UNIVERSIDAD DE LAS PALMAS
DE GRAN CANARIA

ULPGC
GRUPO FEAM

Fundamentals of photocatalysis applications for water detoxification, trends and limitations

Group of Photocatalysis and Spectroscopy for Environmental Applications.

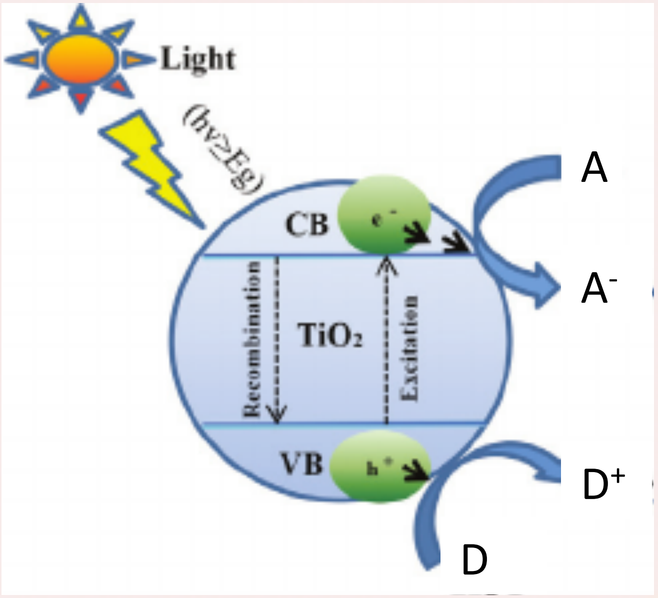
University of Las Palmas de Gran Canaria

2nd Summer School on Environmental Applications of Advanced Oxidation Processes

***Heterogeneous Photocatalysis* can be understood as a photoinduced redox process on the surface of a light activated solid catalyst.**

The catalyst should be a wide band gap semiconductor to photo-generate highly reducing electrons and highly oxidizing holes

The catalyst should have a high specific surface area.



PHOTOGENERATION:

$TiO_2 + h\nu \rightarrow TiO_2\ (e^-_{CB} + h^+_{VB})$

MIGRATION:

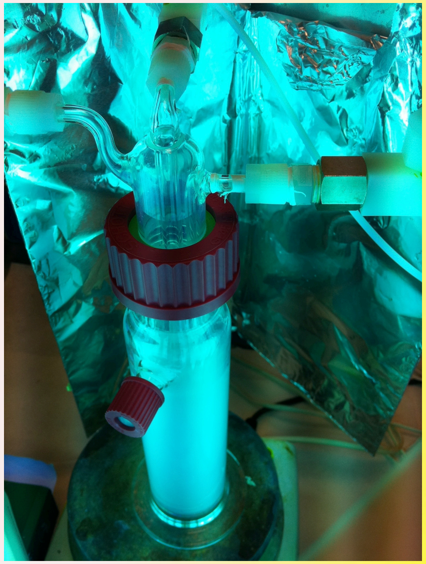
$(Ti^{IV})_{SURFACE} + e^-_{bc} \rightarrow (Ti^{III})_{SURFACE}$

$(Ti^{IV}\text{-}\ O^{2-}\ \text{-}\ Ti^{IV}) + h^+_{VB} \rightarrow (Ti^{IV}\text{-}\ O^{\cdot -}\ \text{-}\ Ti^{IV})$

RECOMBINATION:

$TiO_2 + e^-_{CB} + h^+_{VB} \rightarrow TiO_2 + Q$

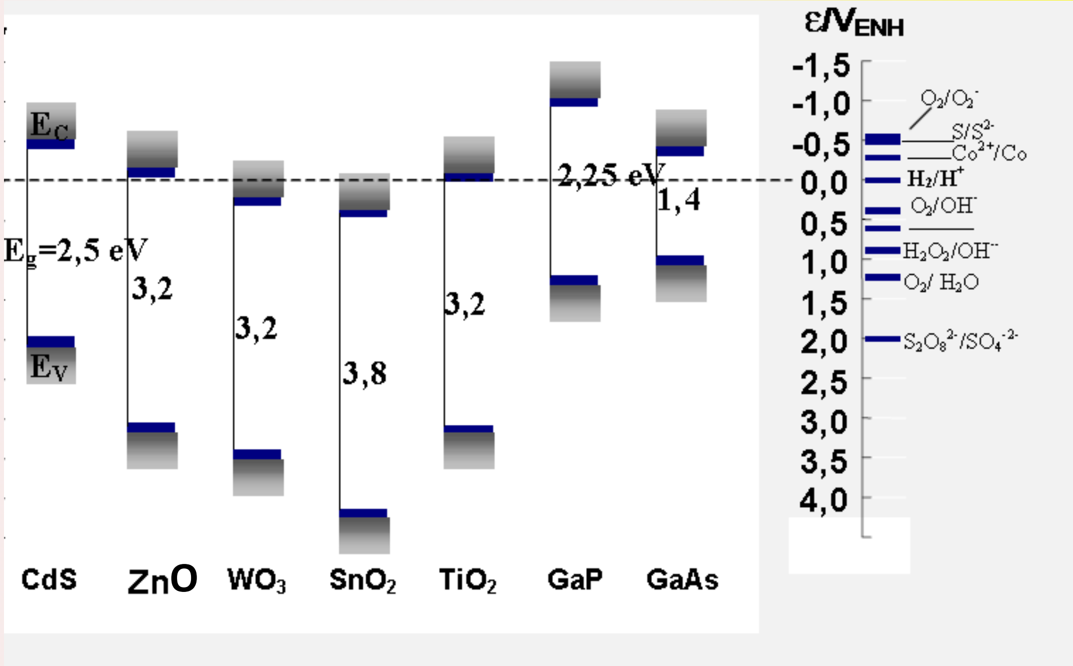
high specific surface area?



In order to have a high specific surface area, normally, a photocatalyst is used as powdery suspended slurry

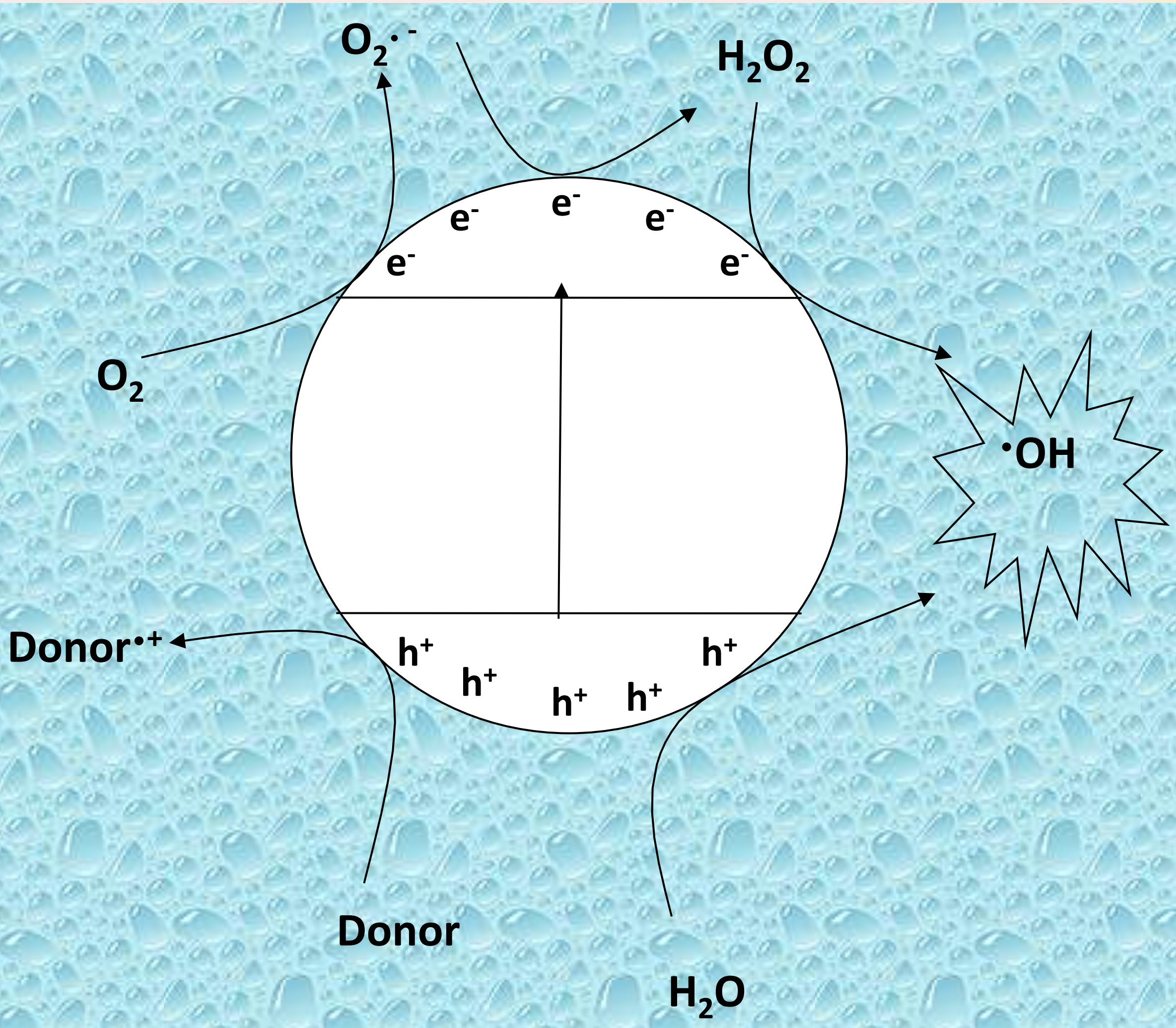
wide band gap semiconductor?

The CB bottom position must be more negative than standard electrode potential of an electron acceptor (oxidant) and the VB top position must be more positive than the standard electrode potential of an electron donor (reductant).

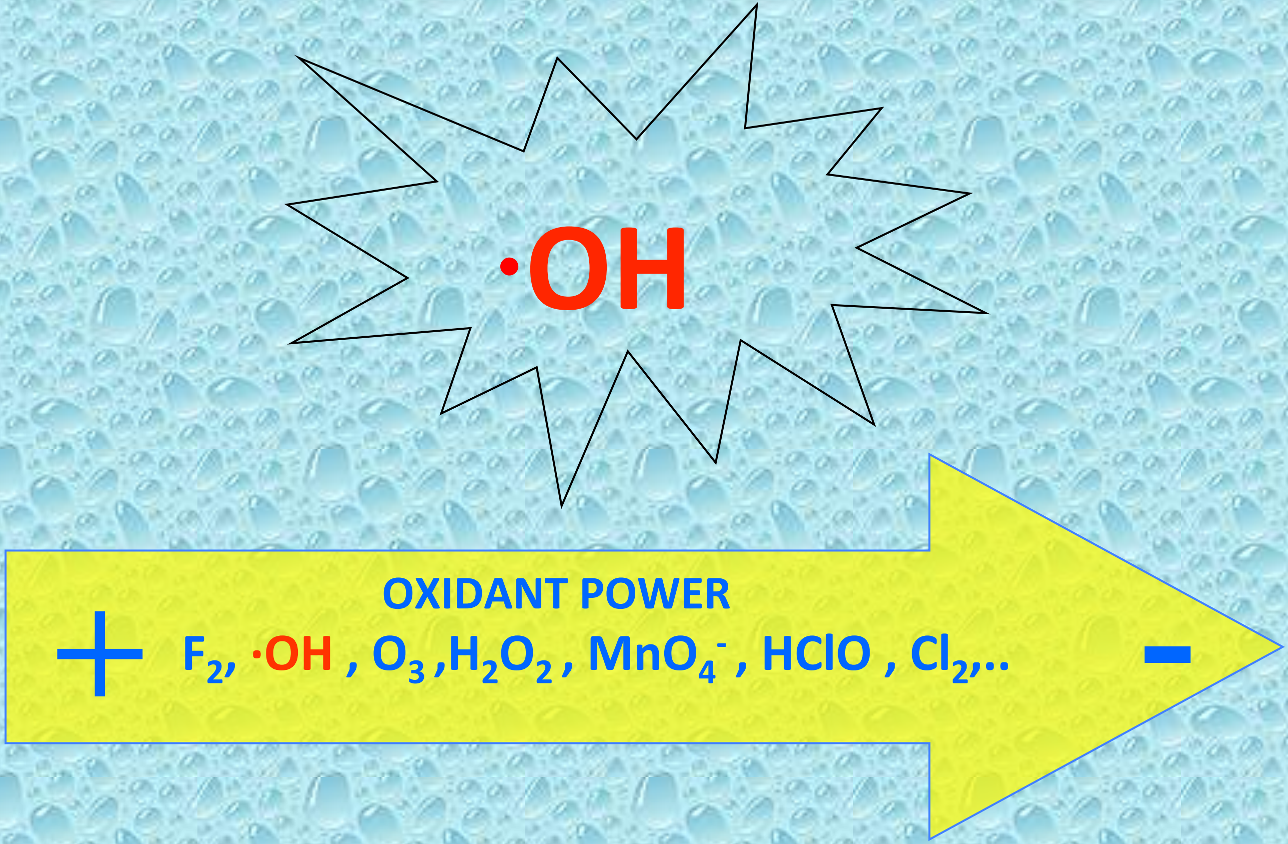


Only a few stable semiconductors have shown adequate characteristics.

For aqueous applications the predominat redox processes are oxidation of water by holes to produce ·OH radicals as a vehicle for the oxidation process and O_2 reduction for scavenging photogenerated electrons.



Semiconductor particle in aqueous media.



$\cdot OH$

OXIDANT POWER

\+ F_2, $\cdot OH$, O_3 ,H_2O_2 , MnO_4^- , HClO , Cl_2,.. –

Oxidation rate constant for different organic substances in presence of ·OH and O_3

Substance	*·OH $k_{oxidation}$ (s^{-1})*	*O_3 $k_{oxidation}$ (s^{-1})*
Chlorinated alkenes	***10^9 - 10^{11}***	***10^{-1} - 10^3***
Phenols	***10^9 - 10^{10}***	***10^3***
Aromatics	***10^8 - 10^{10}***	***1 - 10^2***
Ketones	***10^9 - 10^{10}***	***1***
Alcohols	***10^8 - 10^9***	***10^{-2} -1***
Alkanes	***10^6 - 10^9***	***10^{-2}***

·OH REACTIONS:

- THROUGH THE ADITION TO A C=C:

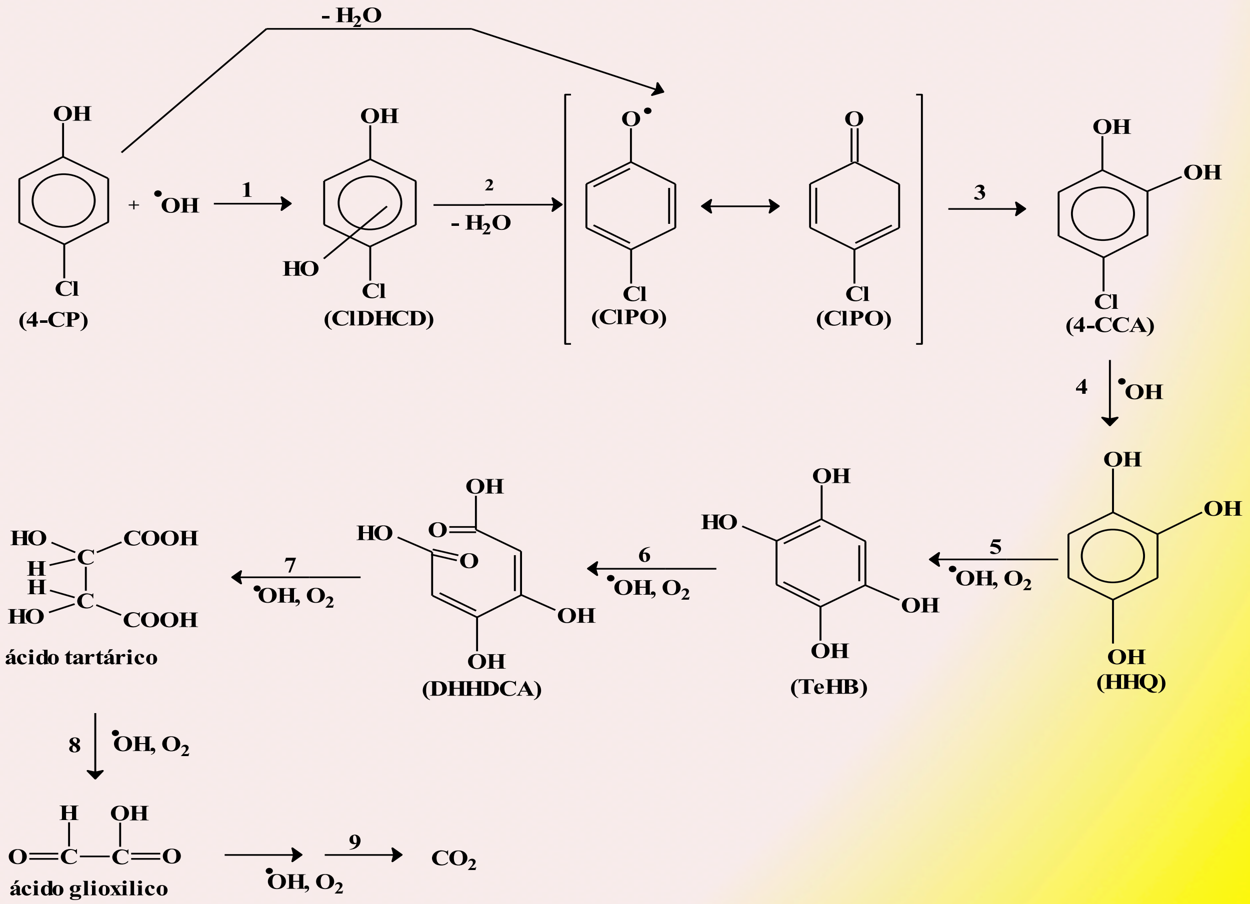
$$\cdot OH + R_1C{=}CR_2 \rightarrow R_1(HO)C\text{-}CR_2\cdot$$

- THROUGH H ABSTRACTION:

$$\cdot OH + RH \rightarrow R\cdot + H_2O$$

C=C ADDITION IS A PROCESS FASTER THAN THE H ABSTRACTION.

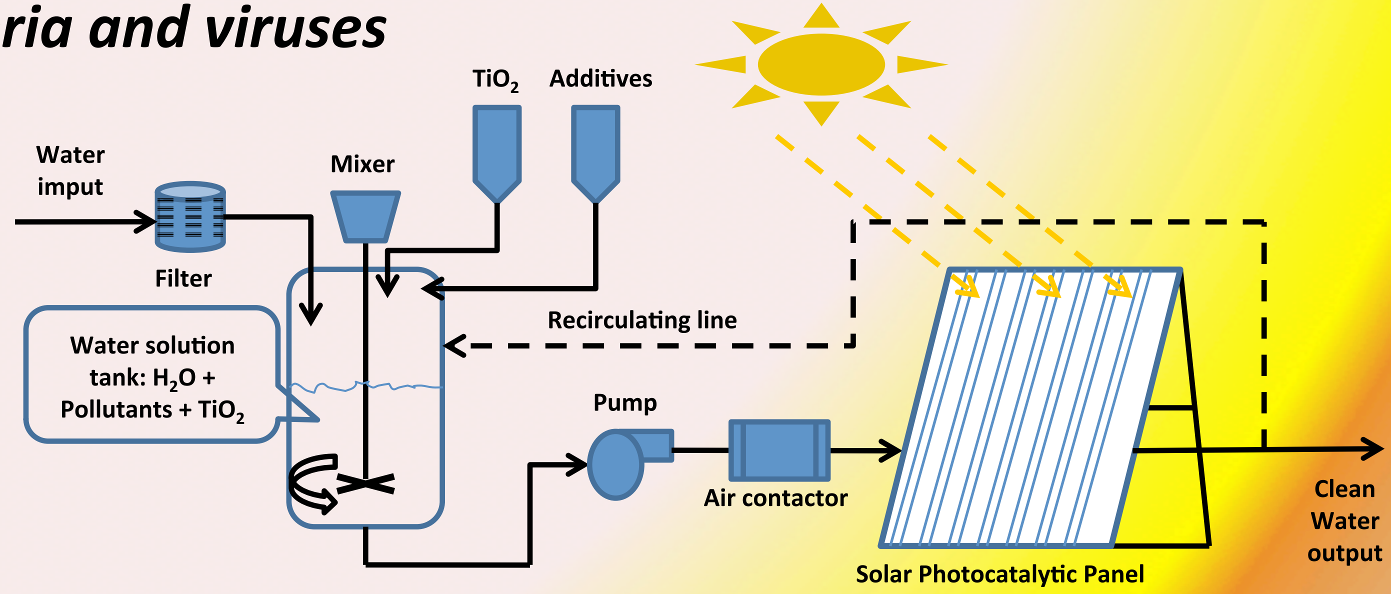
4-CP PHOTOCATALYTIC MINERALIZATION MECHANISM



$$C_nH_mO_zX_y \; + \; p\,O_2 \rightarrow n\,CO_2 + y\,HX + \; w\,H_2O$$

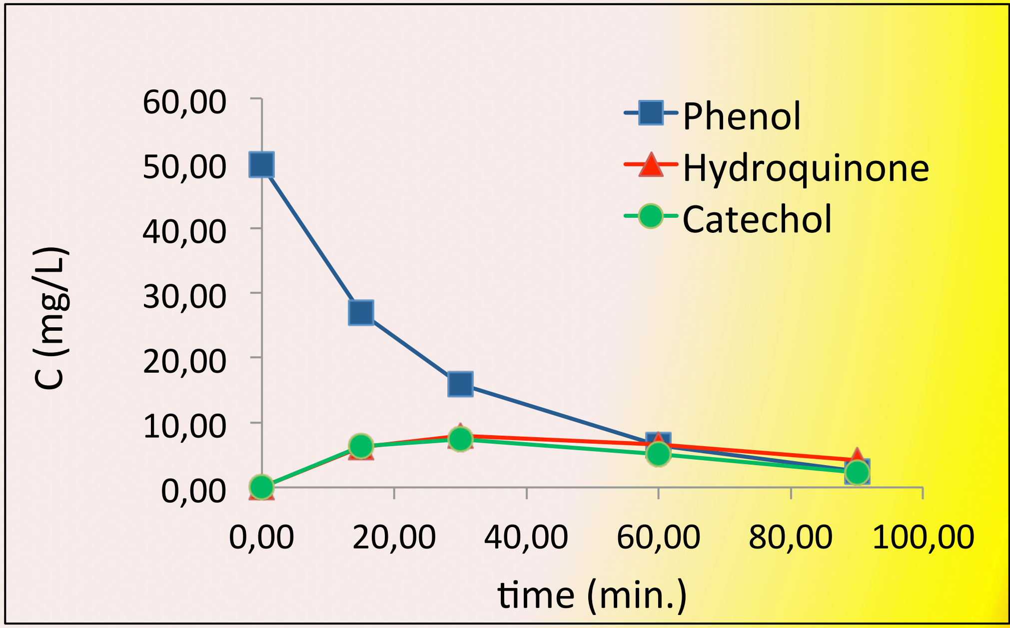
At laboratory scale this process has been tested with success using for many applications:

- ***Phenols and phenol derivatives***
- ***Halogen organic compounds***
- ***Pesticides***
- ***Surfactants***
- ***Emerging pollutants (pharmaceutical and cosmetic products, flame retardants,…)***
- ***Bacteria and viruses***
- ***…***



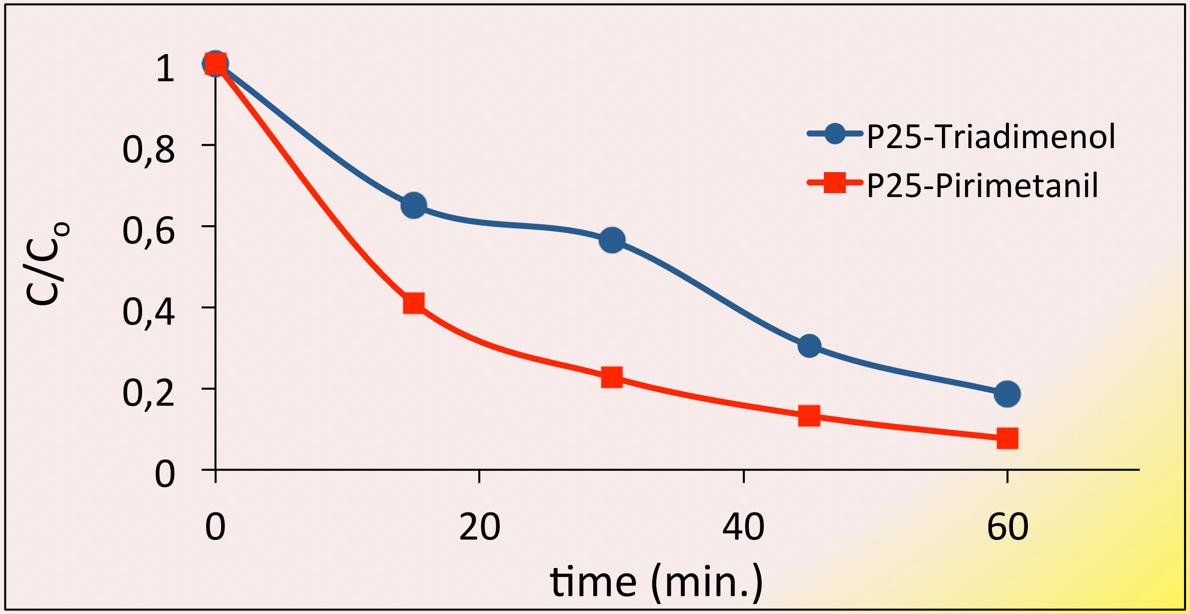
The systems are operated in a discontinuous manner by recirculating the wastewater with an intermediate reservoir tank and centrifugal pump

Phenol, hydroquinone and **catechol** concentration evolution during the phenol photocatalytic mineralization using TiO_2 (ECT 1023t)



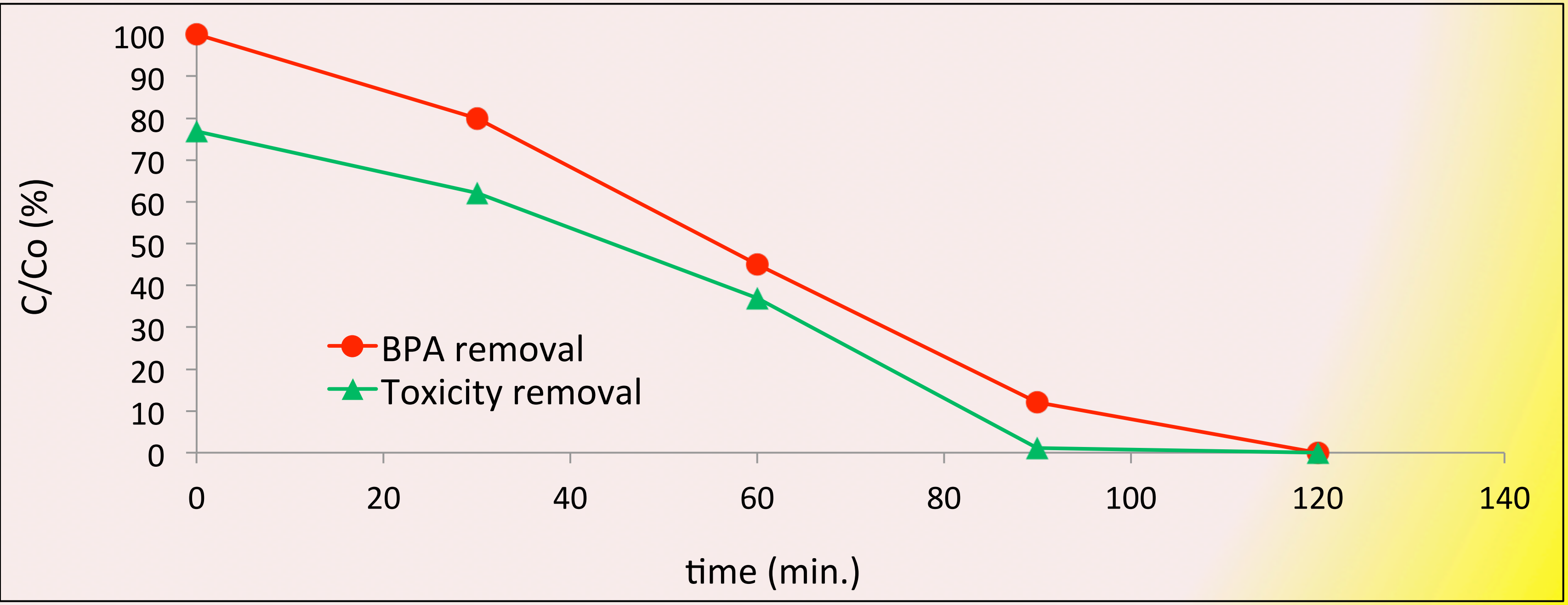
*** [Phenol] = 50 ppm , $[TiO_2]$ = 1 g/L , pH = 5 , T=25°C**

Pesticides photocatalytic removal

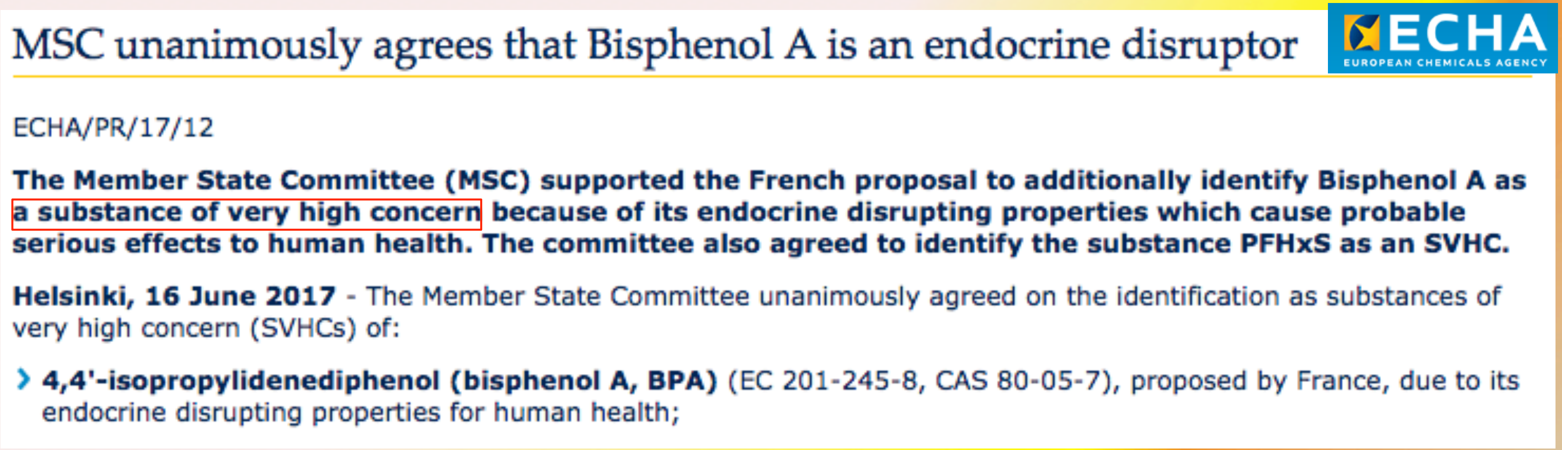


*** [Pesticide] = 0,53 mM , $[TiO_2]$ = 1 g/L , pH = 5 , T=25°C**

Bisphenol A photocatalytic removal



*** [BPA] = 50 ppm , [TiO$_2$] = 1 g/L , pH = 5 , T=25°C**



MSC unanimously agrees that Bisphenol A is an endocrine disruptor

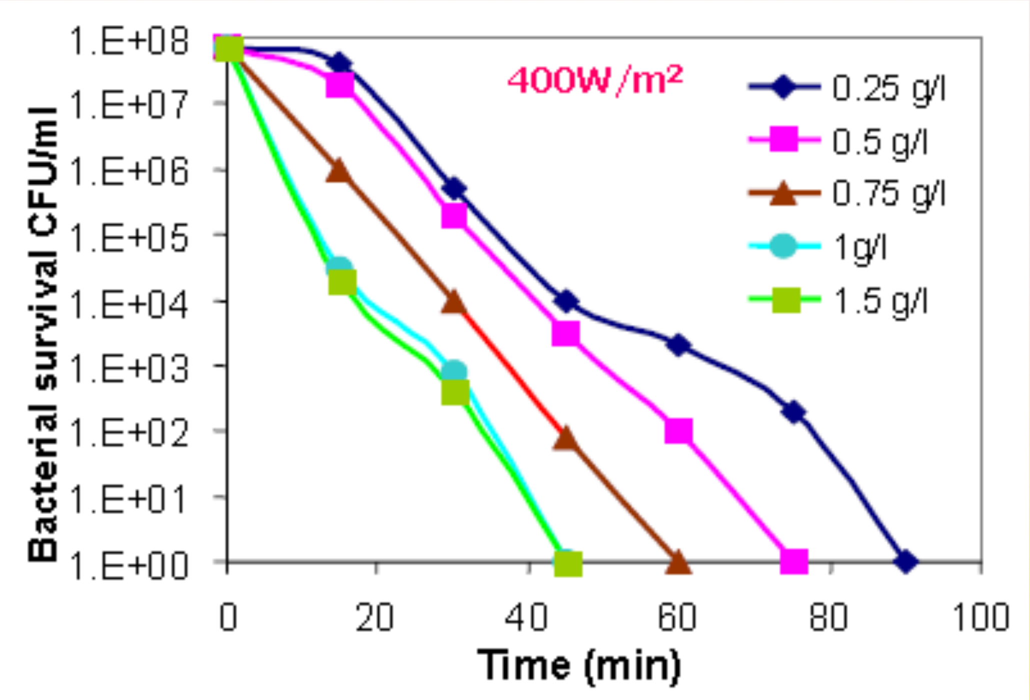
ECHA/PR/17/12

The Member State Committee (MSC) supported the French proposal to additionally identify Bisphenol A as a substance of very high concern because of its endocrine disrupting properties which cause probable serious effects to human health. The committee also agreed to identify the substance PFHxS as an SVHC.

Helsinki, 16 June 2017 - The Member State Committee unanimously agreed on the identification as substances of very high concern (SVHCs) of:

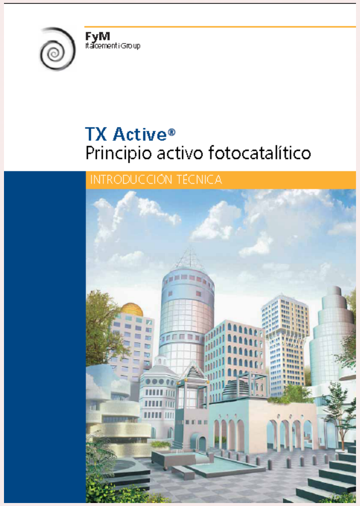
- **4,4'-isopropylidenediphenol (bisphenol A, BPA)** (EC 201-245-8, CAS 80-05-7), proposed by France, due to its endocrine disrupting properties for human health;

Photocatalytic disinfection*



- **Photocatalytical inactivation of *E. coli*: effect of (continuous–intermittent) light intensity and of (suspended–fixed) TiO_2 concentration.** Rincón, A.G and Pulgarin C. *Appl. Catal. B: Environ. 44 (2003), 263.*

TX Active® (FyM- Italcementi Group)



FyM
Italcementi Group

TX Active®
Principio activo fotocatalítico

INTRODUCCIÓN TÉCNICA

PHOTOCATALYTIC PAINTS -
PAINT A BREATH OF FRESH AIR

TACKLING INDOOR AIR QUALITY ISSUES

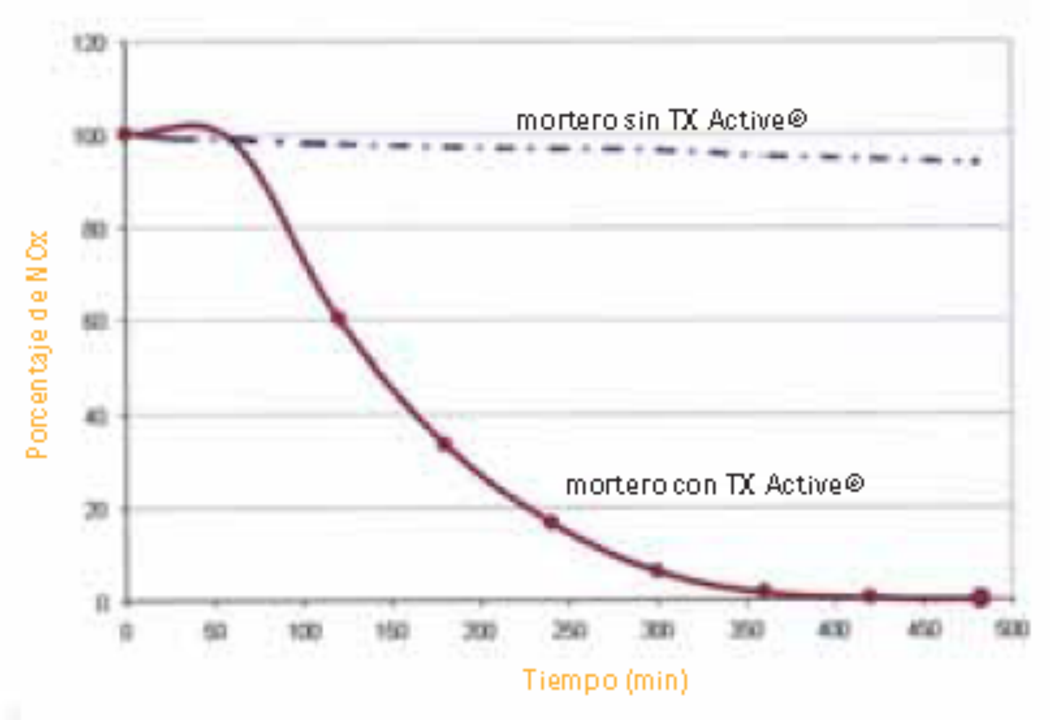
KEIM ECOSIL®-ME

Completely VOC free, odourless, high quality interior Photocatalytic paint which removes airborne pollutants improving indoor air quality.

The Photocatalytic properties allow Keim Ecosil-ME to reduce levels of Nitrogen Oxides, Benzene, Toluene, Formaldehyde and Acetaldehyde off gassed by many different building components and materials.

www.keimpaints.co.uk
info@keimpaints.co.uk

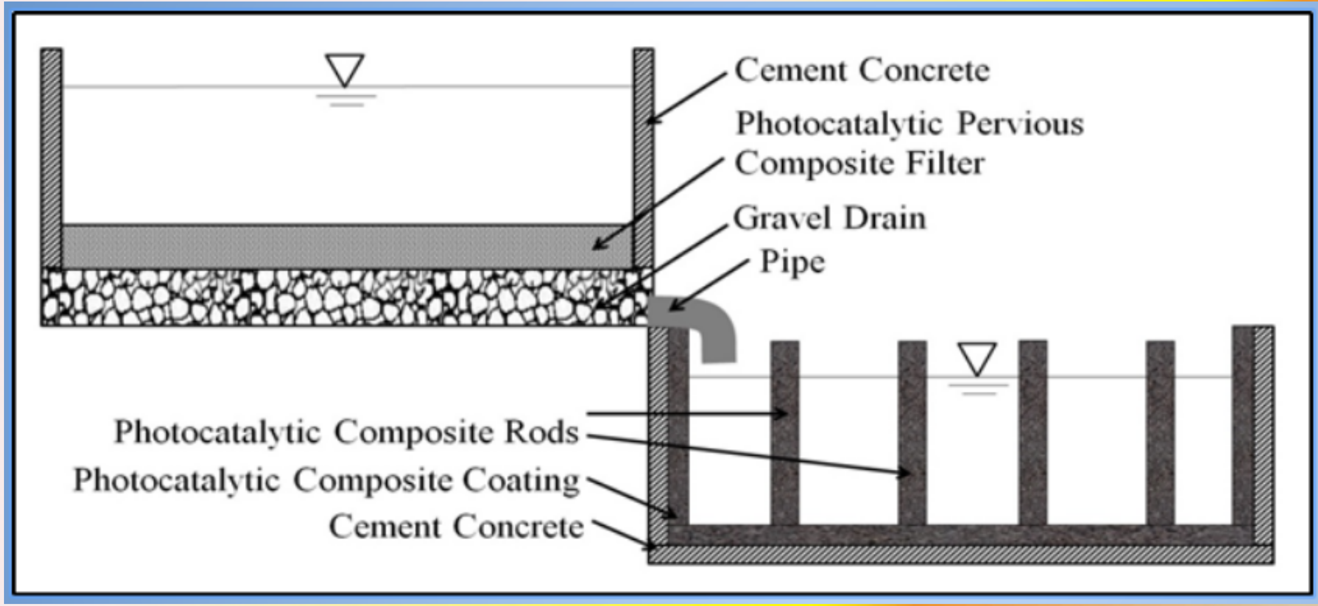
http://www.fym.es/ES/Prensa/Galeria+de+Im%C3%A1genes/2009ProductosTXActive.htm



**Deepika Kurup,
U.S. winner of 2014 Stockholm Junior Water Prize**

A novel silver doped photocatalytic pervious composite was synthesized using uniformly graded sand, Portland cement, titanium dioxide and silver nitrate (Photocatalytic Composition for Water Purification US 20140183141 A1) Deepika Kurup

Prototype for real world application



Oxatur

Oxatur is a floating or permanent establishment and, for example, positioned at discharge sources or central water systems.

The surface has been treated with a special photocatalytic coating. That accelerates the decomposition (photocatalytic cleaning) of organic (micro) contaminants, alcohols, algae and bacteria.

Fully autonomous operating unit

The pumped water is brought back to the water system. The return water is enriched with oxygen

Equipped with floatlands planted with a unique crop that removes nutrients N and P from the water and stores it in the green parts.

Photocatalyst UBE TiO_2/SiO_2

Natural Helth Center. Almería

"TOKYO, February 25, 2005--Ube Industries,Ltd. has been awarded the Minister of Environment Prize of the Fourth Annual Green Sustainable Chemistry (GSC) Awards by the Green Sustainable Chemistry Network (GSCN), in recognition of the company's major contribution to reduction of environmental impact through its development of the world's first high-strength photocatalytic fiber utilizing surface gradient structures, and of a water decontamination system that makes use of this material."

http://www.ube-ind.co.jp/english/products/index.htm

Nature **416**, 64-67 (7 March 2002) | doi:10.1038/416064a. **A general process for *in situ* formation of functional surface layers on ceramics.** Toshihiro Ishikawa, Hiroyuki Yamaoka, Yoshikatsu Harada, Teruaki Fujii & Toshio Nagasawa

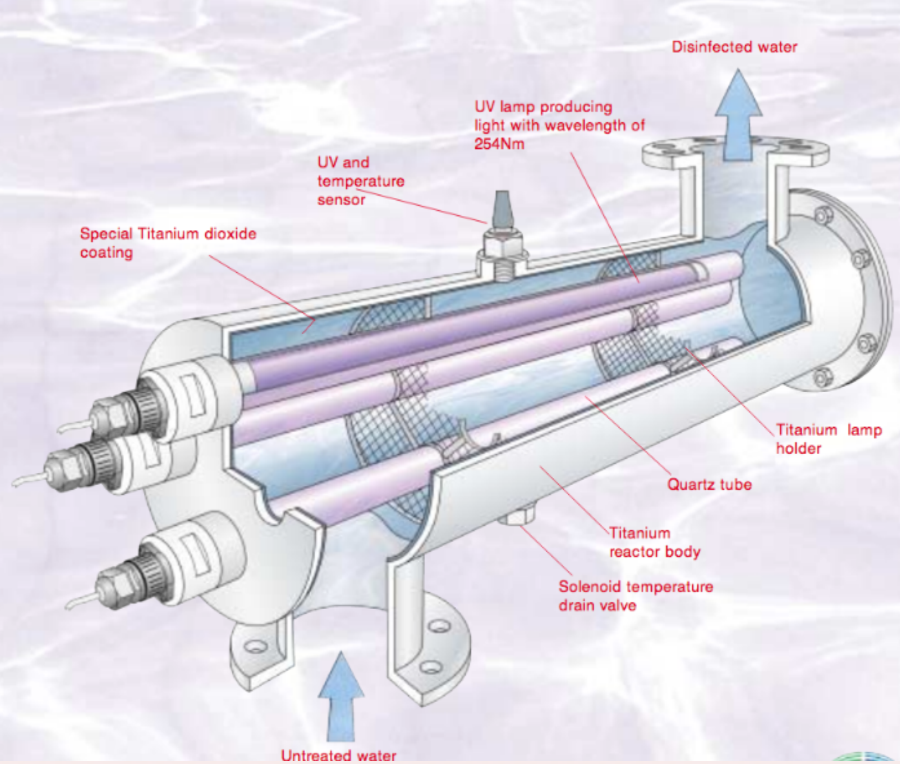
Photocatalyst UBE TiO_2/SiO_2

Indoor pool at the Paraplegic Hospital of Toledo, equipped with an UBE Photocatalytic system which has demonstrated 99.9% efficiency in removing pathogens*

* http://www.borrmart.es/articulo_limpiezas.php?id=224&numero=54

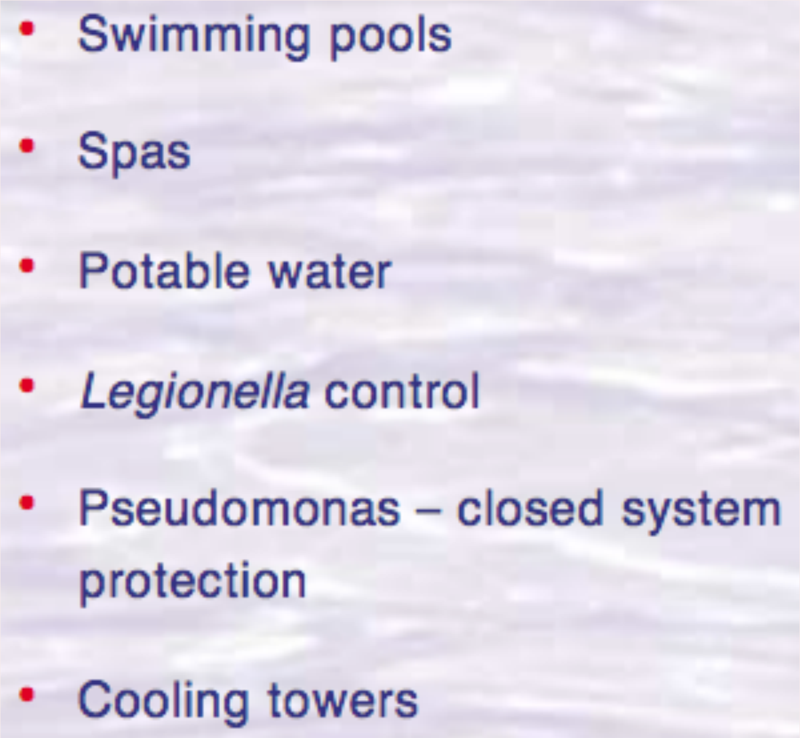
AOP.TITANIUM® Brightwater

Titanium AOP is an environmentally friendly 'gatekeeper' solution that prevents Legionella and other organisms from entering the water system within the building.



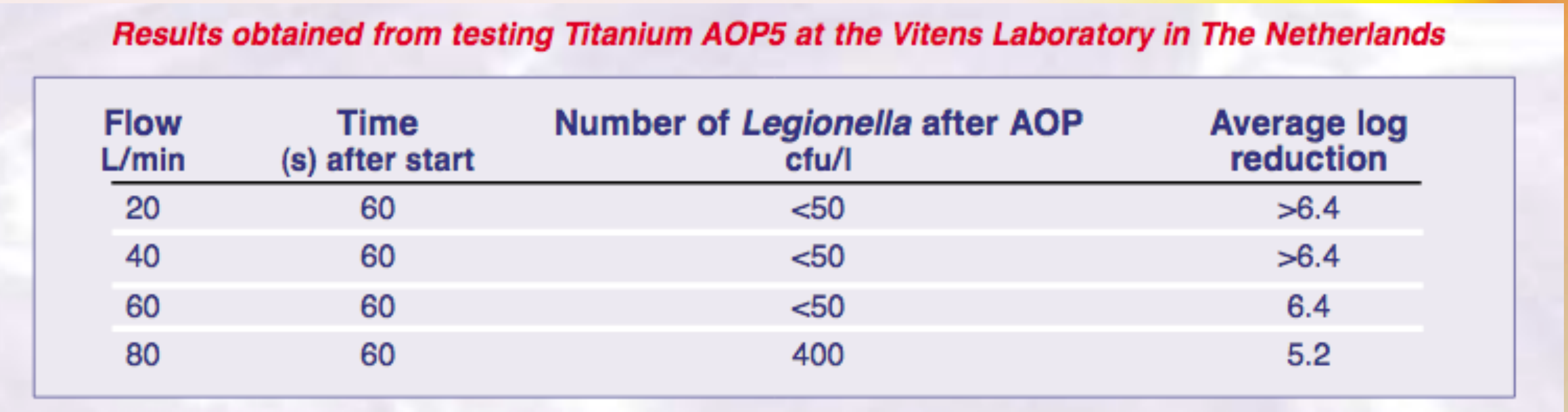
http://www.bwater.eu/aop/titanium-aop/titanium-aop-page/#

AOP.TITANIUM® Brightwater



- Swimming pools
- Spas
- Potable water
- *Legionella* control
- Pseudomonas – closed system protection
- Cooling towers

- Humidifiers
- Recycling of grey water
- Rainwater harvesting
- Bore hole water disinfection
- Process applications – food & beverage industry



Results obtained from testing Titanium AOP5 at the Vitens Laboratory in The Netherlands

Flow L/min	Time (s) after start	Number of *Legionella* after AOP cfu/l	Average log reduction
20	60	<50	>6.4
40	60	<50	>6.4
60	60	<50	6.4
80	60	400	5.2

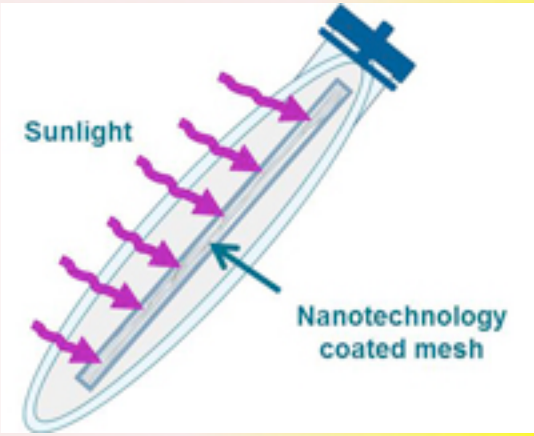
PhotoCat® Purifics

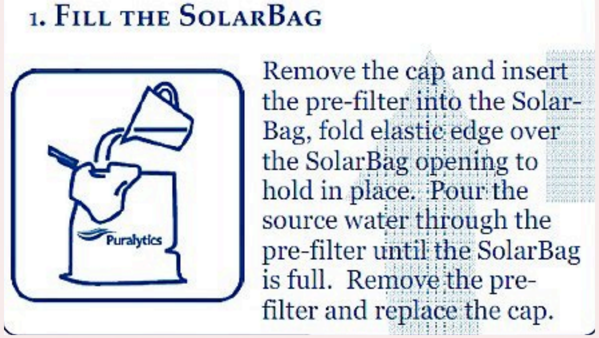
PhotoCat is a photocatalytic, ceramic membrane process that **combines** the best of "chemical free" **advanced oxidation** (AOP+) & ceramic **ultrafiltration**.

PhotoCat is a photocatalytic membrane system that destroys organic pollutants when they are mixed with the titanium dioxide (TiO_2) slurry, and activated by full spectrum UV light. The patented continuous TiO_2 separation process allows the catalyst to be completely recaptured and reintroduced into the inlet stream.

http://www.purifics.com/photo-cat-photocatalytic-membrane-system

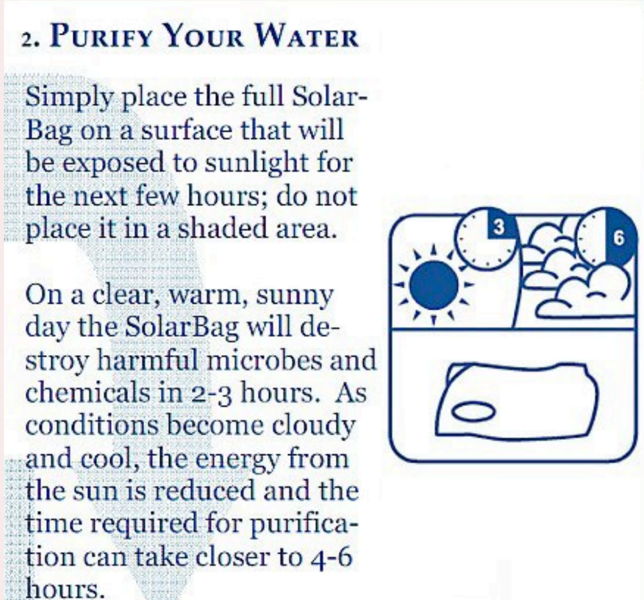
Portable Drinking Water Purifier





1. FILL THE SOLARBAG

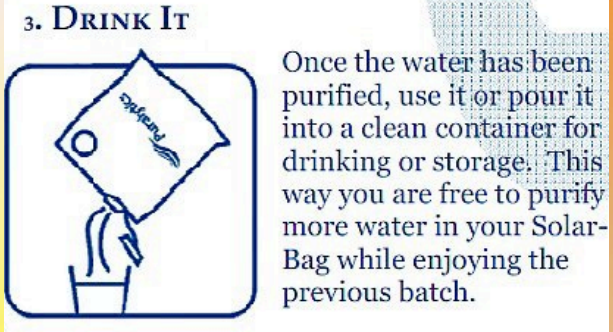
Remove the cap and insert the pre-filter into the SolarBag, fold elastic edge over the SolarBag opening to hold in place. Pour the source water through the pre-filter until the SolarBag is full. Remove the pre-filter and replace the cap.



2. PURIFY YOUR WATER

Simply place the full SolarBag on a surface that will be exposed to sunlight for the next few hours; do not place it in a shaded area.

On a clear, warm, sunny day the SolarBag will destroy harmful microbes and chemicals in 2-3 hours. As conditions become cloudy and cool, the energy from the sun is reduced and the time required for purification can take closer to 4-6 hours.



3. DRINK IT

Once the water has been purified, use it or pour it into a clean container for drinking or storage. This way you are free to purify more water in your SolarBag while enjoying the previous batch.

Shield 1000® de Puralytics

Shield 1000 ©
LED Activated Point of Entry / Use Purifier

LilyPad ©
Sunlight Activated Floating Treatment Device

http://www.roddenberrydrt-handbook.com/uploads/2/6/8/9/26891397/doc10133_rev_1.3-_manual_shield_1000_owners.pdf


Solar photocatalytic panels in Albaida (La Mojonera, Almería)

What is the extent of commercialization of TiO_2 supported solar photocatalysis?

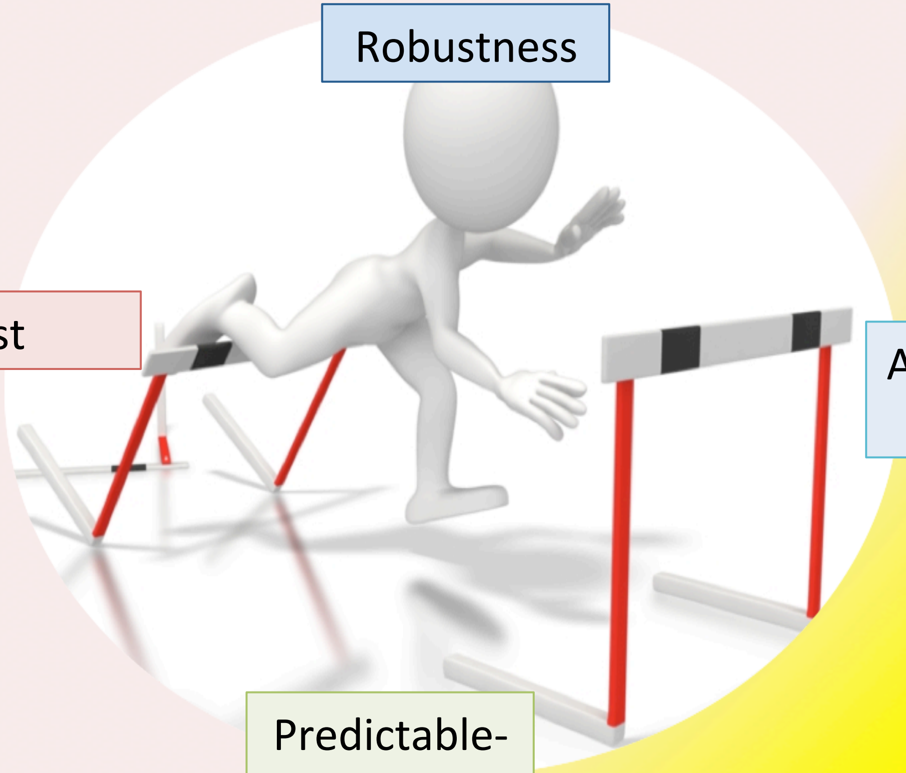
SODIS AFRICA NET

Solar Water Disinfection

Photocatalytic Disinfection Plant for drinking water production in Kenya

Obstacles for industrial application

- The current lack of data for comparison of solar photocatalysis with other technologies (technoeconomic studies, environmental impact)➔is it it a promising technology compared to others?



Robustness

Cost

Processes based on UV activated TiO_2 are about four times more expensive as RO (Al-Bastaki, 2004, Chem. Eng. Proces, 43, 935)

Automation-Safety

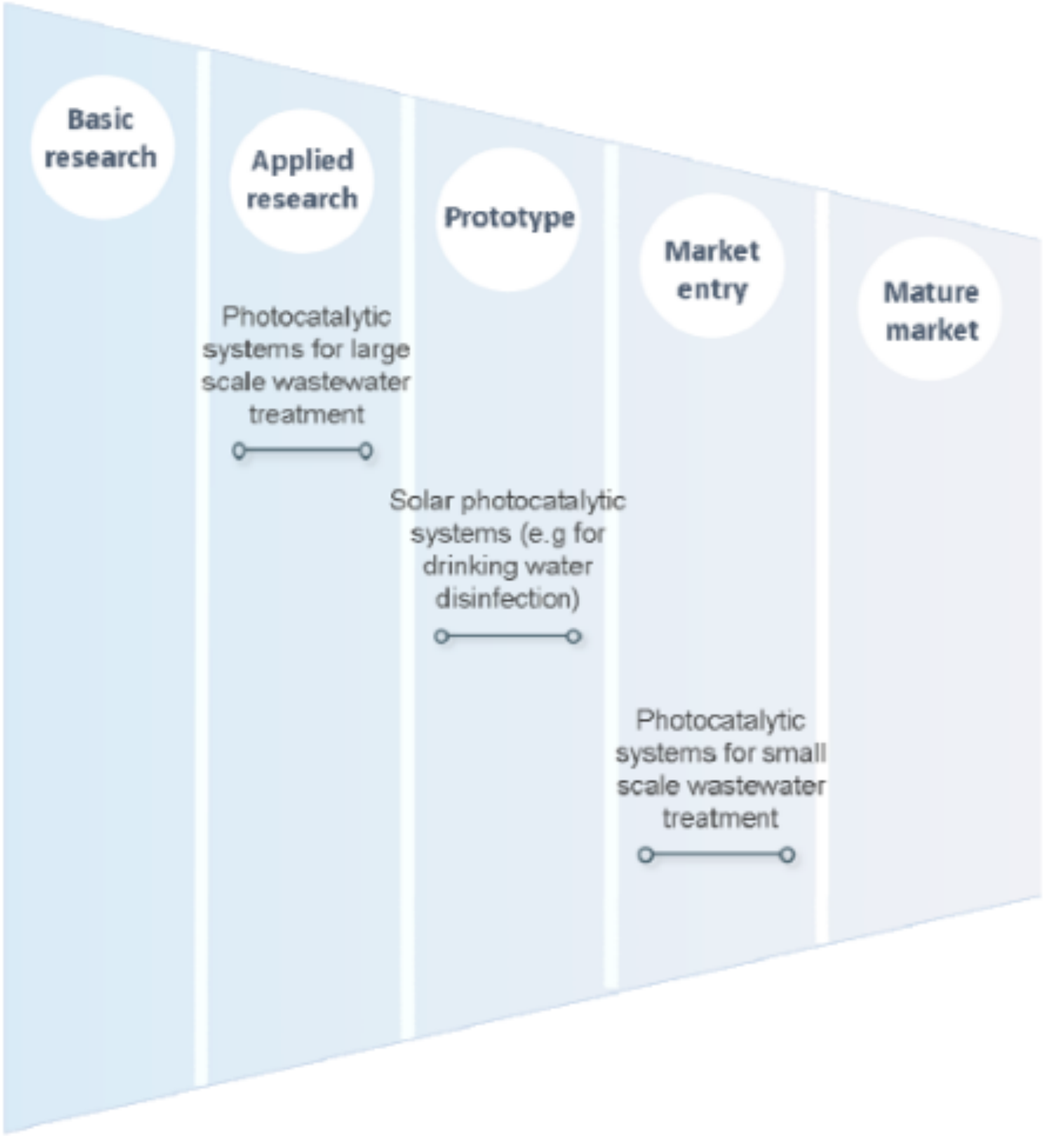
Predictable-Extensive

Wastewater from banana post-harvest

- Fungicide: imazalil (prevent fruit from rotting)
- 10 m^3 per week

cost	Solar Photo-Fenton	Solar Photocatalysis
Investment/€	123282.37	126370.84
Invesment/€/m³	23.71	24.30
operation/€/m³	2.25	2.58

- Combined use of TiO_2-based technologies with other technologies (e.g., biological, ultrafitration)➔ Integrated techniques can ameliorate the drawbacks of individual processes. Case: Membrane photoreactor as secondary treatment
- Additional values: hydrogen



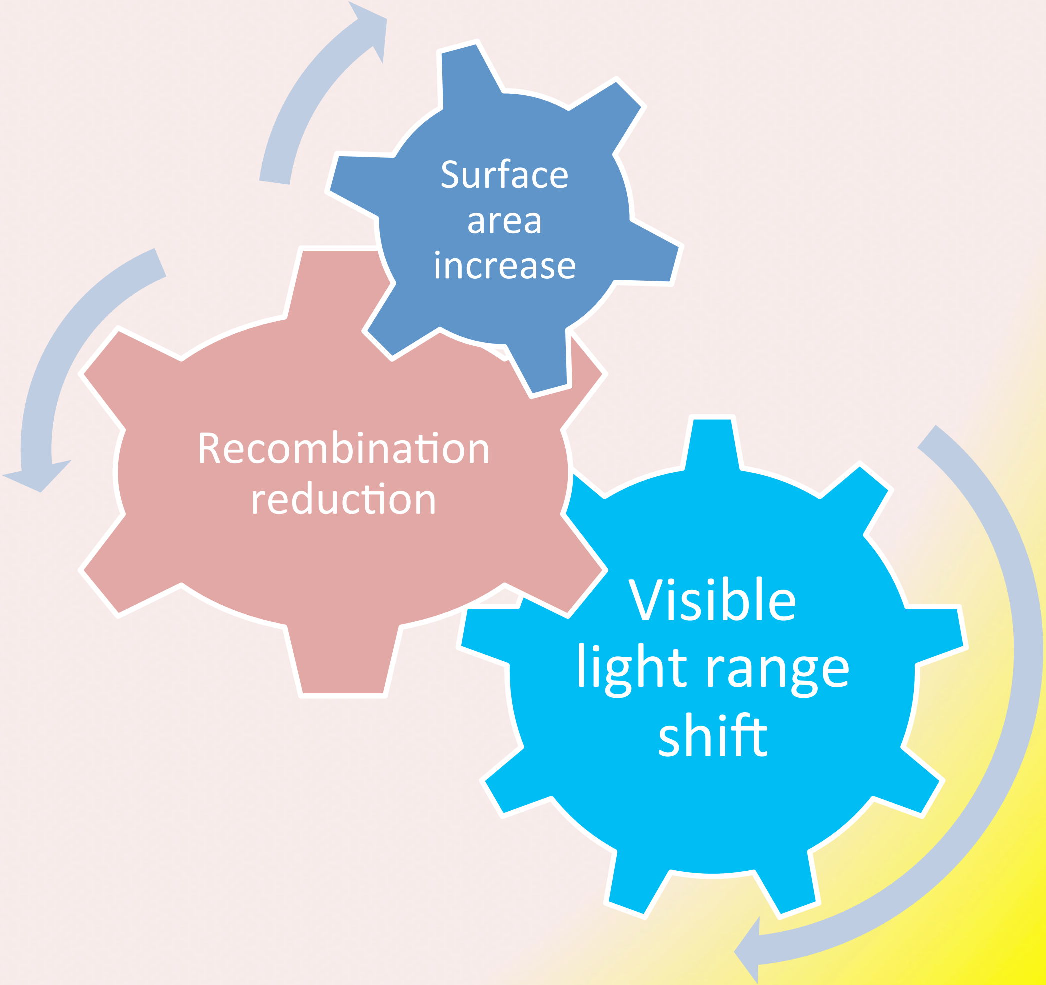
Technology Readiness Levels for photocatalytic applications for water treatment

Despite all these applications, there are some limitations that prevent greater degree of implementation of the heterogenerous photocatalytic technology.

- ***Catalyst low efficiency***

- ***Difficulties for catalyst recovery and reuse (long sedimentation/ filtration periods and reactivation treatments required).***

➢ *Catalyst low efficiency*



Surface area increase

Recombination reduction

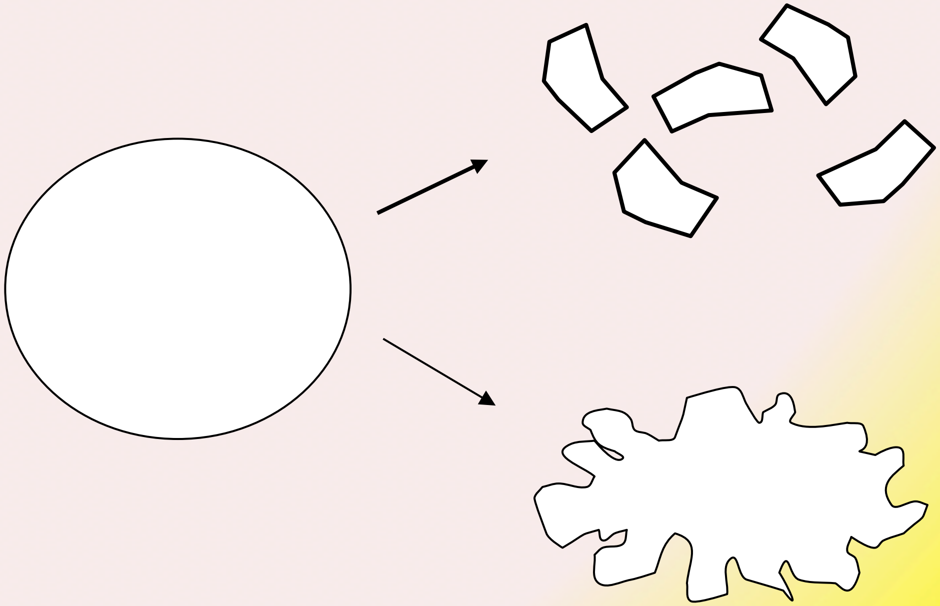
Visible light range shift

S

SURFACE AREA INCREASE

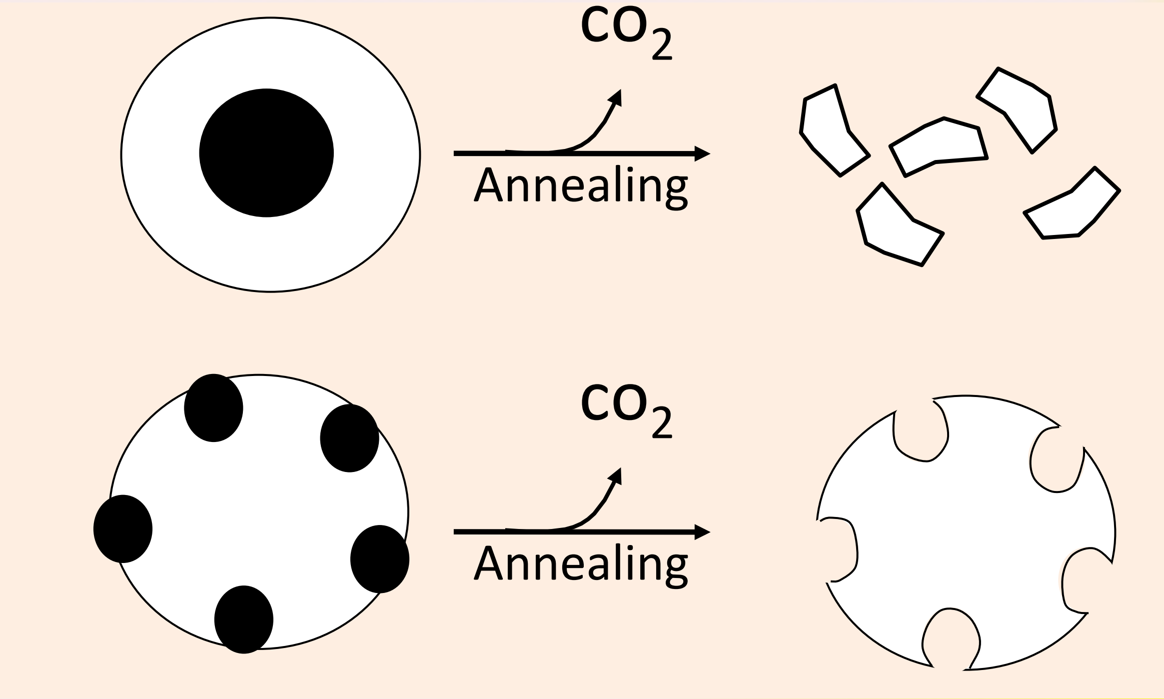
Many researches have tried in recent years to develop and optimize thermal, chemical or combined treatments to obtain photocatalysts with a larger surface area.

This purpose has been tried via obtaining materials composed of smaller particles or by the synthesis of porous particles.



SURFACE AREA INCREASE (I)

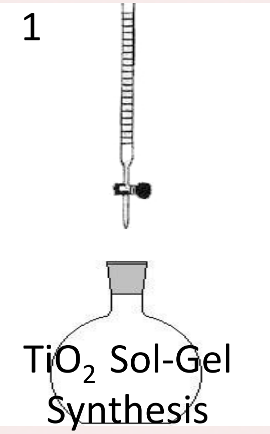
One interesting way to address this objective is synthesizing of TiO_2 in presence of molecular templates. These are chemically or physically removed once the preparation step is completed leaving a void on the surface.

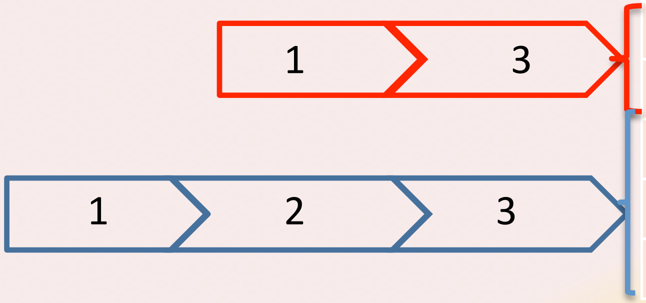


SURFACE AREA INCREASE (II)

Another** interesting way **to address this objective is the** synthesis via sol-gel **of TiO_2 and subsequent** hydrothermal treatment **.

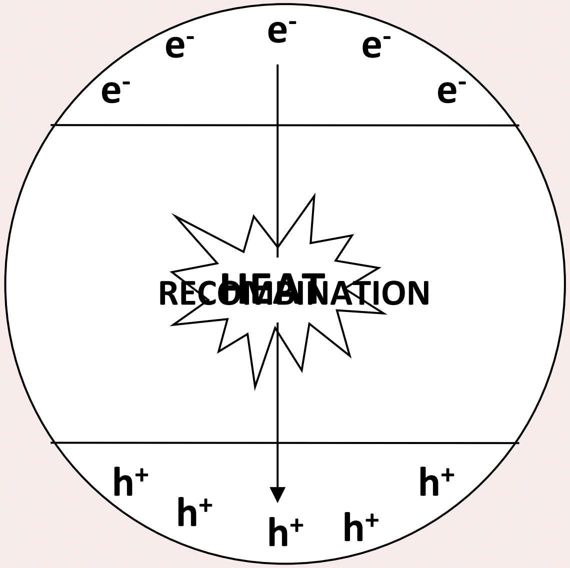
<u>Hydrothermal treatment</u>: The precipitate obtained by sol gel is placed in an autoclave at 150 °C for 24 hours just before calcinations treatment*.





Catalyst	Anatase(A) /Rutile (R)	Crystallite size (nm) (A)	Crystallite size (nm) (R)	BET surface area (m^2/g)
nHT-773	100% A	21.7	----	38.4
nHT-873	100% A	36.9	----	27.9
HT	100% A	6.5	----	182.3
HT-773	100% A	11.9	----	88.3
HT-873	100% A	26.2	----	37.7

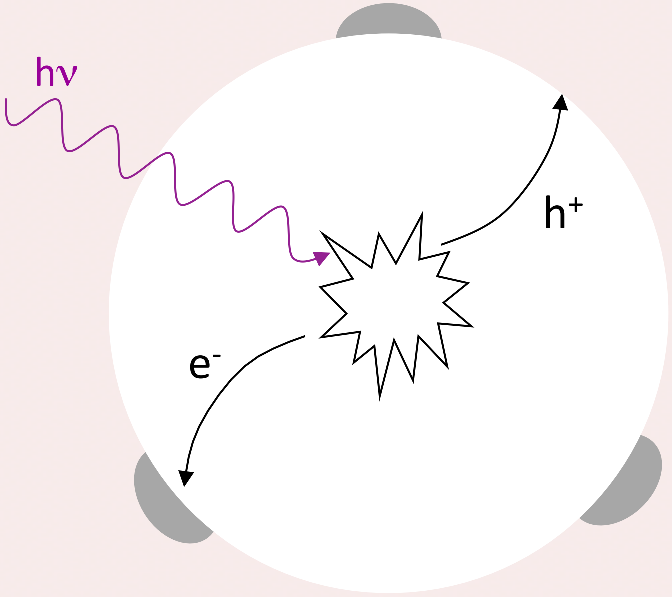
RECOMBINATION PROCESSES MINIMIZATION

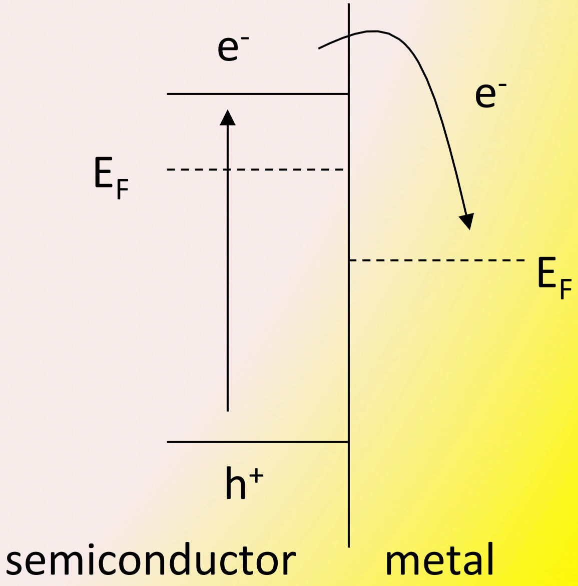


In order to increase the lifetime of photogenerated electrons and holes some strategies can be adopted , for example:

- ***Reducing the recombination centers (defects) density➔ high crystallinity.***
- ***Using fast electron scavengers (Fe^{3+}, $S_2O_8^{2-}$…).***
- ***Using effective electron traps.***

RECOMBINATION PROCESSES MINIMIZATION

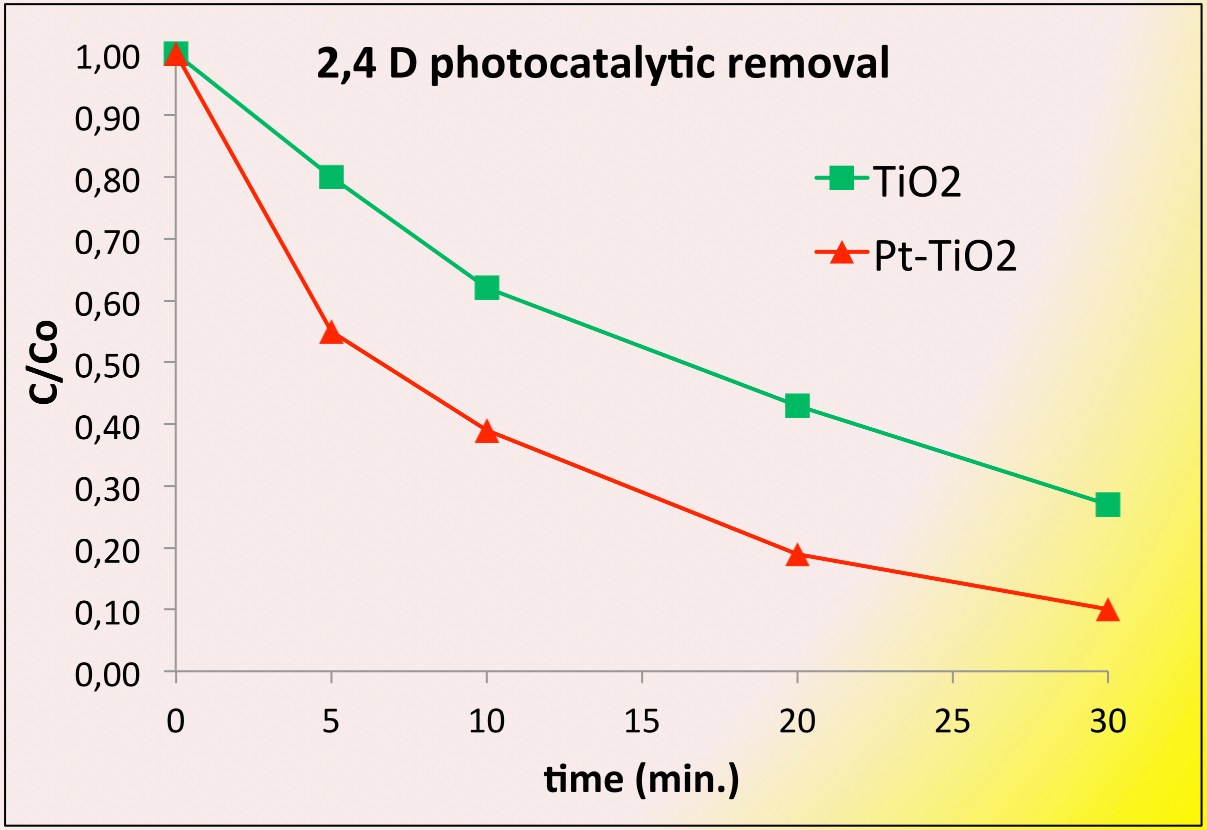




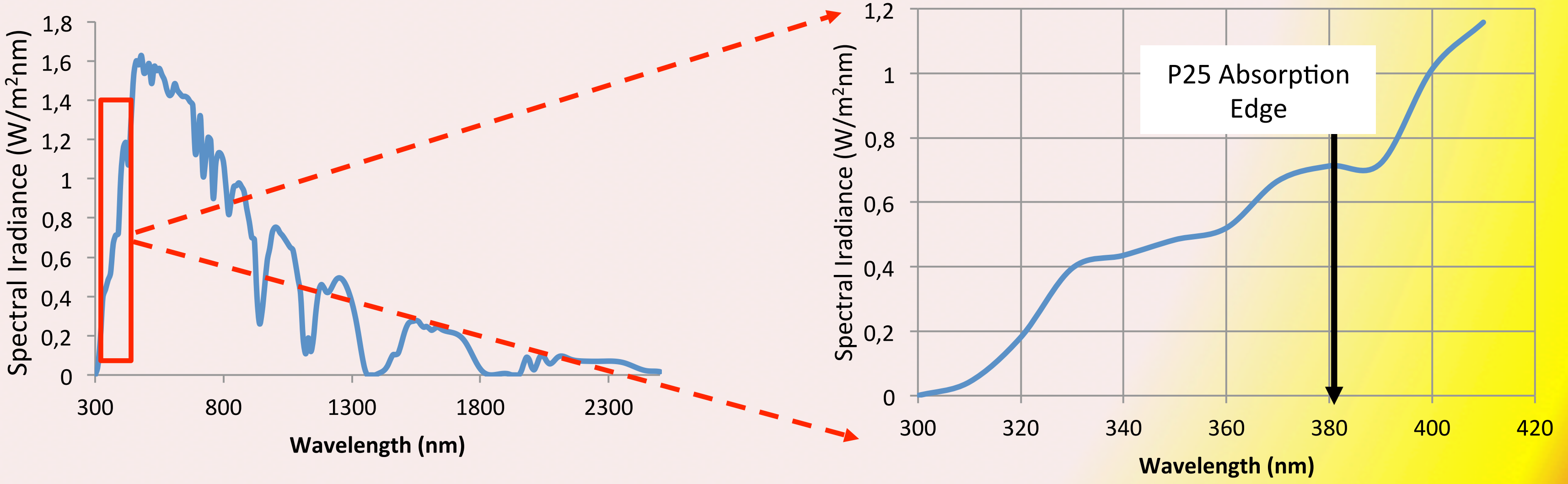
One of the most common used ways has been the photodeposition of noble metals with Fermi levels comprised between the valence and conduction bands of the semiconductor

R

RECOMBINATION PROCESSES MINIMIZATION

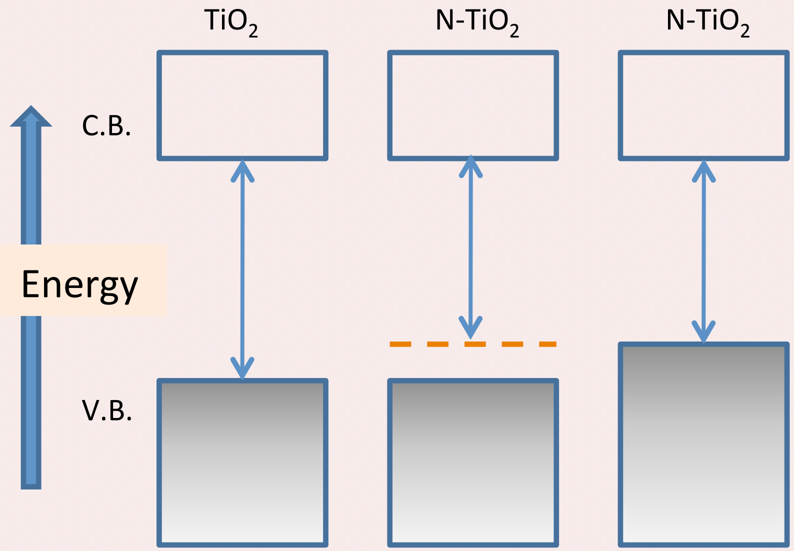


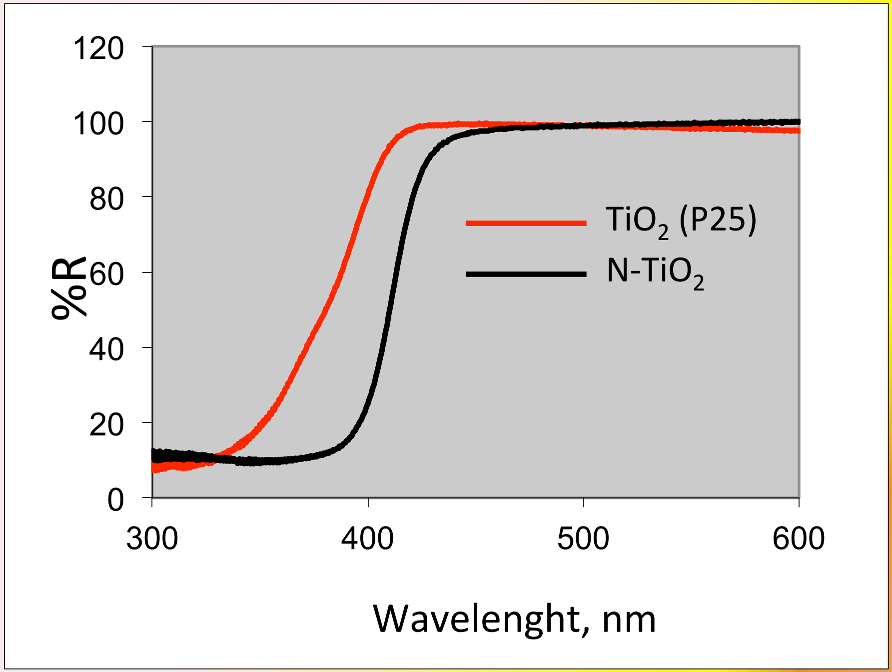
Visible light range shift



P25 can only use around 5 – 8 % of solar photons. Simply reducing the band gap around 0.2 eV (30 nm shift to visible range) the useful photons increase is around 30 %.

non-metal-doping-TiO_2 (e.g. N- TiO_2) *can be an interesting way to reduce the band gap and consequently shifting the absorption edge to visible light by the introduction of localized levels in the band gap or by broadening the valence band**.





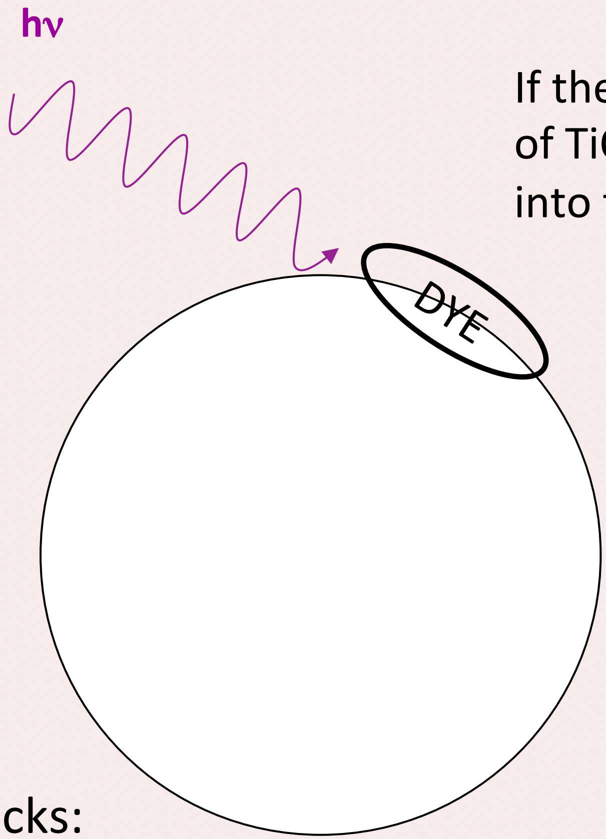
Drawbacks:

- Generate oxygen vacancies in the bulk. These defects can act as massive recombination centers of photo-induced electron e hole pairs
- Unstable: Deactivation has been observed
- Unfavorable in energy: The doping process of the non metal elements always involves thermal treatment at high temperatures or a long time of hydrothermal treatment

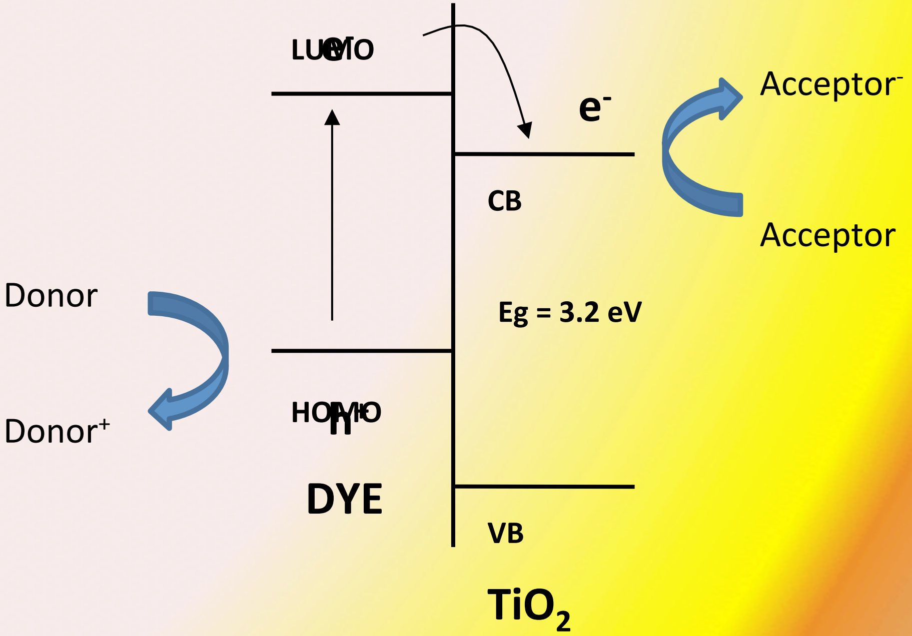
V

Combination with photosensitizer

Examples: erythrosin B, thionine, bipyridine, phthalocyanine



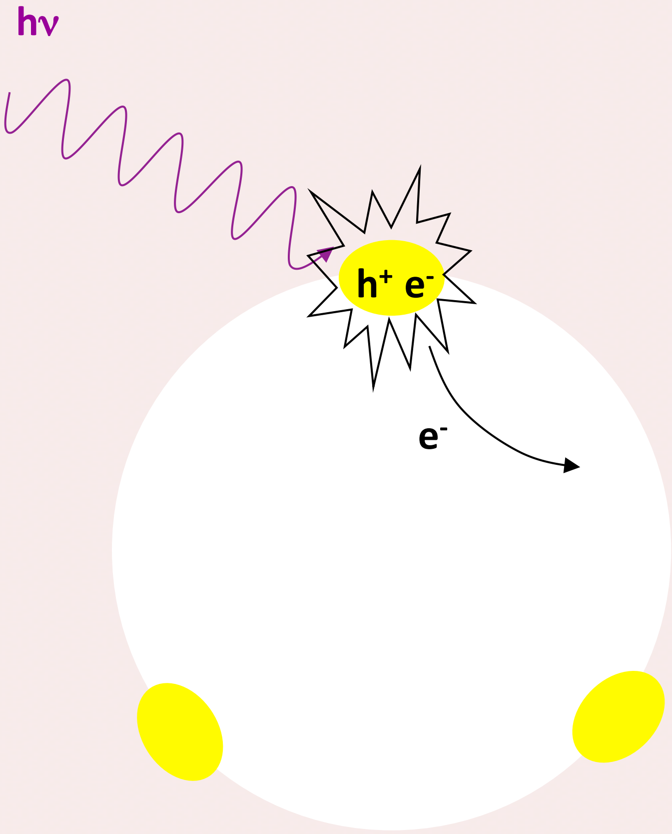
If the redox potential is lower than the conduction band (CB) of TiO_2, an electron may be injected from the excited state into the CB

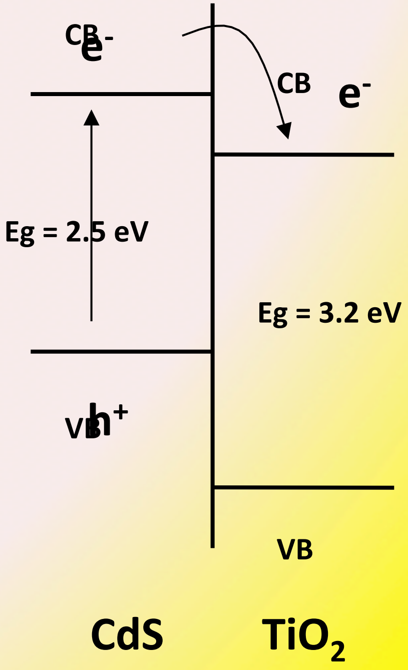


Drawbacks:

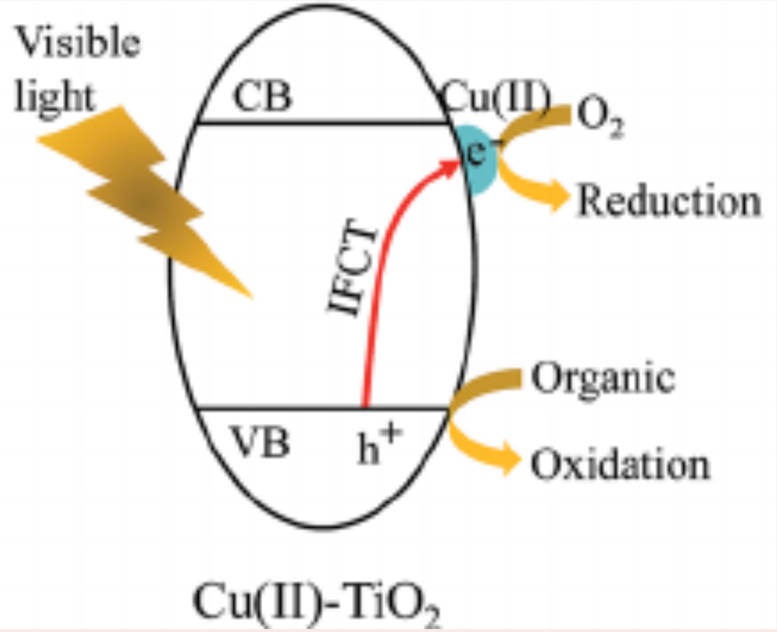
- The electron transfer from excited dye to TiO_2 usually depends strongly on the adsorption efficiency of the dye molecule. In this case the dye molecules are only absorbed onto the TiO_2 surface by physical/chemical adsorption. So the dye molecules as sensitizers tend to partially desorb.
- Dyes are toxic and unstable.

Semiconductors combination





Interfacial charge transfer process (IFCT)



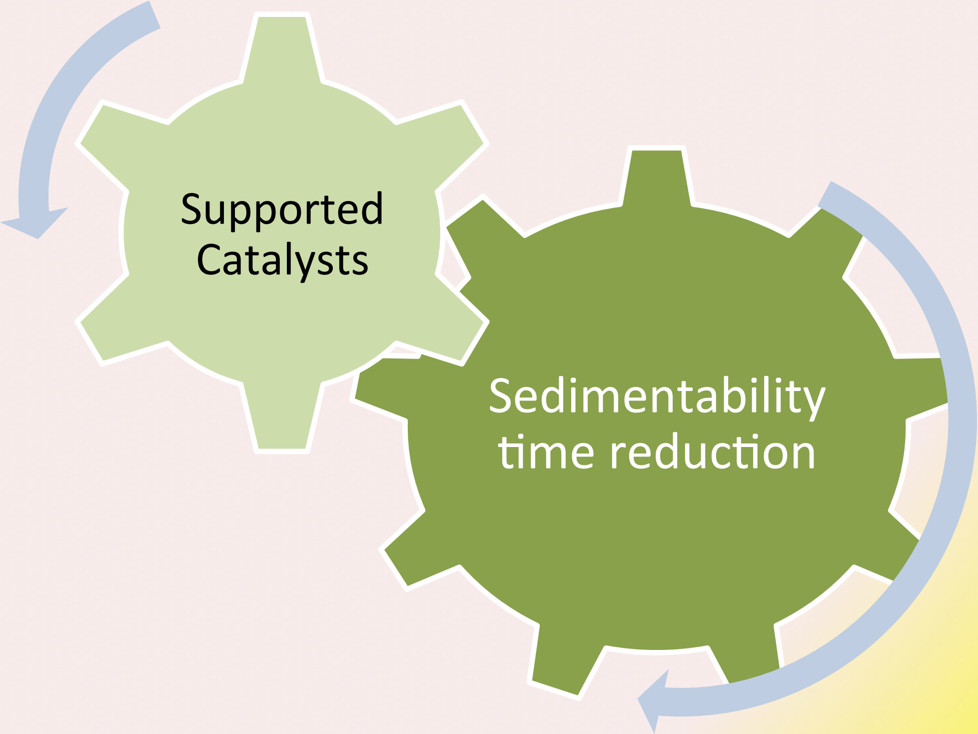
DOI: 10.1039/C4TA02211D

The surface modification of TiO_2 with Cu(II) or Fe(III) nanoclusters increases the visible-light-sensitivity of the resulted material without inducing impurity levels in the band gap.

Electrons in the valence band (VB) of TiO_2 are excited to the Cu(II) nanoclusters under visible-light irradiation through an **interfacial charge transfer (IFCT) process**. The introduction of excited electrons into the Cu(II) nanoclusters leads to the formation of Cu(I) species, which efficiently reduce oxygen molecules.

During the IFCT process, holes with strong oxidative power for the decomposition of organic compounds are generated in the deep VB of TiO_2.

➢ *Catalyst recovery*



Supported Catalysts

Sedimentability time reduction

S

SUPPORTED CATALYSTS

- ***ELECTION OF SUPPORT AND METHOD OF FIXING THE CATALYST TAKING INTO ACCOUNT:***
  - ***Maximum possible surface in contact with the reactive medium.***
  - ***Maximum possible surface area exposed to radiation.***
  - ***Thermal and Chemical inert.***
  - ***Cheap and durable (adherence)***
  - ***Have a low pressure drop***

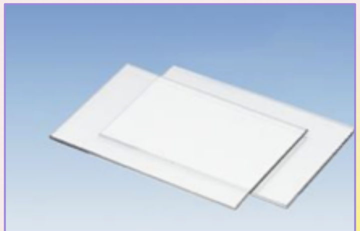
"studies performed to date have not yet identified a fixed-catalyst system that performs as efficiently as slurry systems, at least for the solar treatment of water".

Book Photocatalysis and Water Purification. From Fundamentals to Recent Applications. Chapter 15.

S

SUPPORTED CATALYSTS

- ***COMMON SUPPORTS:***
  - ***Packed beds:***
    - ***Glass beads (hollow or bulk), glass tubes, glass Raschig rings***
    - ***Polymeric materials***
    - ***Porous lava, natural porous silica pumice, exfoliated vermiculite, zeolites***
    - ***Lattice monolithic solids: foams***
  - ***Reactor walls***
  - ***Glass tubes***
  - ***Paper (e.g.*** *paper* provided by *Ahlstrom Com*
  - ***Metal fibers, steel mesh, aluminum plates***
  - ***Optical fibers as light distributing guide***
  - ***…***



S

Immobilization techniques (I)

Binders: The binder directly fixes the photocatalyst onto the substrate or support physically isolating it from the active TiO_2. Fully inorganic binders are preferred (e.g. SiO_2), polymers and organosilane polymers containing organic functional groups can also be used.

Thermal treatment*:* The simplest immobilizing method. The photocatalyst is mainly deposited first on the support surface by impregnation of the photocatalyst suspension at an optimized concentration.

Sol–gel methods are among the most widely used immobilization methods, due to the relatively low processing costs as well as the flexible and tunable implementation onto a wide range of substrates in terms of shape, size, and chemical nature. Dip-coating and spreadcoating are the two main processing methods for immobilizing sol–gel TiO_2 onto substrates.

Immobilization techniques (II)

CVD method: Substrates are subjected to a gaseous flow of a single or multicomponent volatile precursor in an inert atmosphere at controlled pressure and controlled temperature, and decomposition of the volatile precursors takes place at the substrate surface, resulting in the formation of thin films.

Electrophoretic deposition: Application of a potential between two electrodes (the substrate to be coated acting as cathode, whereas anode being usually platinum). This method is restricted to metallic substrates, or at least conductive ones.

S

SEDIMENTATION TIME REDUCTION:

- ***Adjusting pH***

In the case of TiO_2 (Degussa P25), at concentrations of 200mg/l, the PZC is obtained at about pH 7 and only 5 h of storage is needed to recover 90–95%.

- ***Increasing the size of the catalysts aggregates in suspension or particles density increase***

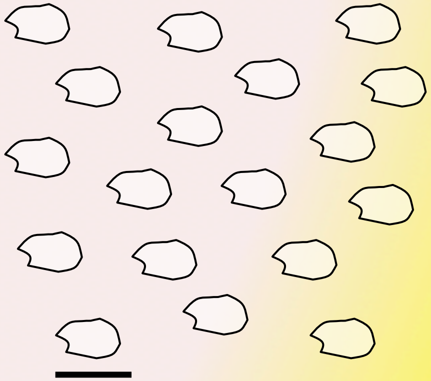
Catalyst recovered can be reused but not indefinitely

Slurry lifetime has been tested with satisfactory results under laboratory conditions but with real water treatments catalyst lifetime would be diminished due to poisoning by contaminants.

D

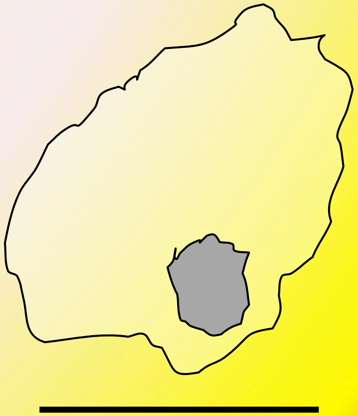
CASE: TiO_2 COMBINED WITH AC:

LASER SCATTERING STUDIES OF TiO_2 SUSPENSIONS ALONE, INDICATED THAT THEY ARE FORMED BY HOMOGENEOUS AGGREGATES WITH AN AVERAGE SIZE OF ABOUT **3 µm**.



SIMILAR STUDIES FOR A 7 %AC CONTAINING CATALYST INDICATED THAT IT IS FORMED BY HOMOGENEOUS AGGREGATES WITH AN AVERAGE SIZE OF approx. **6 µm**.

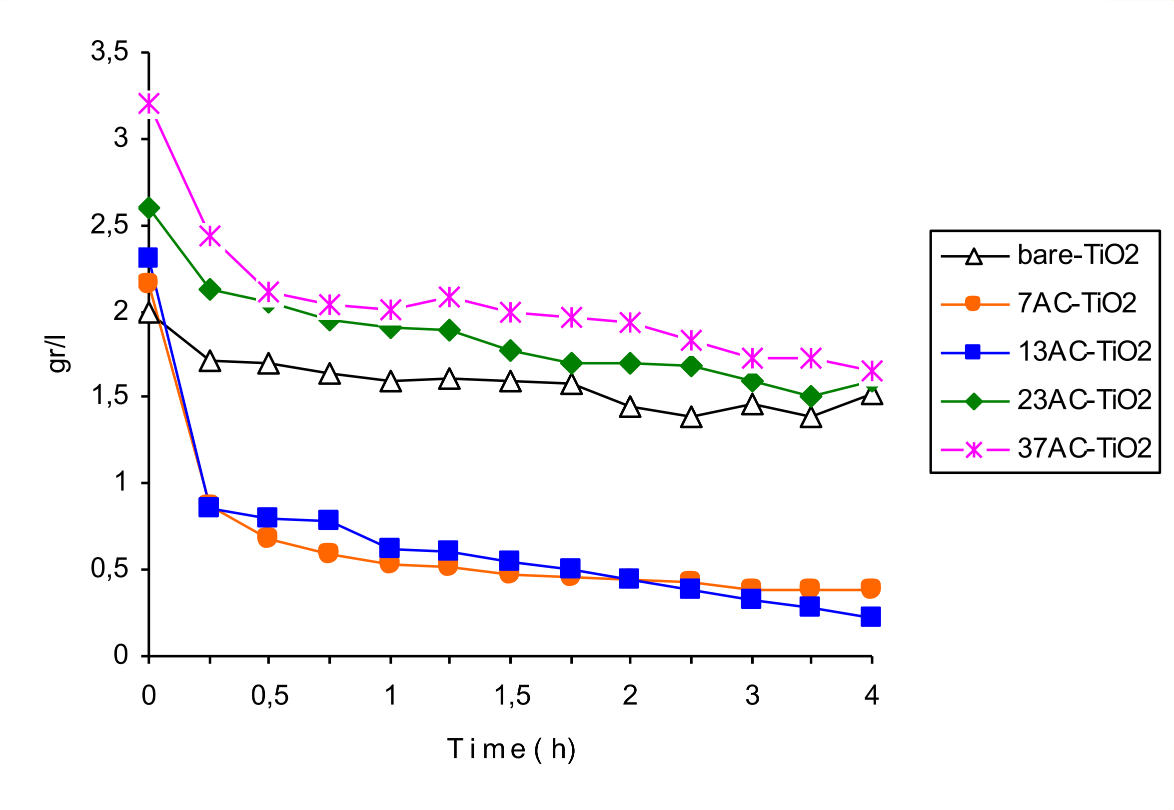
BIGGER AND MORE DENSE AGGREGATES, THAT PRODUCE A HIGHER SEDIMENTABILITY OF THESE SAMPLES.



D

CASE: TiO$_2$ COMBINED WITH AC:

TURBIDIMETRIC SEDIMENTABILITY STUDIES SHOWED THAT THE LOWER AC CONTAINING CATALYSTS PRESENT A CONSIDERABLY HIGHER SEDIMENTABILITY THAN TiO$_2$ ALONE



S

CATALYST SEPARATION. OTHER OPTIONS

- ***Ultrafiltration?***

P25 powder elementary particles are about 30 nm, or even smaller in other TiO_2

- ***Microfiltration?***

In water, the particles always agglomerate into larger ones.

- ***Microfiltration combined with sedimentation?***

About 90% of the catalyst can easily be recovered by sedimentation and the rest by microfiltration.

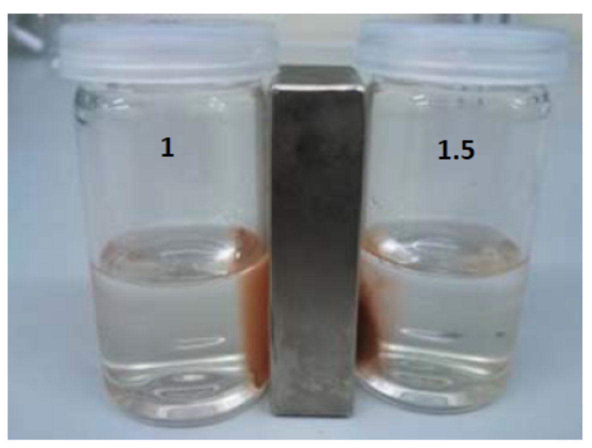
D

CATALYST SEPARATION. OTHER OPTIONS

Composite nanoparticles with magnetic core and photoactive shell.

Separation is obtained from slurry photoreactors when an external field is applied.

Materials used as the magnetic core: **Fe_3O_4**, Fe_2O_3, $NiFe_2O_4$, $CoFe_2O_4$, FeCo, and Co_3O_4.



UNIVERSIDAD DE LAS PALMAS
DE GRAN CANARIA

ULPGC

GRUPO **FEAM**

THANS FOR YOUR KIND ATTENTION