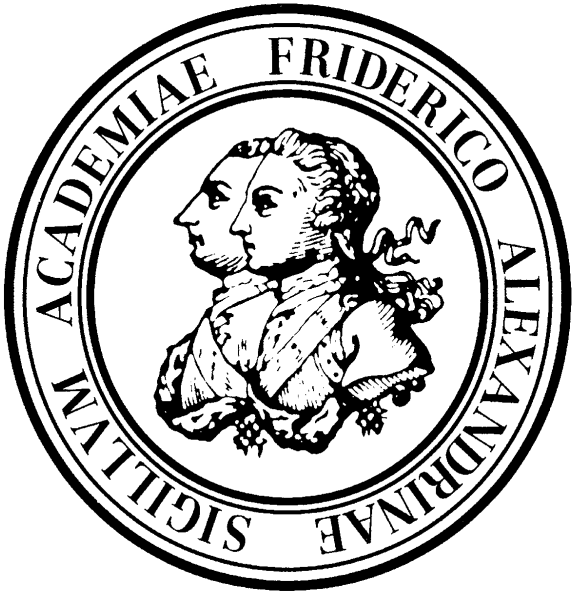
C- and C,N – Modified Titania for Visible Light Photocatalysis



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Direct and Indirect SC Photocatalysis

TiO_2

Aerobic photooxidation

UV!

Primary Processes

Rates and Quantum Yields

*Angew. Chem. 2010 (*problem of comparison*)*

Light Absorbing species ?

C-H Activation

$$R\text{-}H + SO_2 + 1/2\ O_2 \xrightarrow{UV} RSO_3H$$

Industry: UV light is essential
10-14 kW High Pressure Mercury Lamps !

Photoinduced radical chain reaction (Bunsen!)

Titania / n-heptane: Vis (!) Addition Reaction

Proposed Mechanism

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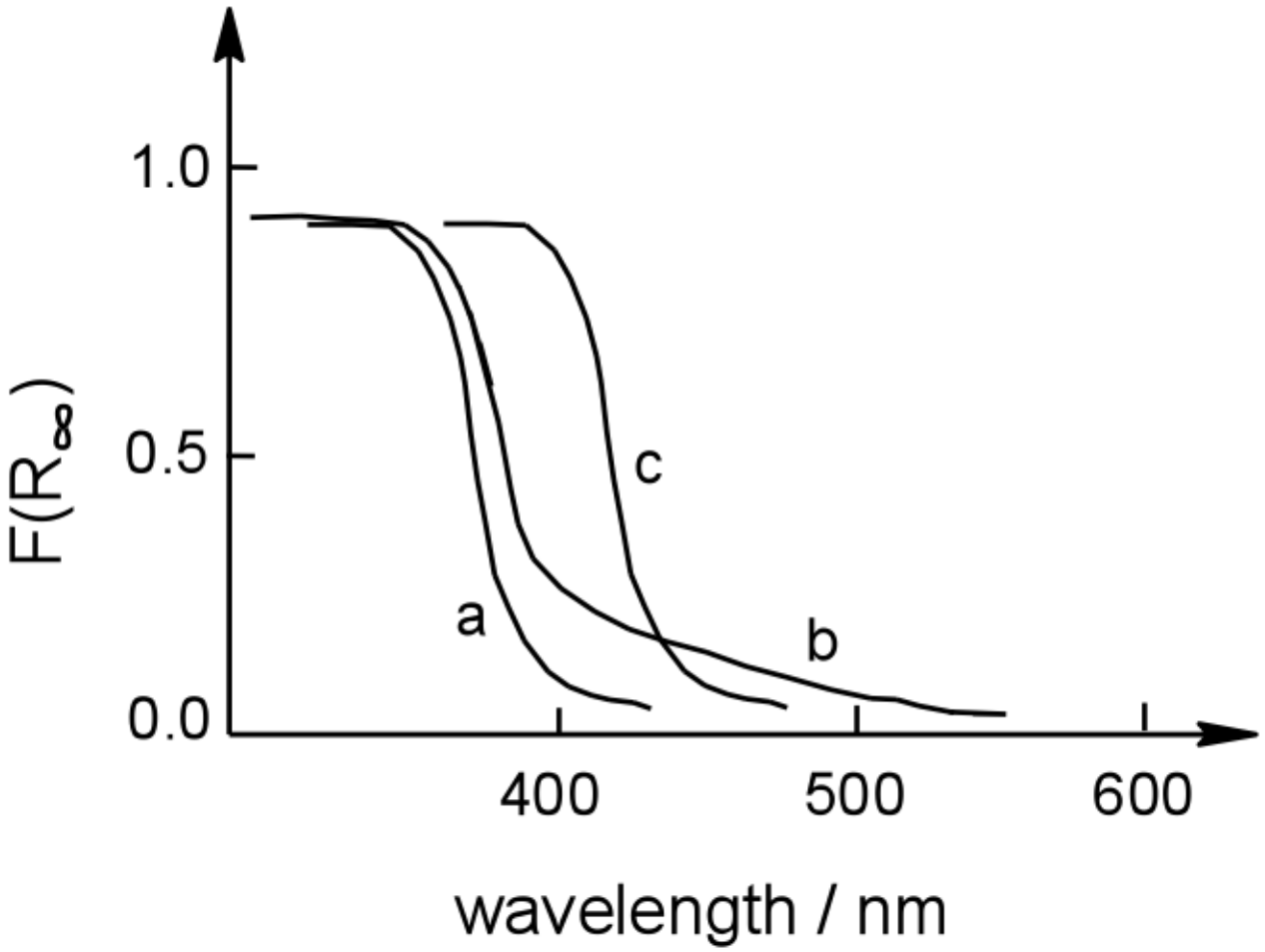
Self sensitization.

„Carbon“ and „Nitrogen“ Modified Titania

- Weak visible absorption
- Doping?
- Sensitization?
- Nature of „C-“ and „N-doped“ titania?
- Location of new energy levels?

Diffuse Reflectance Spectra

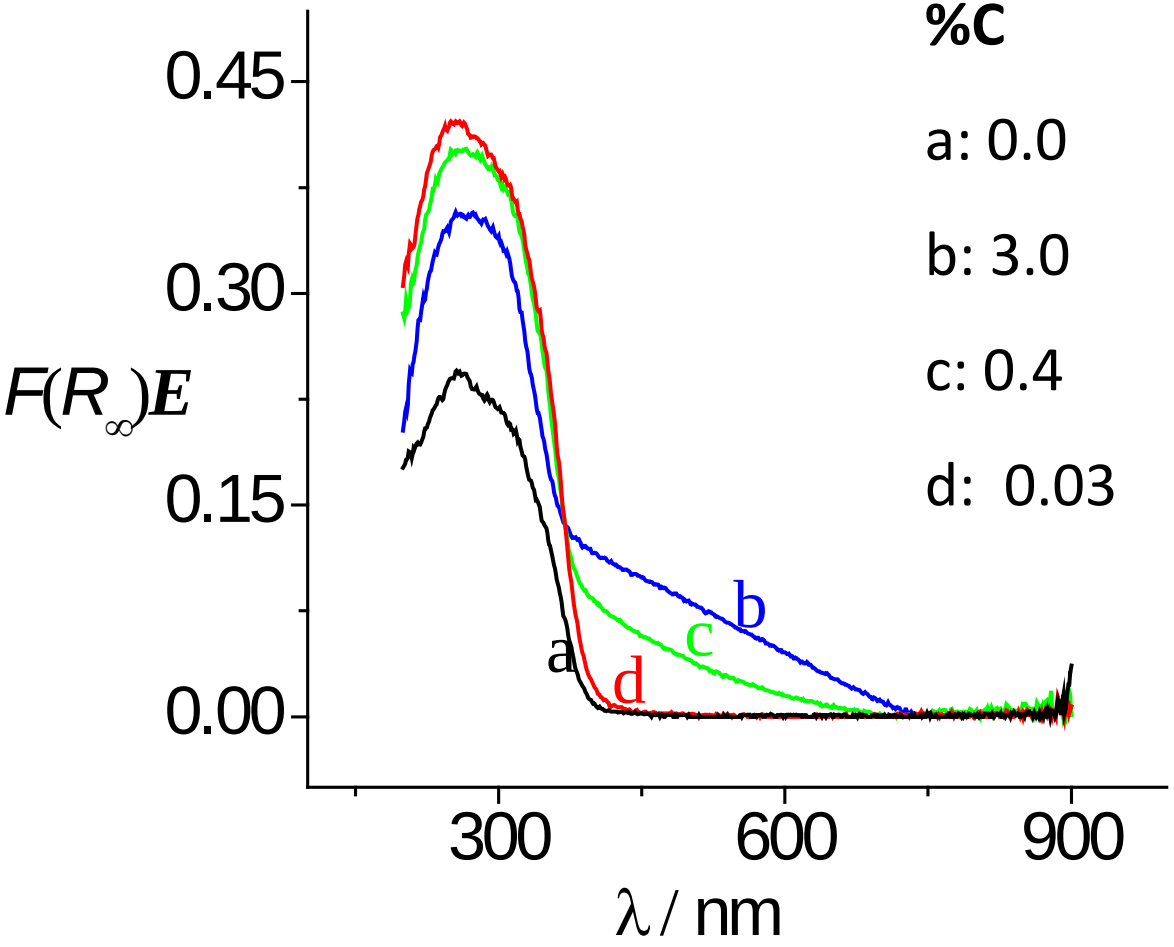


C-Modified Titania

- $TiCl_4$ + NBu_4OH, 400 °C. (Or surface modification)
- 0.4 – 3% C, anatase
- XPS C1s: 285 eV (C); 287, 288 eV (carbonate)
- Quasi Fermi Level shift from -0.54 to -0.48 / -0.39 V
- Bandgap narrowing ~ 0.14 eV, E_{vb} = 2.63 V (const.)
- Improved Daylight Photocatalytic Activity (rel. to TiO_2-N)

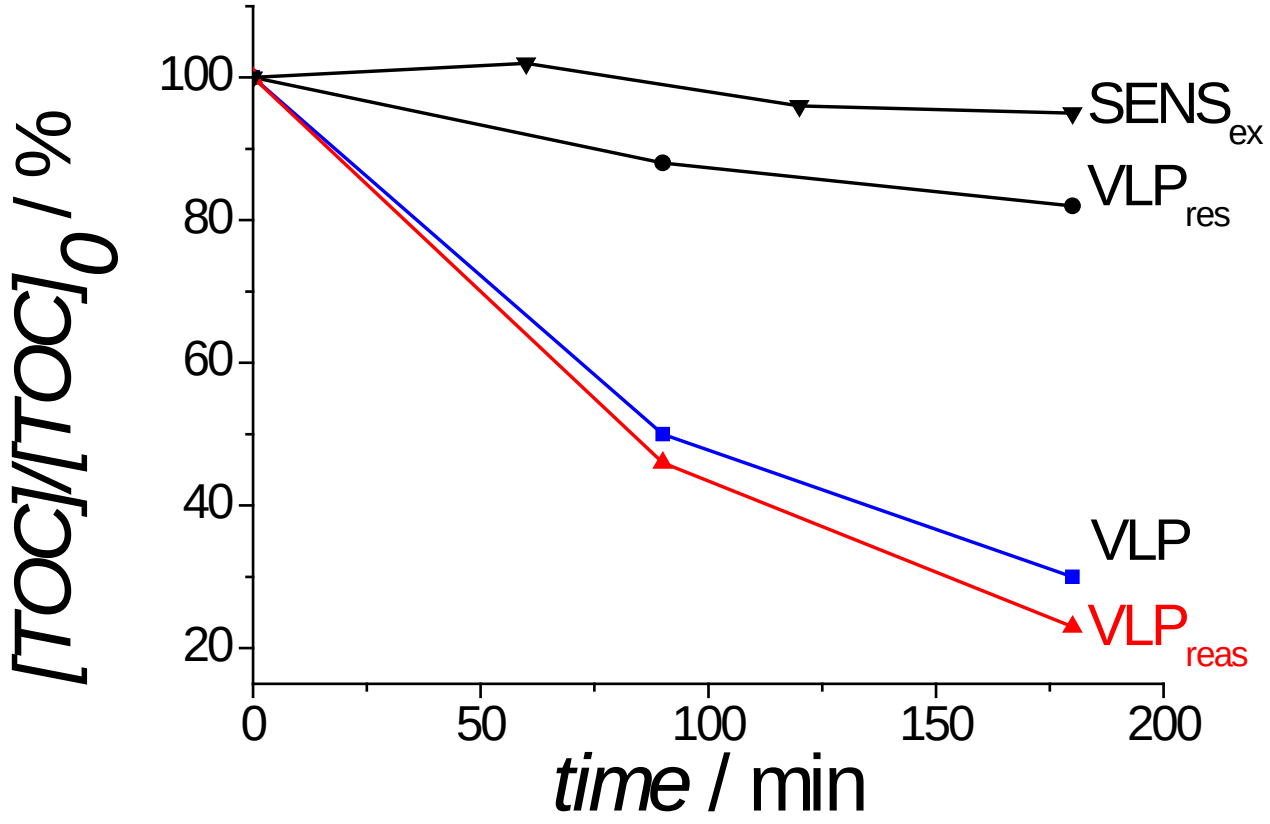
Appl Catal. B. 2001 (H.K., F.-W. Maier), Angew.Chem. 2002

TiO_2-C - Absorbance and Activity



%C	rel. Rate (4-CP)
a: 0.0	1
b: 3.0	37
c: 0.4	76
d: 0.03	1

Mineralization of 4-Chlorophenol



[TiO_2]-O-CO-Ar / sensitizer!

J. Coord. Chem. 2010

„Nitrogen Doped“ (Modified?) TiO_2

- TiO_2 + $(NH_2)_2CO$ or Melamine, 400 °C, 1 h
- N 0.8-2.0, C 0.4-1,2%, anatase, 170 m2/g
- 7 – 10 nm crystals, μm aggregates
- XPS N1s: 400 eV (br, w), no peak at 396 eV (nitridic N)
- Quasi Fermi Level shift from -0.54 to -0.48 V
- beige, turns white upon alkali treatment at 100 °C

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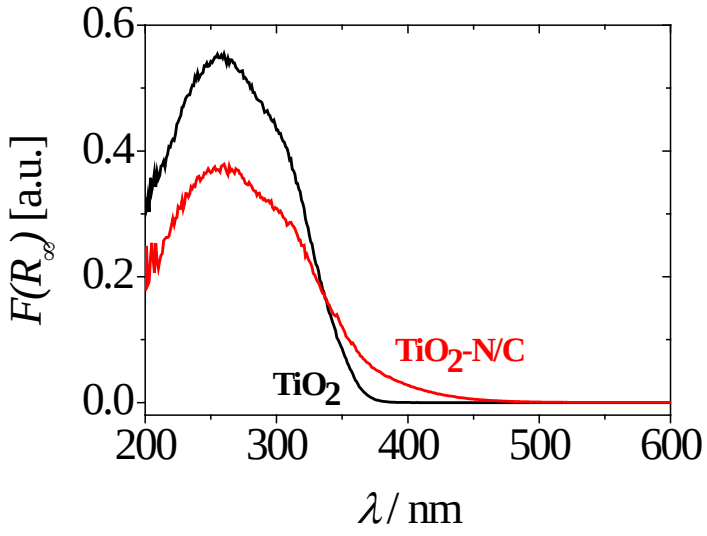
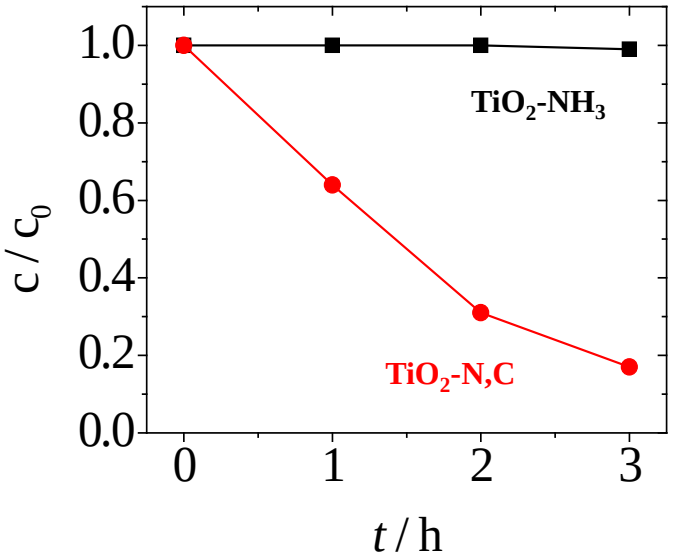
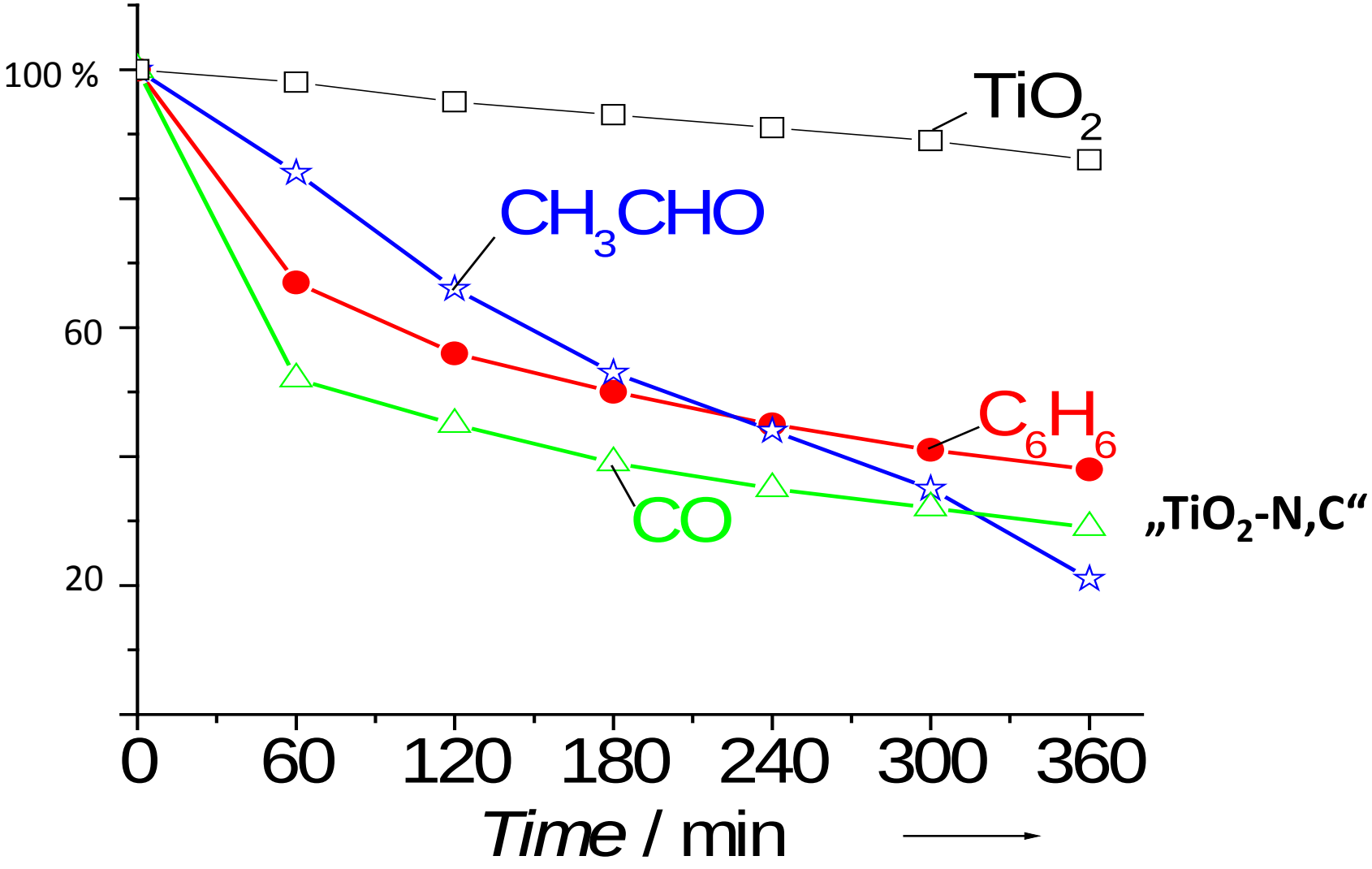
Nature of N-Precursor vs. Activity





$\lambda \geq 420$ nm

Diffuse Indoor Daylight Photocatalysis
Gas Phase



Melamine from Urea

Modification Mechanism

TiO_2-N (from NH_3) is inactive in HCOOH oxidation

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Desorption of Cyameluric Acid

TiO_2-N,C *Extract* *TiO_2-R*


AK
KISCH