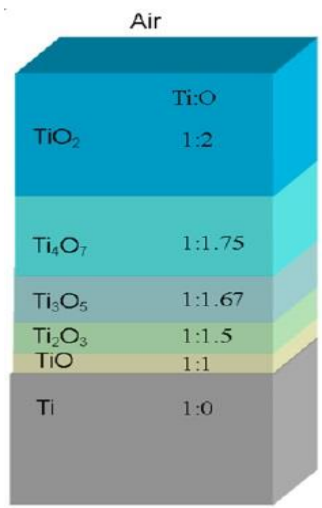
Нанопористый диоксид титана для фотокаталитических приложений



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Ш-К «Фотокатализ», Новосибирск, 07 октября 2022, пленарный доклад

Aim of this talk is

to pay attention on rapidly growing field of science devoted to the search and the synthesis of highly active semiconductor photocatalysts acting under **visible light**

This is important for: material science, green chemistry, hydrogen generation, clean water and clean air.

Photocatalysis under solar light gives

Green energy storage due to hydrogen production

Green purification of water and atmosphere

Green chemistry of selective organic synthesis, oxidation or reduction

Titanium dioxide is good for suncream

Plan of talk

1. **Introduction: which photocatalyst is good ?**
2. **Titania photocatalyst TiO_2, main properties**
3. **Synthesis and catalytic activity of TiO_2**
4. **Nonstoichiometry in TiO_{2-x}**
5. **Summary and mechanism of catalytic activity**

Which solar photocatalyst is good ?

1. Photocatalyst should be able to absorb visible light (E_g < 3.0 eV)

2. Ability of the catalyst to create electrons and holes

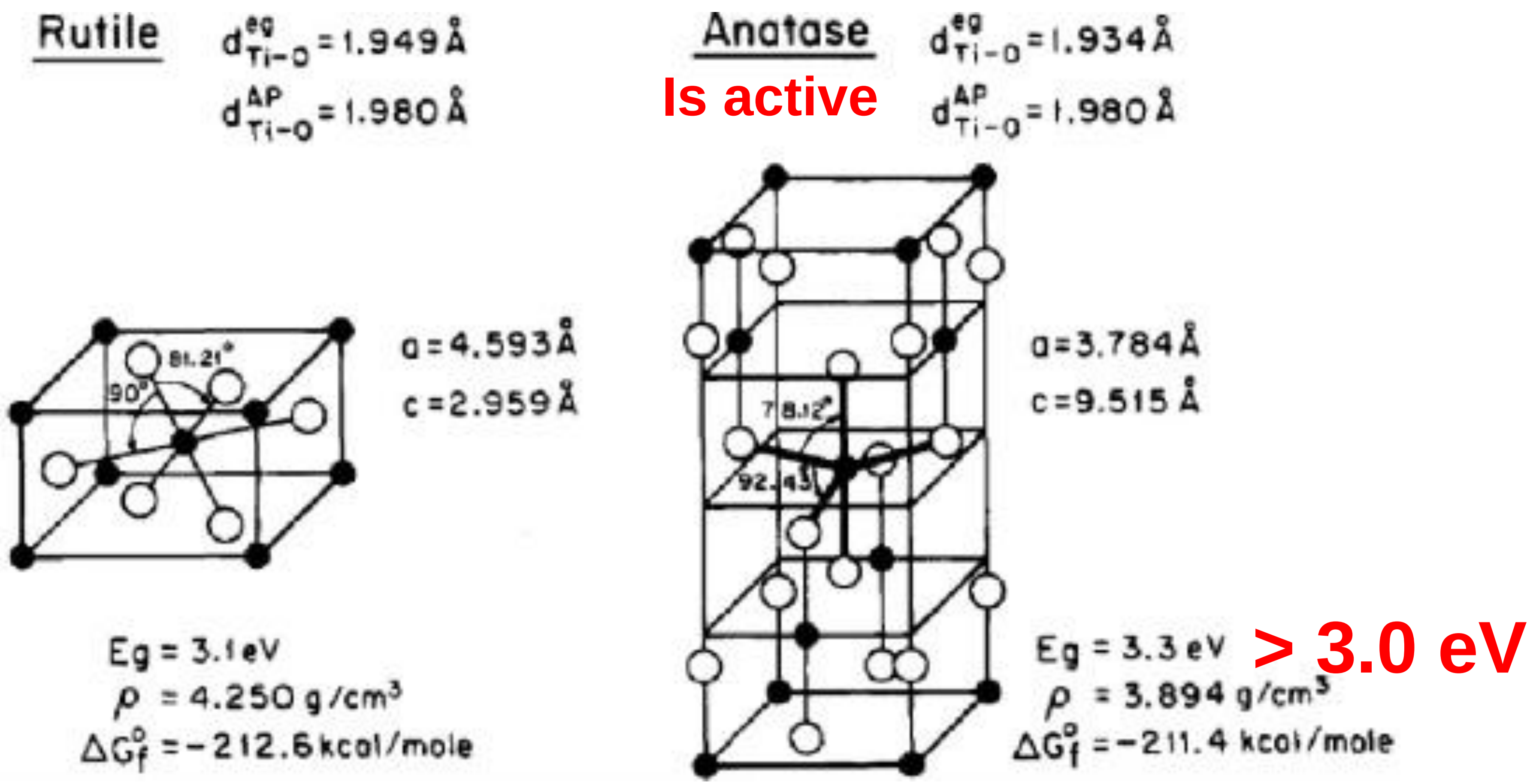
3. Created electrons and holes should be separated in space to avoid their recombination

4. Free radicals, which are generated by electrons and holes, for example, hydroxyl radicals, OH, should be able to undergo secondary reactions

5. Photocatalyst should be nanostructured (positive and negative size effect)

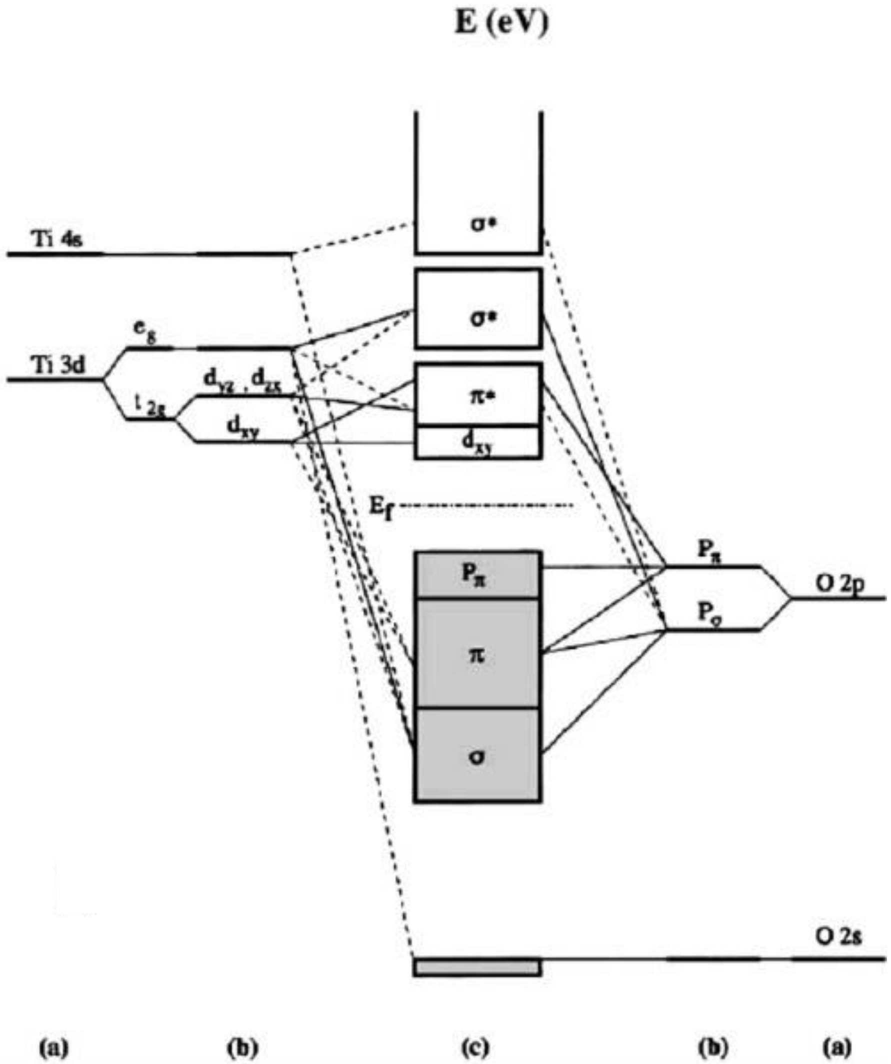
6. Photocatalyst should be chemically stable and catalytically active within operating time

Structure and semiconductor properties of TiO_2 modifications



The two crystal structures differ in the distortion of each octahedron and by the assembly pattern of the octahedra chains. In rutile, the octahedron shows a slight orthorhombic distortion; in anatase, the octahedron is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are larger, whereas the Ti-O distances are shorter than those in rutile.

Band gap of bulk and nano-TiO_2



Molecular-orbital bonding structure for anatase TiO_2: (a) atomic levels; (b) crystal-field split levels; (c) final interaction states. The thin-solid and dashed lines represent large and small contributions, respectively.

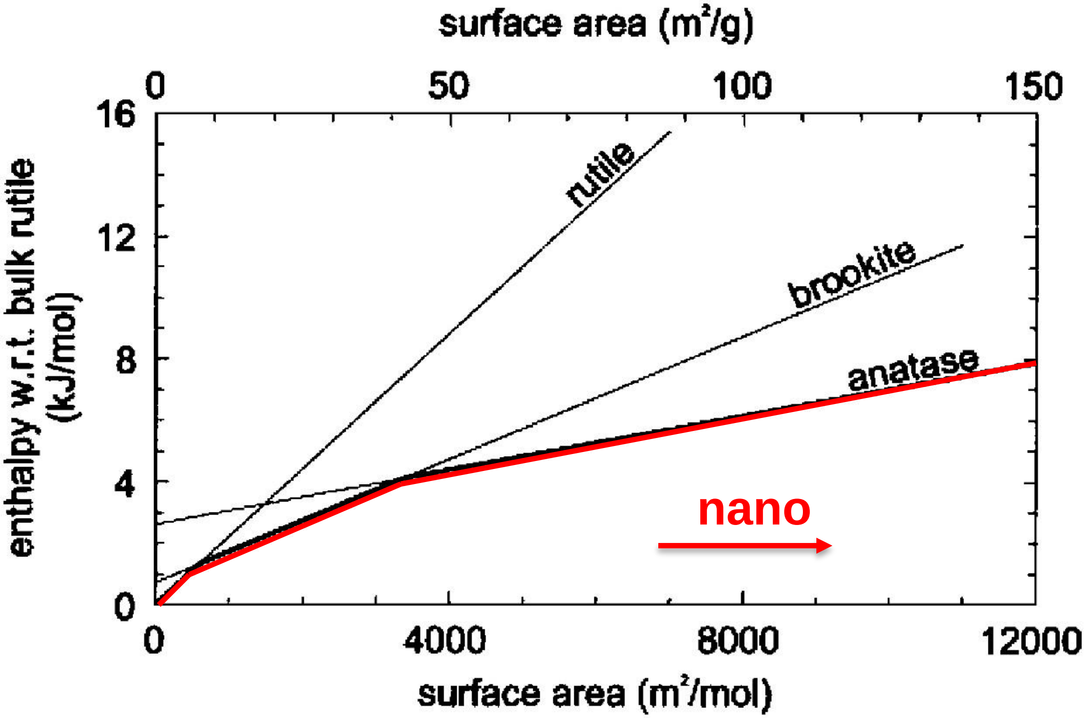
Quantum confinement size effects were observed for TiO_2 nanoparticles with a small apparent band gap blue shift (<0.1-0.2 eV) caused by quantum size effects for spherical particles sizes down to 2 nm. (due to the relatively high effective mass of carriers in TiO_2 and an exciton radius in the approximate range 0.75-1.90 nm)

Blue shift for nanosheets

$$\Delta E_g = \frac{h^2}{8\mu xz}\left(\frac{1}{L_x{}^2} + \frac{1}{L_z{}^2}\right) + \frac{h^2}{8\mu_y L_y{}^2}$$

where *h* is Plank’s constant, *μxz* and *μy* are the reduced effective masses of the excitons, and *Lx*, *Ly*, and *Lz* are the crystallite dimensions in the parallel and perpendicular directions with respect to the sheet, respectively.

Enthalpy of diferent modifications of nano-TiO_2

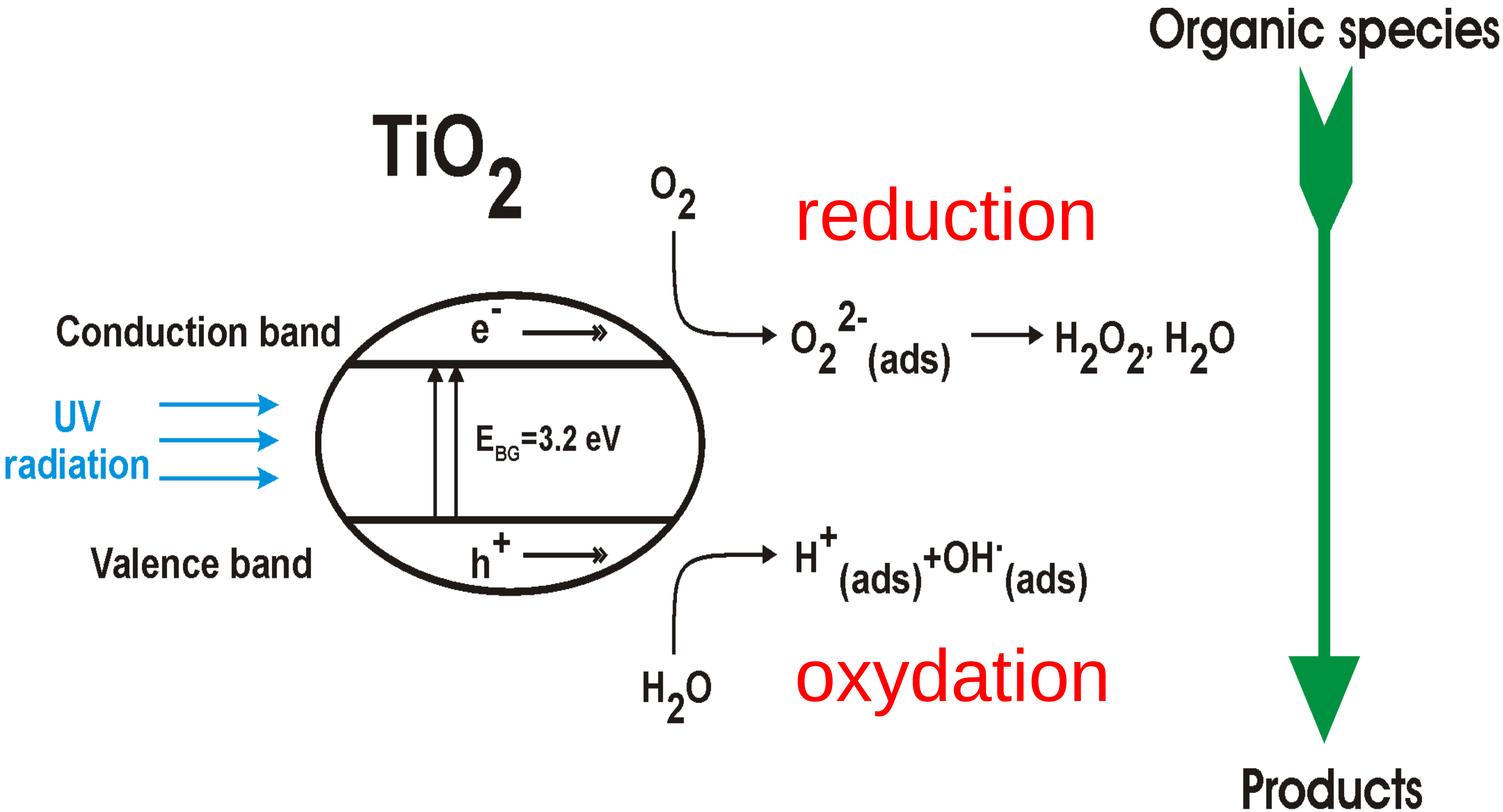


On heating concomitant with coarsening, the transformations are all seen: anatase to brookite to rutile, brookite to anatase to rutile, anatase to rutile, and brookite to rutile.

The transformation sequence and thermodynamic phase stability depended on the initial particle sizes of anatase and brookite

The **red** solid line represents the phases of lowest enthalpy as a function of surface area. Rutile was energetically stable for surface area < 592 m^2/mol (7 m^2/g or >200 nm), brookite was energetically stable from 592 to 3174 m^2/mol (7−40 m^2/g or 200−40 nm), and anatase was energetically stable for greater surface areas or smaller sizes (<40 nm).

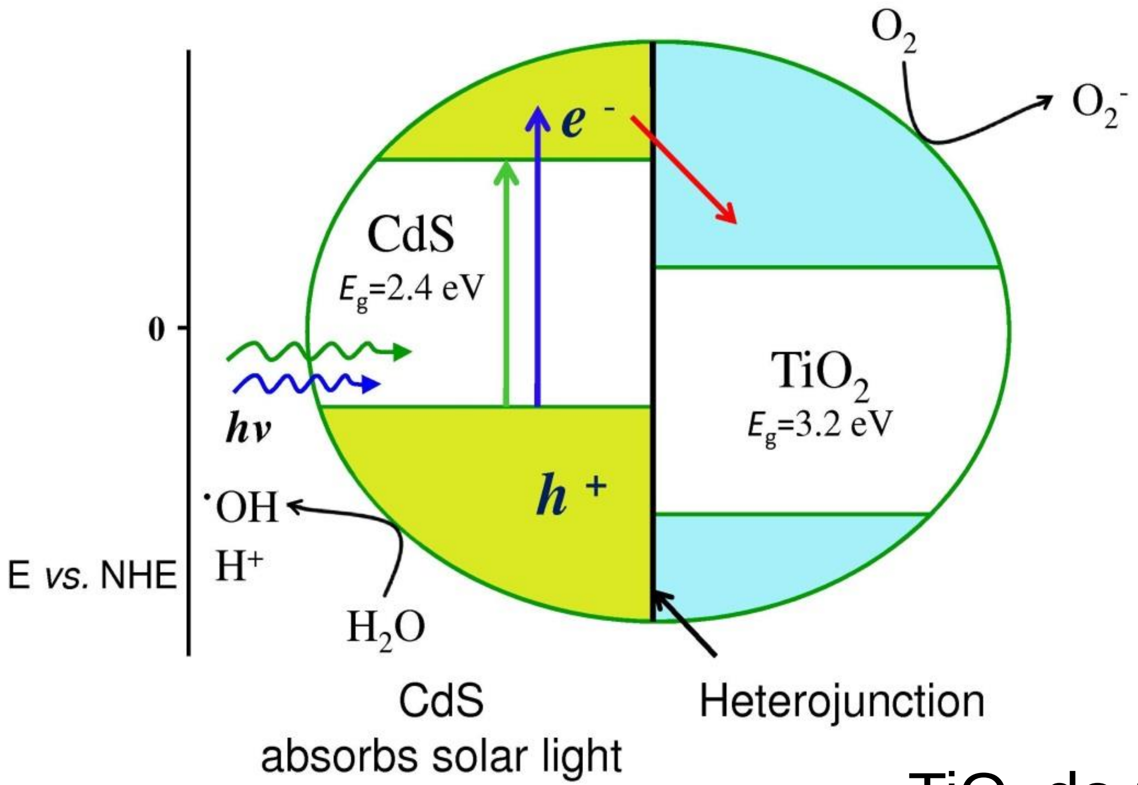
Titanium dioxide photocatalyst



Main disadvantage of TiO_2:
functioning exclusively under UV-irradiation (wave length shorter than 390 nm)

Model for catalytic activity of semiconductor nanocomposites under sunlight (λ < 515 nm)

$$2C_2H_5OH + O_2 = 2CH_3COH + 2H_2O$$



TiO_2 do not absorbs sunlight

Rempel A.A., Kozlova E.A. et al, CatCom. 2015

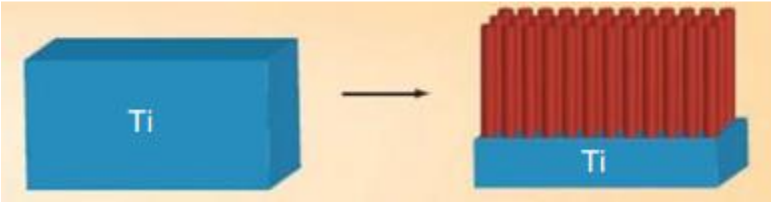
Synthesis techniques of nanoporous photocatalyst active under visible light

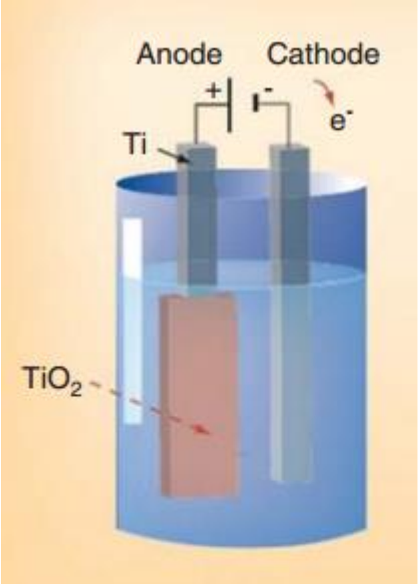
1. Anodization of metal at low temperatures to produce gradient of chemical composition or hetero-structure

2. Reduction of stoichiometric oxide in hydrogen atmosphere at elevated temperatures

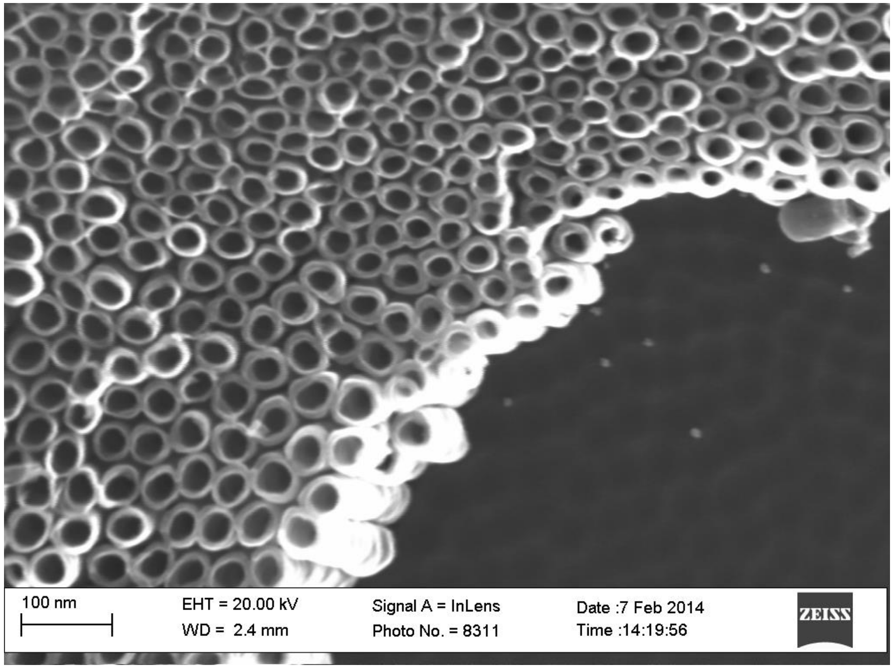
Nanotubular titanium dioxide film synthesis

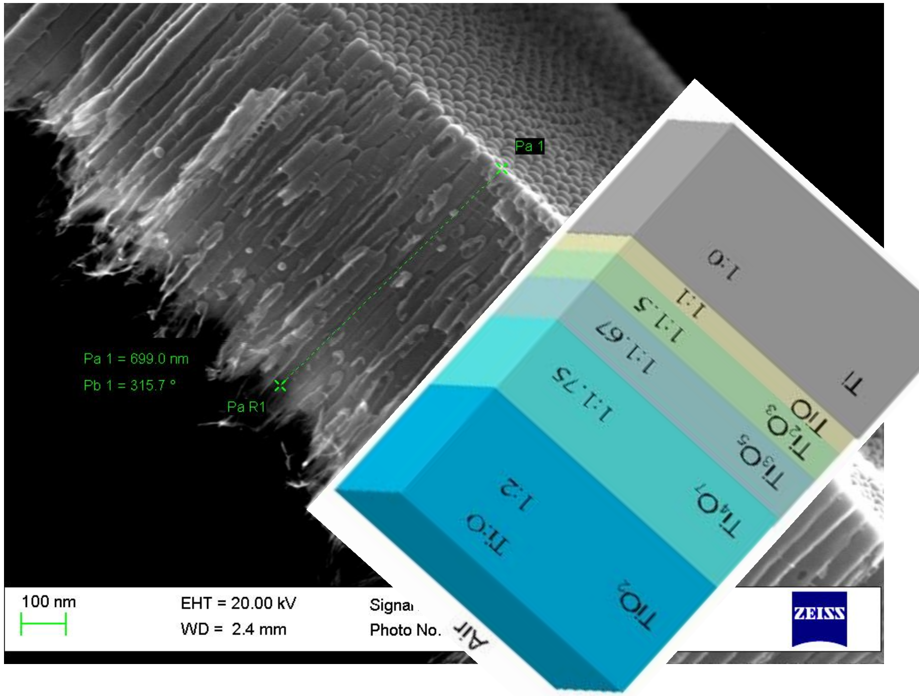
- Nanotubular TiO_2 film was synthesized by the anodic oxidation of a 100 μm thick titanium foil.
- Anodization was carried out potentiostatically at a voltage of 20 V and anodization time of 15, 30, 60, 120, 180 or 360 min.
- A solution of ethylene glycol and ammonium fluoride with the concentration equal to 1 wt. % was employed as the electrolyte.
- The area of the anodization for every sample was about 4 cm^2.

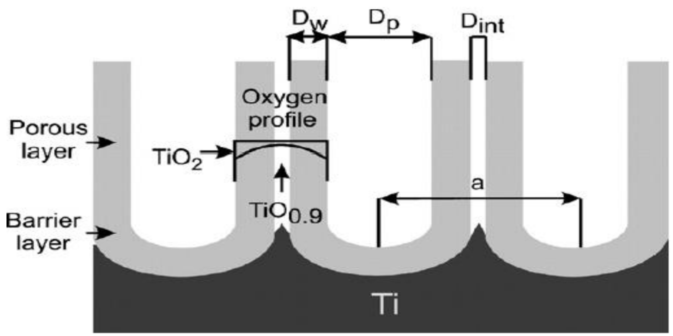




Nonstoichiometric titania nanotubes, produced by anodization of a Ti-foil







NH_4F (1 wt.%) + $C_2H_4(OH)_2$, 20 V, 300 K, 2 h

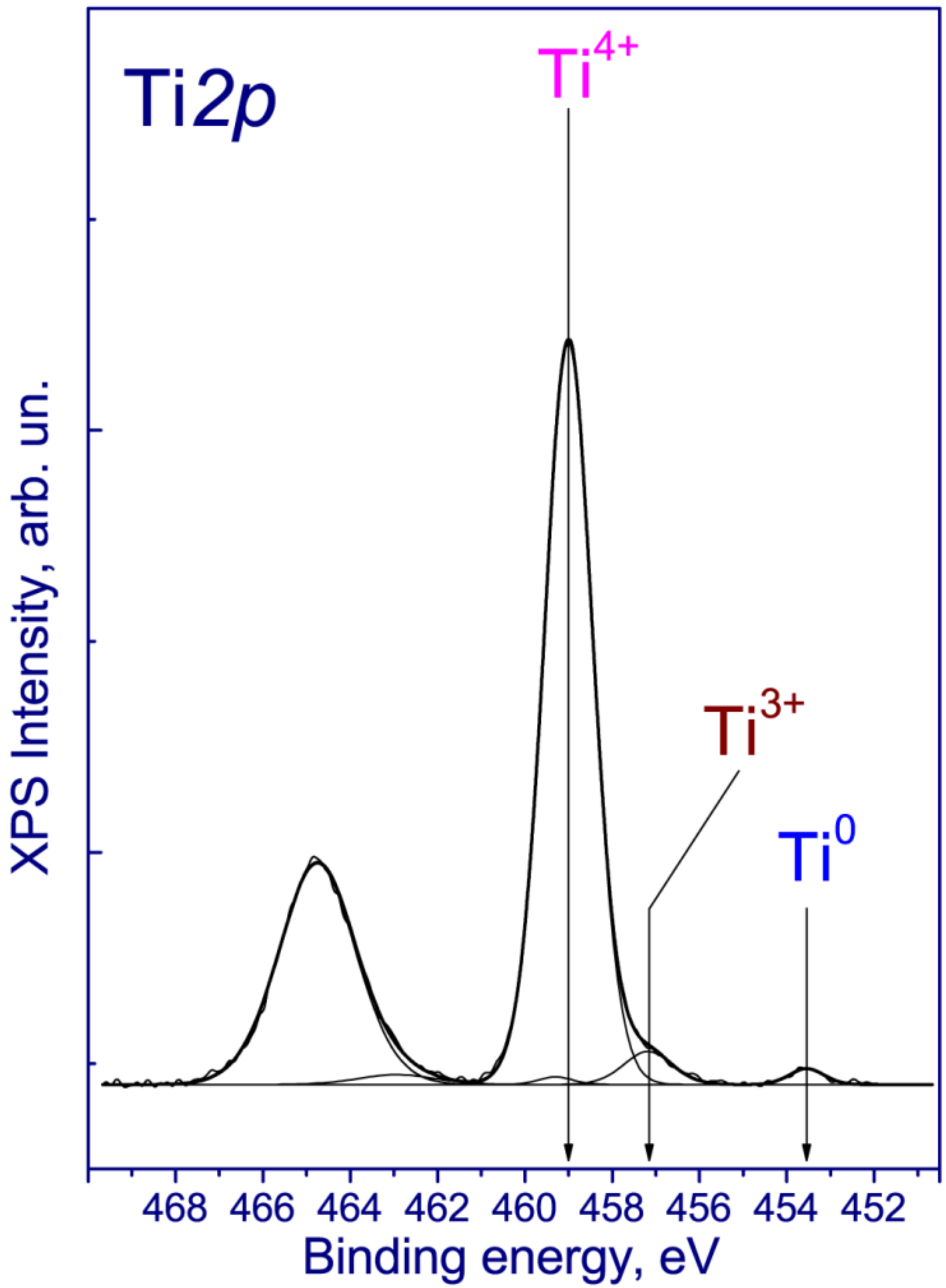
$Ti + xO^{2-} \longrightarrow TiO_x + 2xe^-$, $(1 < x < 2)$

$C_3H_5OH + 4O_2 \rightarrow 3CO_2 + 3H_2O$

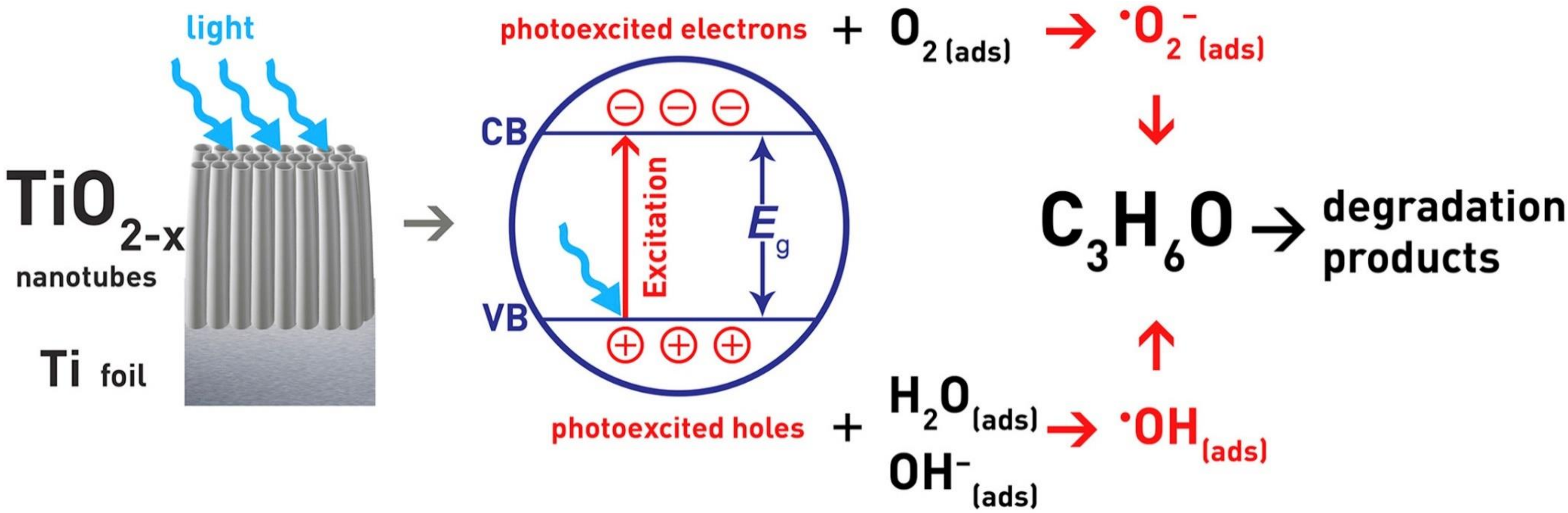
Catalytic activity is 5 times higher in compare to standard Degussa P25

Non-stoichiometry is approved by XPS of TiO_{2-x}

Ti^{3+} state appears in the vicinity of oxygen vacancy

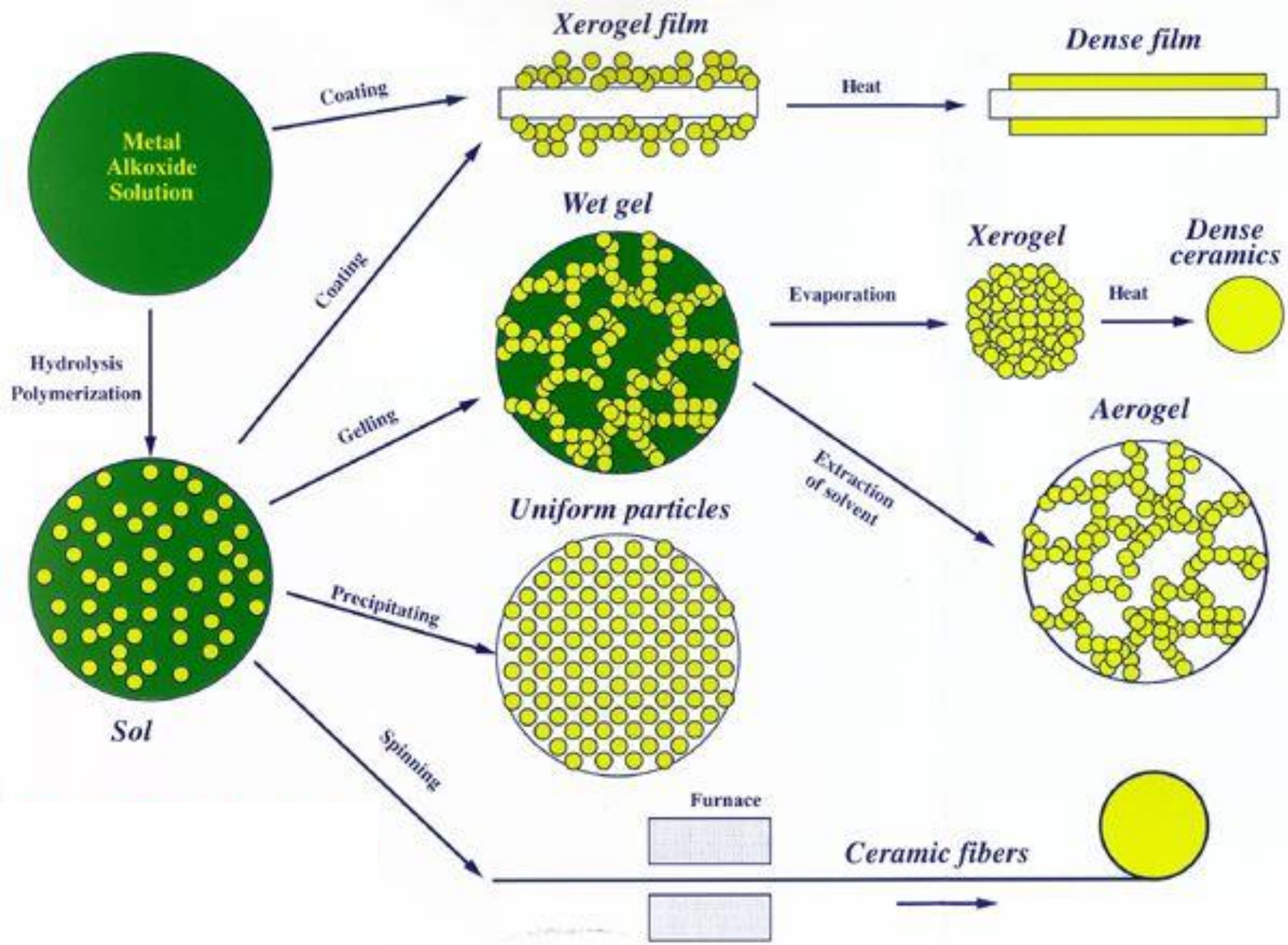


Catalytic reaction on TiO_{2-x} NTs

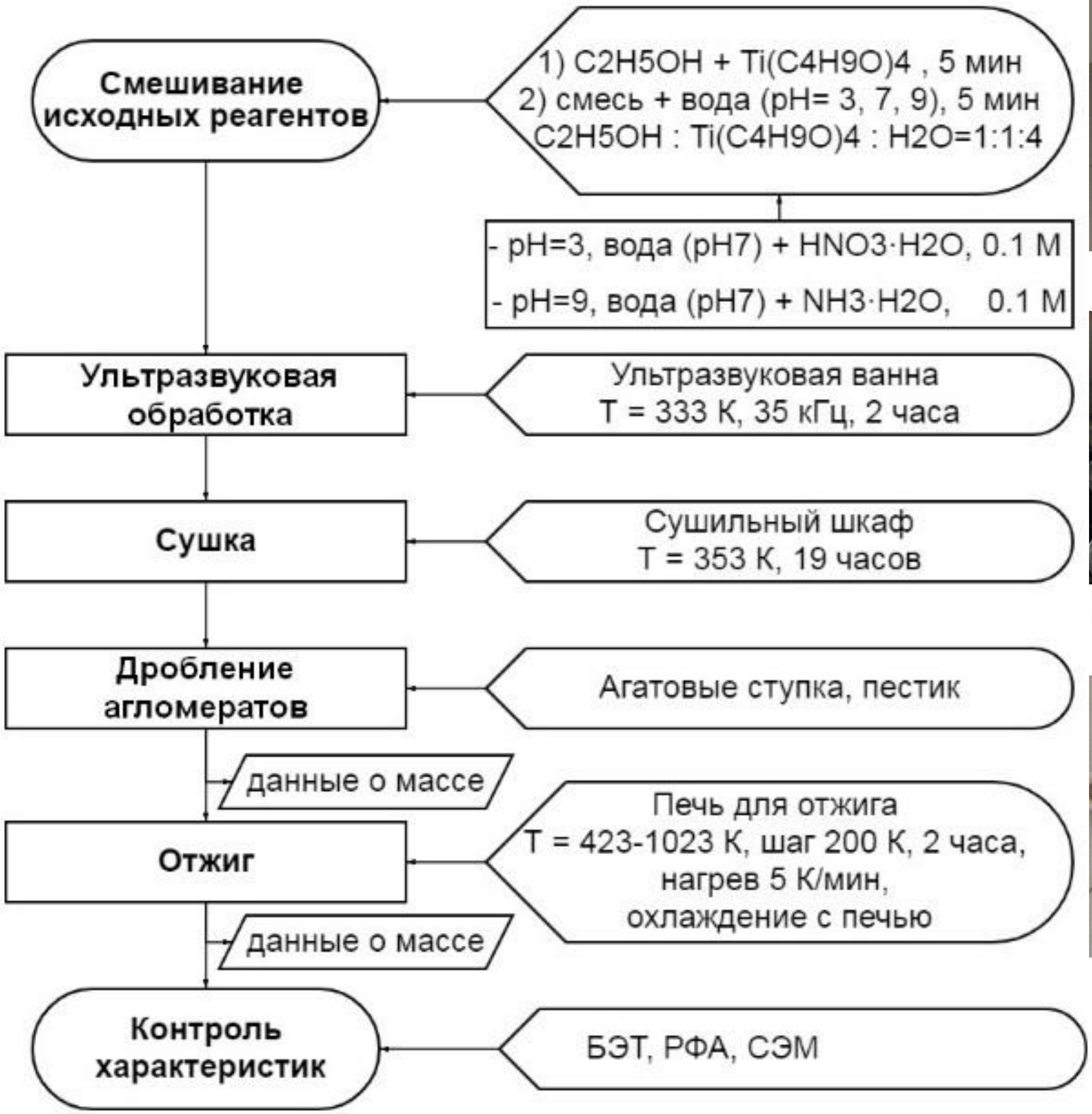


Journal of Alloys and Compounds, 2019

Sol-gel technology and products



Синтез нанопористого диоксида титана



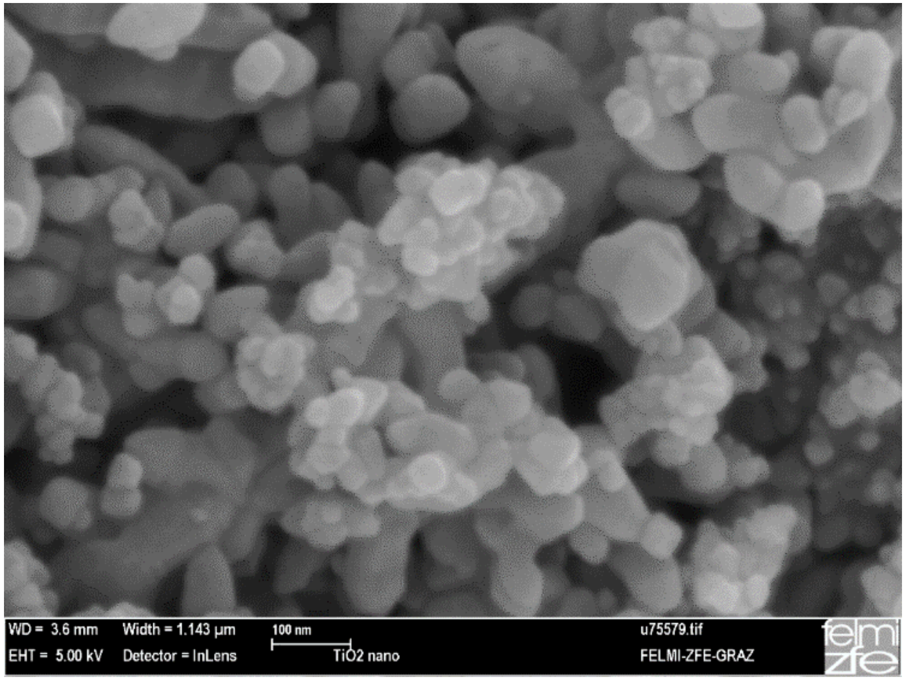
423 К и 623 К
после отжига

Sol-gel synthesis of TiO_2

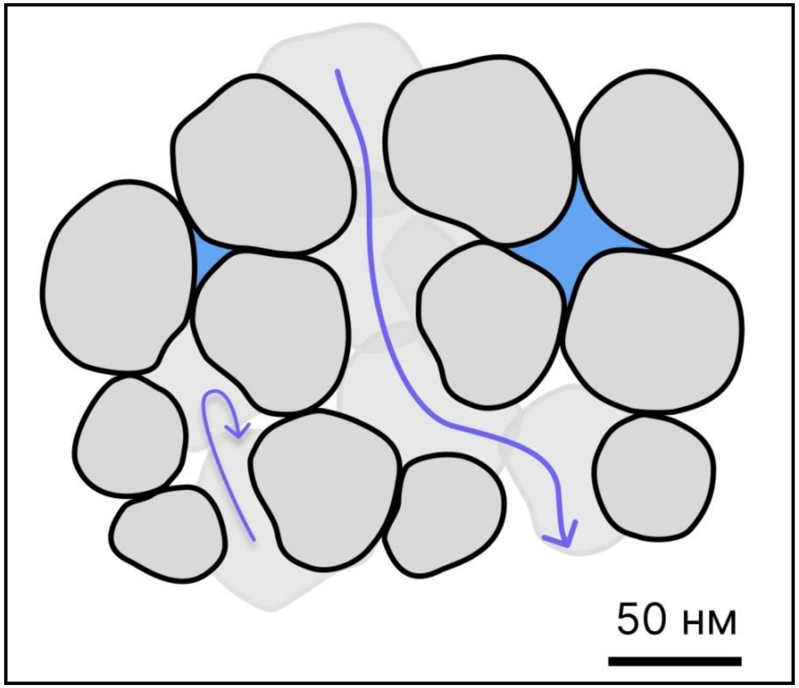
$Ti(OBu)_4$ was hydrolyzed according to the following procedure:

few mmol of $Ti(OBu)_4$ were added into the conical flask equipped with magnetic stirrer, water condenser and dropping funnel.

Stoichiometric titania

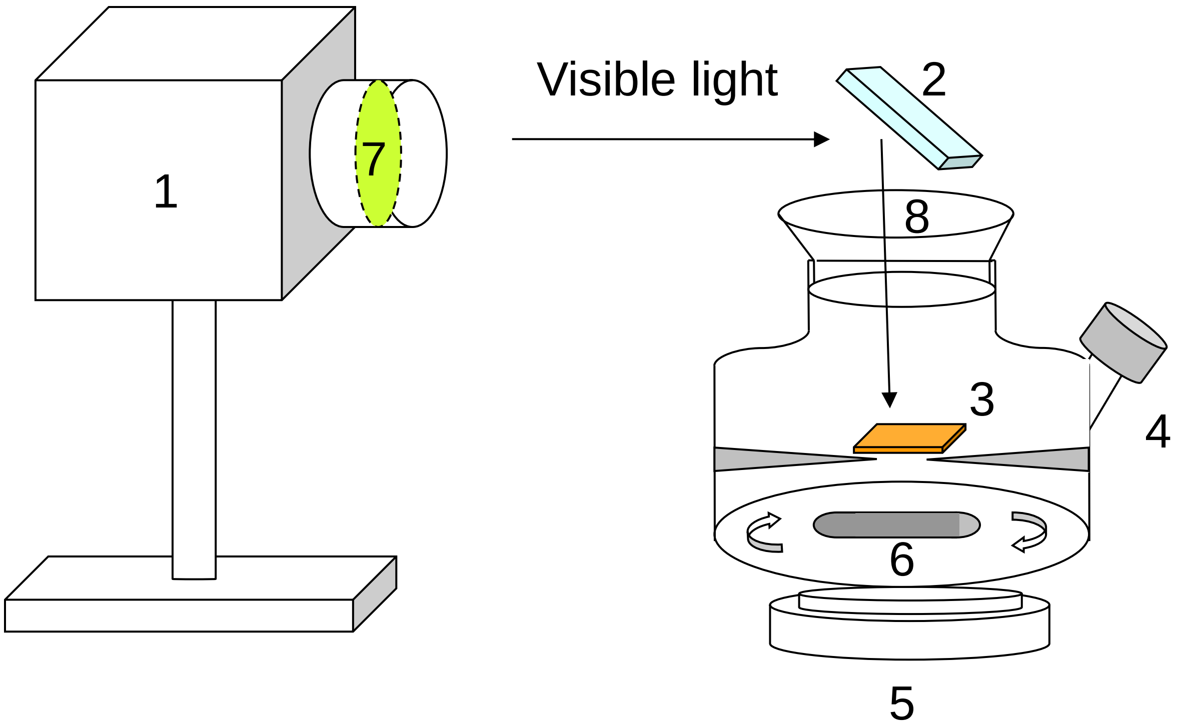


+ Annealing in hydrogen stream



Reaction setup

$$2CH_3\text{-}CH_2OH + O_2 = 2CH_3\text{-}COH + 2H_2O$$

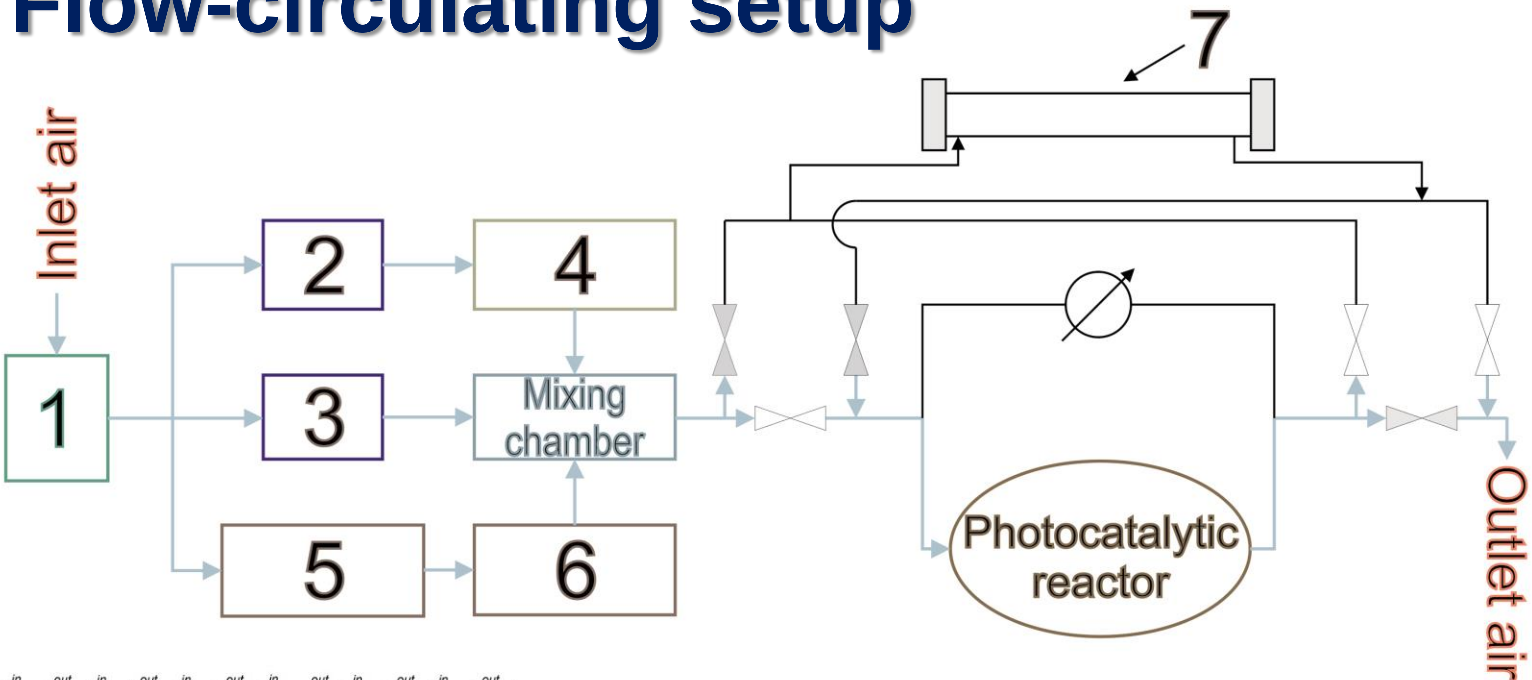


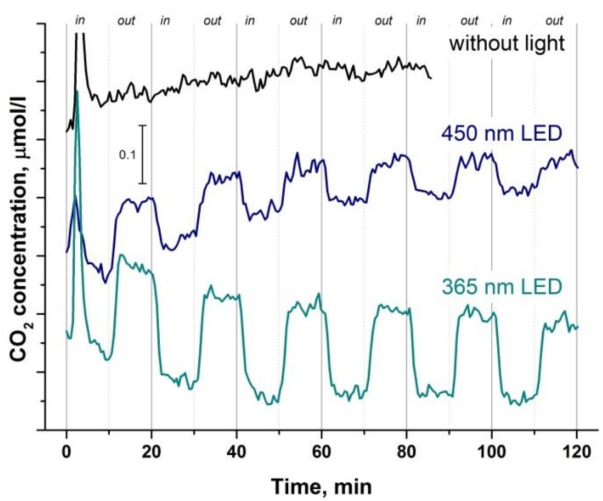
Reaction set-up:
1 – high pressure mercury lamp,
2 – mirror,
3 – supported photocatalyst,
4 – injector,
5 – magnetic stirrer,
6 – anchor,
7 – cut-off filter,
8 – quartz window

λ> 420 nm
Gas chromatography

Boreskov Institute, Novosibirsk

Flow-circulating setup





1. **Air purification system**
2. **Mass flow controller**
3. **Mass flow controller**
4. **Saturator with dist. water**
5. **Saturator with acetone**
6. **Microdispenser**
7. **Gas cell installed in IR spectrometer**

LEDs – 450 and 365 nm

$$C_3H_5OH+4O_2 \rightarrow 3CO_2+3H_2O$$

Aerobic oxidative C–H/C–H coupling of azaaromatics with nucleophiles by TiO_2 as a photocatalyst

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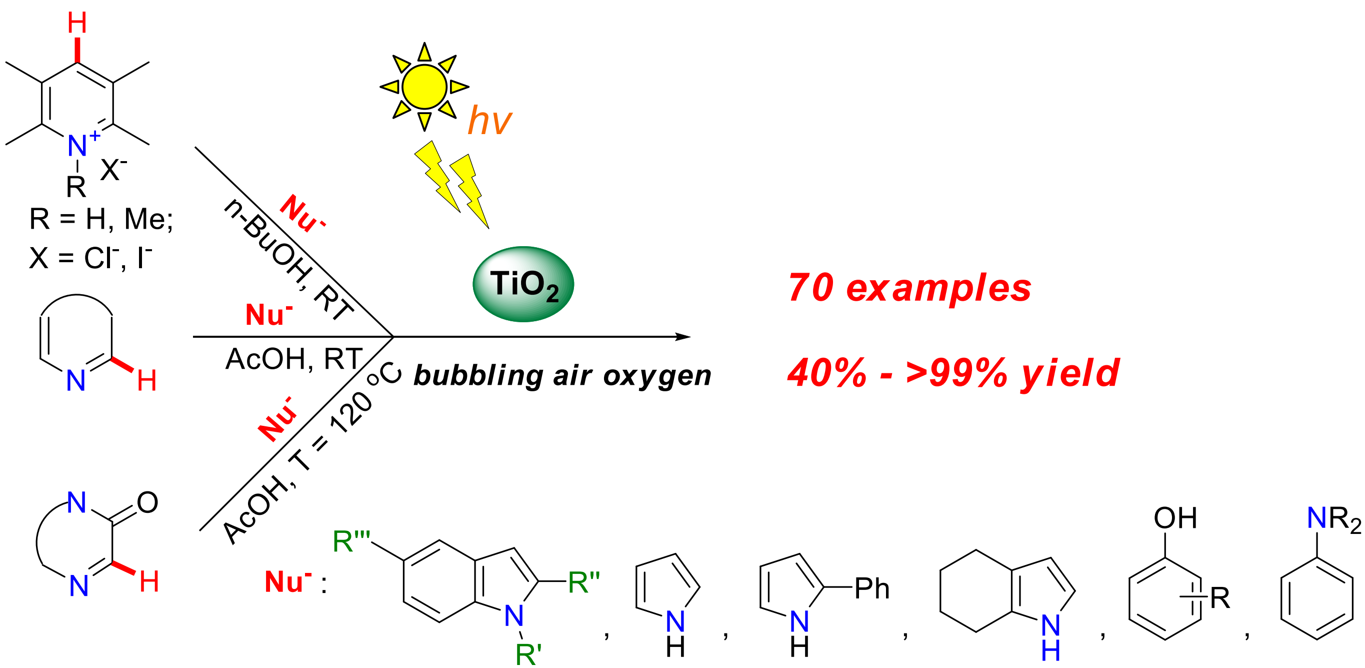
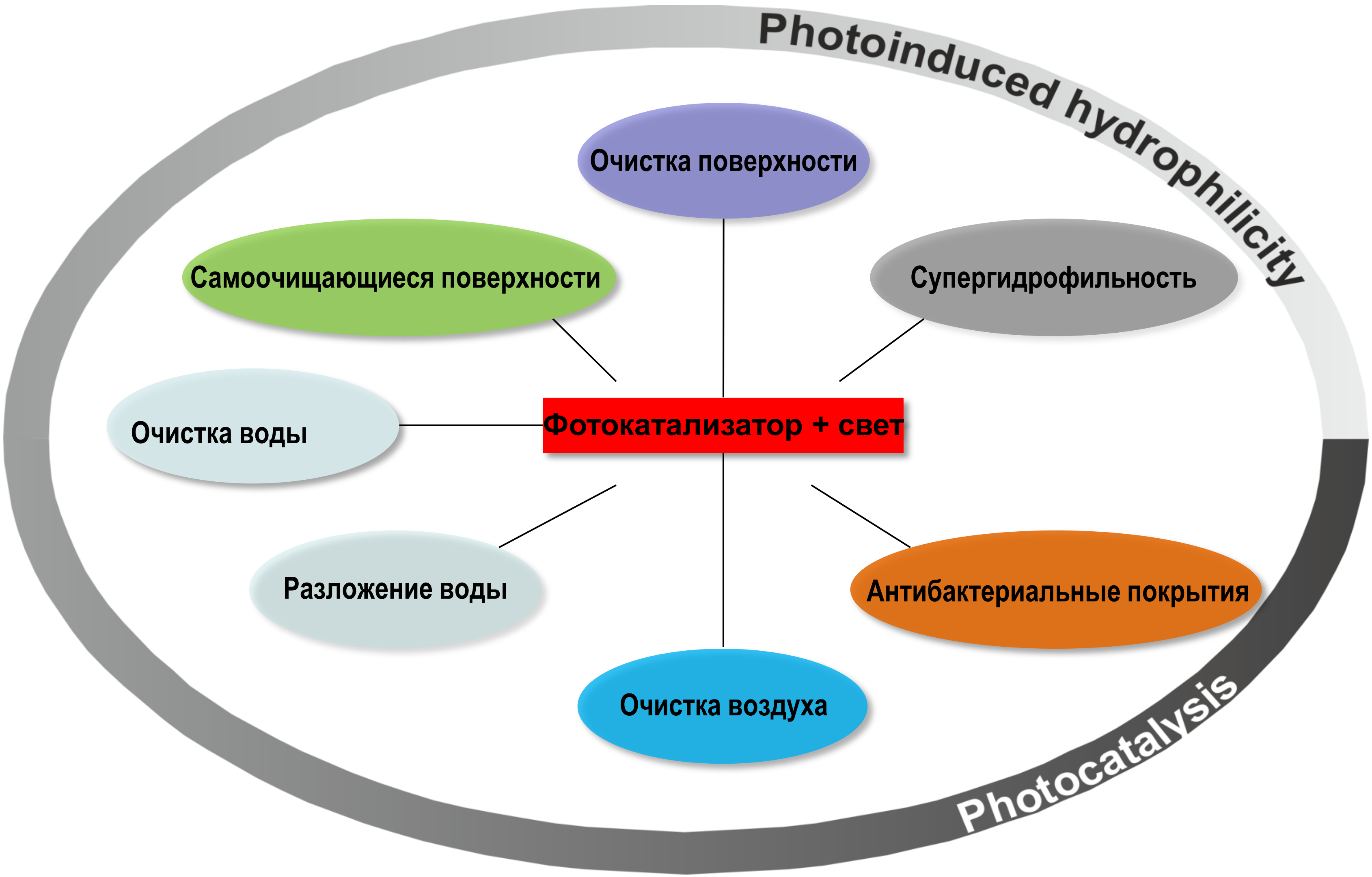
[a]Ural Federal University
[b]Institute of Organic Synthesis, the UB of the RAS
[c]Institute of Solid State Chemistry, the UB of the RAS



Published in 2015

Области применения фотокатализаторов



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