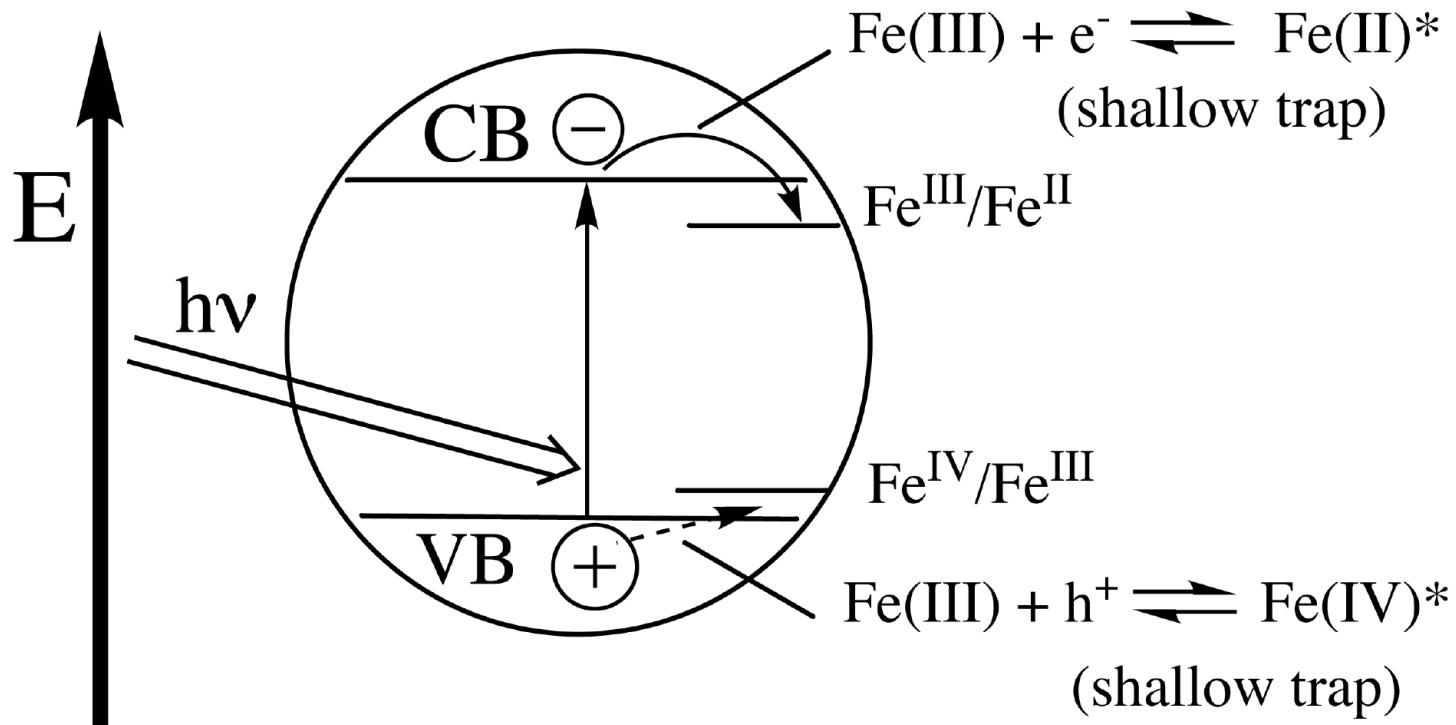
Laser Flash Photolysis: TiO_2/Pt -Colloids

Proposed Reaction Mechanism with DCA



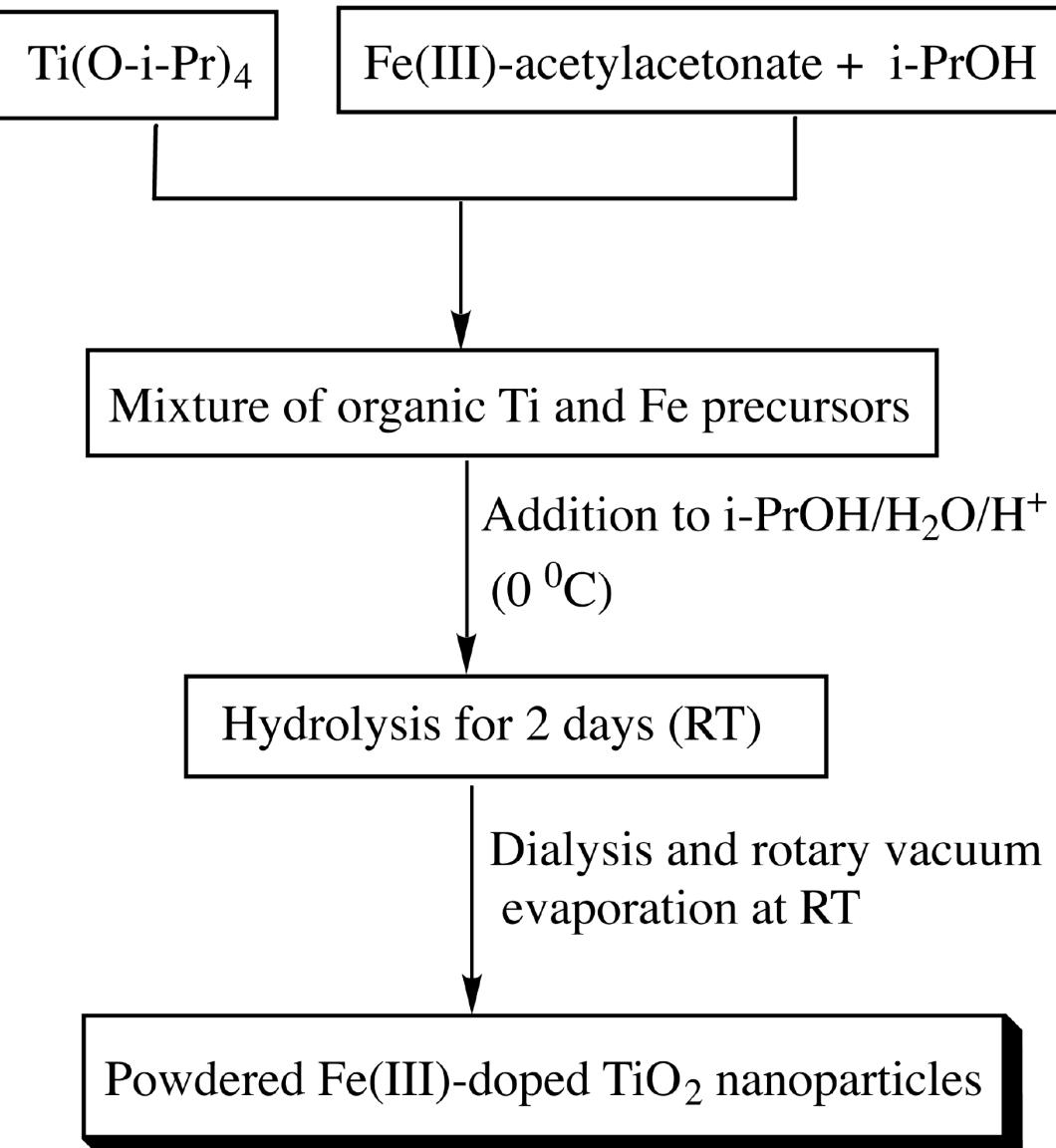
Fe(III)-doped TiO₂-Particles

Energy Levels



Semiconductor (TiO₂)

(c)



Fe(III)-doped TiO₂-Colloids: *Novel Synthetic Method*

(c)

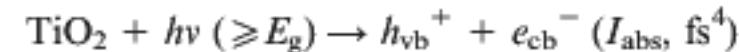
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Fe(III)-doped TiO₂-Particles: The Methanol/ Formaldehyde- System (to determine the yield of hydroxyl radicals)

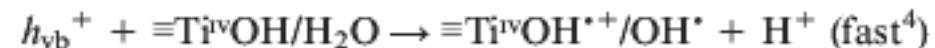
Charge carrier generation



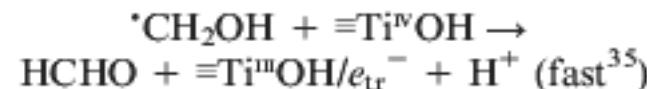
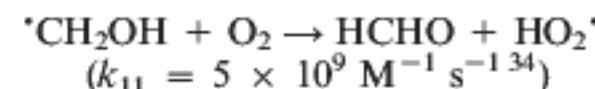
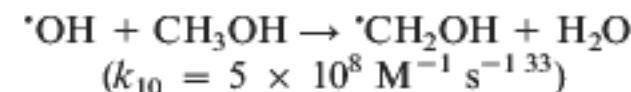
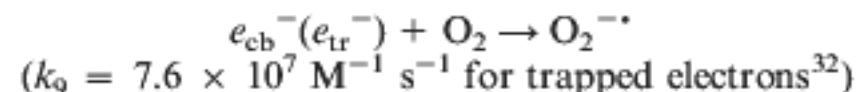
Charge carrier recombination



Production of hydroxyl radicals

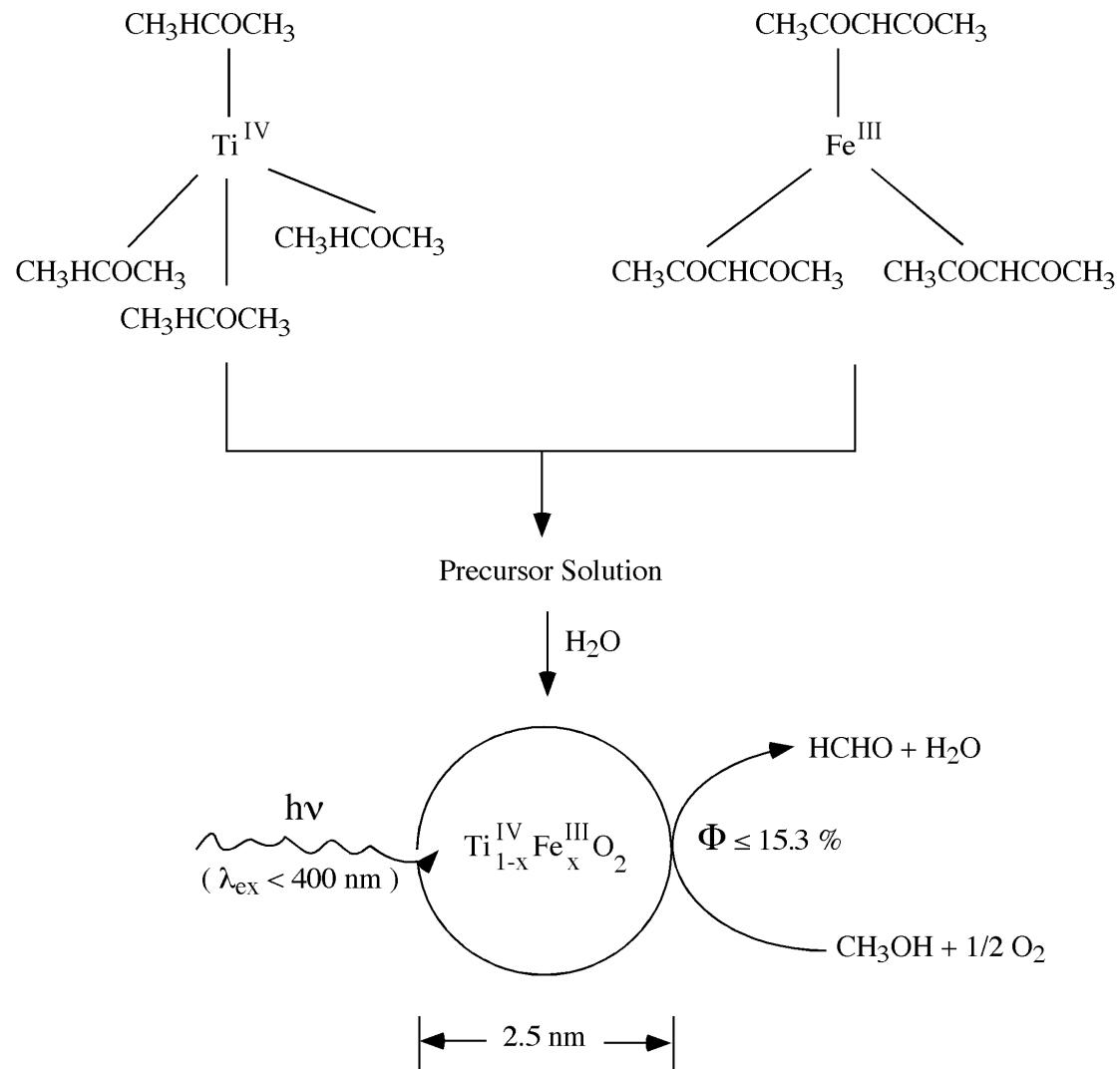


Interfacial charge transfer



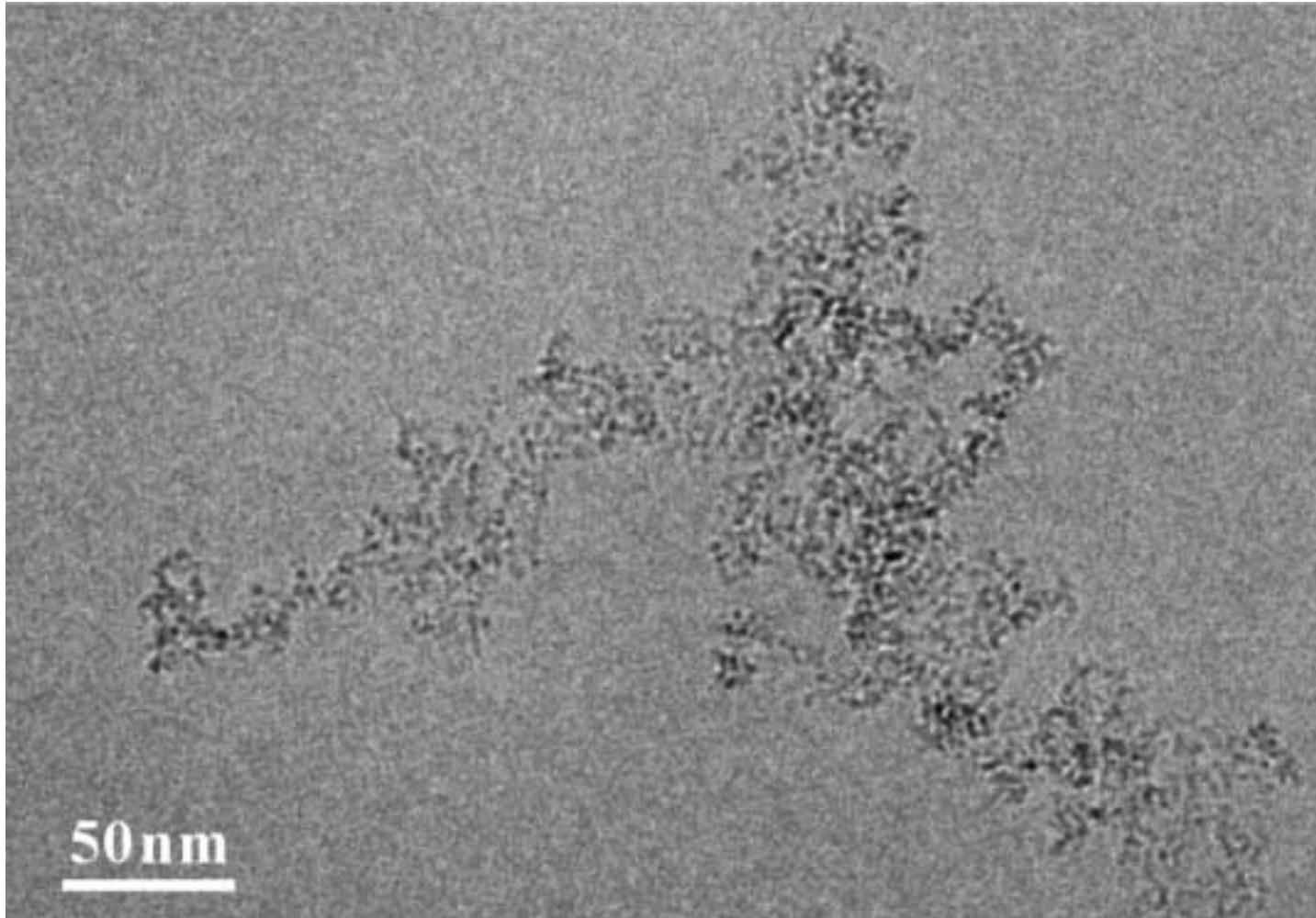
Fe(III)-doped TiO₂-Particles:

Can we explain this
high quantum
yield of
formaldehyde
formation?



Fe(III)-doped TiO₂-Colloids

Cryo-TEM Picture (0.5 at% Fe(III))



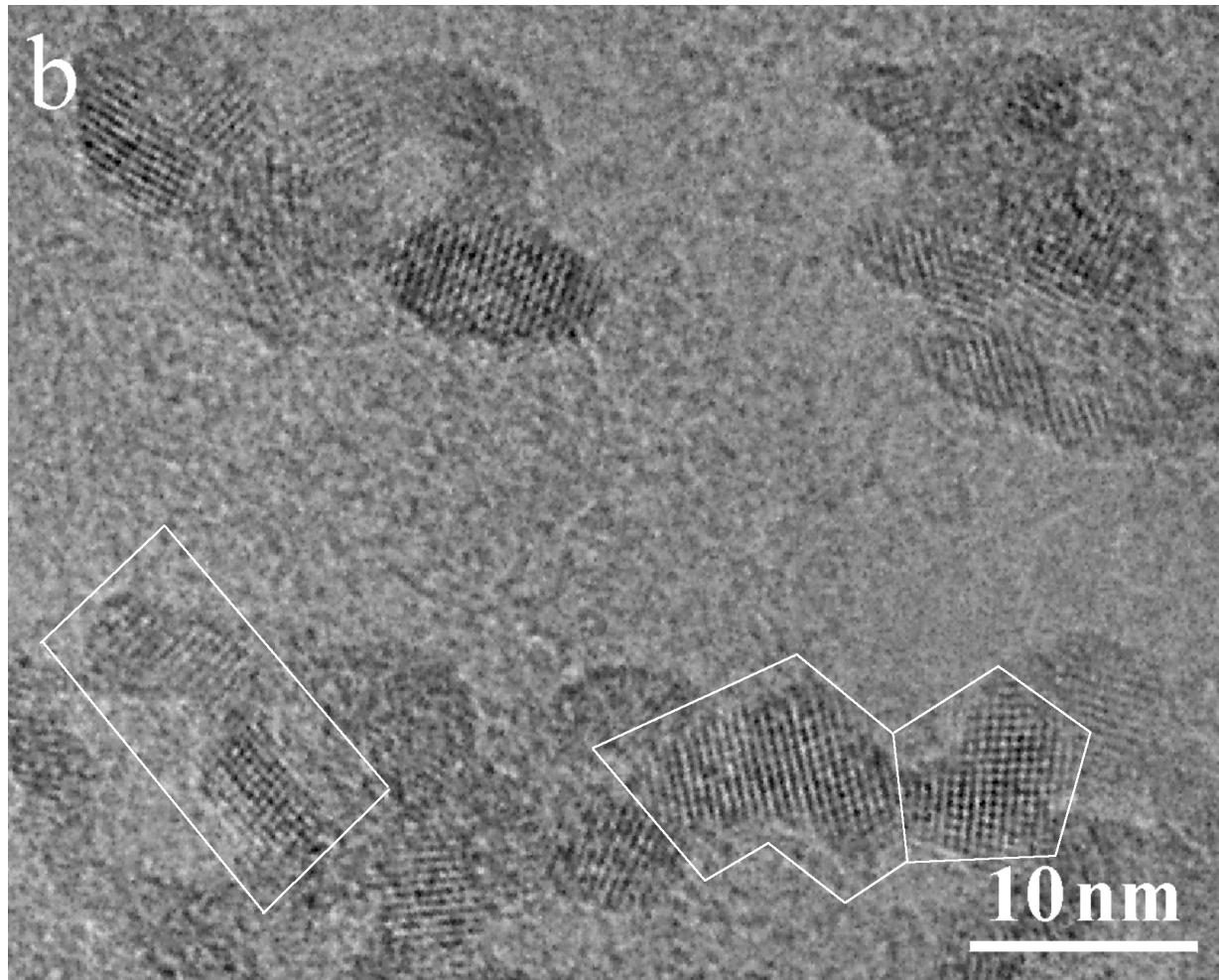
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Fe(III)-doped TiO₂-Colloids

Cryo-TEM Picture



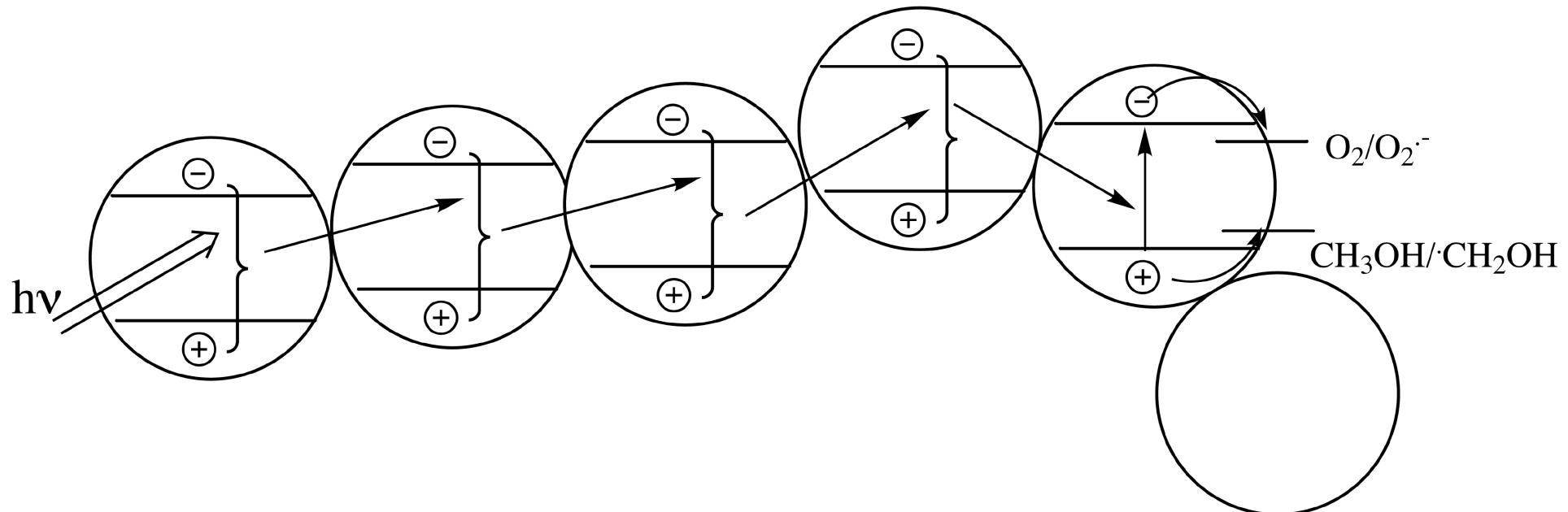
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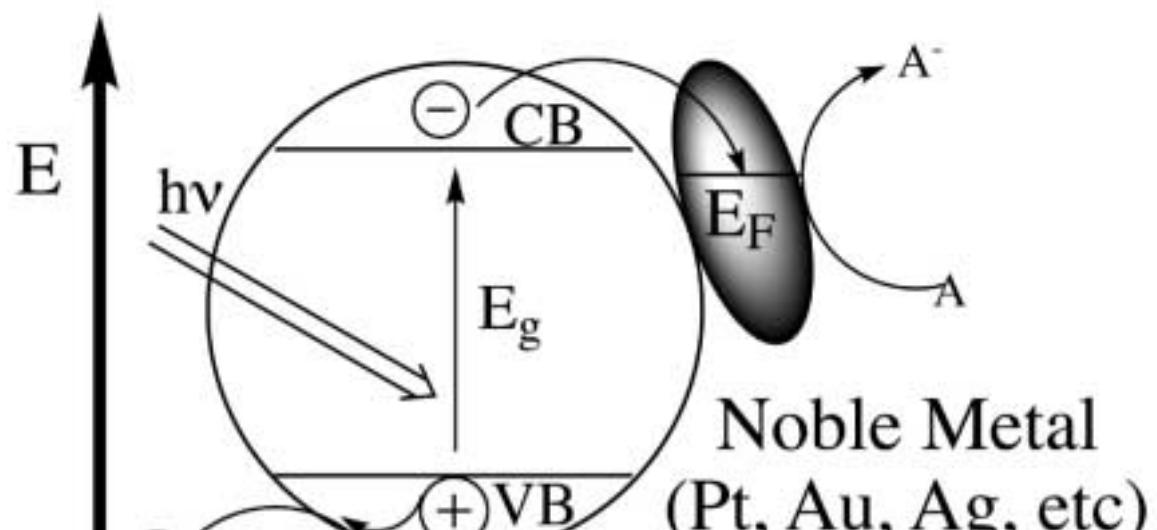
The Antenna Mechanism

(An attempt to explain the high quantum yields of formaldehyde formation during the CH₃OH–Oxidation at TiO₂/Fe(III)–Colloids)



Enhancing the Photocatalytic Activity

(a) Metal Nano-Contacts

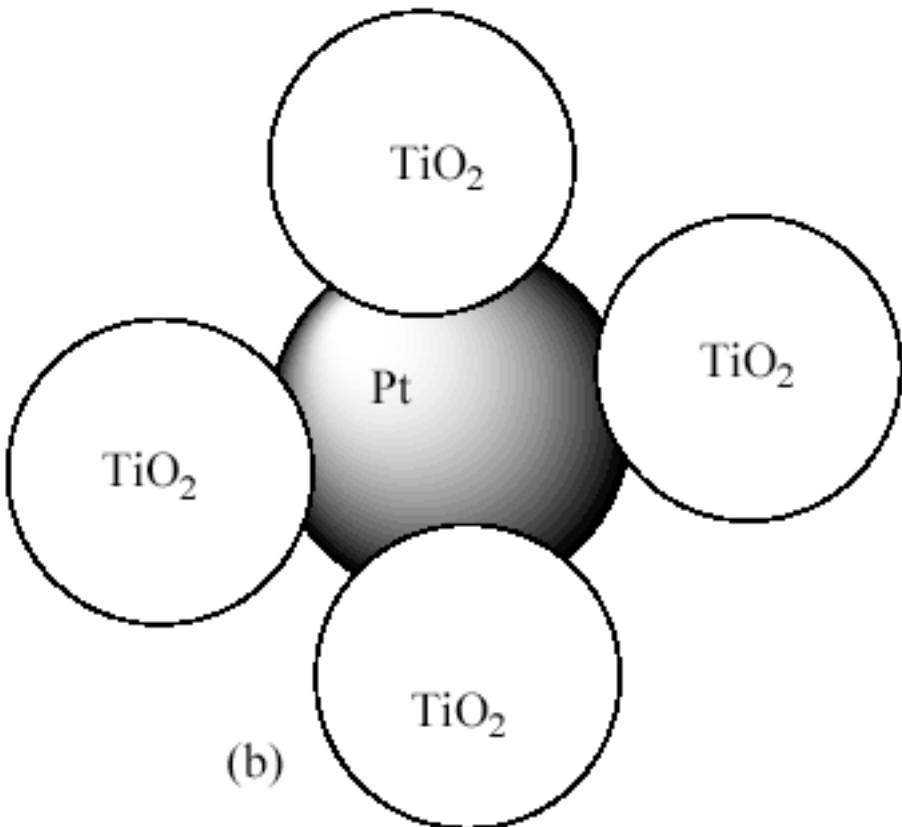
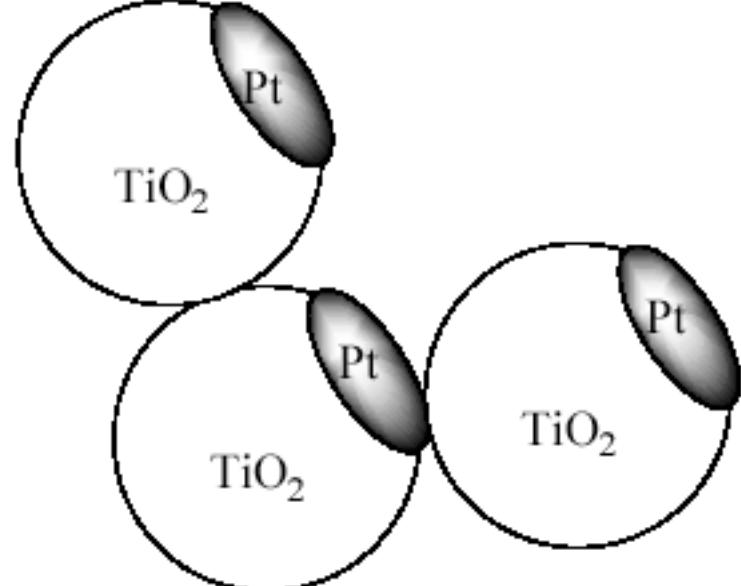


Semiconductor (TiO_2)

(a)

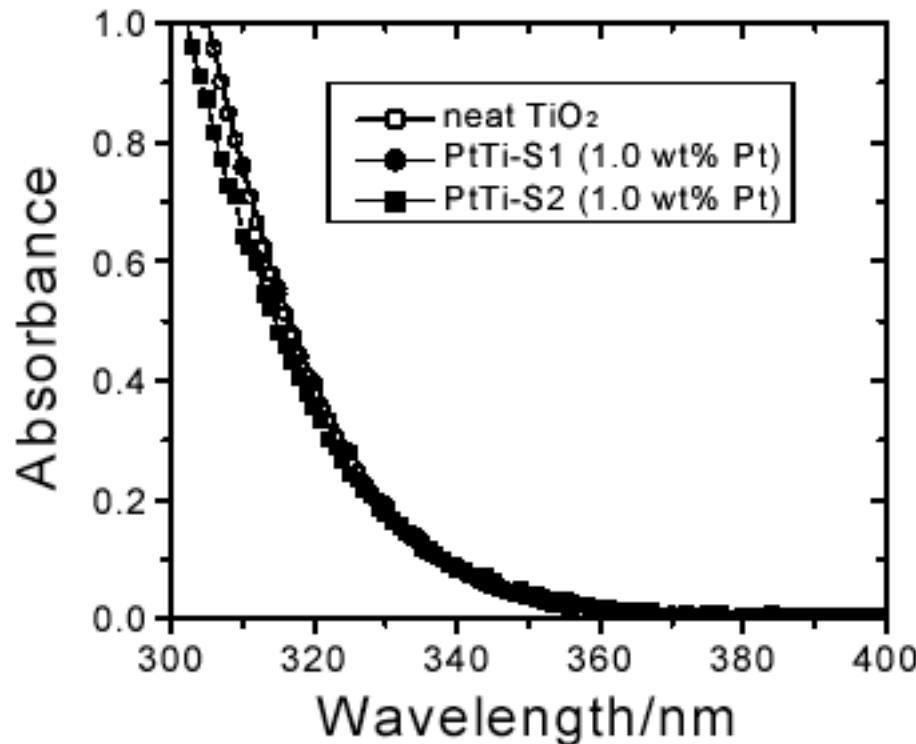
Platinization of TiO_2 -Particles

Photoplatinization (PtTi-S1) vs. Colloidmixing (PtTi-S2)



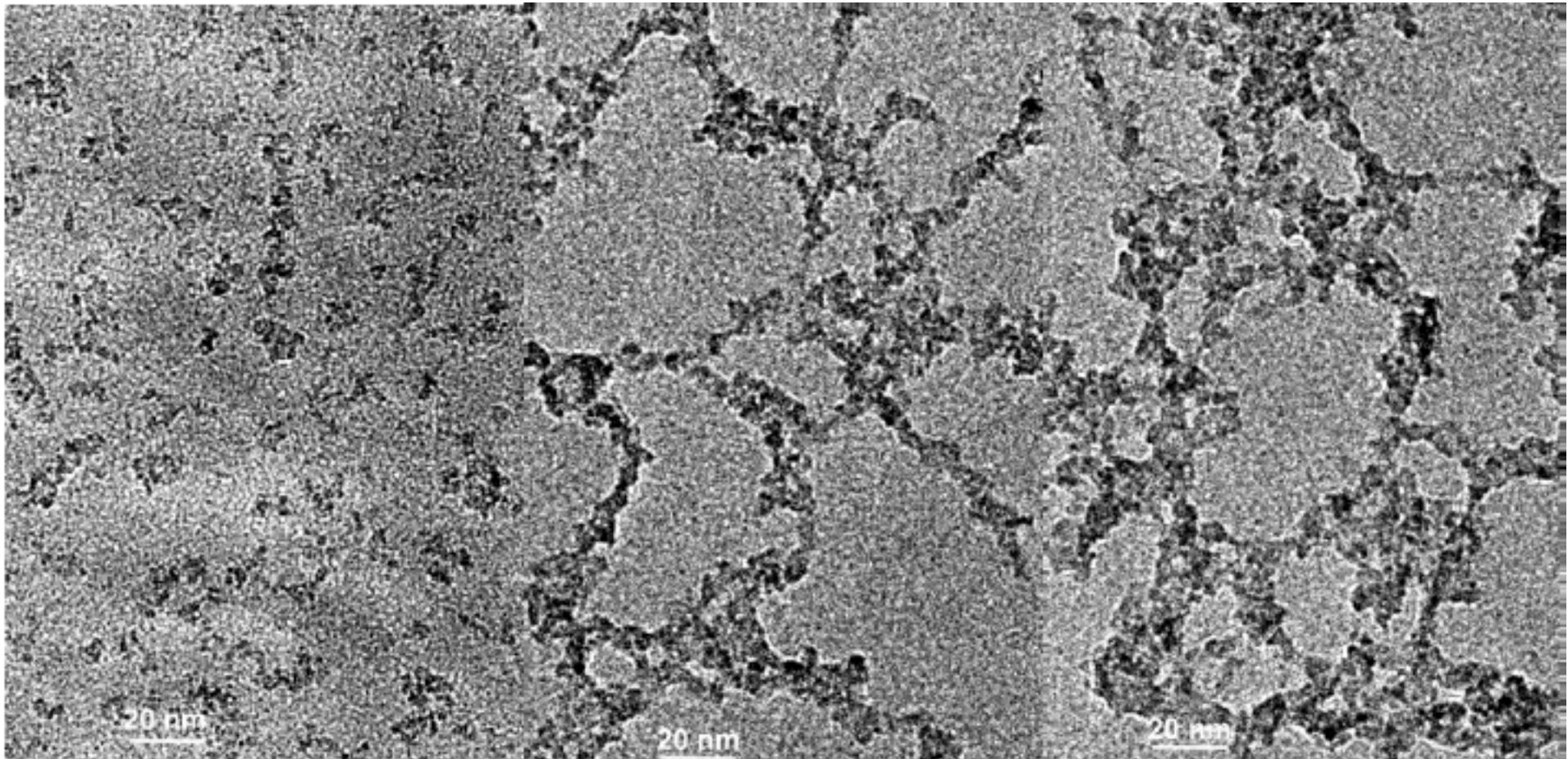
Platinization of TiO_2 -Particles

UV-vis-Spectra of the Colloids



Platinization of TiO_2 -Colloids

Cryo-TEM Picture (1.0 wt% Pt)



TiO_2

PtTi-S1

PtTi-S2

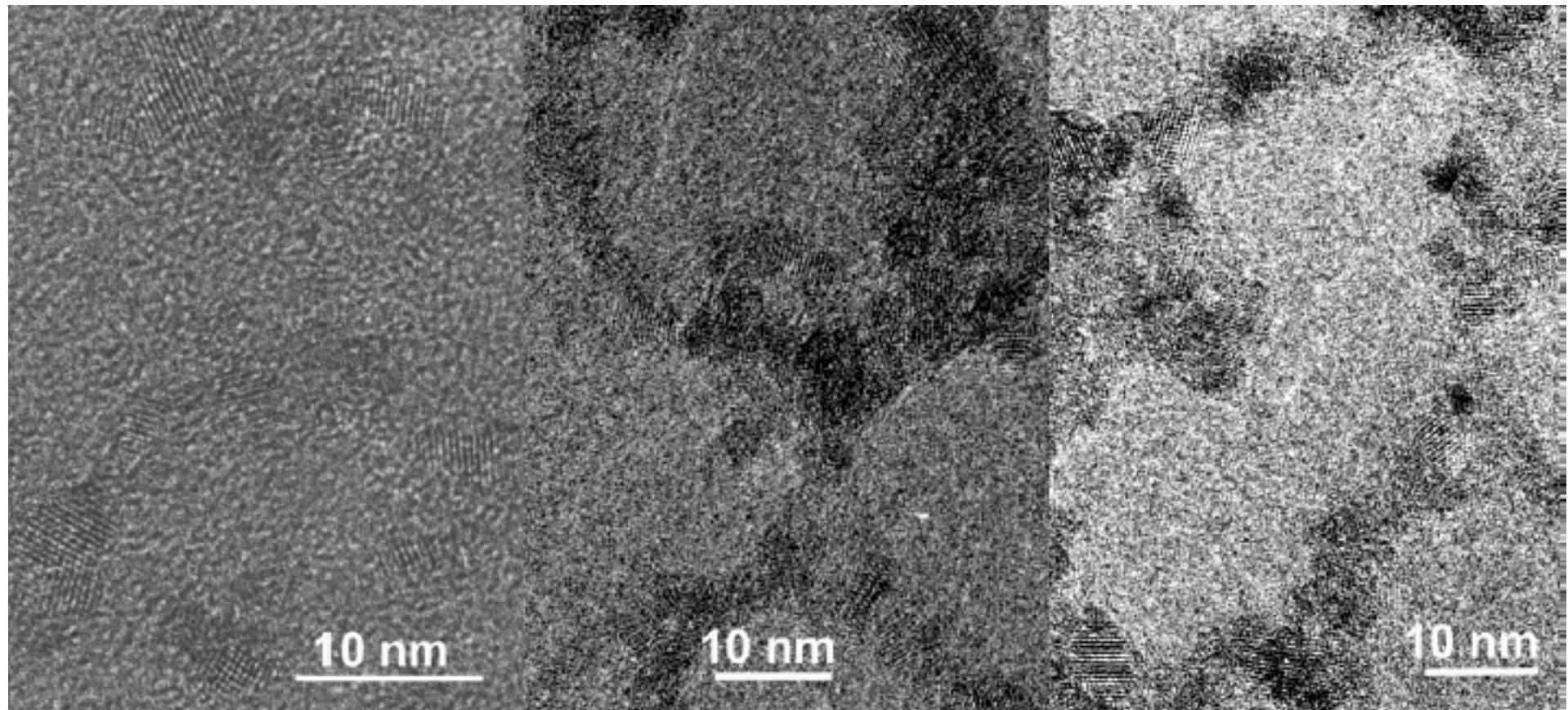
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Platinization of TiO_2 -Colloids

Cryo-HRTEM Picture (1.0 wt% Pt)



TiO_2

PtTi-S1

PtTi-S2

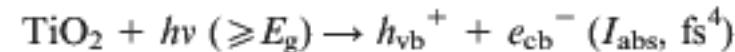
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Platinized TiO₂-Particles: The Methanol/ Formaldehyde- System (to determine the yield of hydroxyl radicals)

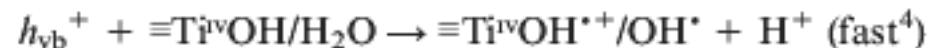
Charge carrier generation



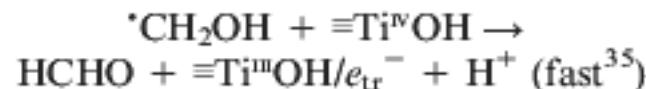
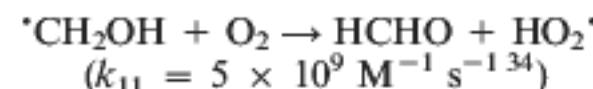
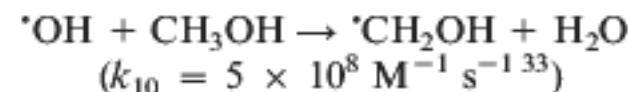
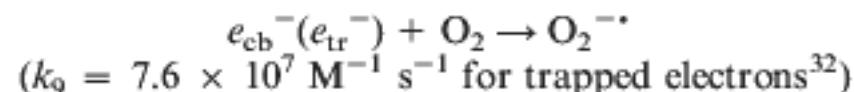
Charge carrier recombination



Production of hydroxyl radicals

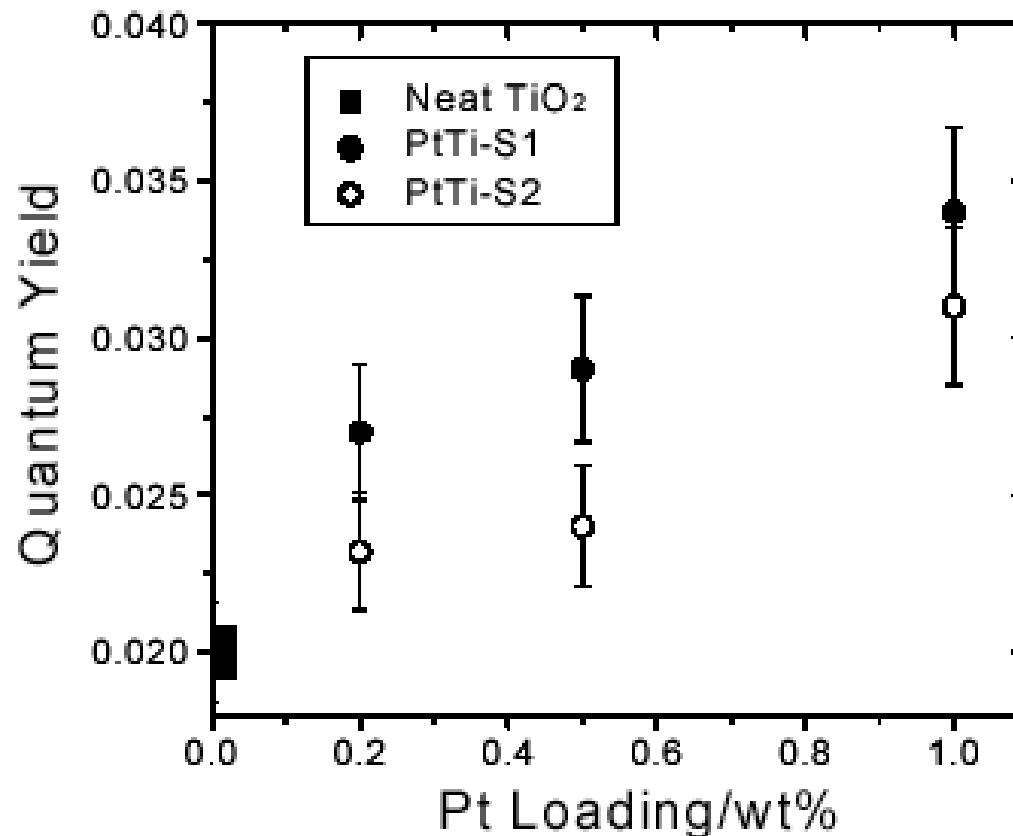


Interfacial charge transfer



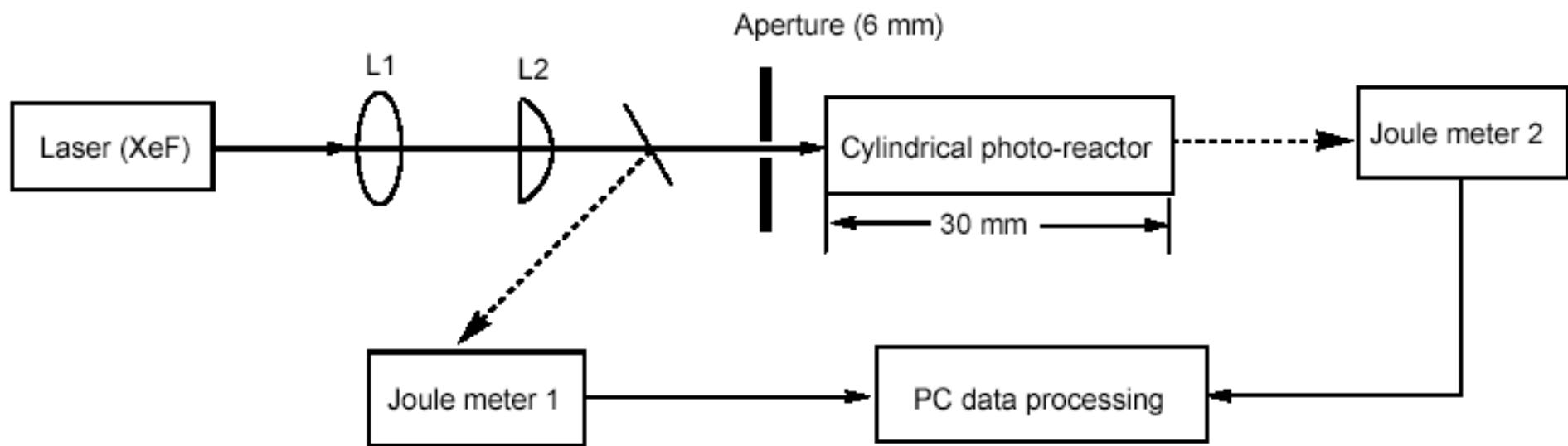
Platinized TiO_2 -Particles

Formaldehyde Yield vs. Pt-Loading (CW Photolysis)



Platinized TiO₂-Particles

Set-up for Intermittent Laserphotolysis



Platinized TiO₂-Particles

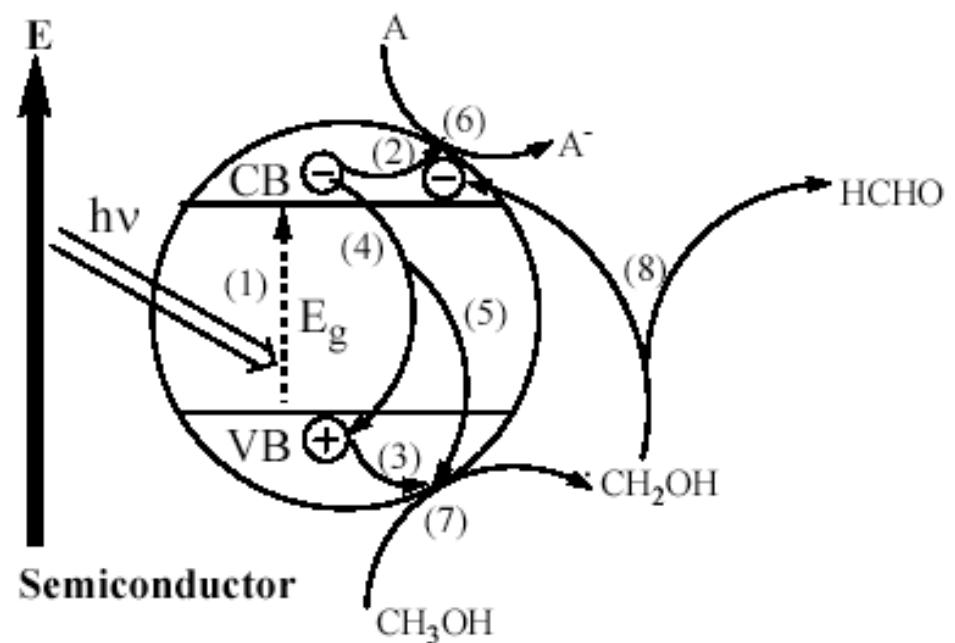
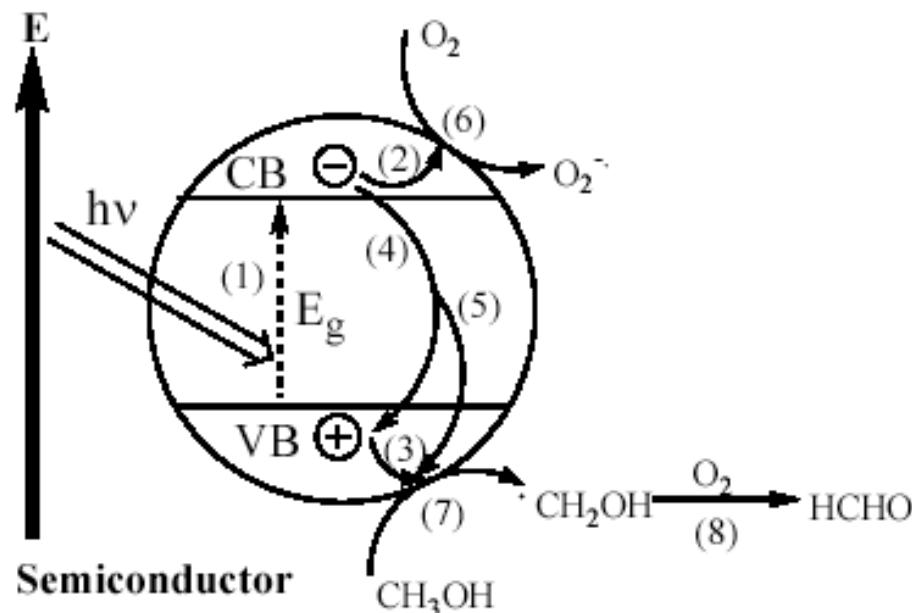
Formaldehyde Yield: CW vs. Laserphotolysis

	CW photolysis ^b 300-400 nm, O ₂ -sat'd	Laser (XeF) pulse photol. ^c 351 nm, O ₂ -sat'd	Laser (XeF) pulse photol. ^d 351 nm, N ₂ -sat'd
2.4 nm TiO ₂	0.020 ± 0.001	0.032 ± 0.002	0.027 ± 0.002
1.5-4 nm PtTi-S1 (1 wt % Pt)	0.034 ± 0.003	0.047 ± 0.002	0.049 ± 0.002
1.5-4 nm PtTi-S2 (1 wt % Pt)	0.031 ± 0.002	0.048 ± 0.002	0.033 ± 0.002

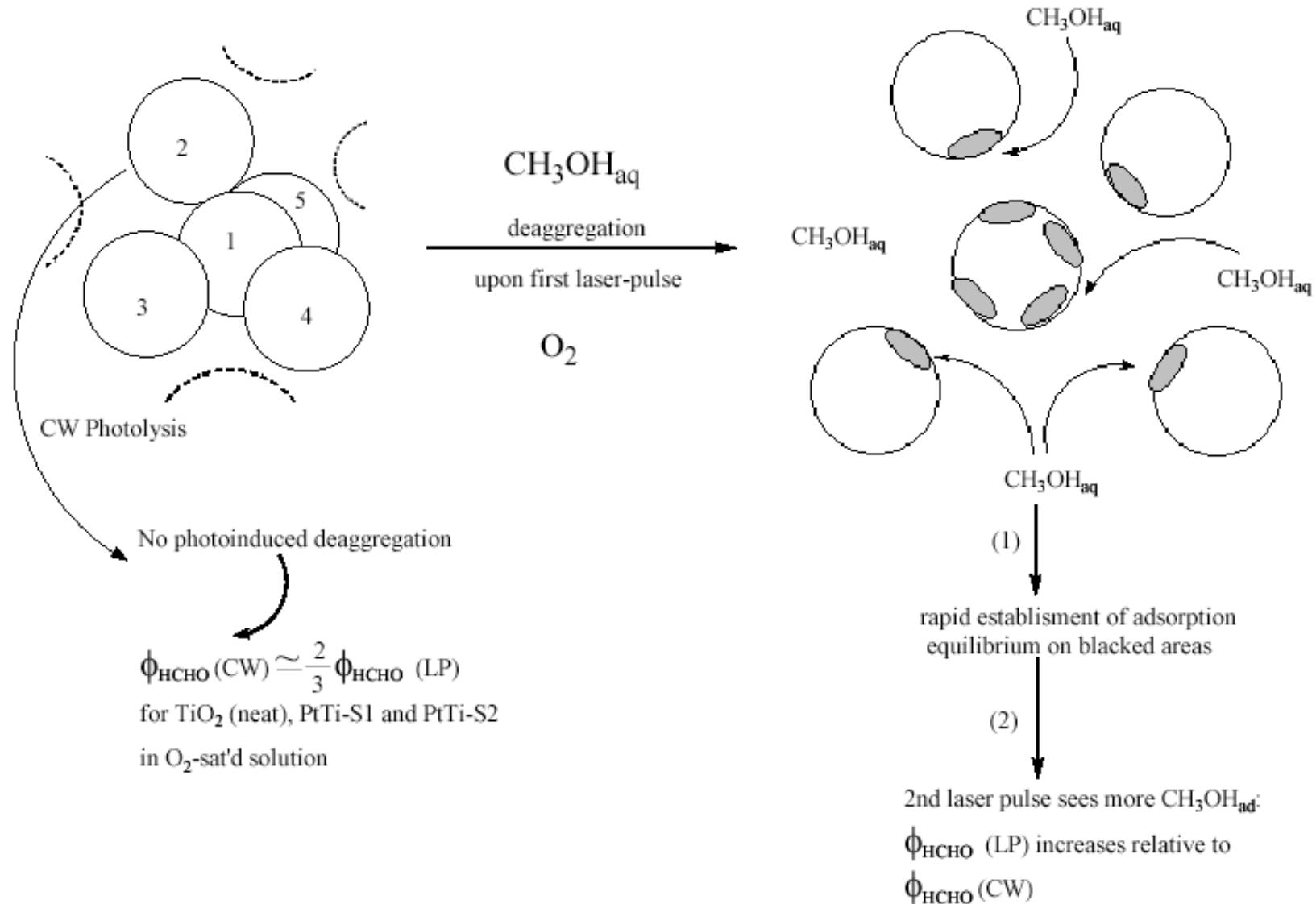


Platinized TiO₂-Particles

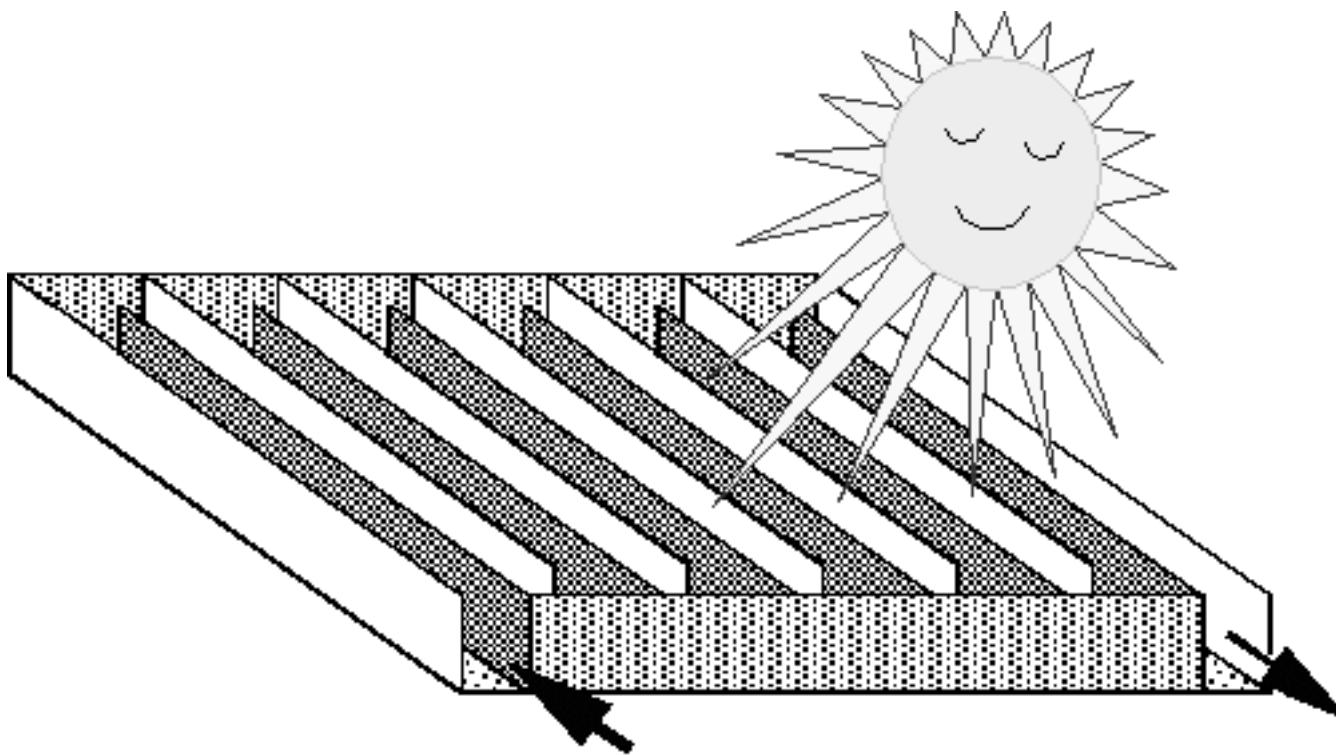
Formaldehyde Formation: O₂ vs. N₂



The De-Aggregation Concept



The Double Skin Sheet Reactor (DSSR)

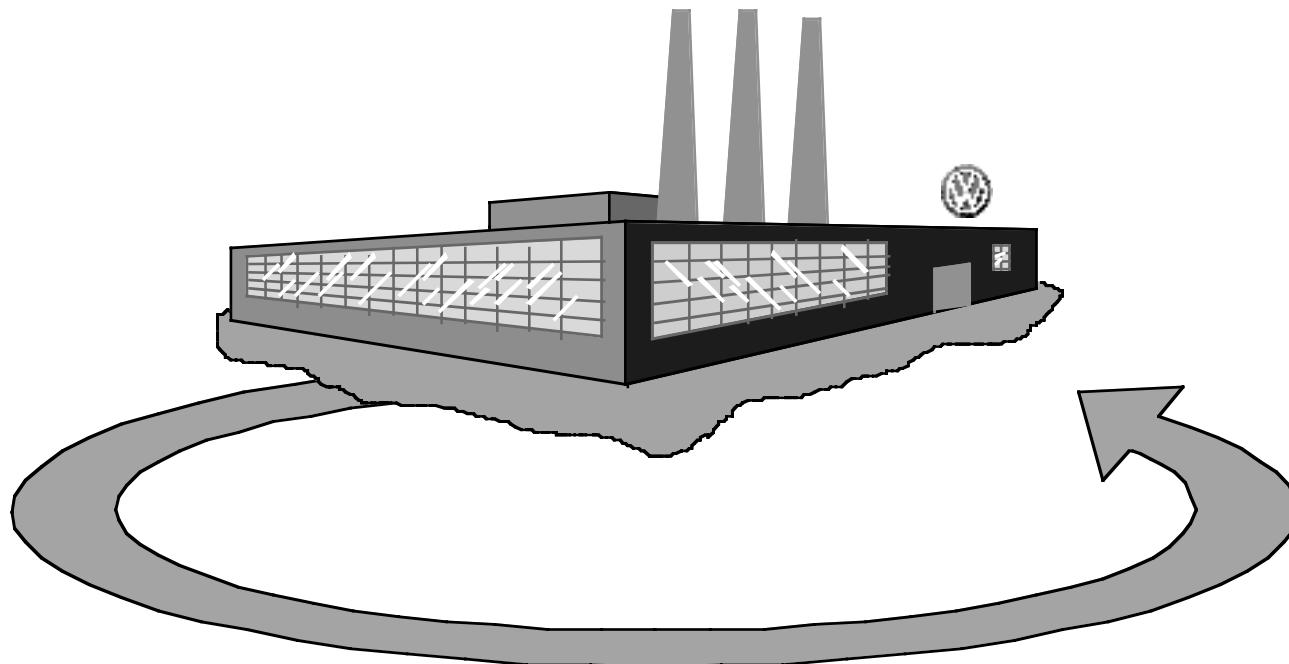


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Recycling of Industrial Wastewater

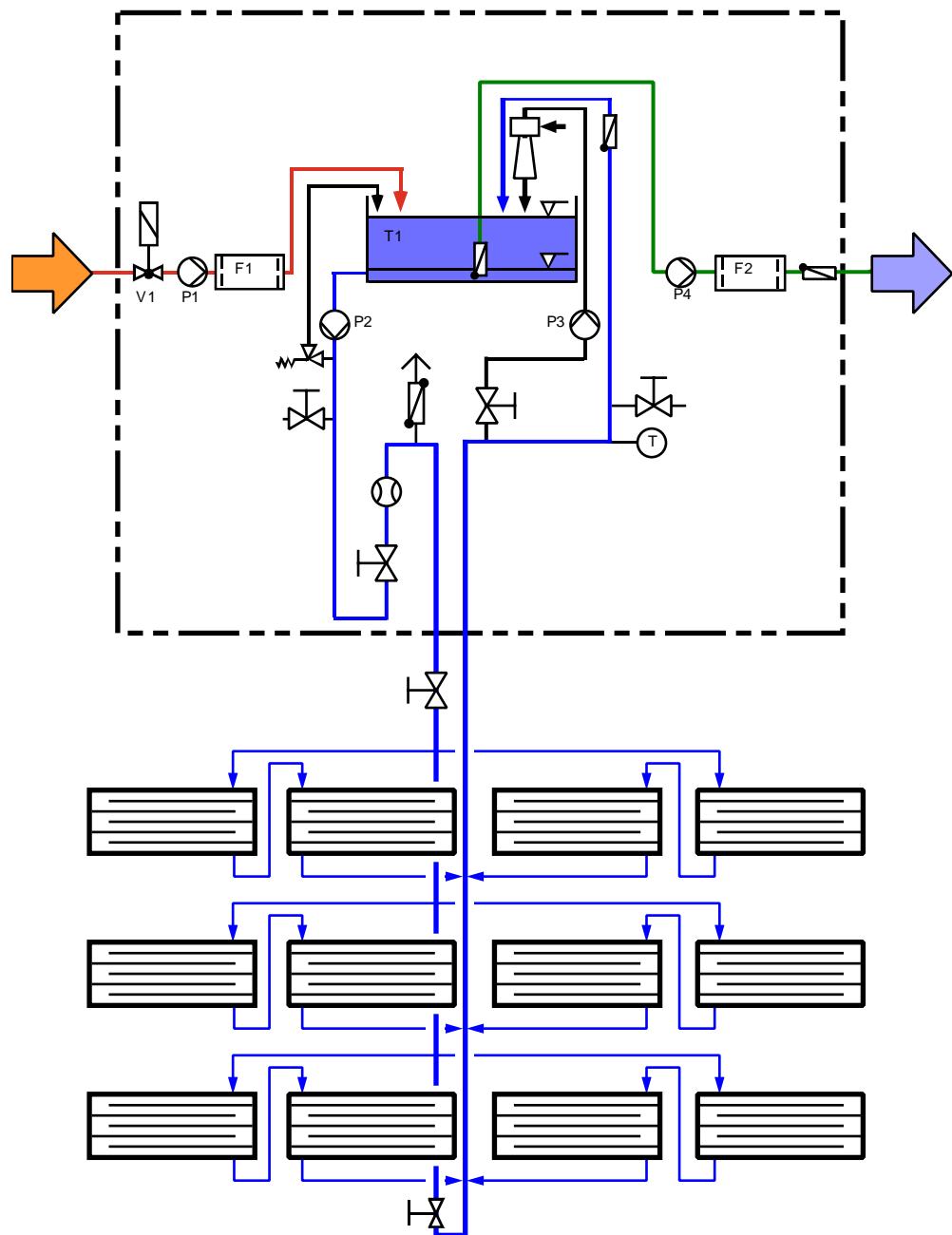


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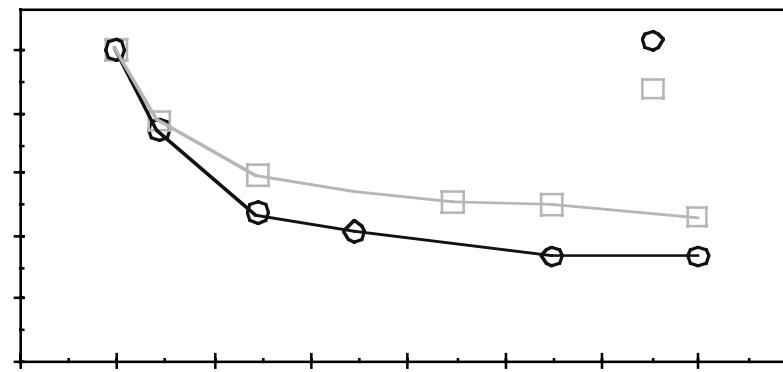
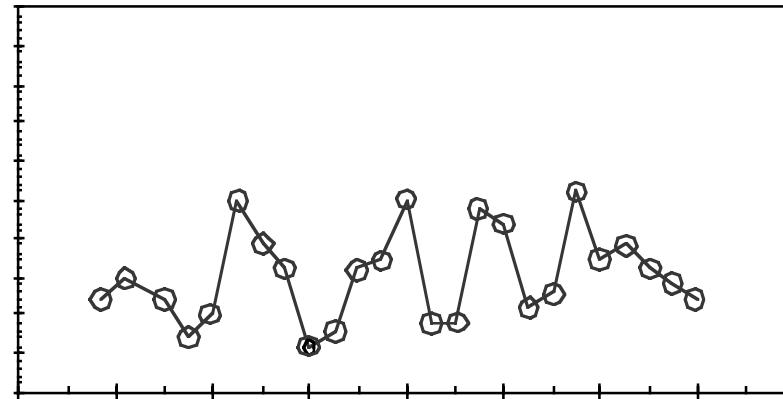
DSSR-Pilotplant I

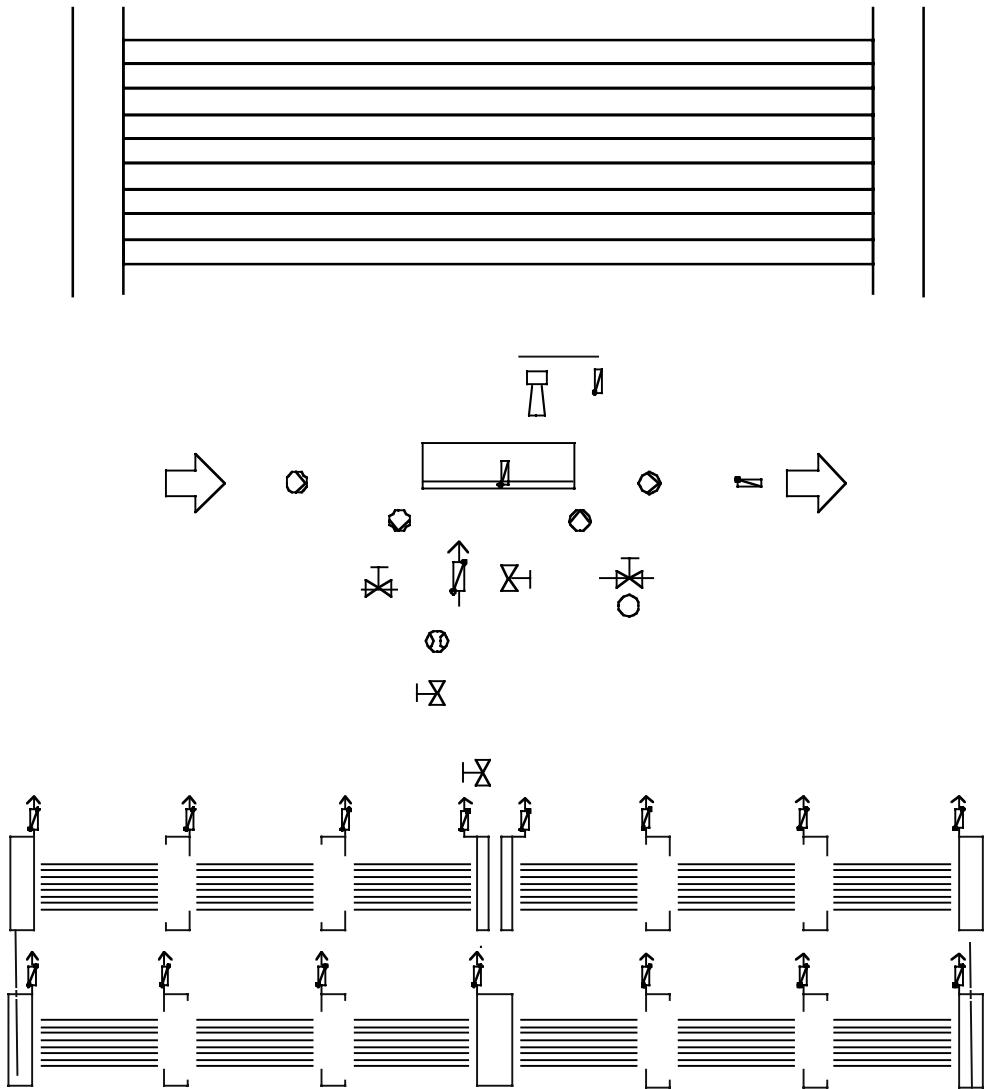


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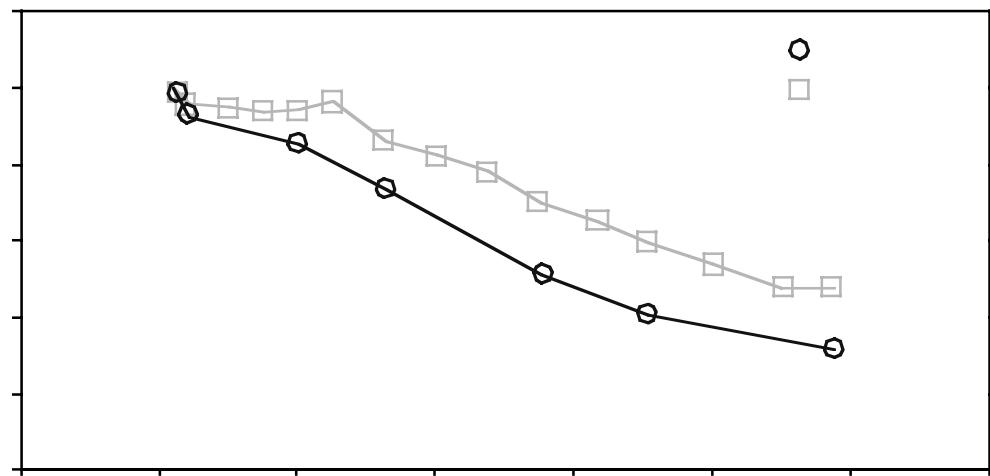
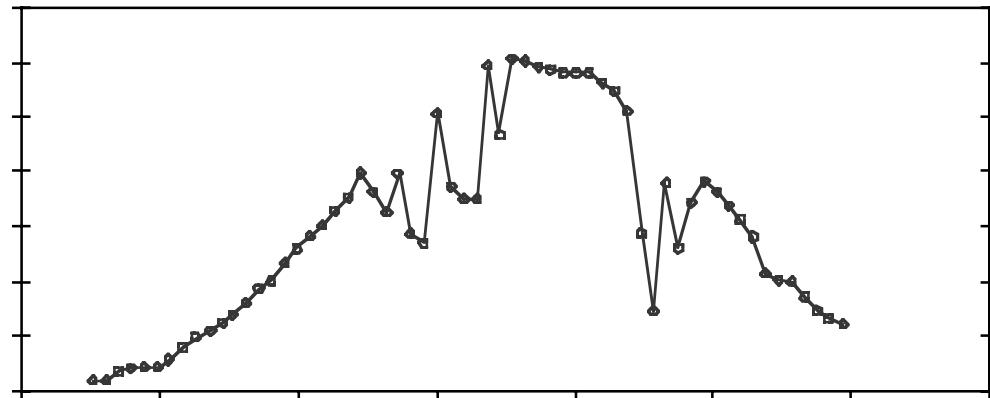
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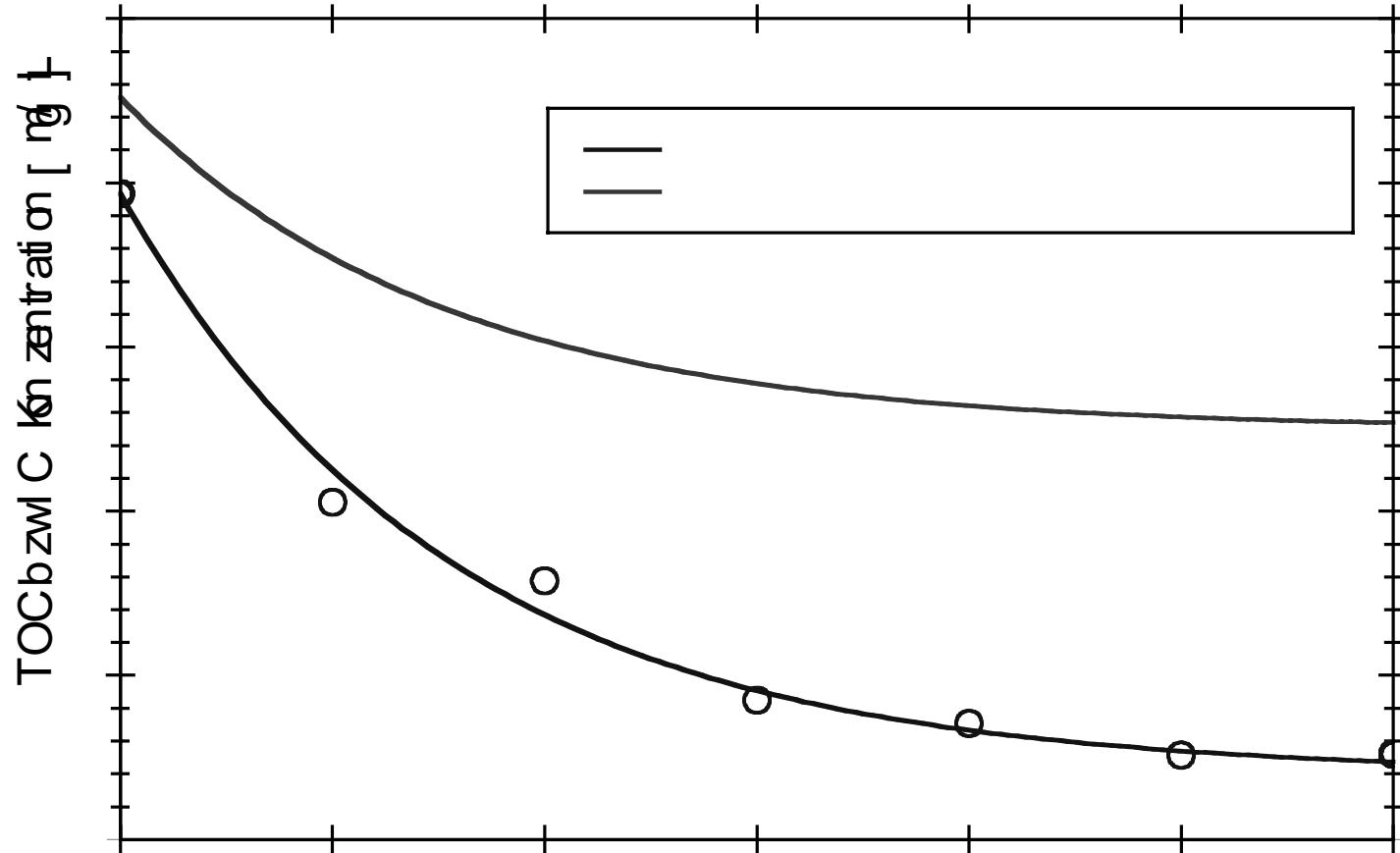


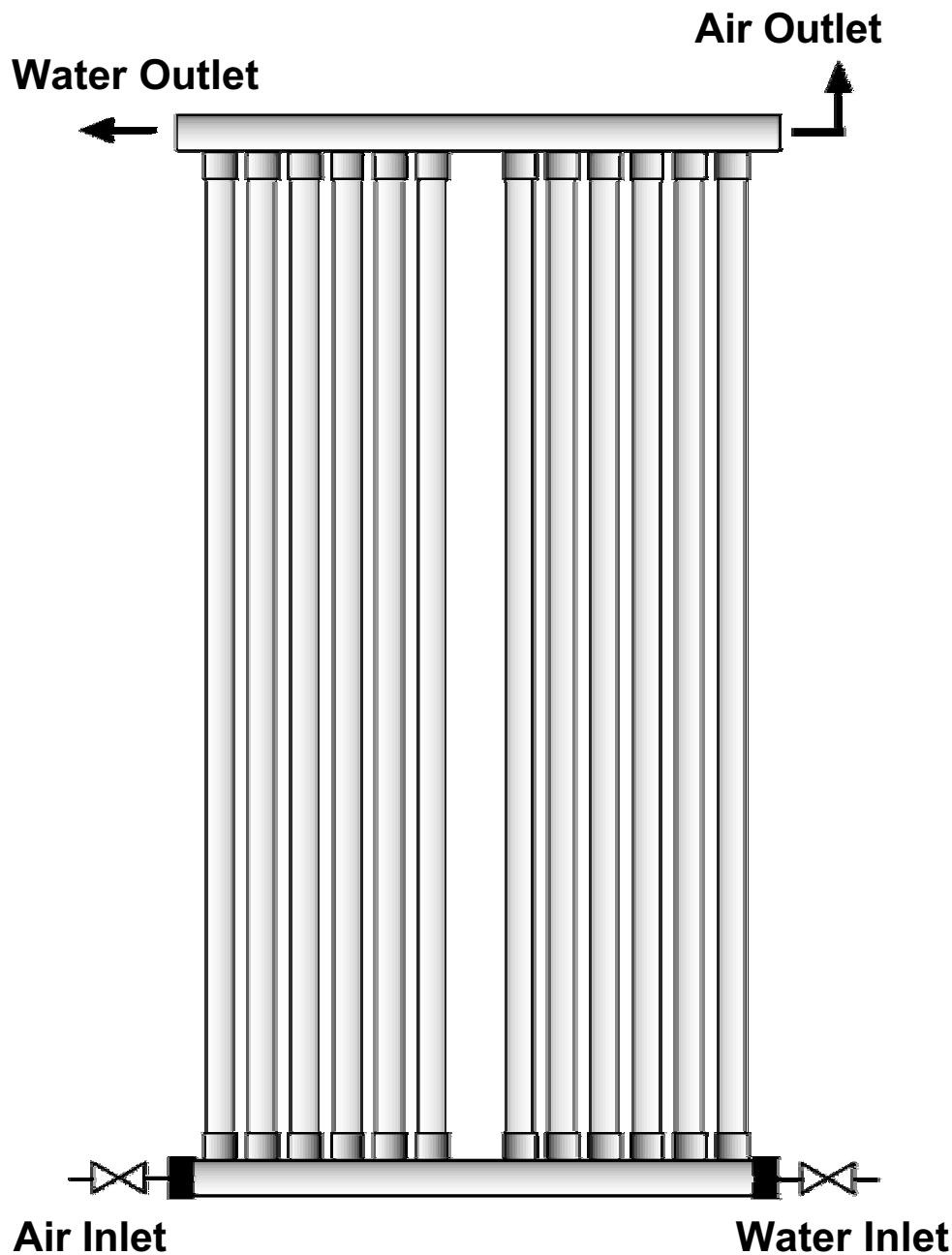












Industrial Production of an ACP–Reactor (Scheme)

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Industrial ACP–Reactor Production (Realization)

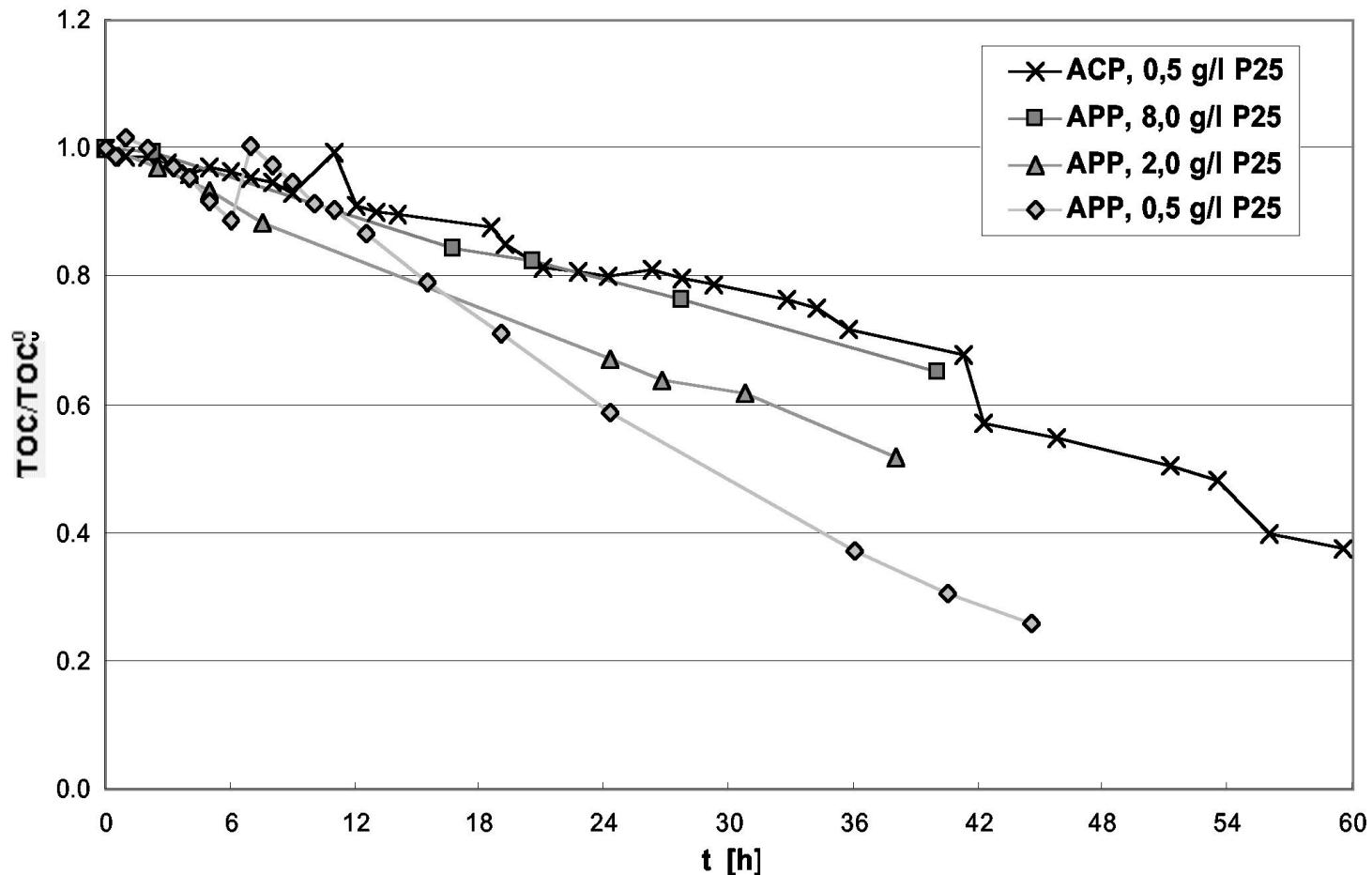


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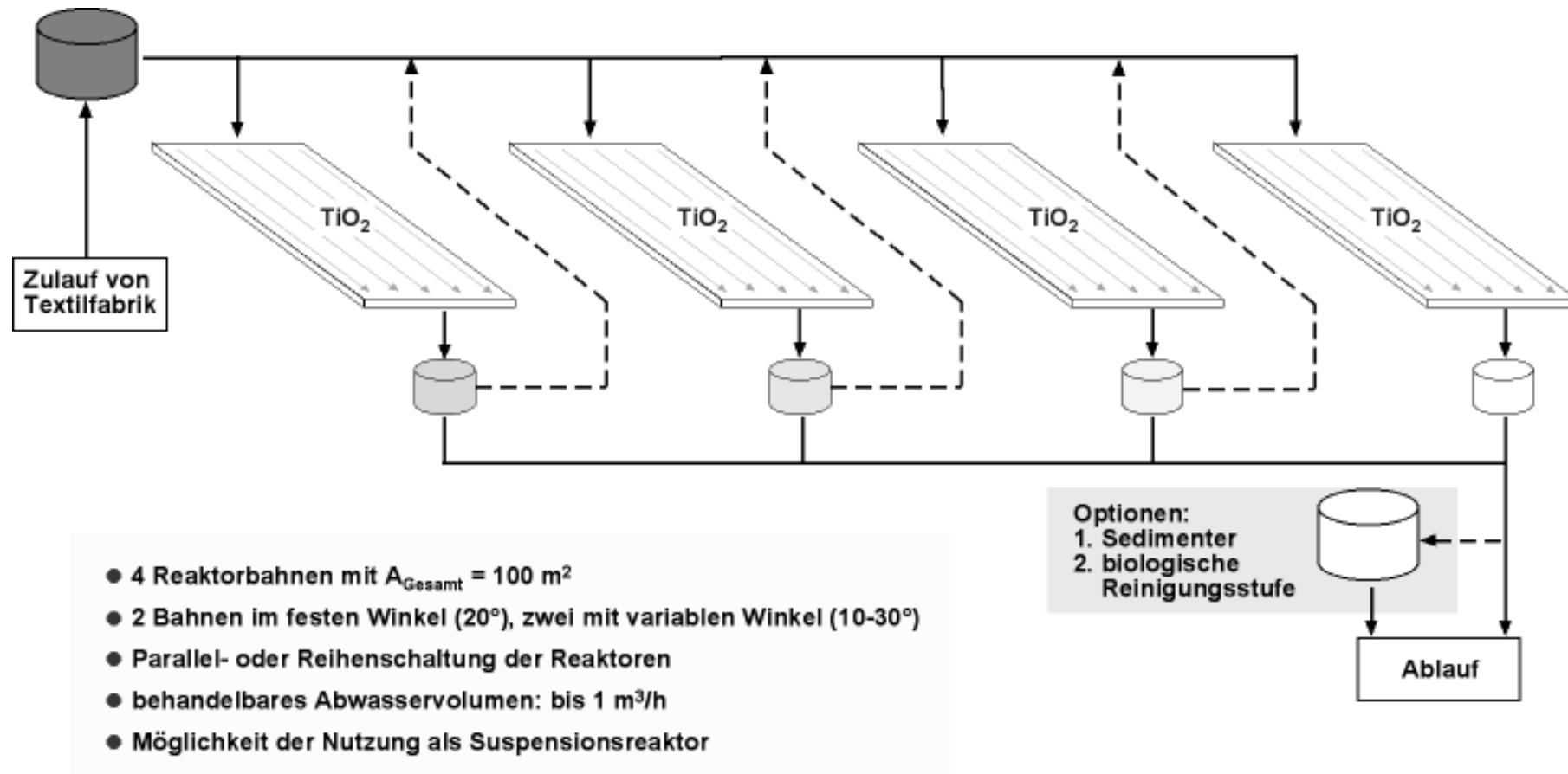
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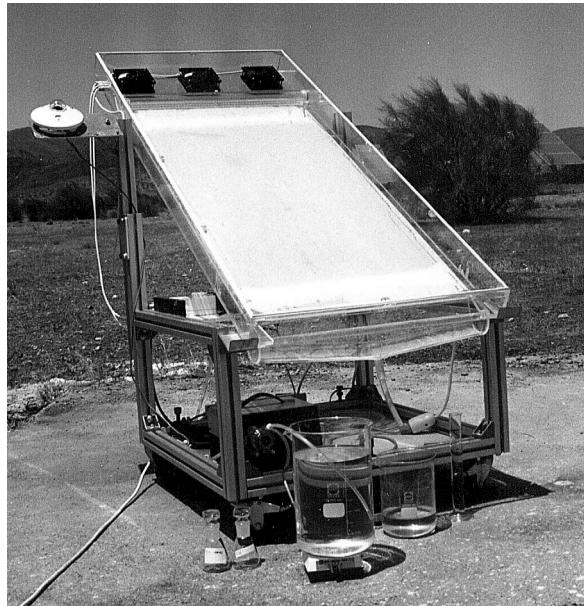
Comparison of the ACP and the APP Reactor for the Degradation of DCA



Thin-Film Fixed Bed Reactor (TFFBR)



Thin-Film Fixed Bed Reactor (TFFBR)



1995 in Almeria/Spanien



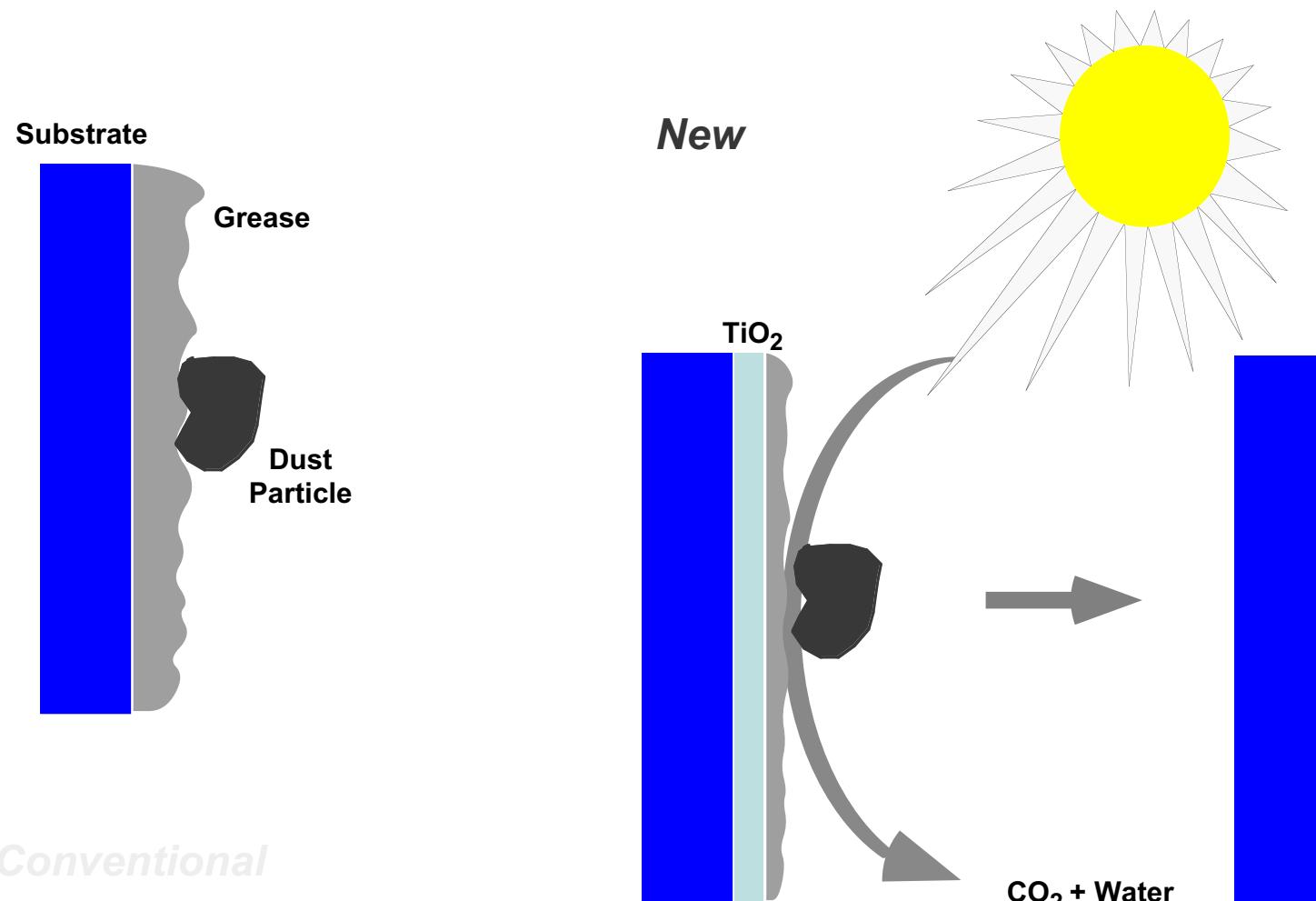
2003 in Tunis/Tunesien

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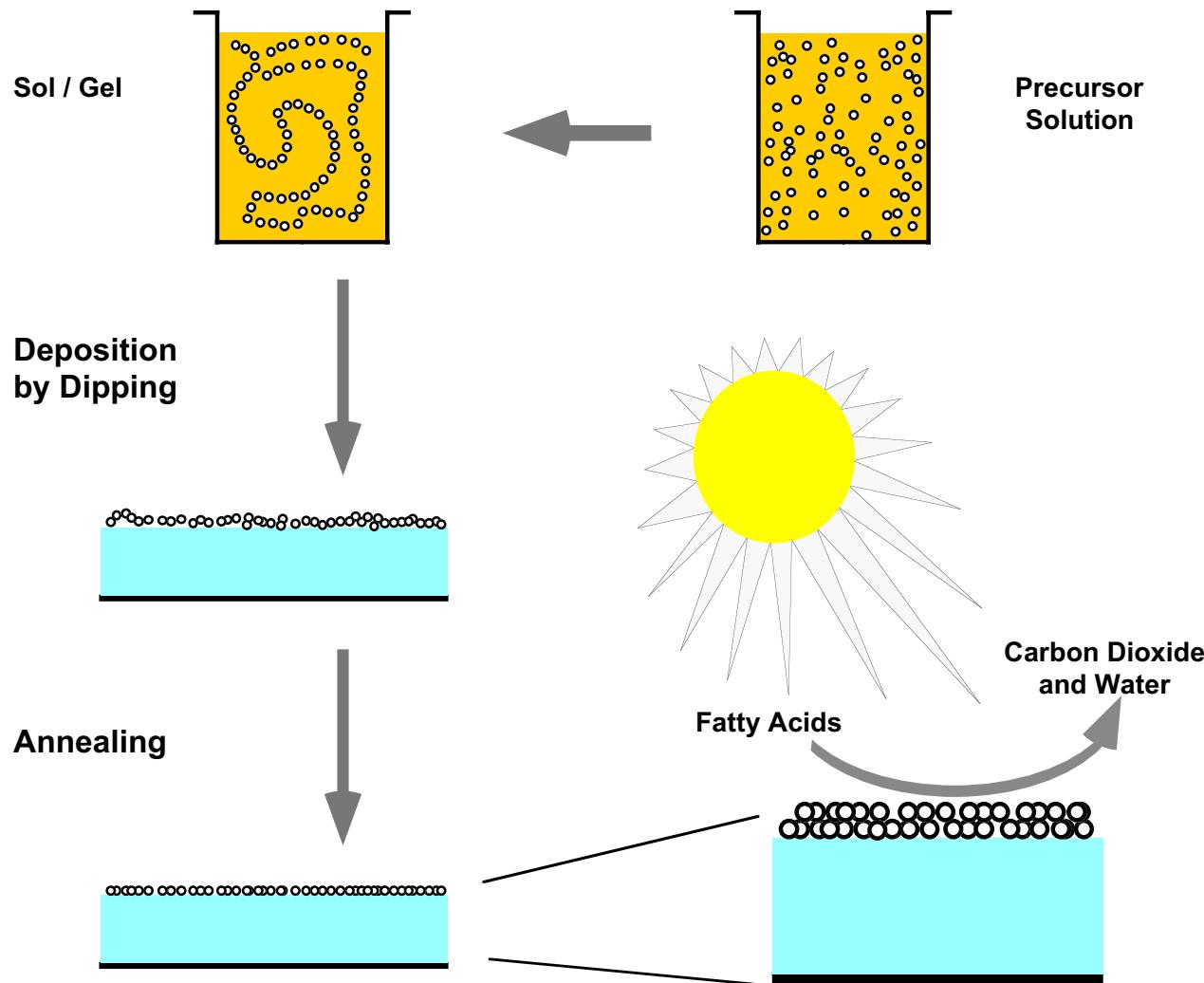
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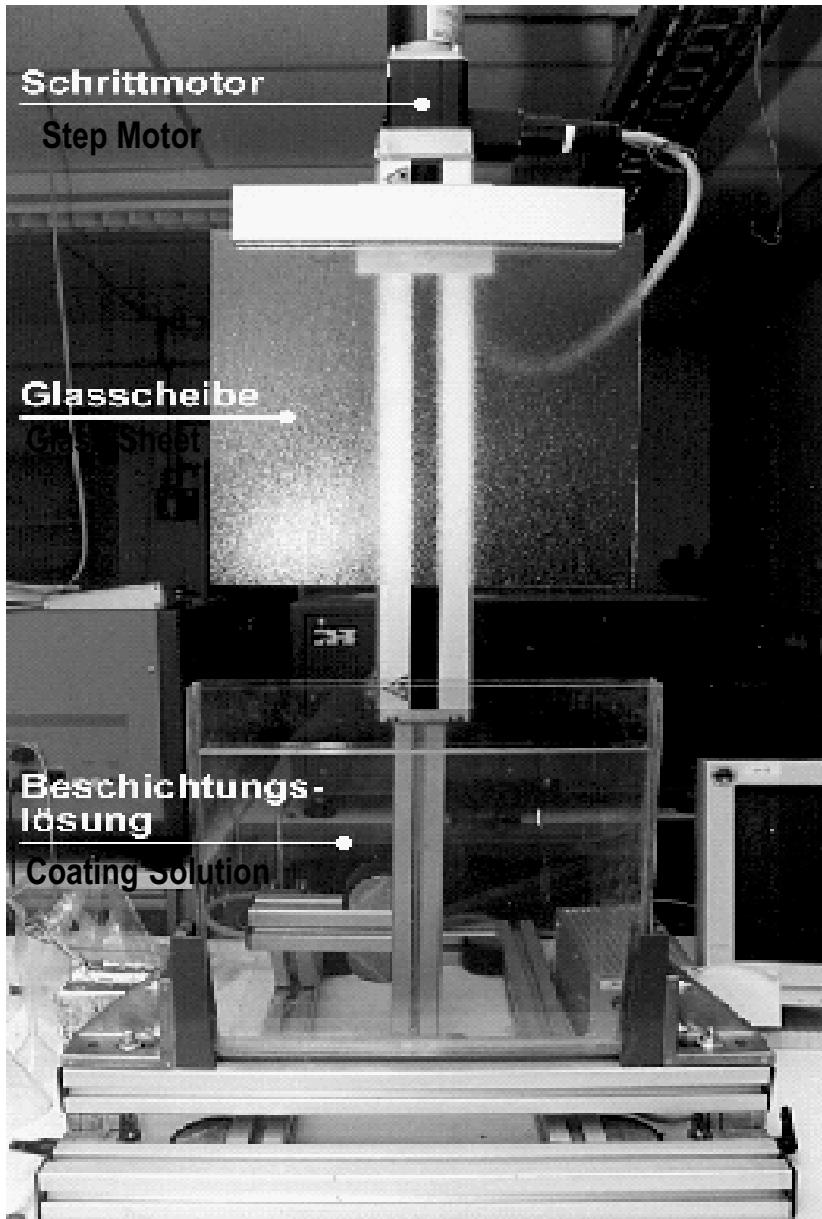


The „Self“-Cleaning Principle



Sol–Gel Film Synthesis



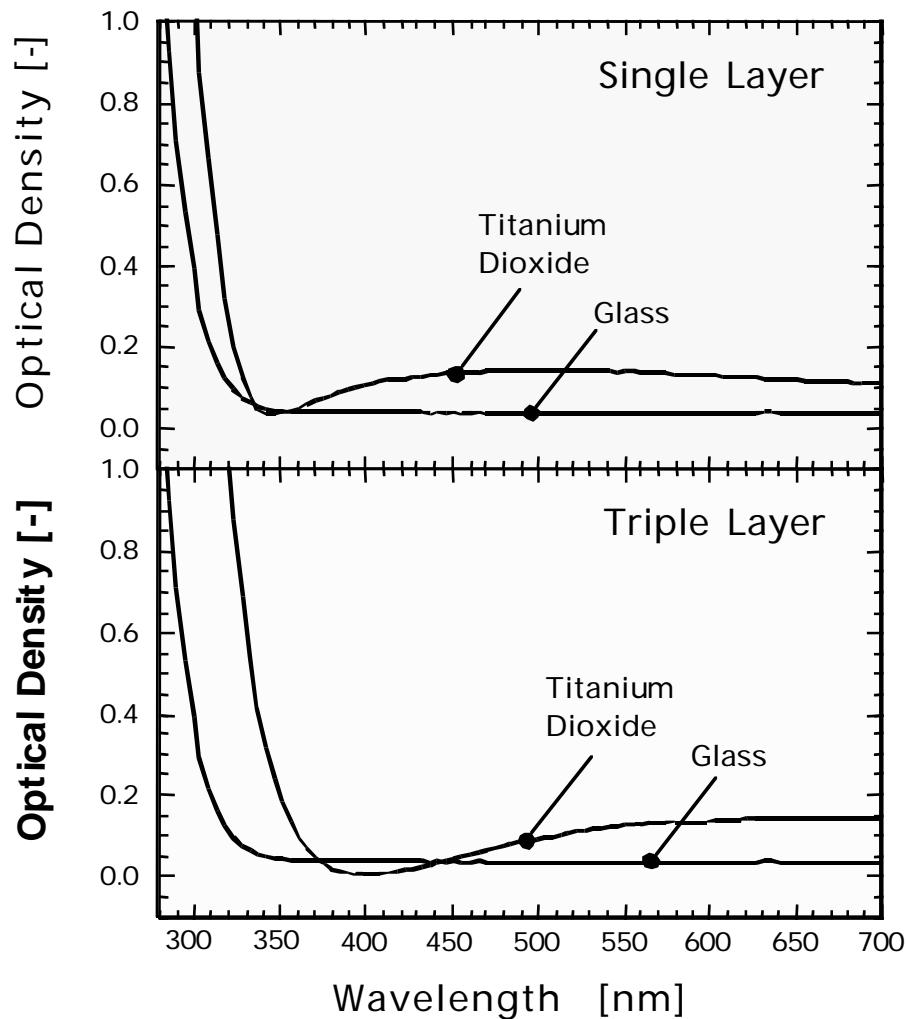


Sol-Gel Film Synthesis: *The Apparatus*

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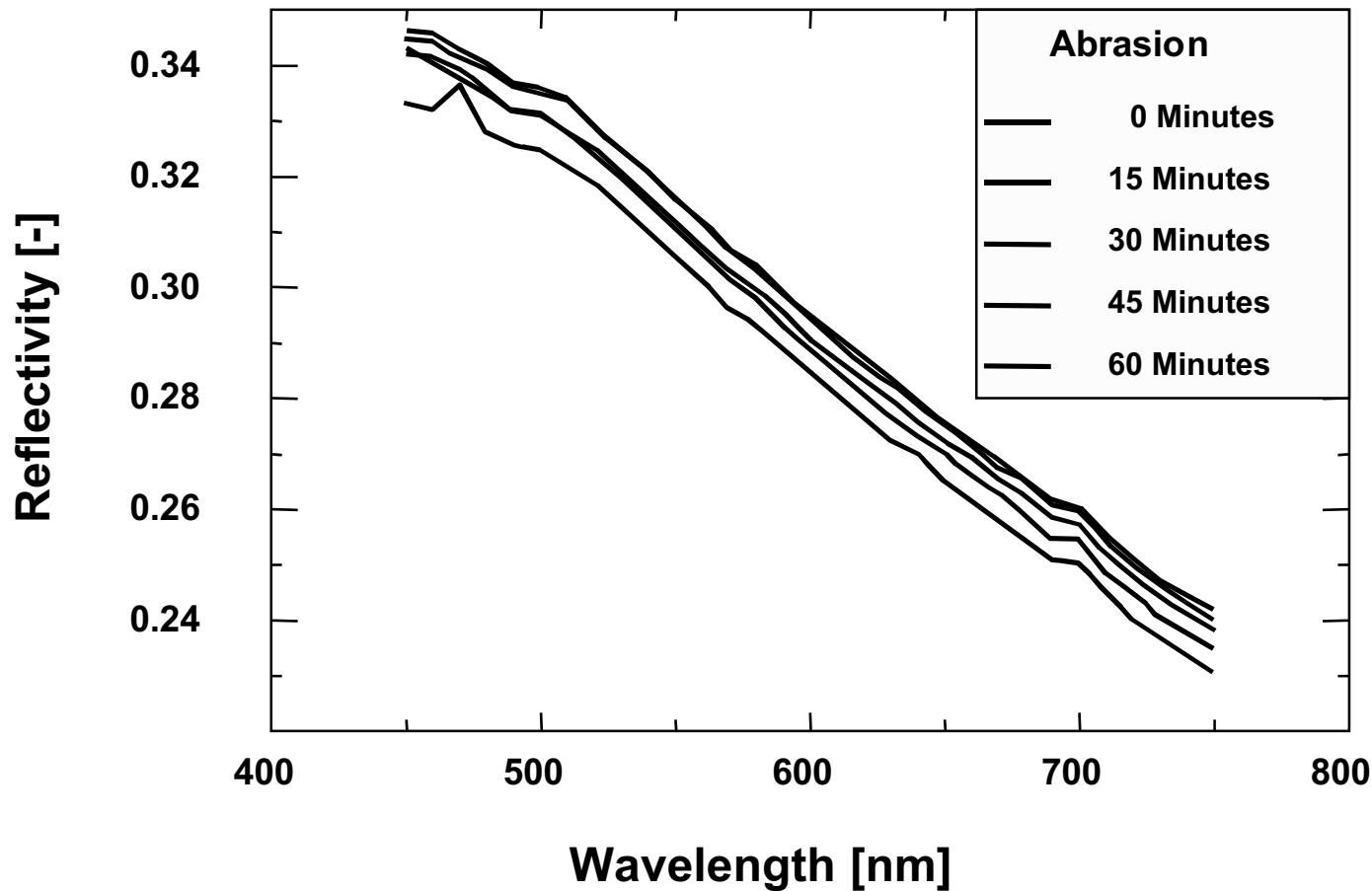




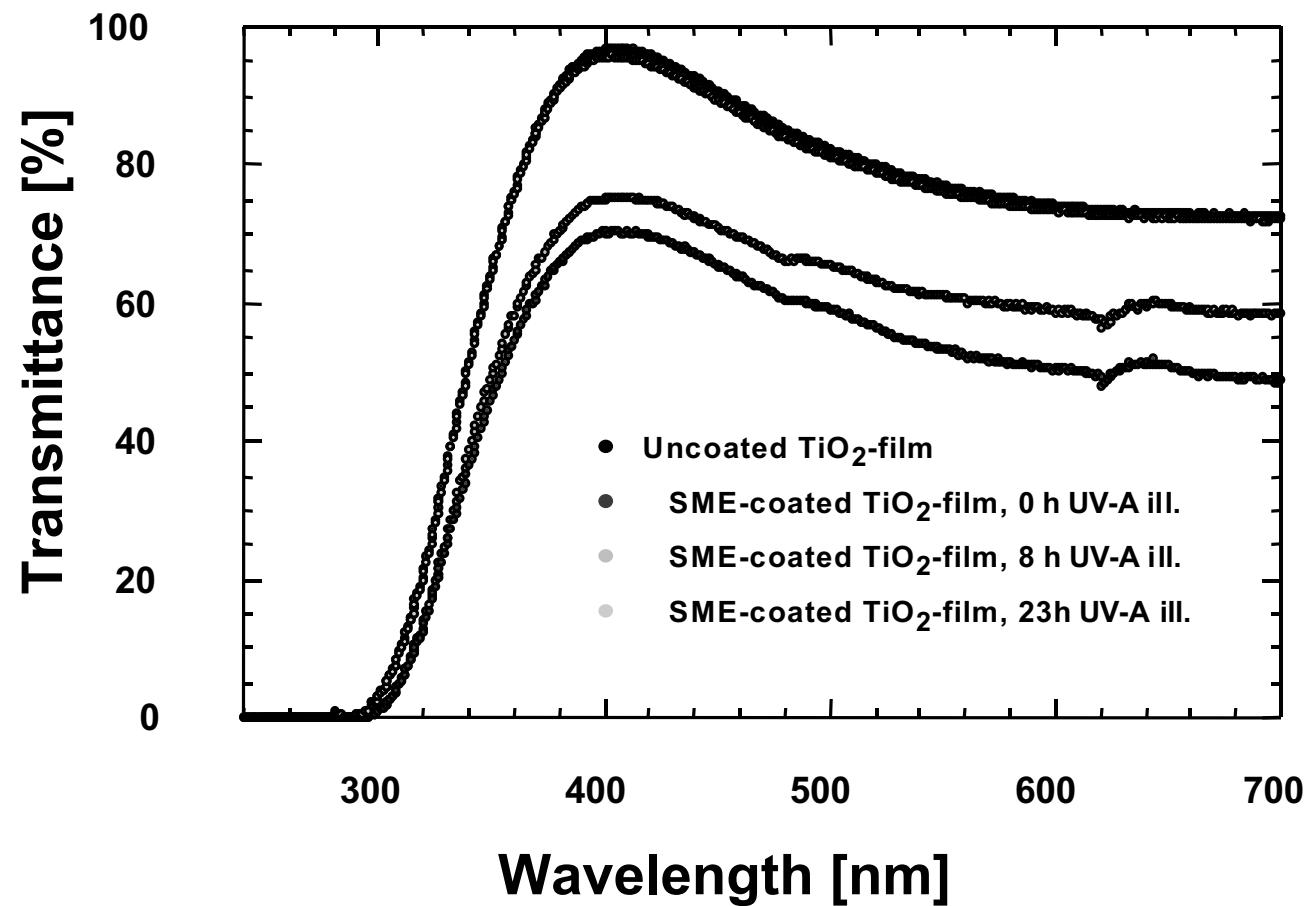
TiO₂ Films on Glass: *60 nm per Dip*



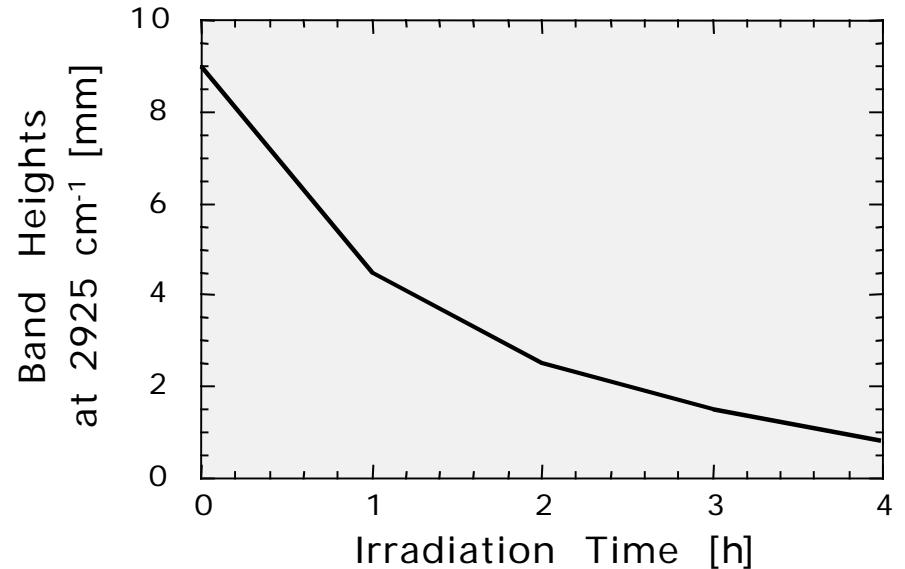
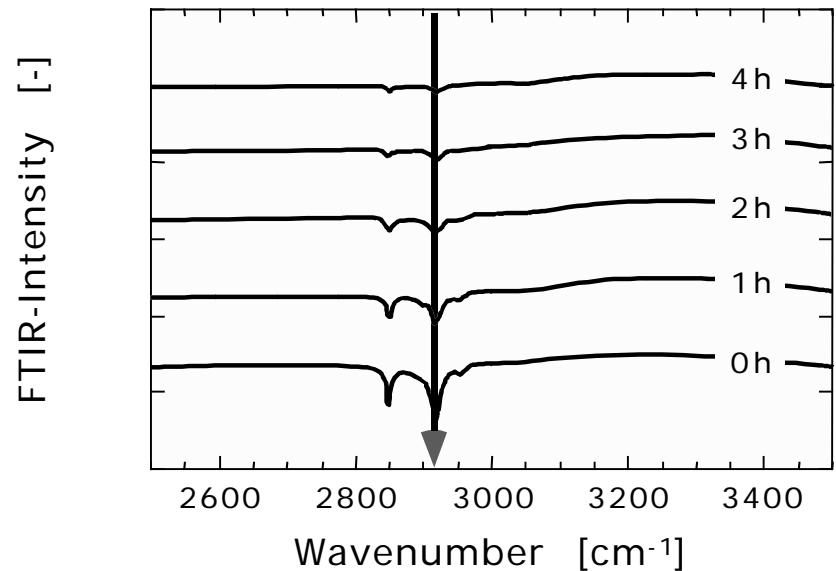
Stability of Sol/Gel-Derived TiO_2 -Films



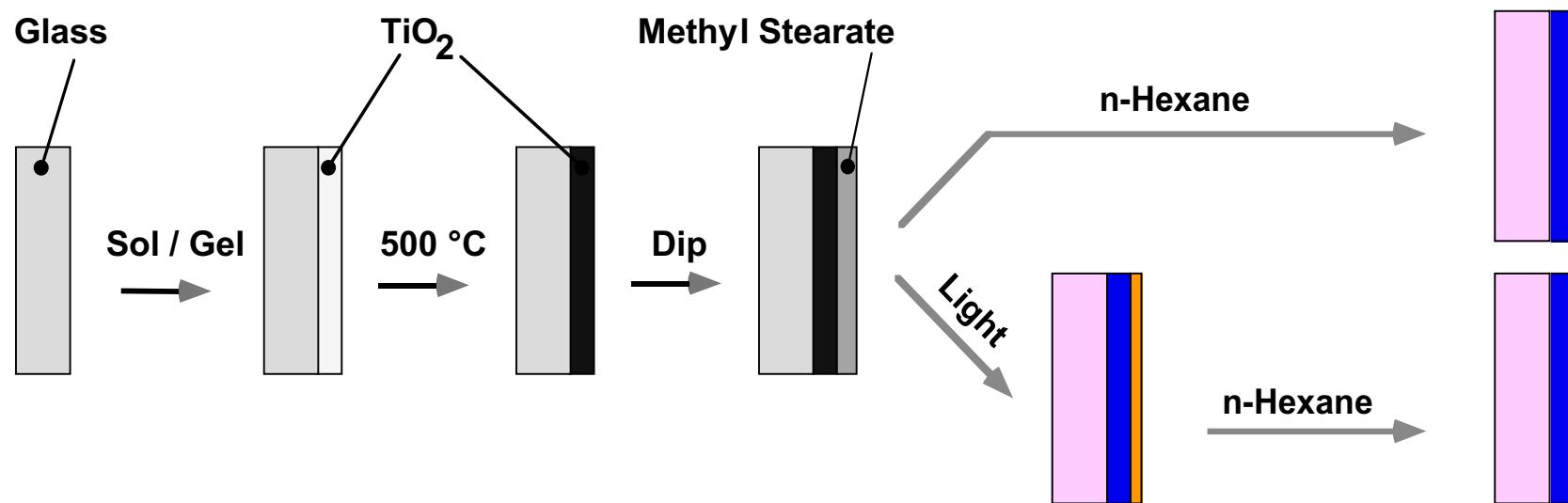
Testing the Photocatalytic Activity: UV/vis-Spectra of Methylstearate adsorbed on the TiO_2 -Films



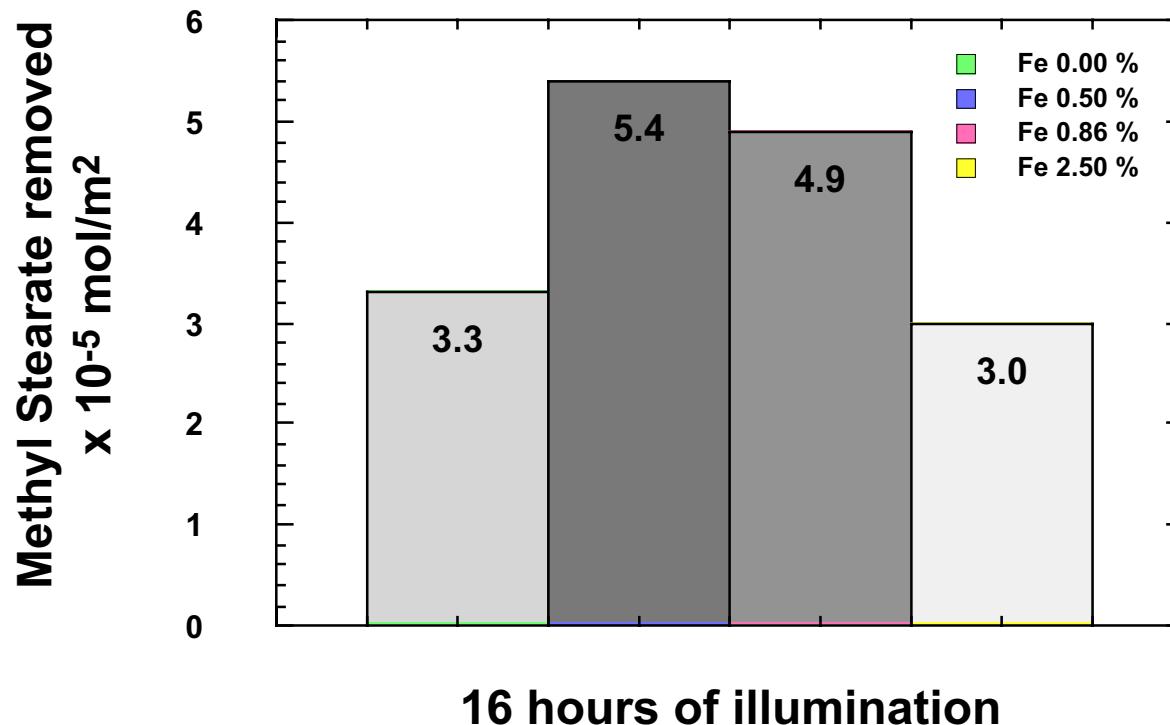
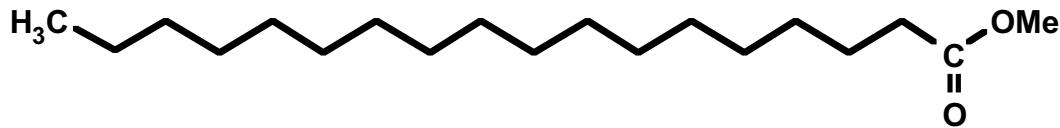
Testing the Photocatalytic Activity: FTIR-Signals of Methylstearate adsorbed on the TiO_2 -Films



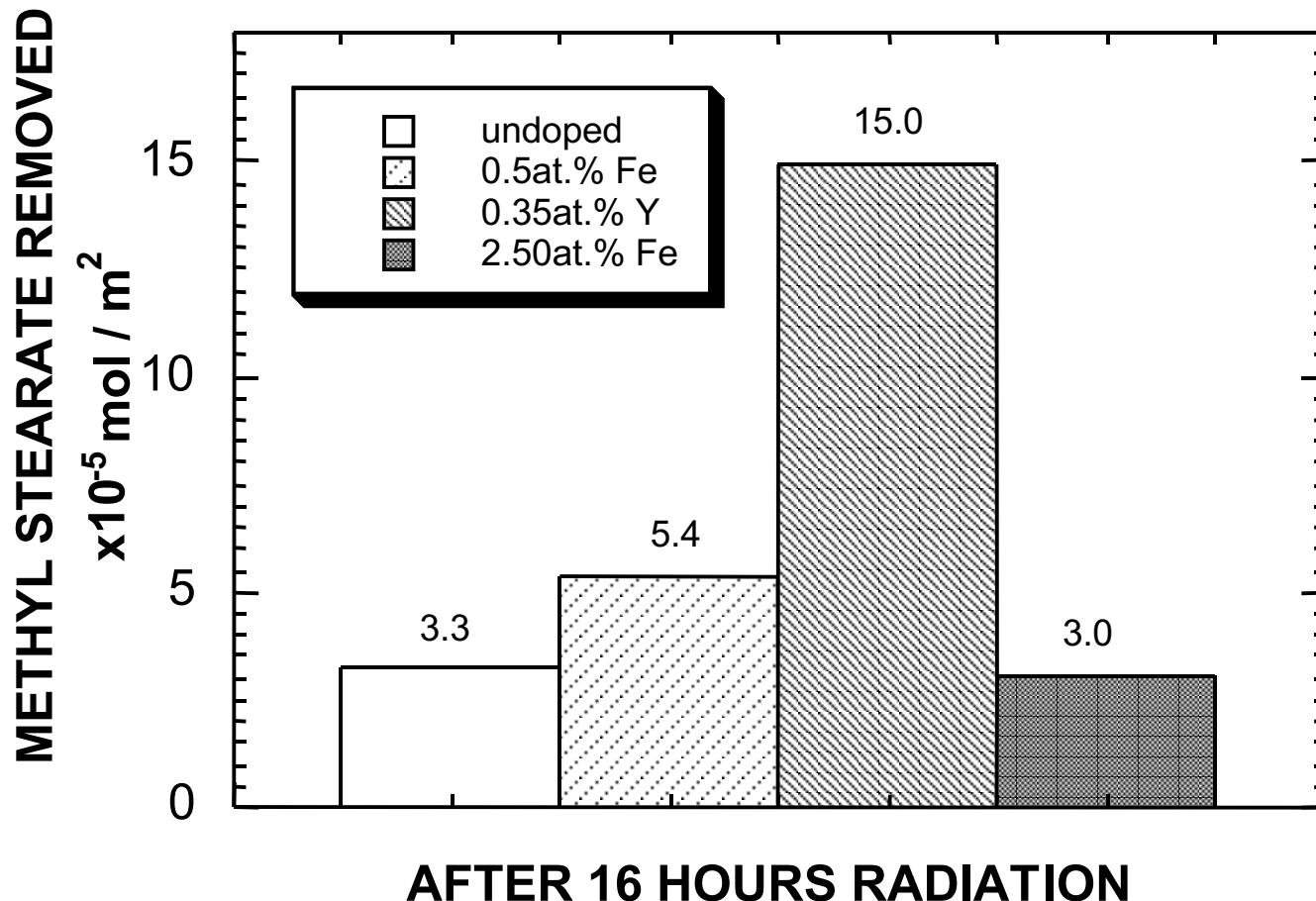
Testing the Photocatalytic Activity: Quantitative GC-Analysis of Methylstearate adsorbed on the TiO_2 -Films



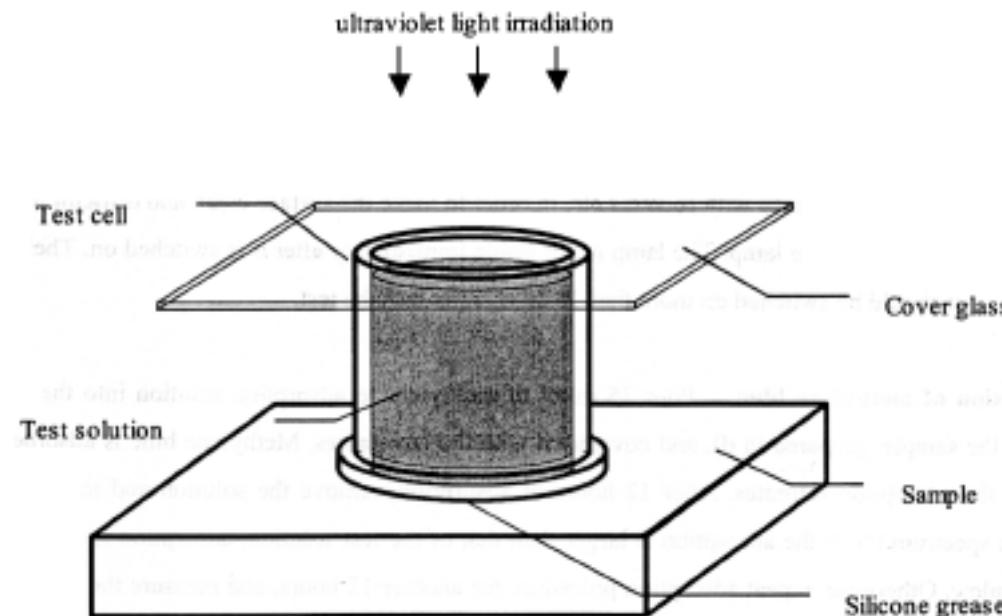
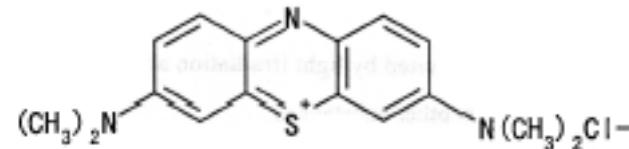
Testing the Photocatalytic Activity: Rates of Methylstearate Removal



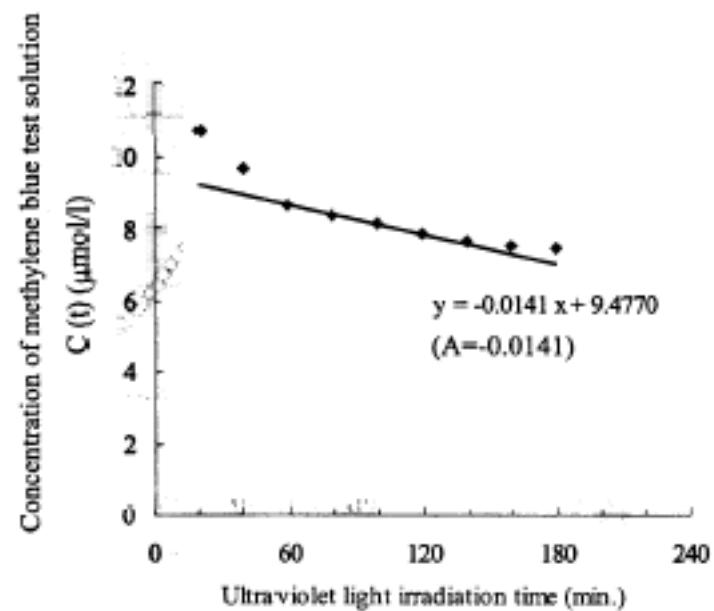
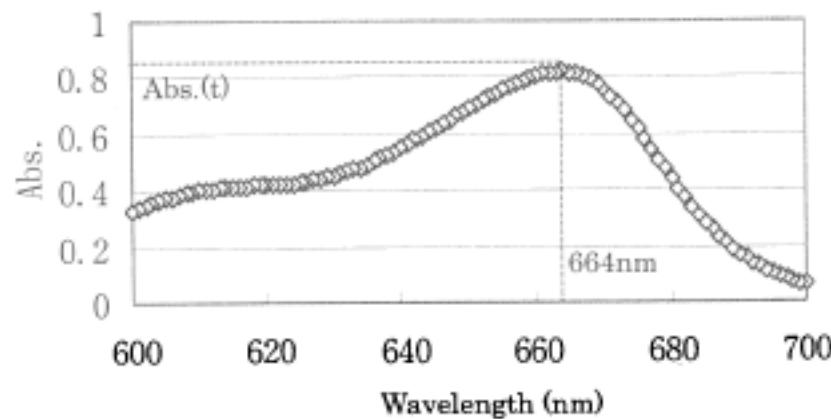
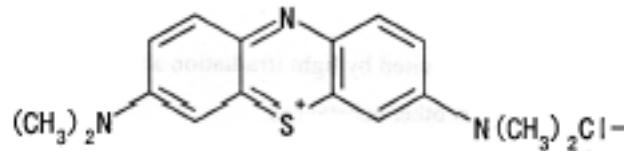
Photocatalytic Activity of Fe³⁺- and Y³⁺-doped TiO₂



Photocatalytic Activity Tests: Methylenblue Degradation

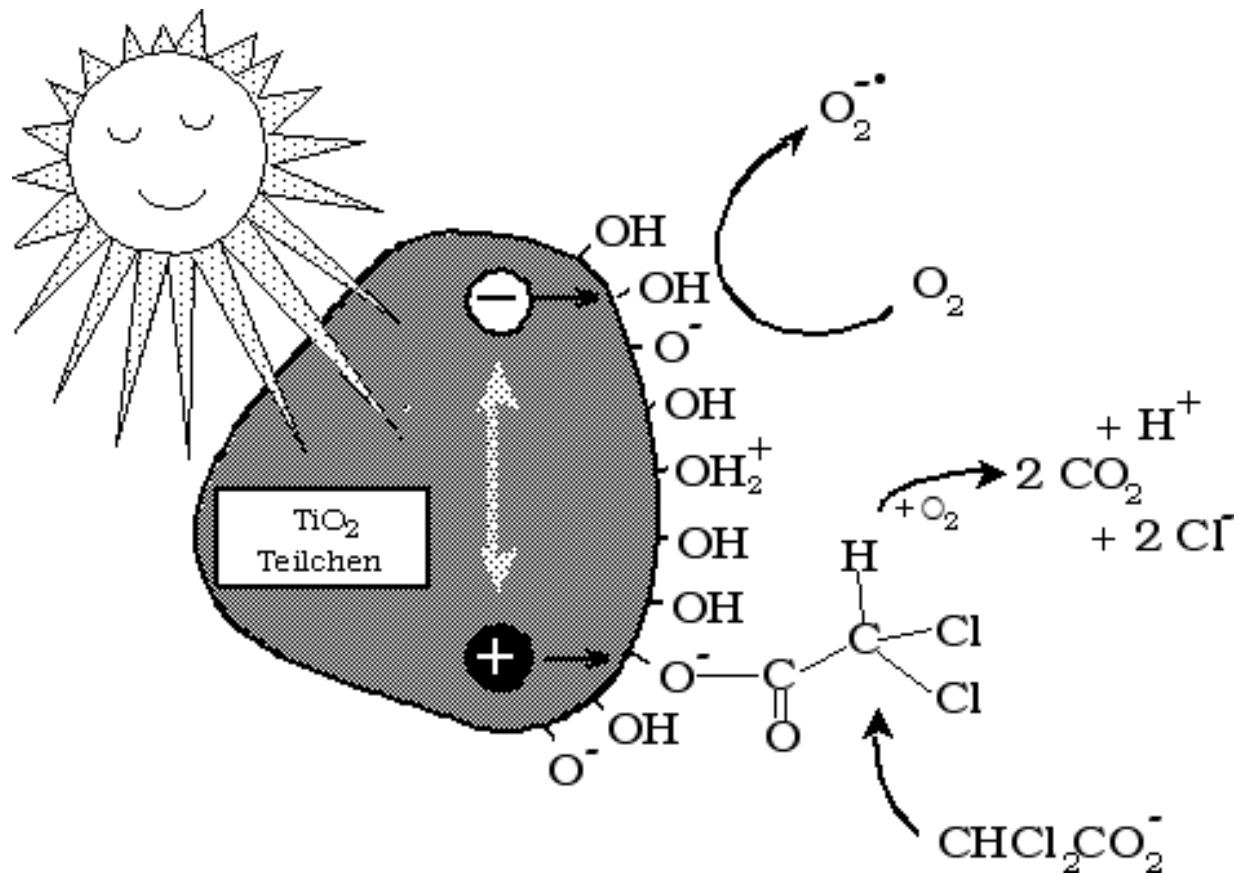


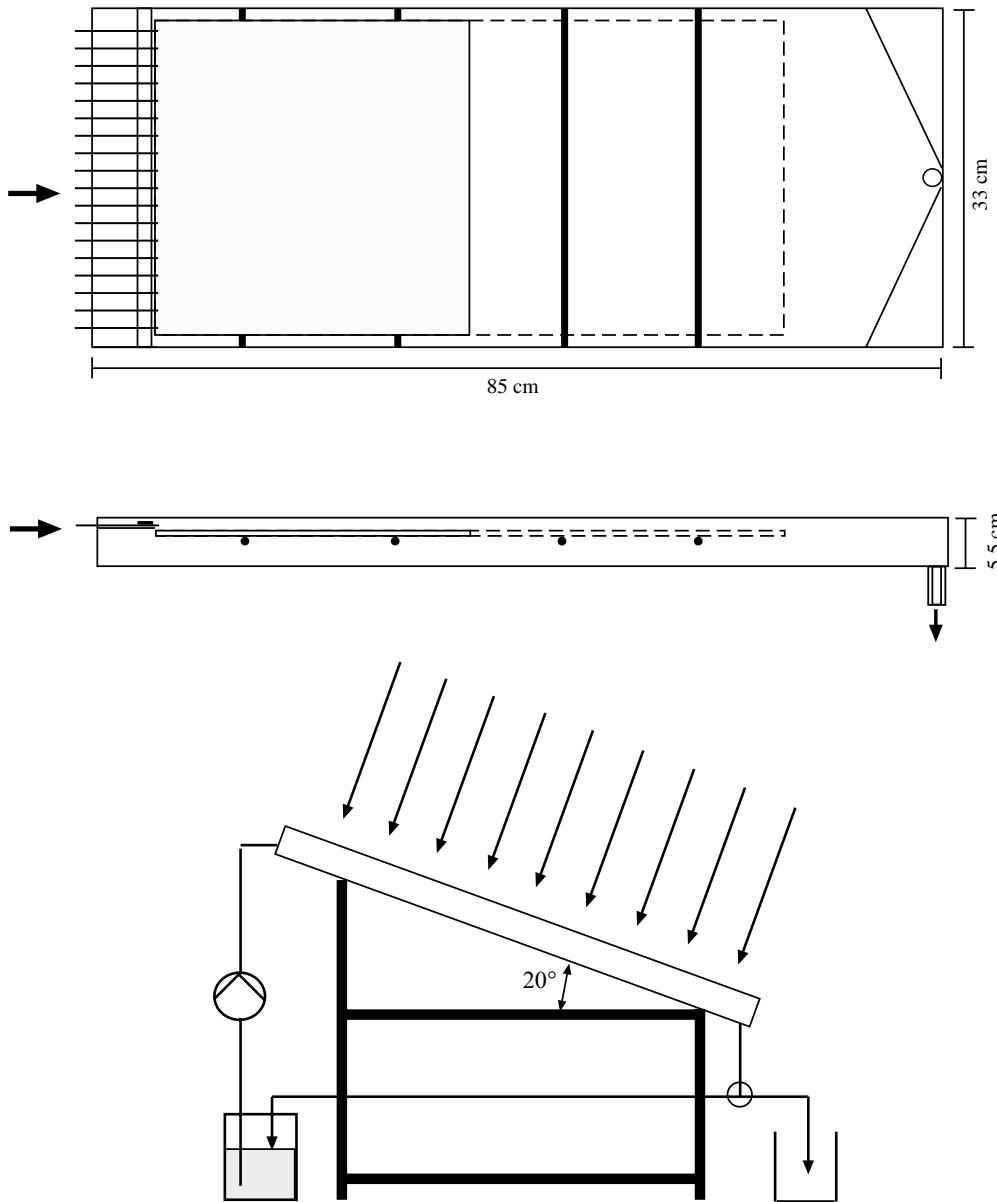
Photocatalytic Activity Tests: Methylenblue Degradation



Photocatalytic Activity Tests:

Dichloroacetate (DCA) Degradation





Photocatalytic Activity Tests: The Thin Film Fixed Bed Reactor (TFFBR)

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Photocatalytic Activity Tests:

The Thin Film Fixed Bed Reactor (TFFBR)

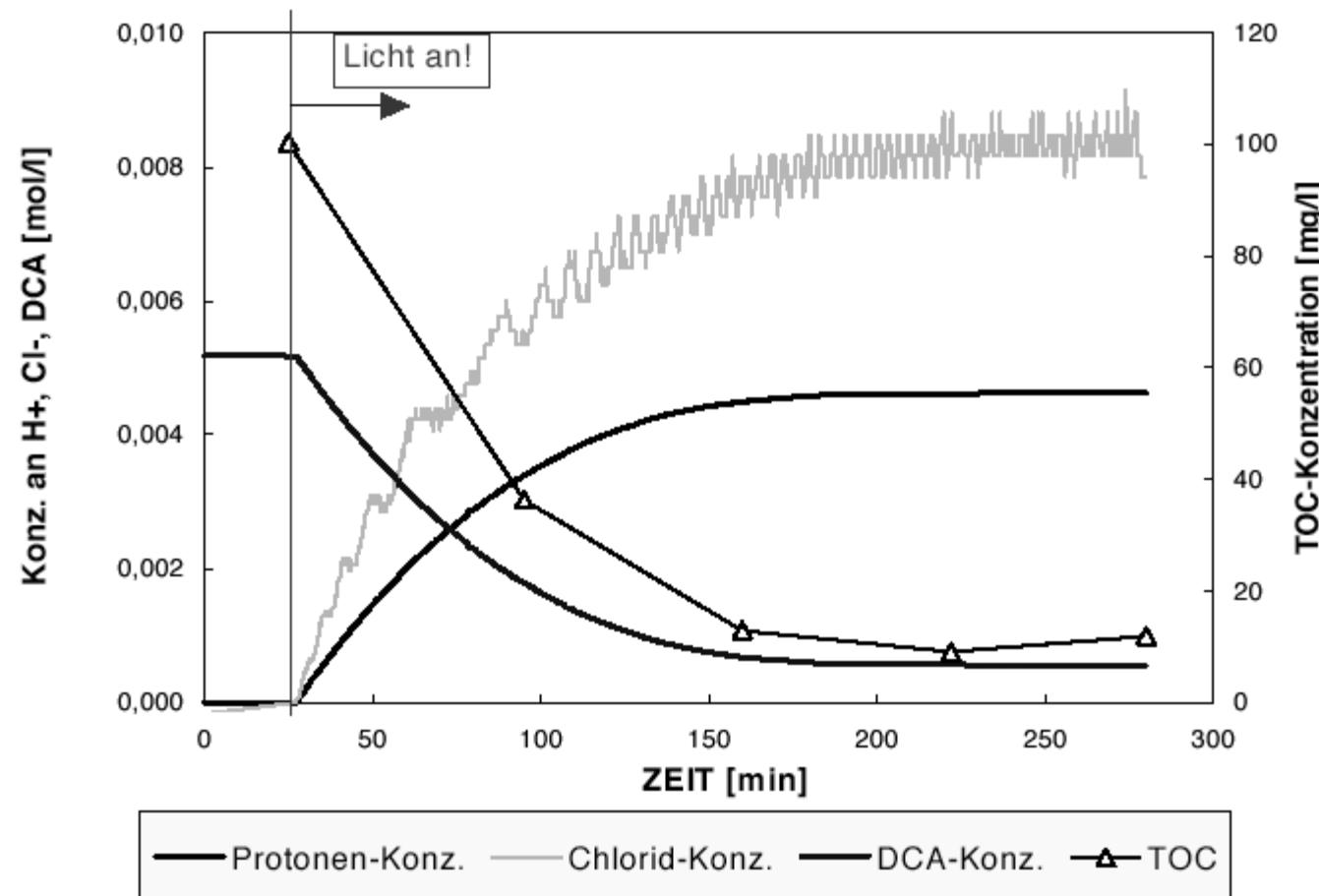


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Photocatalytic Activity Tests: Dichloroacetate (DCA) Degradation



Photocatalytic Activity Tests: DCA Degradation – Effect of Binders

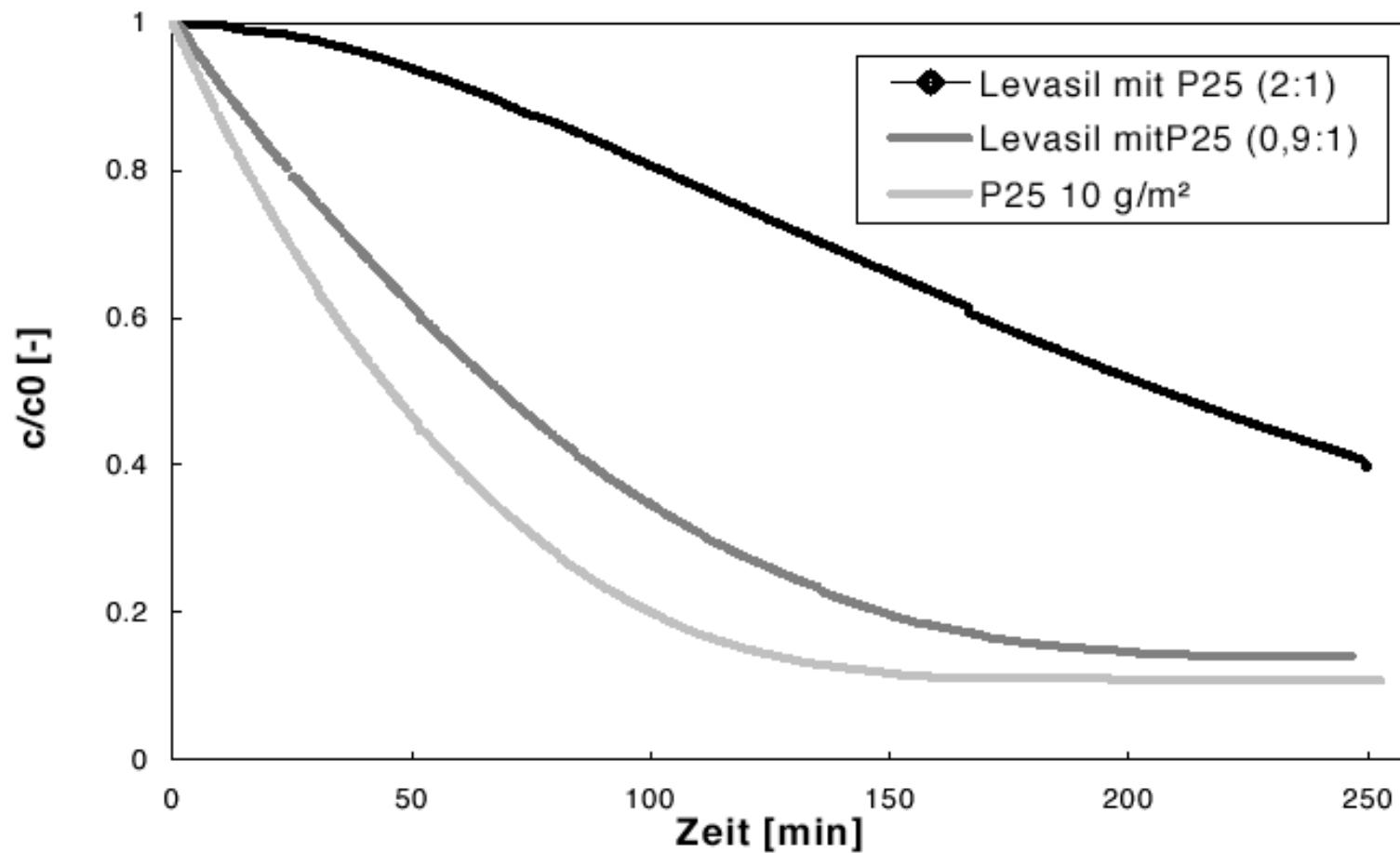


Bild 5-7: DCA-Abbau im TFFBR berechnet aus der Protonenbildung, Modellabwasser: 5mM DCA,
Dauer: 4h, $E = 25 \text{ W} \cdot \text{m}^{-2}$, pH-Wert = 3, Verdunstungstitration: $0,840 \text{ ml} \cdot \text{min}^{-1}$, Spraytechnik auf
Glasplatten, Katalysatoren: P25 (300x600 mm), Levasil® mit P25: $\text{SiO}_2:\text{TiO}_2=2:1$ (300x600 mm),
Levasil® mit P25: $\text{SiO}_2:\text{TiO}_2=0,9:1$ (2 Platten zu 300x300 mm)
bahnemann@iftc.uni-hannover.de

Photocatalytic Coatings: Examples

Selbst-reinigendes Zelt-Dach



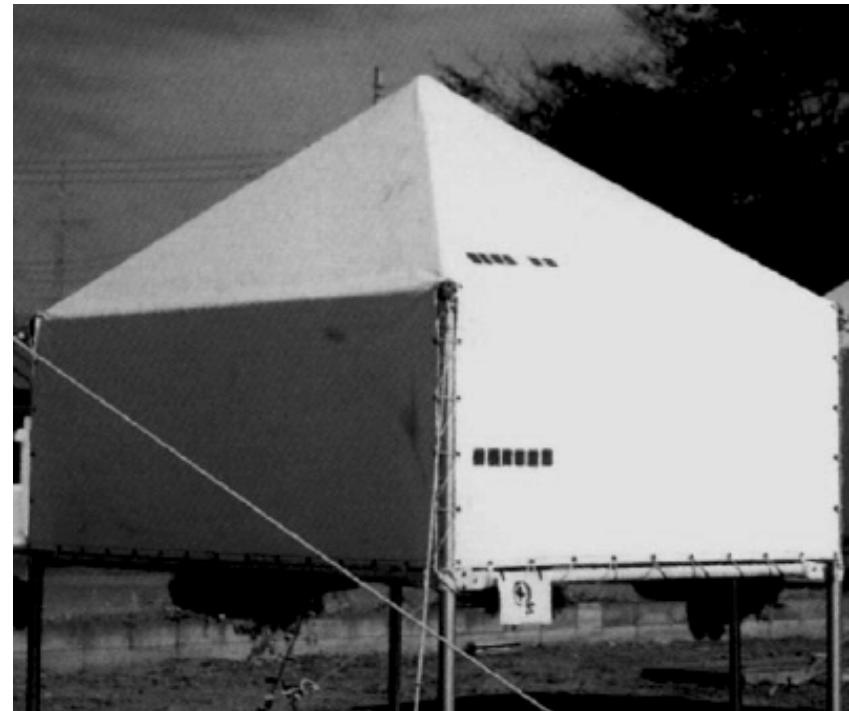
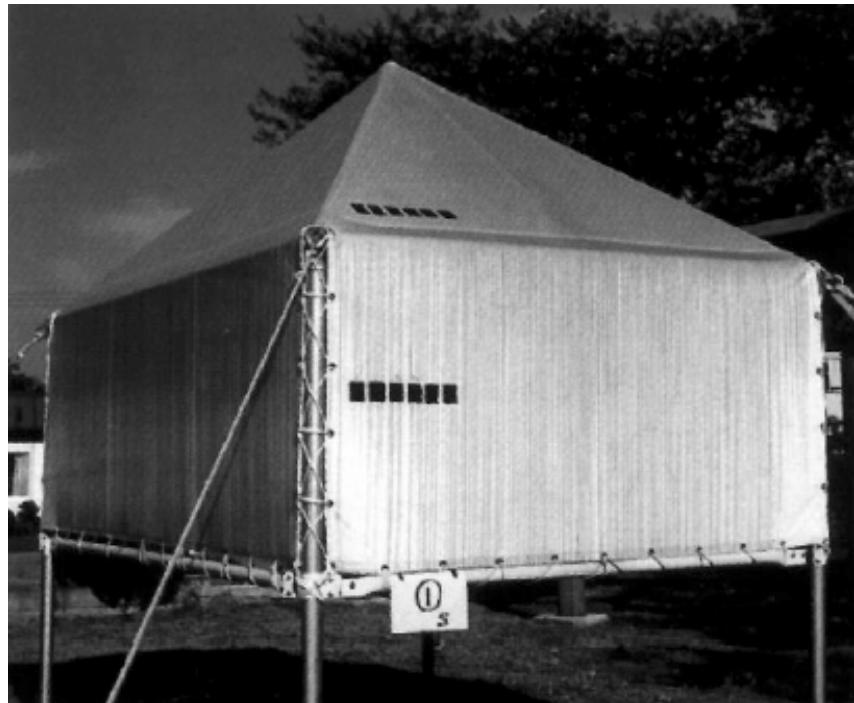
Foto:
Taiyo
Kogyo
Corporation
Corporation

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Photocatalytic Coatings: Examples



Kleine Testzelte
auf dem
Fabrik-Gelände,
Saitama-Präfektur
nahe Tokyo

Photocatalytic Coatings: Examples

Fahrzeug-Lackierung mit "Hydrotect".Beschichtung



Foto: Toto Ltd.

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Photocatalytic Coatings: Examples

Selbst-reinigende Jalousie



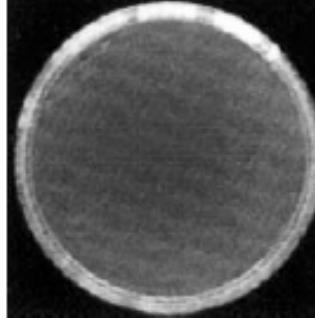
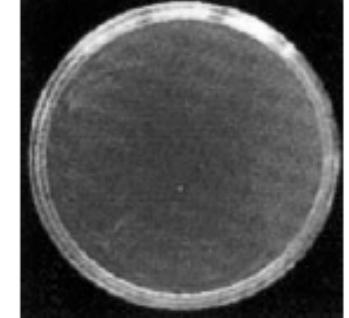
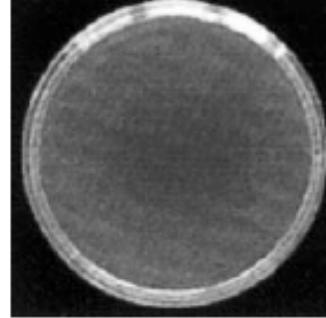
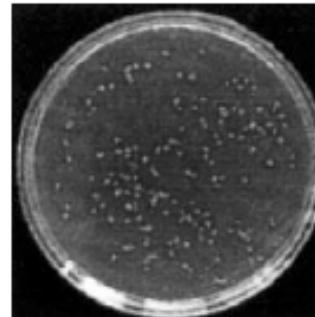
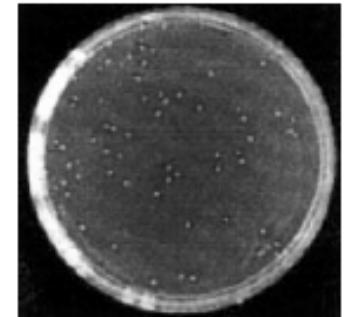
Foto: Nichibei Trading Co., Ltd.

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Photocatalysis: Antibacterial Properties

		E. coli	Methicillin-resistente Staph. aureus	Pseudomonas aeruginosa
Photokatalytisch aktive Kacheln	1 Stunde mit 1000 Lux belichtet			
Normale Kacheln	mit 1000 Lux belichtet			

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Photocatalysis: Antibacterial Tiles

Operationssaal



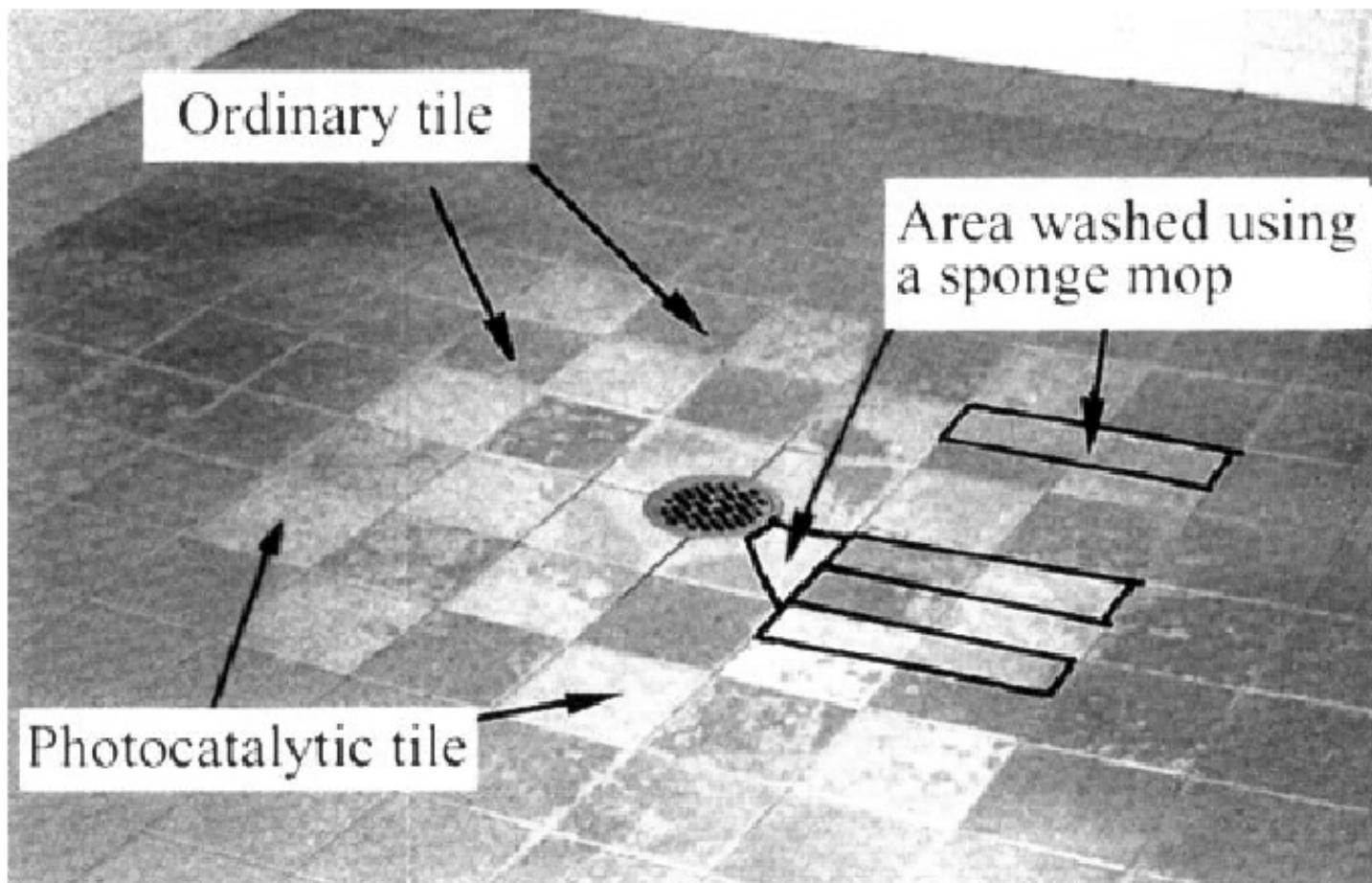
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Photocatalysis: Antibacterial Tiles

Duschräum in Studentenwohnheim



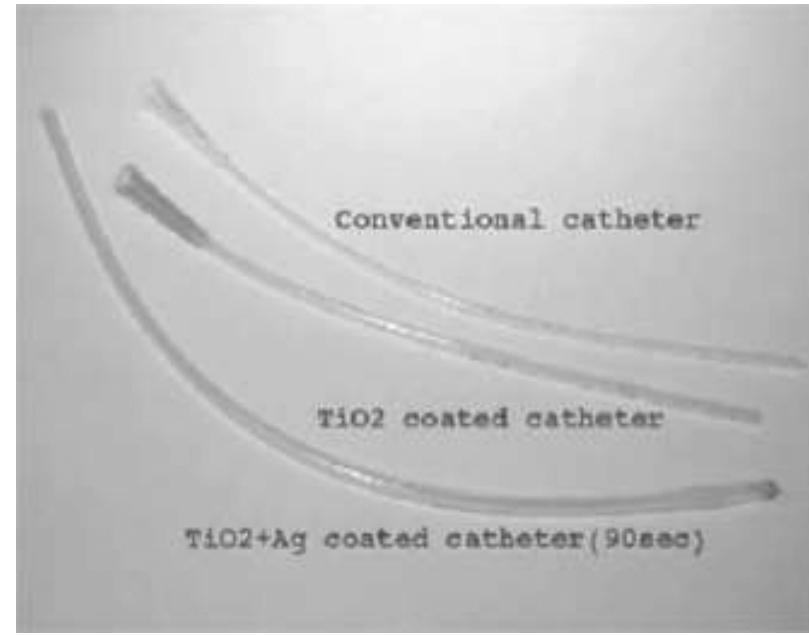
Antibacterial/fungal performance



Medical applications

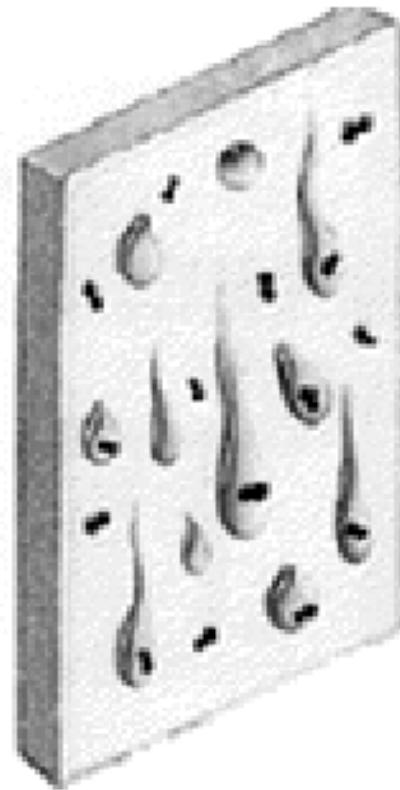


Wall of operating room

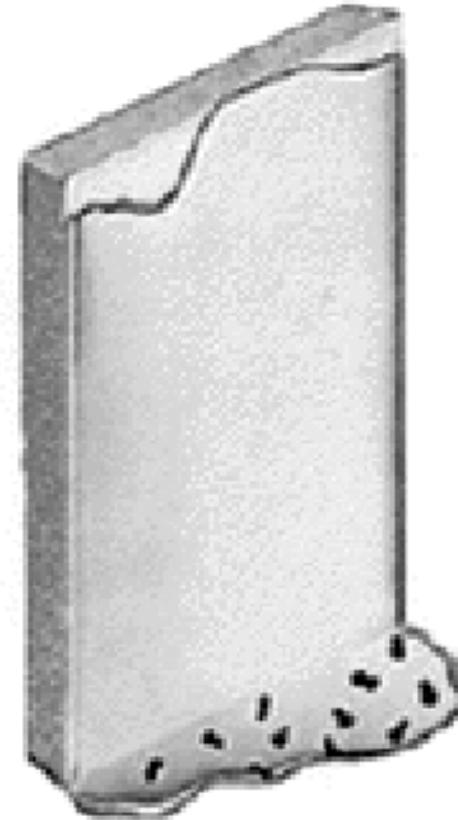


Catheter

Photocatalysis: Superhydrophilicity



ordinary uncoated tile



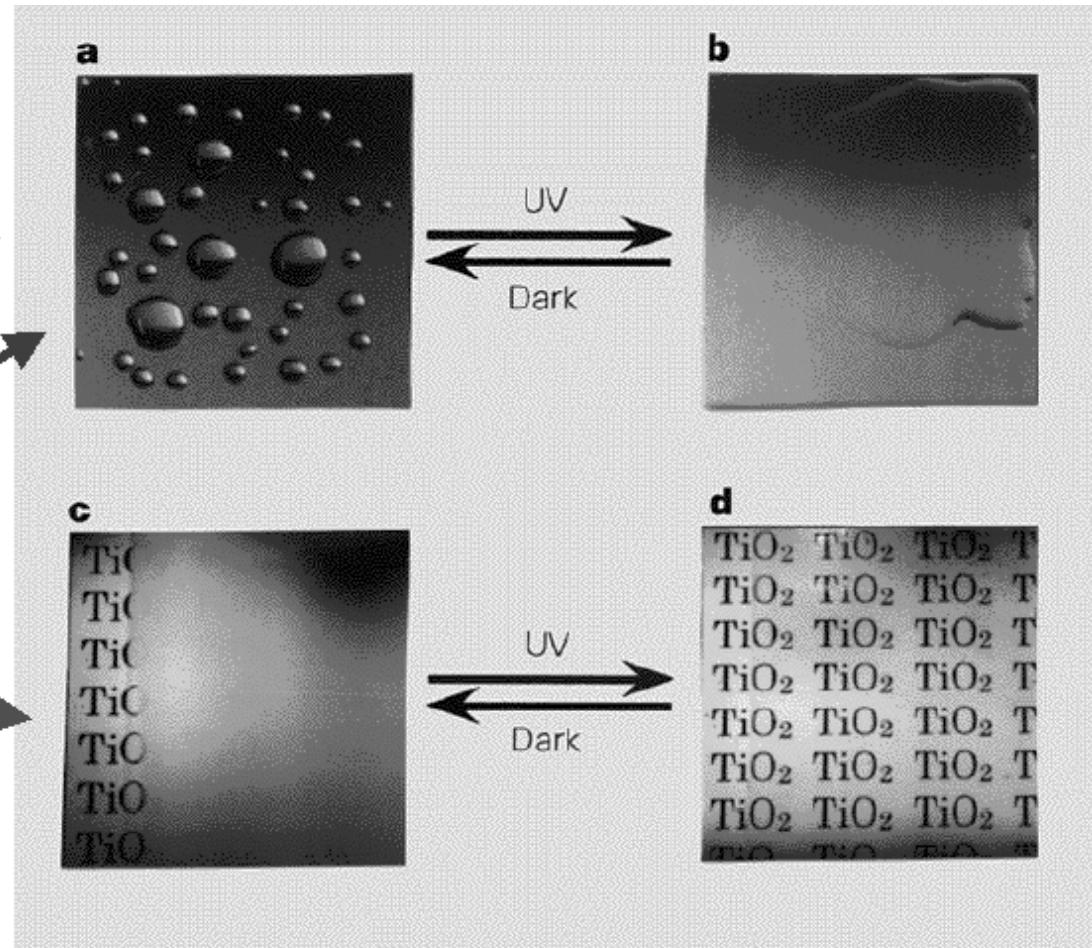
hydrophilic tile coated by TiO₂

Photocatalysis: Superhydrophilicity

Photogeneration of amphiphilic surface through UV irradiation

Water droplets

Water vapor



Wang, et al. Nature, 388 p. 431

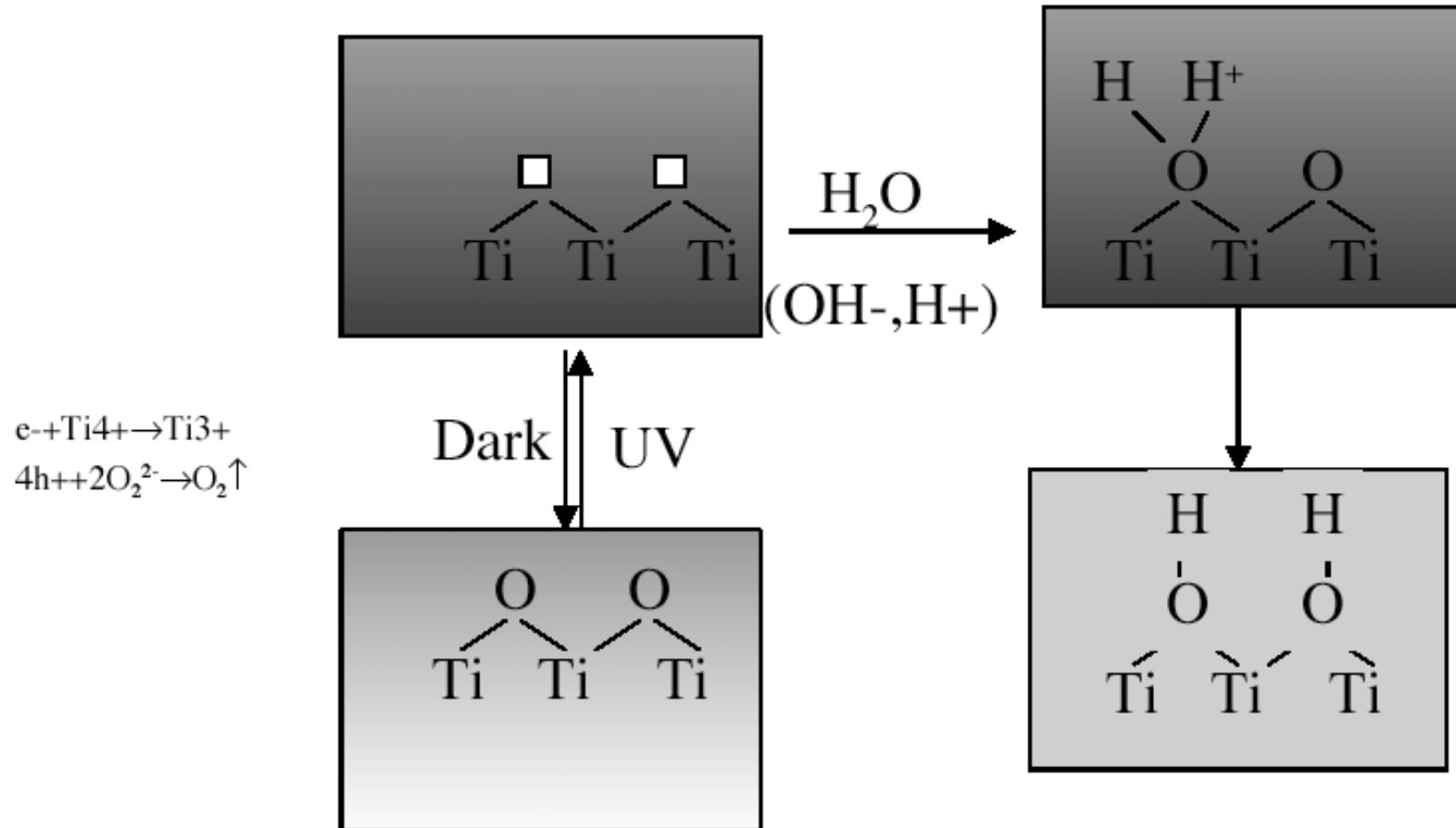
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Photocatalysis: Mechanism of Superhydrophilicity

O vacancies created



Photocatalytic Coatings: Examples of Superhydrophilicity

Halb beschichteter Spiegel



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Photocatalytic Coatings: Examples of Superhydrophilicity

Außenspiegel mit "Hydrotect".Beschichtung



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Saint Gobain Bioclean



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Pilkington Activ



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MACHT SICH SAUBER.

ERLUS 

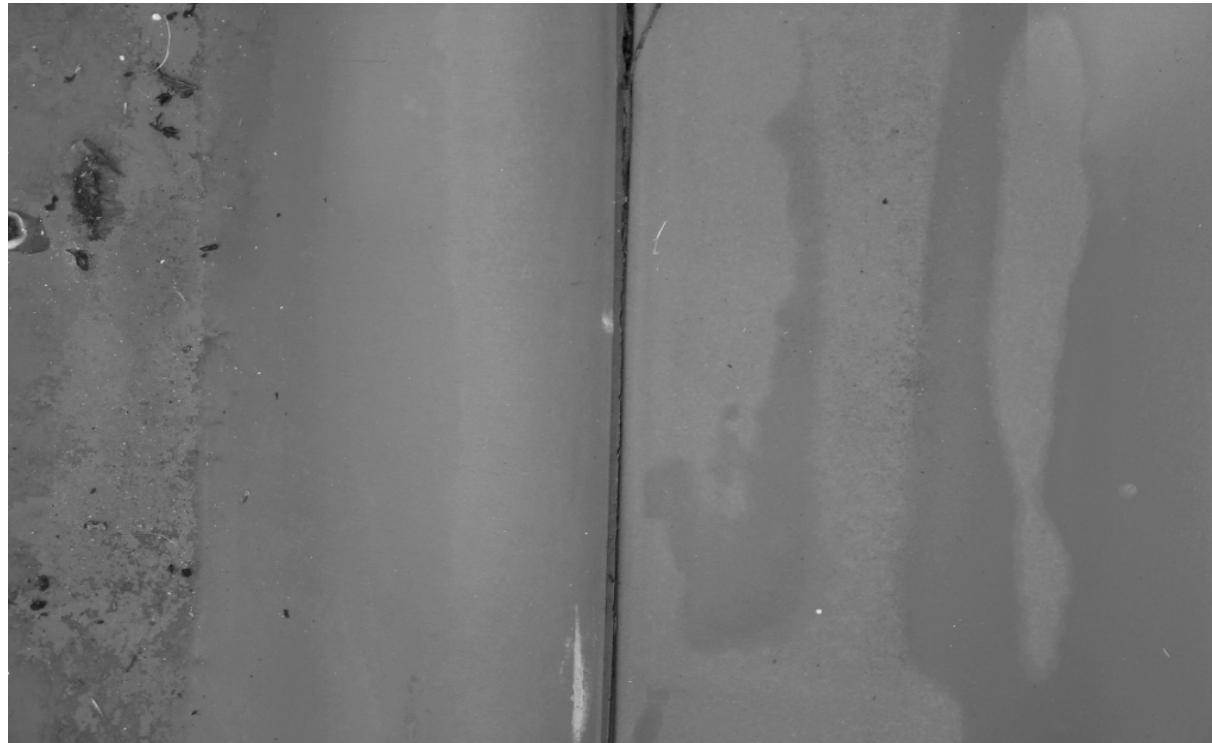


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Comparison



unbeschichtete

beschichtete

Rooftiles after 1 Year Outdoor Exposure

Standardization in Germany:

The DIN Working Committee

DIN Deutsches Institut für Normung e.V.
Normenausschuss Materialprüfung (NMP)

Arbeitsausschuss NMP 293

"Photokatalyse"

Bericht

über die 01. Sitzung des NMP 293

"Photokatalyse"

am 09. Juni 2004 in Berlin

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Universität Hannover
Institut für Technische Chemie
Photochemie und Nanotechnologie



Standardization in Germany:

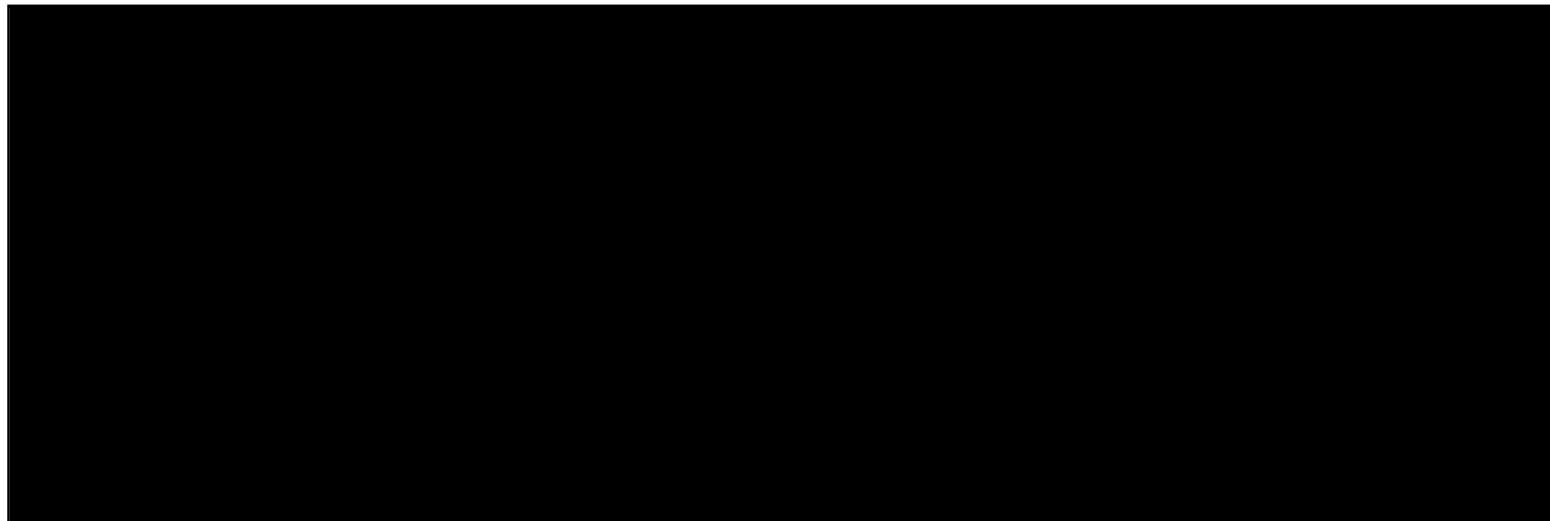
The DIN Working Committee Members

- Herr Ackerhans/Erlus Baustoffwerke AG
- Herr Bahnemann/Universität Hannover
- Herr Biedermann/Titam Oberflächenschutz
- Herr Goer/Pilkington Deutschland AG
- Herr Mannheim/Deutsche Steinzeug AG
- Herr Menzel/Degussa AG
- Herr Plüschke/Dachziegelwerke Nelskamp GmbH
- Herr Proft/SACHTLEBEN Chemie GmbH
- Herr Naumann/CC-NanoChem
- Herr Rubbert/Saint Gobain Glass
- Herr Suthoff/Profine GmbH



Standardization in Germany:

The New DIN Working Committee Members



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Standardization in Germany:

The DIN Working Programme

NMP 293 beginnt mit der Normung von Prüfverfahren für photokatalytische Effekte auf Oberflächen als Grundlage für zu erarbeitende Anforderungsnormen.

Als Rahmen-Arbeitsprogramm wurden folgende Schwerpunkte festgehalten:

- Prüfverfahren für photokatalytischen Abbau von chemischen und biologischen Modellsystemen;
- Prüfverfahren für photoinduziertes Benetzungsverhalten;
- Prüfverfahren für photophysikalische Effekte.

Die Erarbeitung des Arbeitsprogrammes soll mit folgenden Arbeitsschritten vorangebracht werden:

- Bewertung und Vereinheitlichung von bereits vorhandenen, internen Prüfvorschriften;
- Festlegung einer Prioritätenliste;
- Bewertung von internationalen Normungsvorschlägen;
- Definition von Standard-Beleuchtungsbedingungen;
- Initiierung eines Technischen Komitees bei CEN.



Concluding Remarks

Part I: Basic Studies

■ Mechanistic Investigations

- Slow Reaction of e^- with O_2
- Different Energetic Trap Levels for h^+
- The Antenna Mechanism
- The Thermal Deaggregation Mechanism



Concluding Remarks

Part II: Applications

■ Water Treatment

- Complex Reaction Mechanisms
- The DSSR Reactor & the ACP Concept
- The TFFBR Reactor
- Beyond the Pilot Plant Scale

■ Self-Cleaning Surfaces

- Transparent Coatings are (easily?) prepared
- Photocatalytic Properties are quantifiable
- Improvement through Fe and/or Y doping



The Research Team

Research Group during the Sommer 2003

On the picture:

- *Mohammad Muneer*
- *Sven Brumma*
- *Cecilia Mendive-Hansmann*
- *Dirk Scheffler*
- *Detlef Bahnemann*
- *Volker Selzer*
- *Lei Liu*

Not shown:

- *Dirk Hufschmidt*
- *Siham Yousef Al-Qaradawi*
- *Anja Hülsewig*



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Now you may relax...



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...since I am no longer in your way!



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