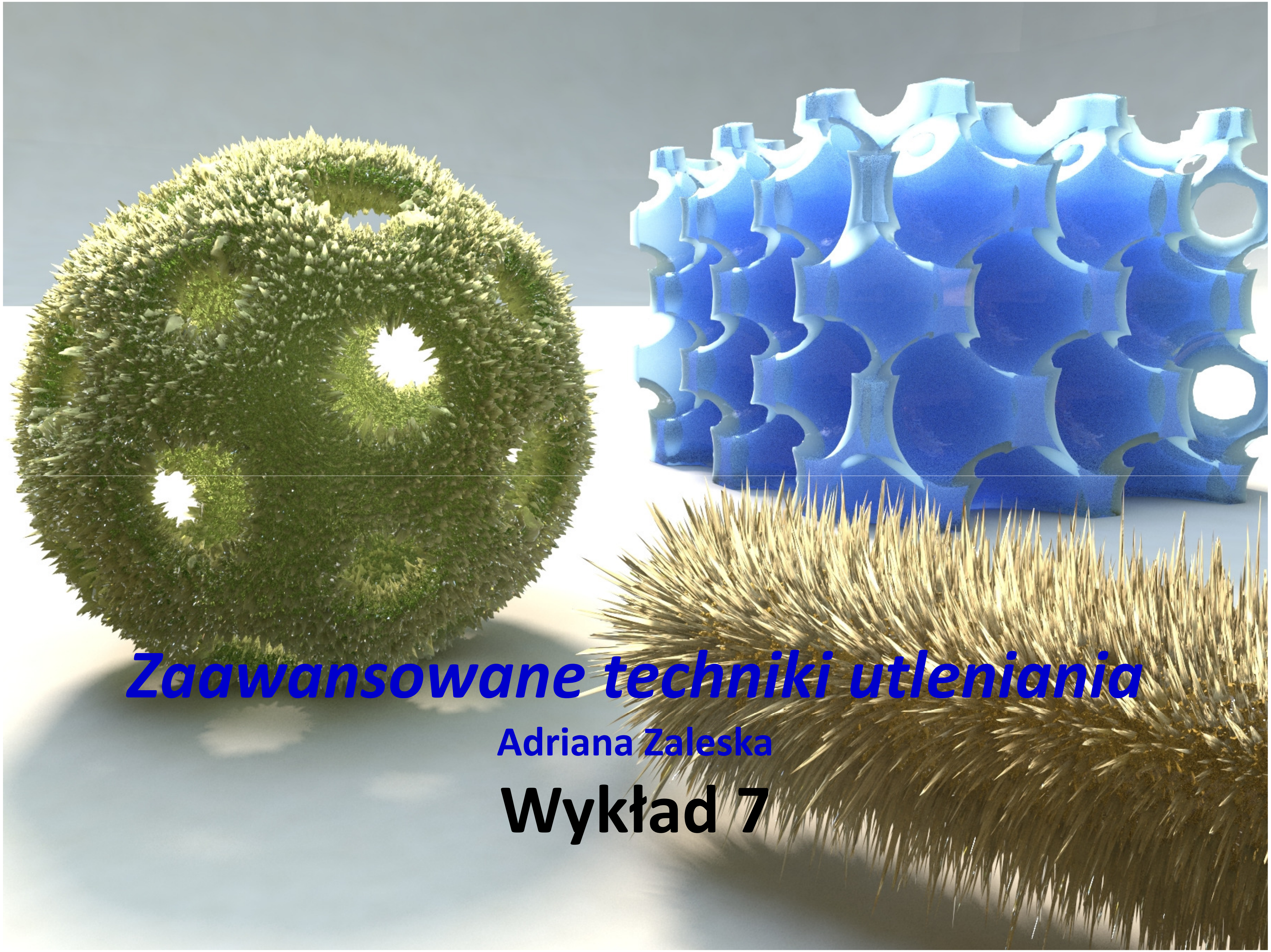


# *Zaawansowane techniki utleniania*

Adriana Zaleska

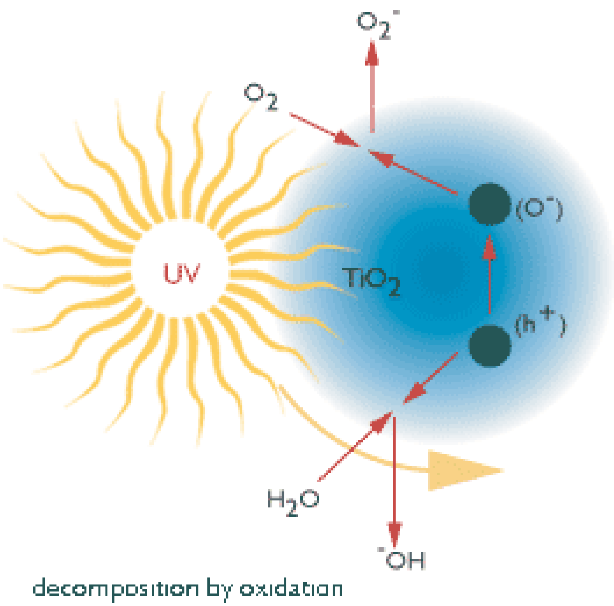
## Wykład 7

# Program wykładu 7

1. Mechanizm wzbudzenia w fotokatalizie heterogenicznej
2. Zastosowanie fotokatalizy heterogenicznej

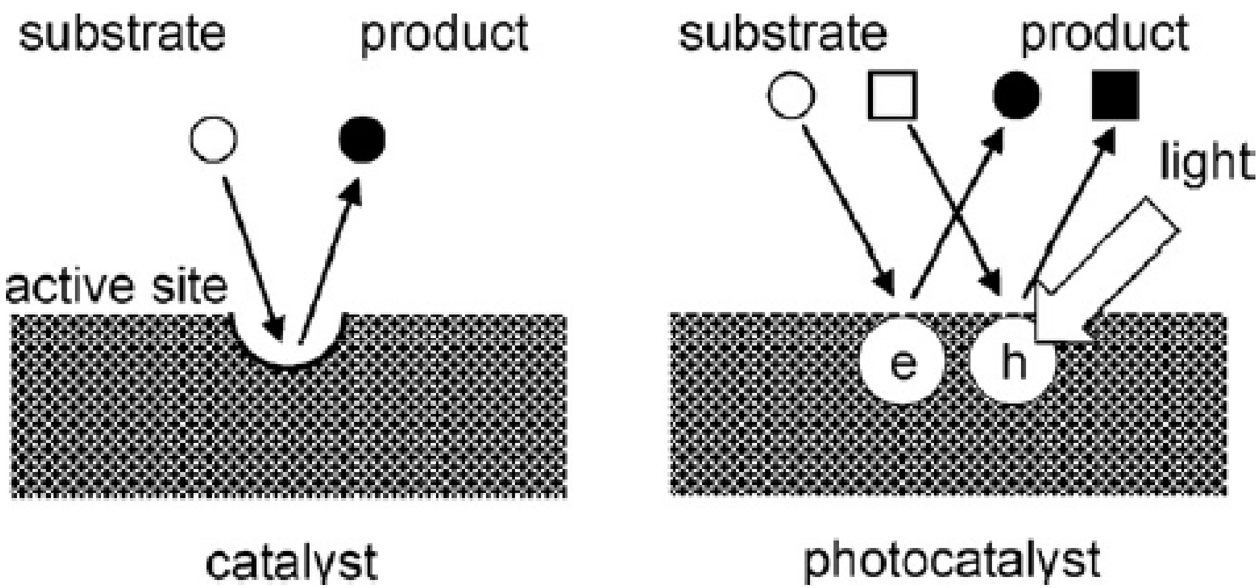
# Fotokataliza heterogeniczna: definicja

"**photocatalytic reaction**" can be defined as a chemical reaction induced by photoabsorption of a solid material, or "photocatalyst", which remains unchanged during the reaction




*Prof. Bunsho Othani*

# Fotokataliza heterogeniczna vs. kataliza heterogeniczna

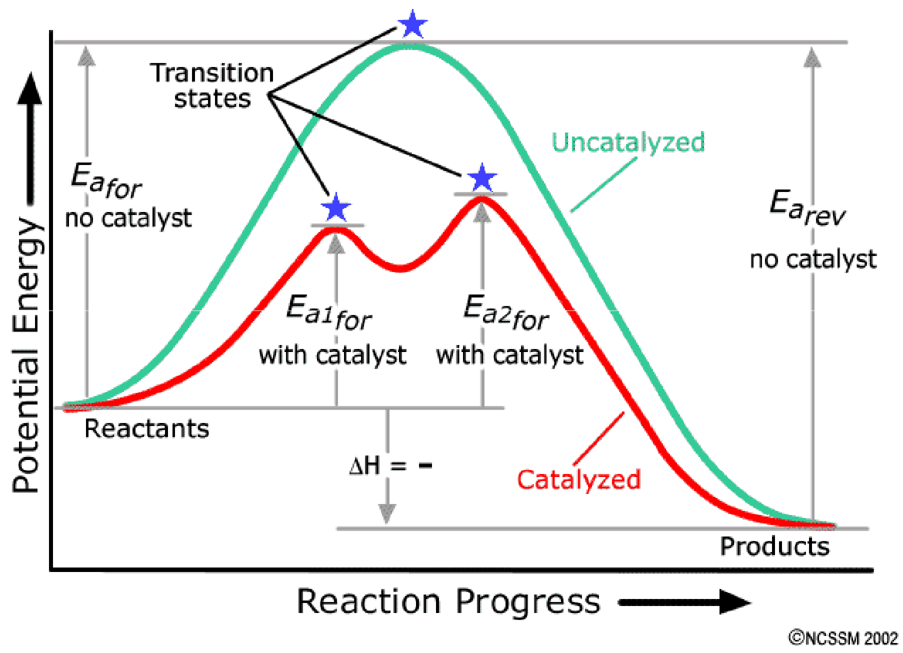



A catalyst contain active site of which a substrate is converted into product

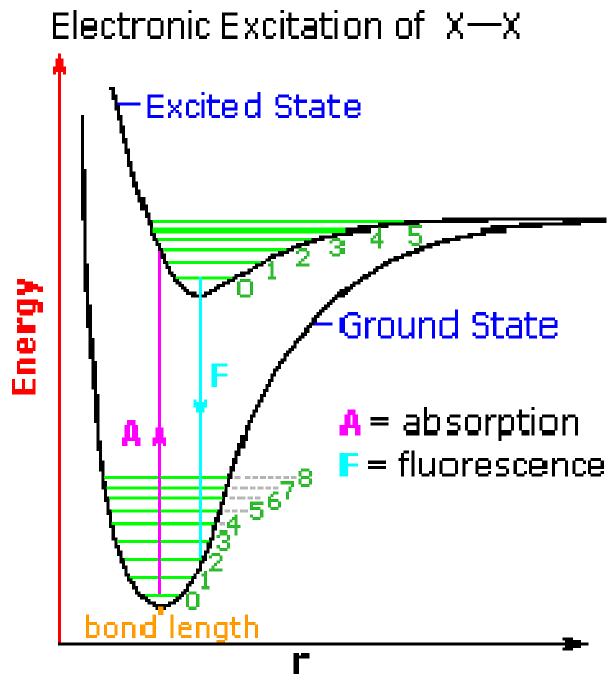
NO ACTIVE SITES are present at the surface of photocatalyst

*B. Ohtani/ J. Photochem. Photobiol. C: 11 (2010) 157-178*

# Fotokataliza heterogeniczna vs. kataliza heterogeniczna
## (diagramy energetyczne)




catalytic reaction




photochemical reaction

*M. Ethirajan et al. / Chem. Soc. Rev. 40 (2011) 340-362*

# Fotokataliza heterogeniczna

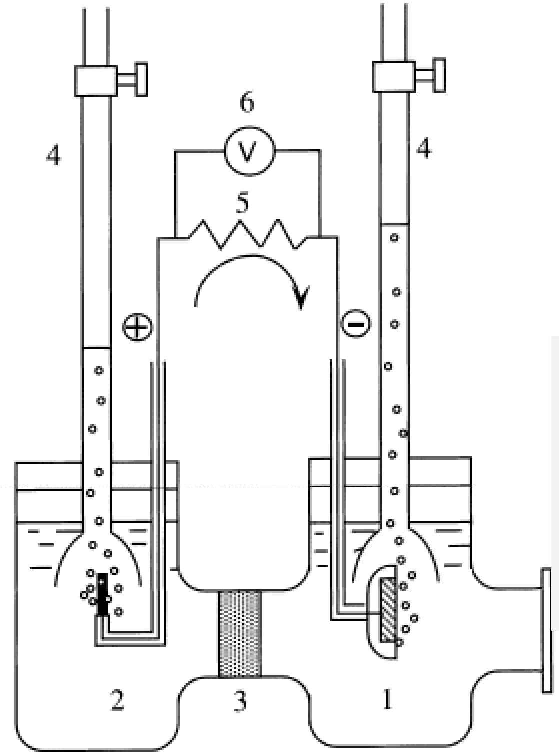



Fig. 1. Schematic diagram of an electrochemical photocell [6]. (1) n-type $TiO_2$ electrode; (2) platinum black counter electrode; (3) ionically conducting separator; (4) gas buret; (5) load resistance and (6) voltmeter.

…de have been measured with a static potentiometer in …rk and under irradiation with light[2] (Fig. 1). Anodic …t which is proportional to the intensity of light begins …v for wavelengths shorter than 415 nm, that is 3.0 eV, …corresponds to the band gap of $TiO_2$. The current …s saturation at potentials positive relative to a saturated …el electrode (SCE). These facts suggest that the anodic …on is related to the formation of holes in the valence …by light excitation. Oxygen evolution was confirmed by …l means of analytical measurements[3,4]. Oxygen evolu… …ccurs at −0.5 V (SCE) in an aqueous electrolyte of pH …his is more negative than the standard potential. We …termed such behaviour "photosensitized electrolytic …ion" (ref. 2). When halogen ions were introduced in the …lyte, they were also oxidized through the suggested …nism of photosensitized electrolytic oxidation. This …curred with other types of n-type semiconductor such as …nd CdS (ref. 5). We believe therefore that the oxygen …ion reaction on the $TiO_2$ electrode under irradiation …s to the first category described above. …then constructed an electrochemical cell in which a $TiO_2$ …de was connected with a platinum black electrode …h an external load (Fig. 2). When the surface of the …

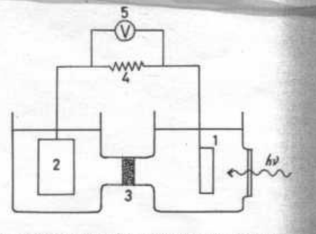



Fig. 2 Electrochemical cell in which the $TiO_2$ electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 $cm^2$.

increase the efficiency of the decomposition process, more reducible species, for example, dissolved oxygen or $Fe^{3+}$ ions, must be added in the compartment of the platinum electrode. When $Fe^{3+}$ ions were added, the current produced under irradiation increased. Currents of a few mA flowed when the …

1976 : chlorobiphenyl and biphenyl were degraded at the surface of irradiated $TiO_2$

*Carey et al. Environ. Contam. Toxicol. 16 (1976) 697*

…starting potential of the oxidation reaction at the $TiO_2$ …de corresponds almost exactly to the flatband potential …is constant in the electrolyte solution of a given pH. To …


1 Coehn, A., Ber. Deutsch. Chem. Gesellschaft, 43, 880 (1910).
2 Fujishima, A., Honda, K., and Kikuchi, S., J. Chem. Soc. Japan (Kogyo Kagaku Zasshi), 72, 108 (1969).
3 Fujishima, A., and Honda, K., J. Chem. Soc. Japan, 74, 355 (1971).
4 Fujishima, A., and Honda, K., J. Institute of Industrial Science, University of Tokyo (Seisan Kenkyu), 22, 478 (1970).
5 Fujishima, A., Sugiyama, E., and Honda, K., Bull. Chem. Soc. Japan, 44, 304 (1971).

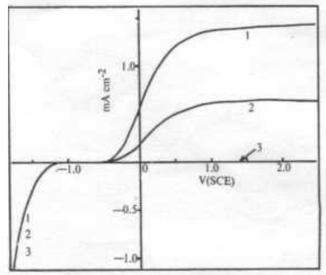




Fig. 1 Current–voltage curves for $TiO_2$ n-type semiconductor. A single crystal wafer of n-type $TiO_2$ (rutile) was used after treatment at 700° C at $10^{-4}$ ~ $10^{-5}$ torr for roughly 4 h to increase the conductivity of the crystal. This wafer was approximately 1.5 mm thick and the exposed (001) surface area was approximately 1.0 $cm^2$. Indium was evaporated on to one side of the surface to ensure ohmic contact and a copper lead wire was connected on the indium layer with silver paste. All other surfaces were sealed by epoxy resin.

…olymers. The mass spectrometer study showed that electron …mpact will fragment the perfluoropolyether molecule, so we …onclude that neither the parent molecule nor its fragments …an be polymerized by electron bombardment either in the …quid or the adsorbed state.

We note that if a mass spectrometer with a nude source, …s used in these experiments, had been operated at room …emperature in the saturated vapour of any of the hydrocarbon …r silicone pump fluids, then serious contamination and failure …f the ion source would have ensued within a few hours.

…decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled. First, oxygen evolution occurs at a potential more negative than that at which hydrogen evolution occurs in normal conditions; second, hydrogen evolution occurs at a potential more positive than that at which oxygen evolution occurs in normal conditions; third, the potential for oxygen evolution is made more negative and that for hydrogen evolution is made more positive, until the former is more negative than the latter.

Current–voltage curves of a semiconducting n-type $TiO_2$

## BIOLOGICAL SCIENCES

### One and Two-dimensional Structure of Alpha-Helix and Beta-Sheet Forms of Poly(L-Alanine) shown by Specific Heat Measurements at Low Temperatures (1.5–20 K)

HOMOPOLYPEPTIDES provide good model systems for various aspects of proteins[1,2]. Recent advances in high polymer and solid state physics have enabled the vibrational aspects of the simpler homopolypeptides to be treated as normal—but complicated—polymers by the theoretical techniques of lattice dynamics based on the experimental methods of neutron, infrared and Raman spectroscopy. Basically, however, these latter methods examine the optical vibrational modes of a system, that is, those modes which are of energy higher than, for example, 70 $cm^{-1}$. The important lower-energy modes are …

*A. Fujishima and K. Honda / Nature 228 (1972) 37-38*

# Fotokataliza heterogeniczna: mechanizm wzbudzenia

## 1s, 2nd and 3rd generation of the photocatalysts

**1960s-1970s**

1990s — *metal doping*

2001 — *nonmetal doping*

**2012**

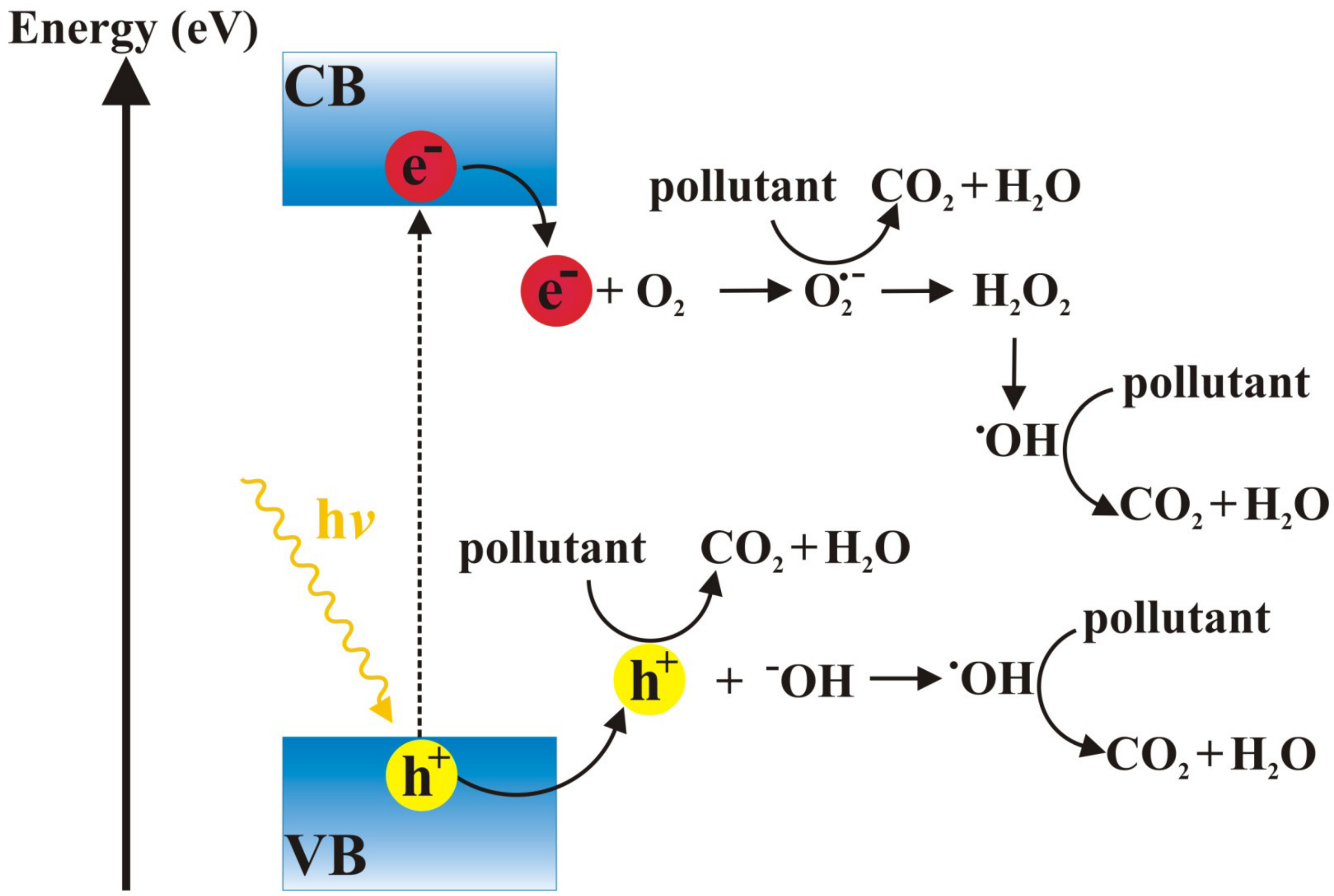
1st generation photocatalysts (**metal oxides**)

2nd generation photocatalyts (**doped and modified $TiO_2$**)

3rd generation photocatalysts (**semiconductors nanocomposites** )

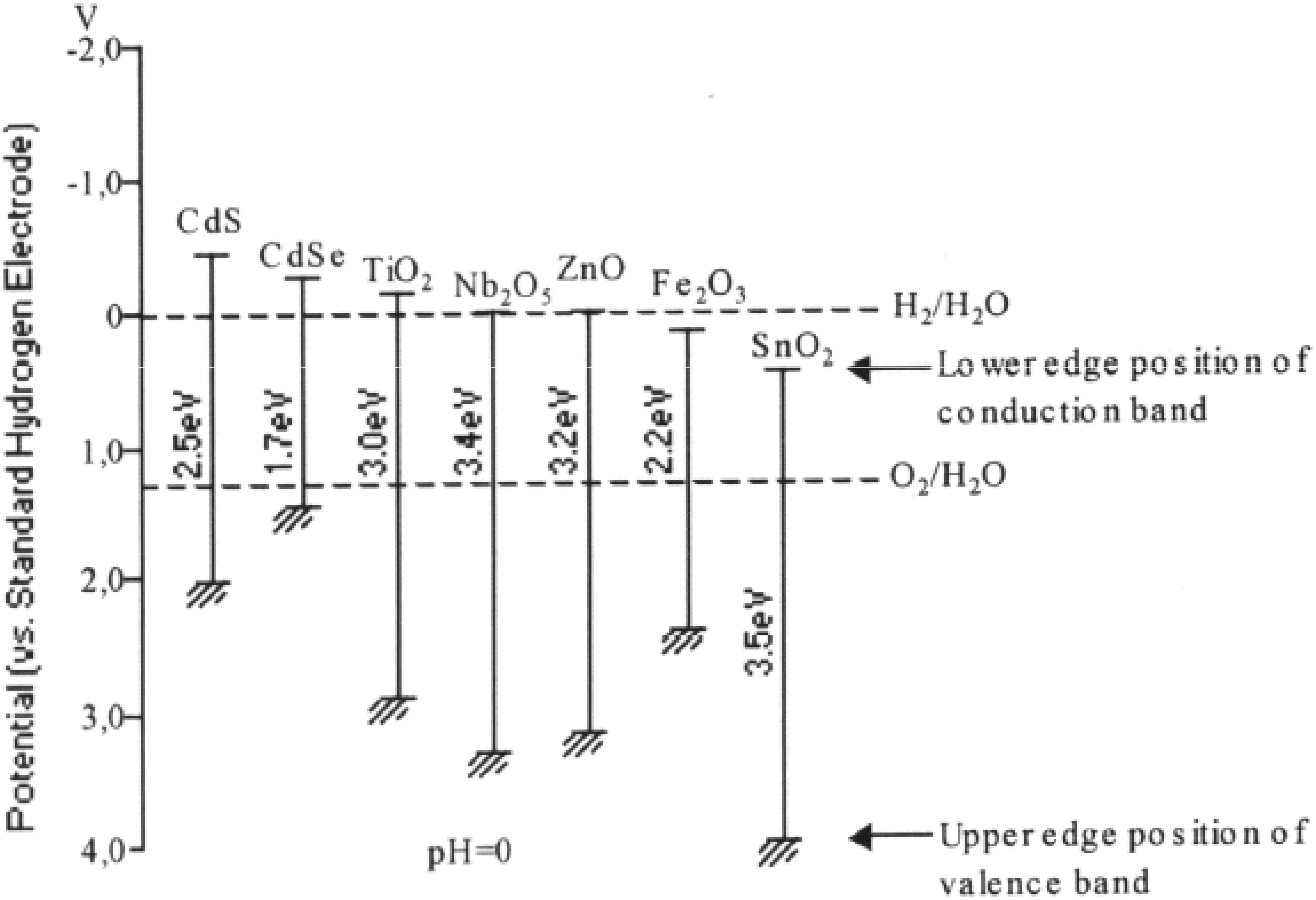
*A.V. Emeline et al. / Environ Sci Pollut Res 19 (2012) 3666-3675*

# Fotokataliza heterogeniczna: mechanizm wzbudzenia




**Wzbudzenie półprzewodnika**

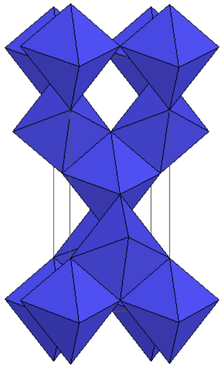
# Półprzewodniki w fotokatalizie heterogenicznej



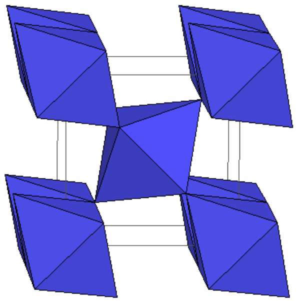
# Właściwości tlenku tytanu(IV)

Struktury krystaliczne:

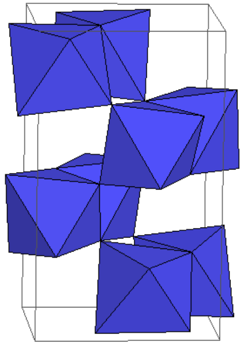
Anataz



Rutyl



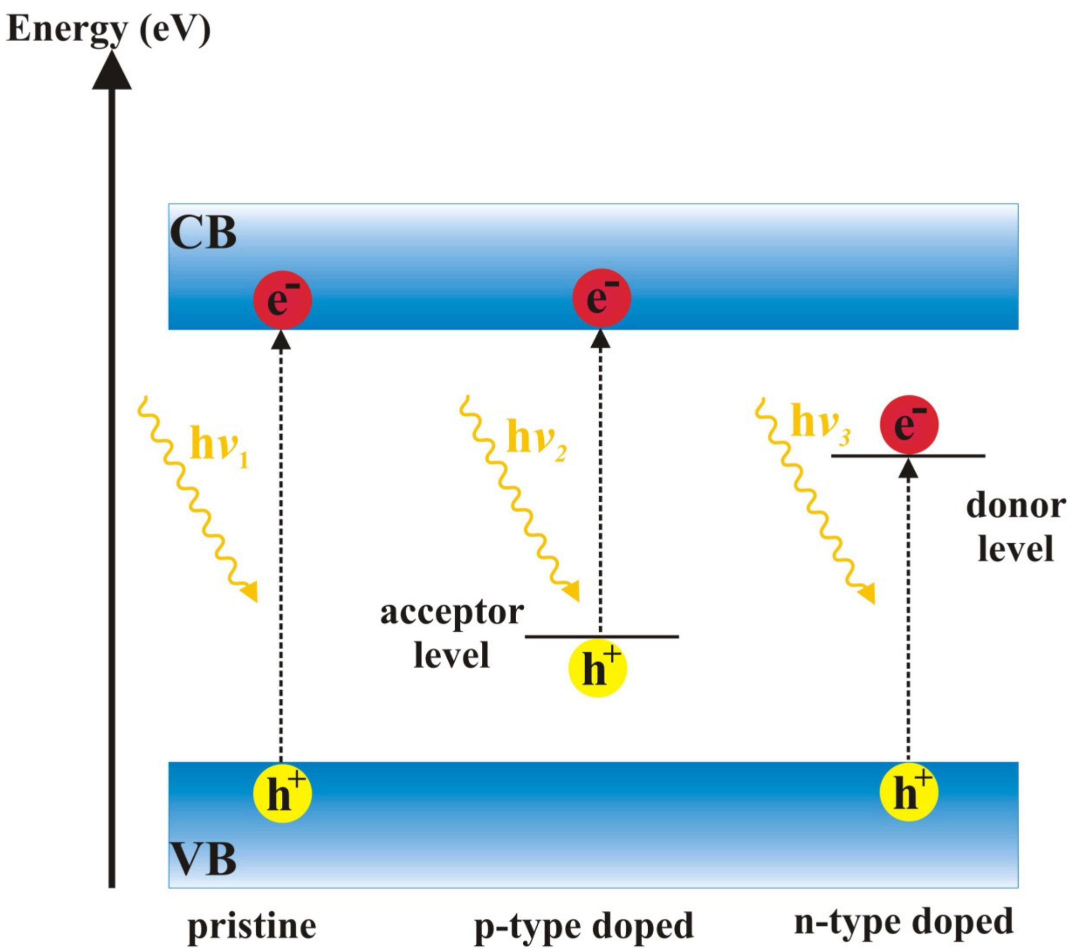
Brukit



**Potencjał fotogenerowanych ładunków:**

**dziury ($h^+$): +2,53 V, elektrony ($e^-$): -0,52 V**

# Fotokataliza heterogeniczna: mechanizm wzbudzenia




**Wzbudzenie półprzewodnika domieszkowanego**

# Domieszkowanie półprzewodnika

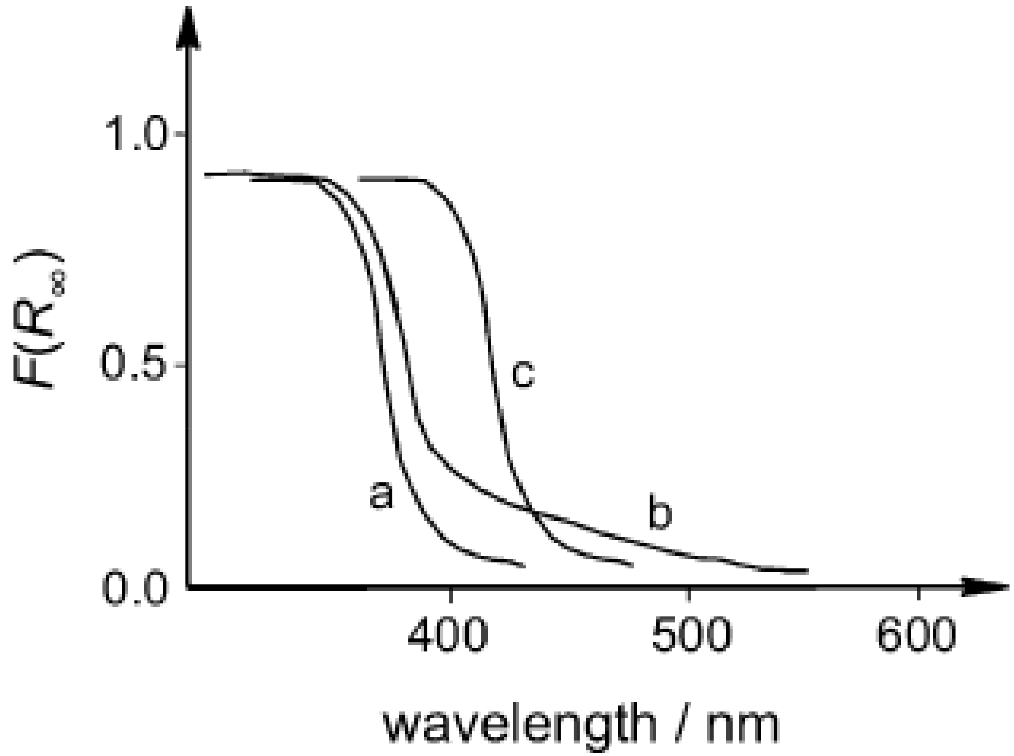
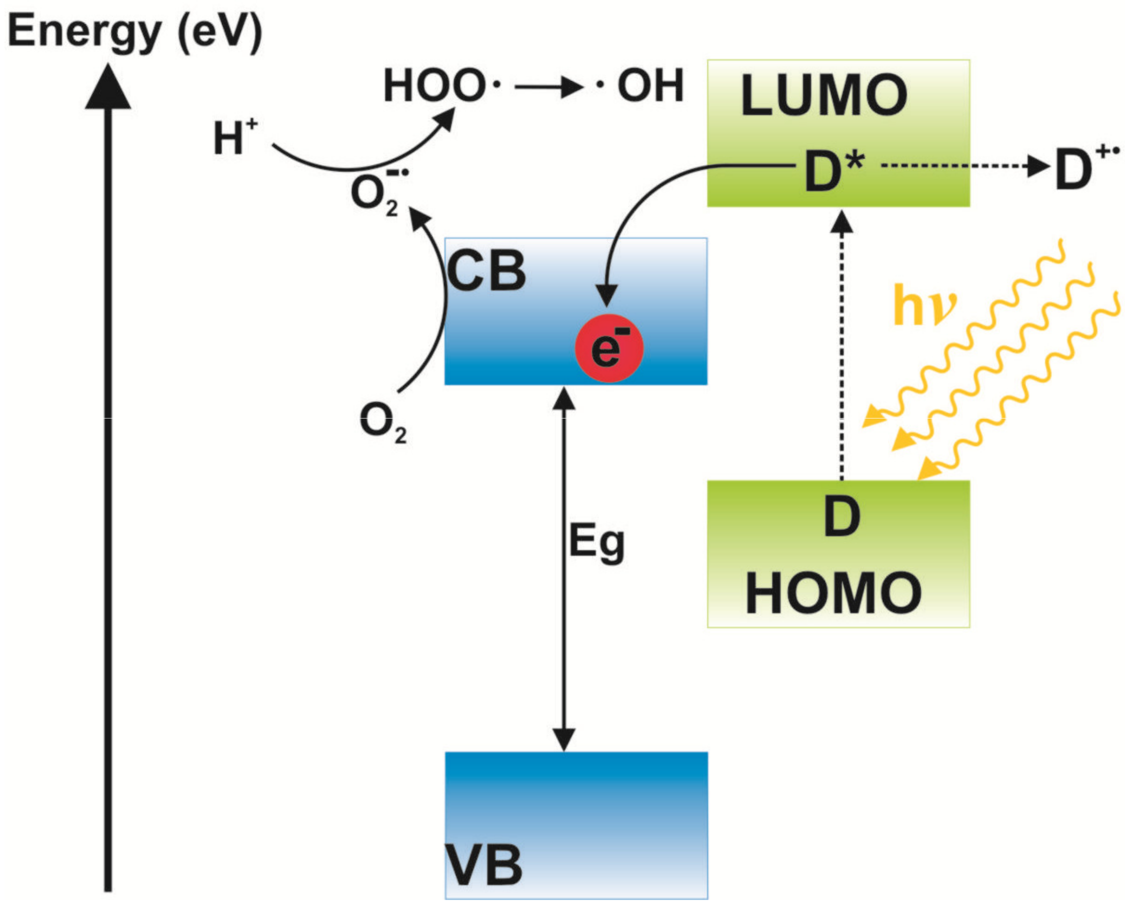



***Figure 8.*** Diffuse reflectance spectra of a) a pristine semiconductor, b) a semiconductor modified by introducing intra-bandgap states, and c) a semiconductor modified by shift of the band edges.

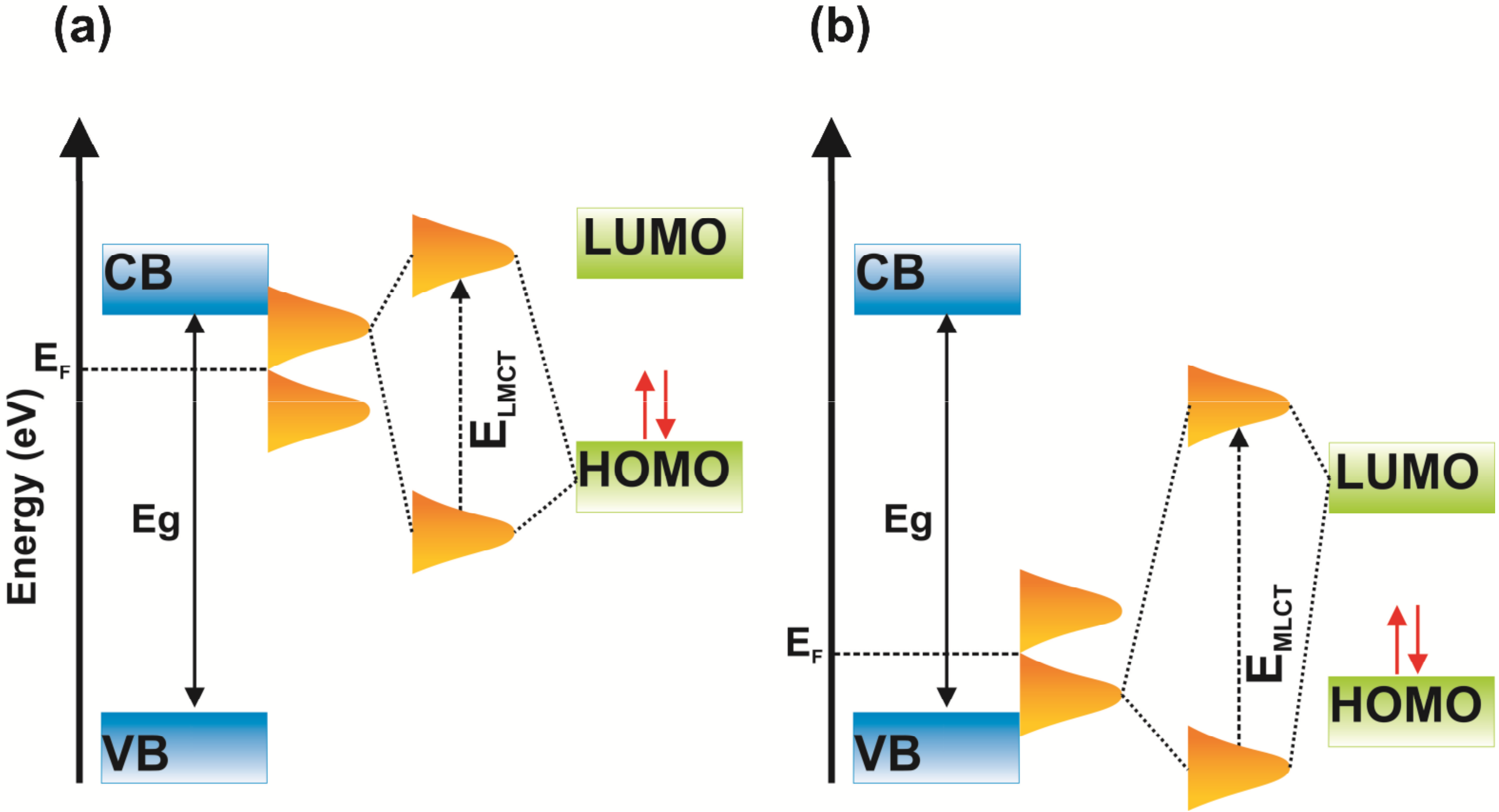
*Angew. Chem. Int. Ed.* **2013**, *52*, 812–847

# Fotokataliza heterogeniczna: mechanizm wzbudzenia



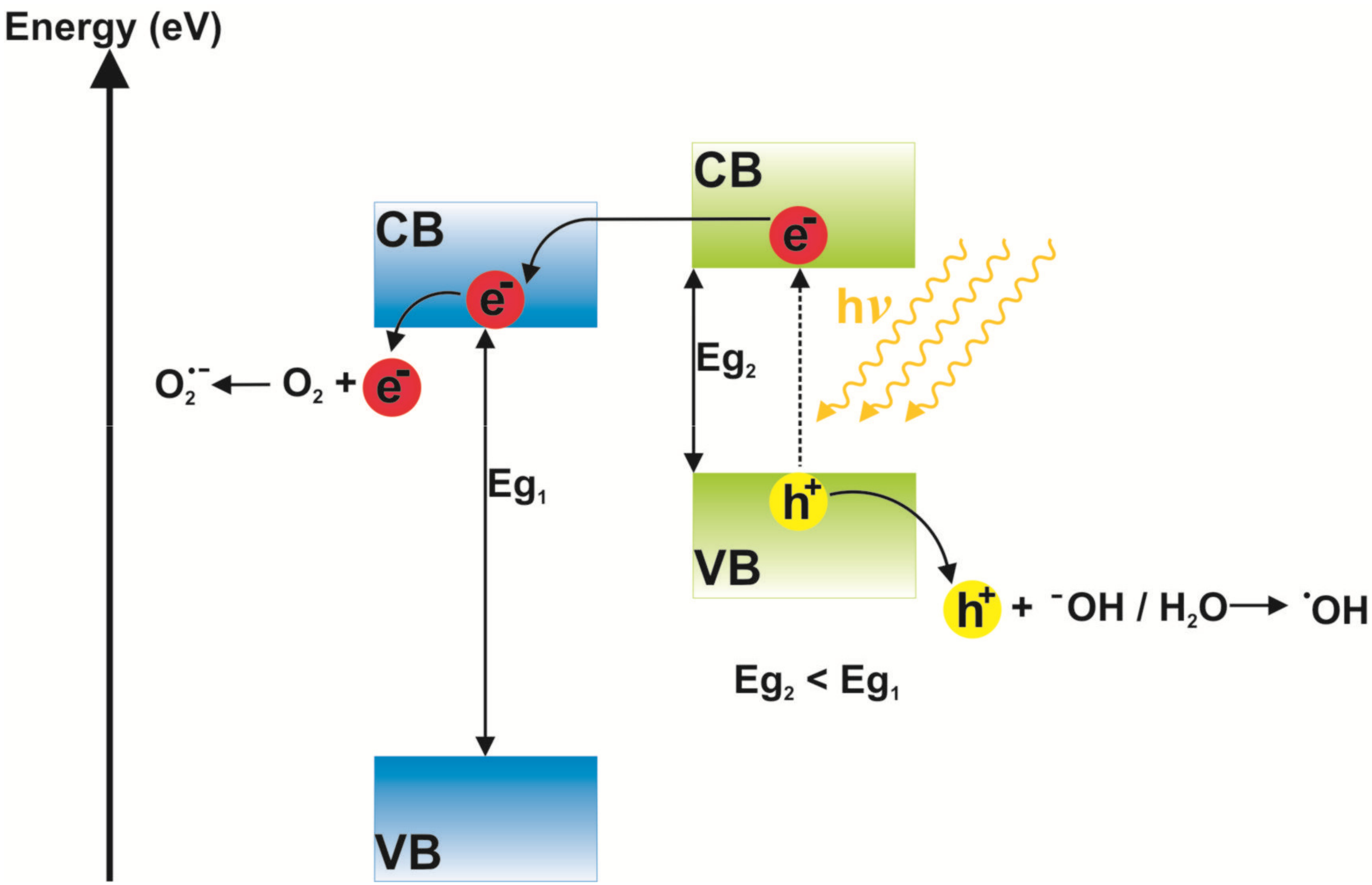

**Wzbudzenie półprzewodnika modyfikowanego barwnikiem (sensybilizatorem)**

# Fotokataliza heterogeniczna: mechanizm wzbudzenia



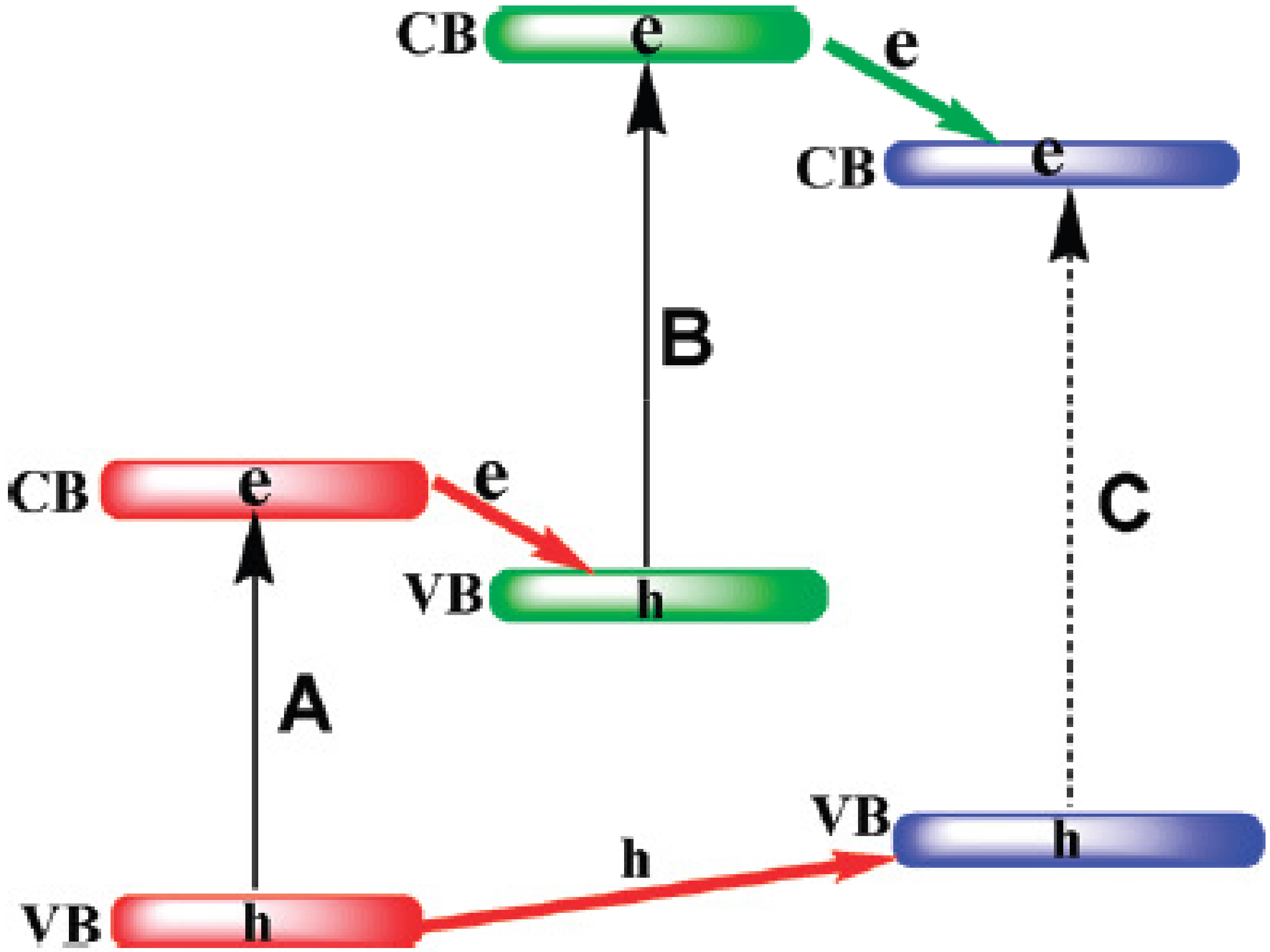

**Wzbudzenie półprzewodnika modyfikowanego związkiem organicznym (kompleks powierzchniowy)**

# Fotokataliza heterogeniczna: mechanizm wzbudzenia



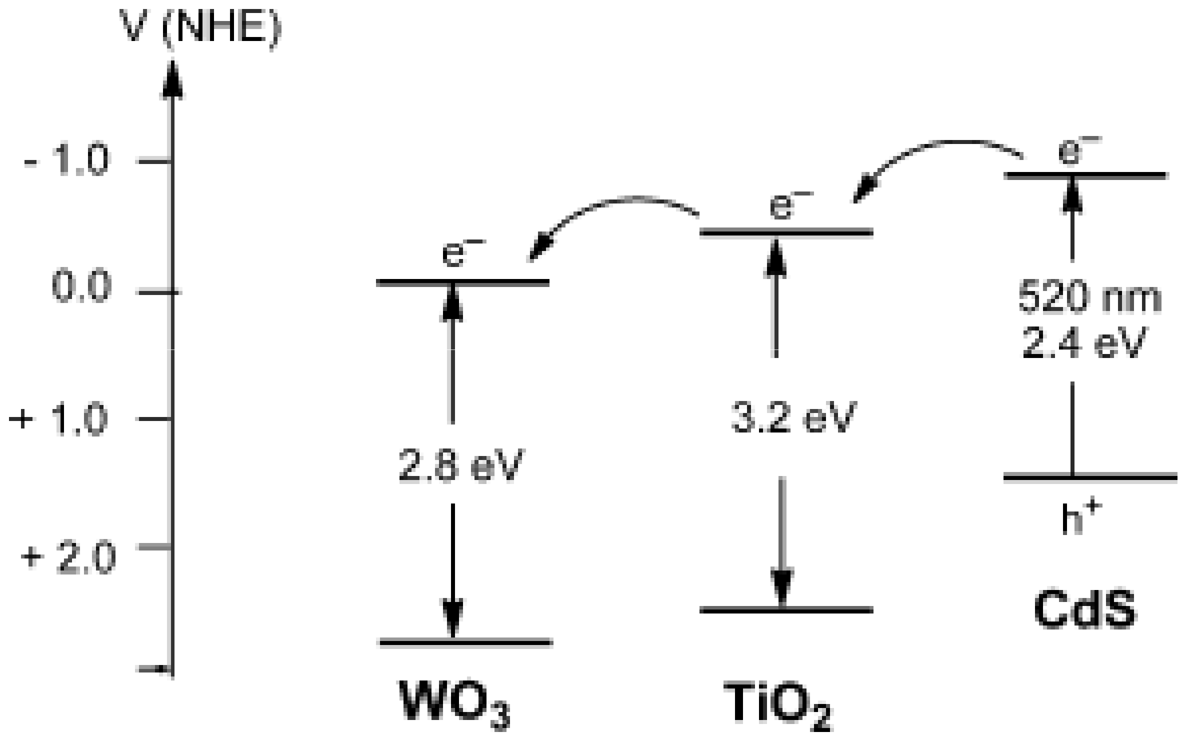

**Wzbudzenie kompozytu dwóch półprzewodników różniących się szerokością przerwy wzbronionej ($E_g$)**

# Fotokataliza heterogeniczna: układy hybrydowe




*N. Serpone & A.V. Emeline / J. Phys. Chem. Lett. 2012, 3, 673–677.*

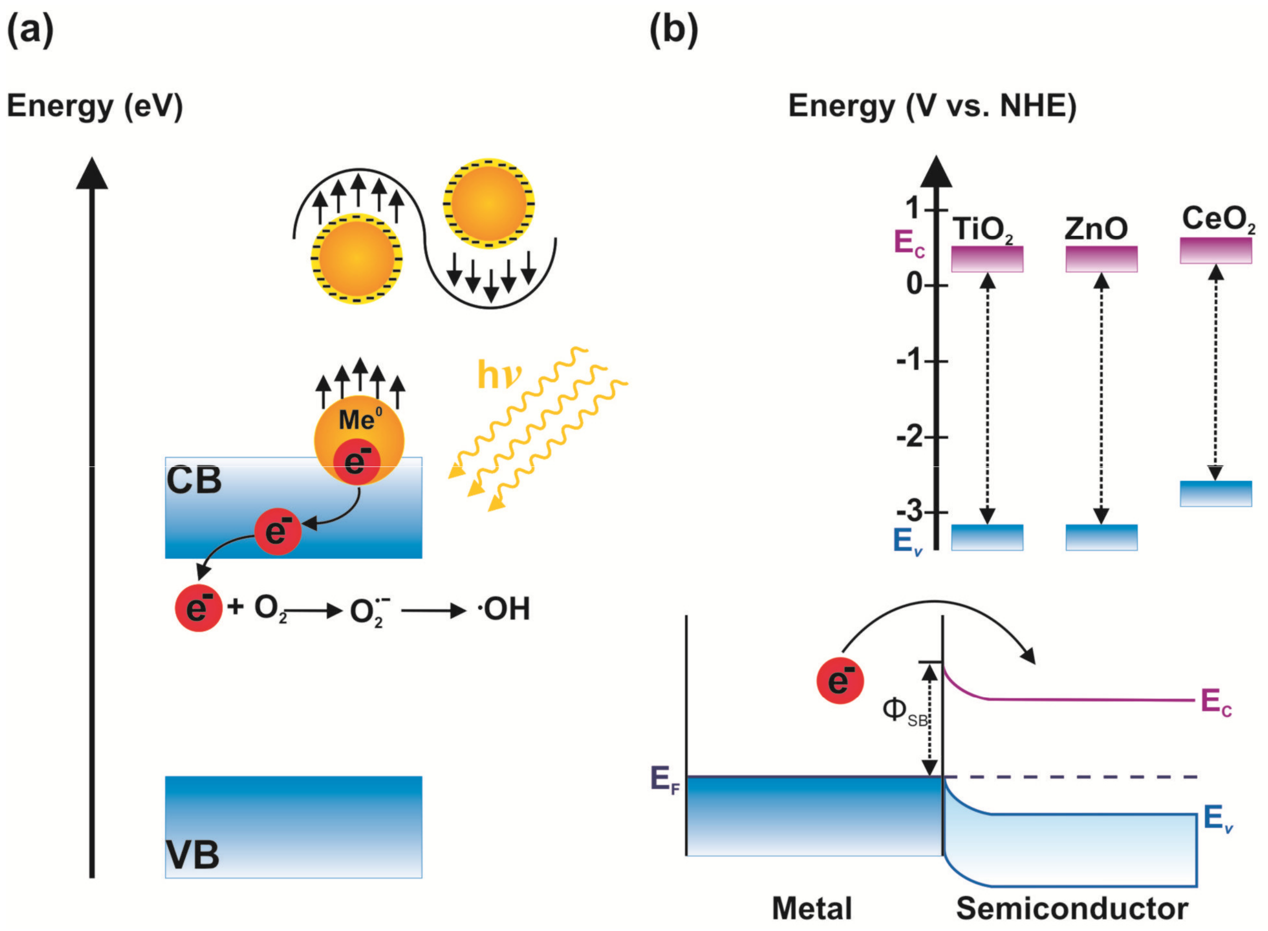
# Fotokataliza heterogeniczna: układy hybrydowe




*Scheme 8.* Schematic description of postulated interparticle electron transfer in the hybrid CdS-O-$TiO_2$-O-$WO_3$.

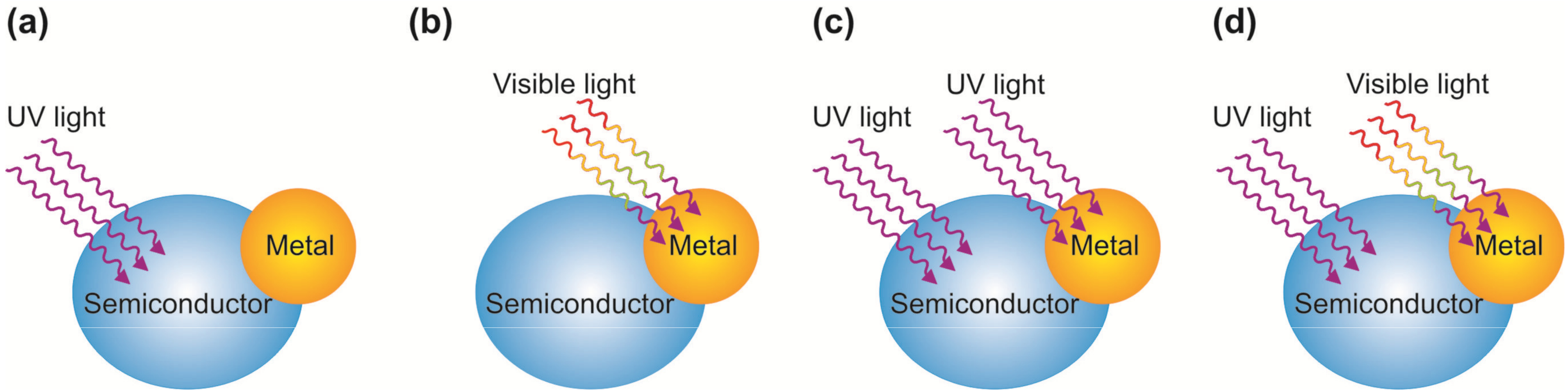
Angew. Chem. Int. Ed. **2013**, 52, 812–847

# Fotokataliza heterogeniczna: mechanizm wzbudzenia



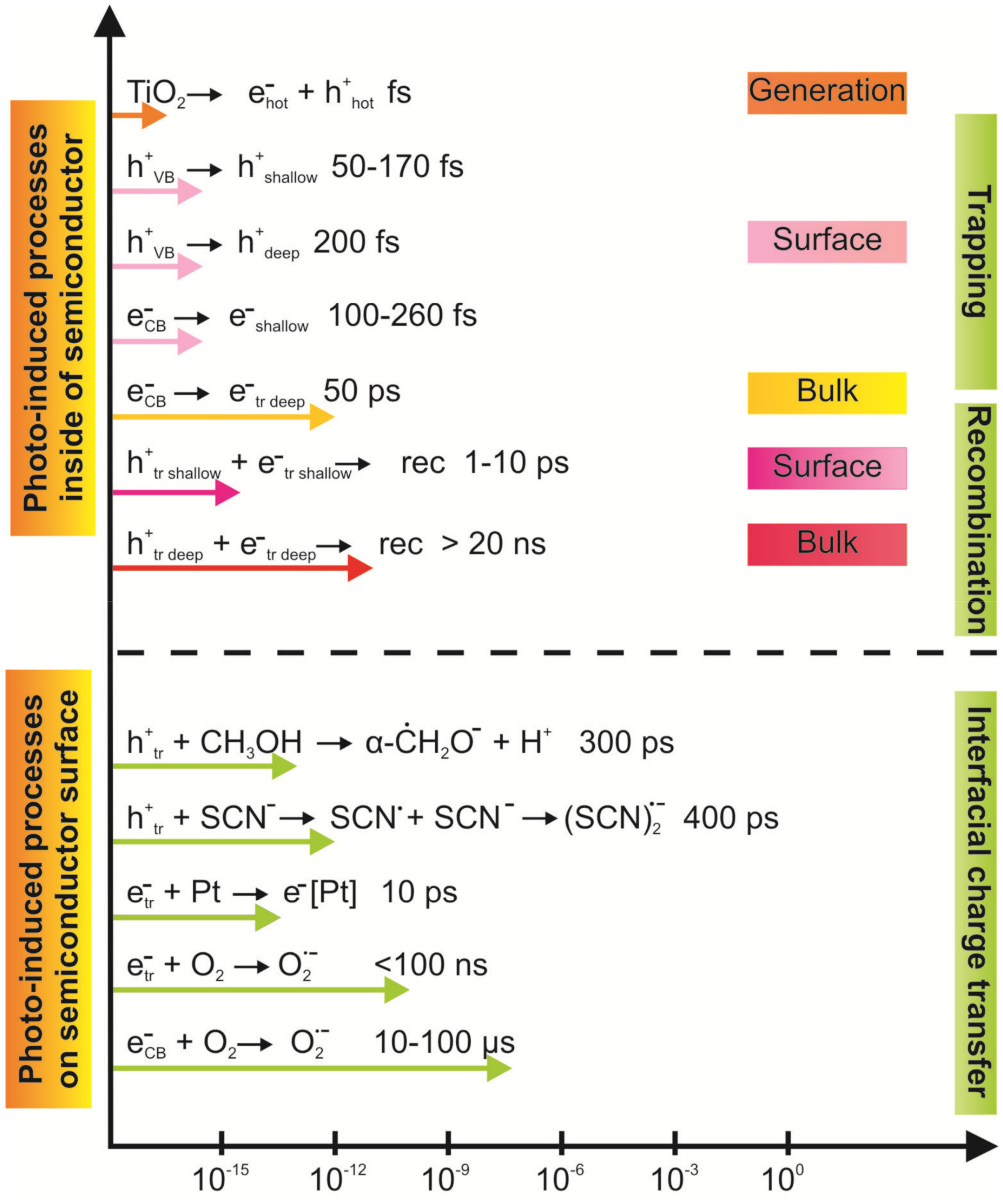

**Wzbudzenie półprzewodnika modyfikowanego nanocząstką metalu szlachetnego**

# Fotokataliza heterogeniczna: mechanizm wzbudzenia



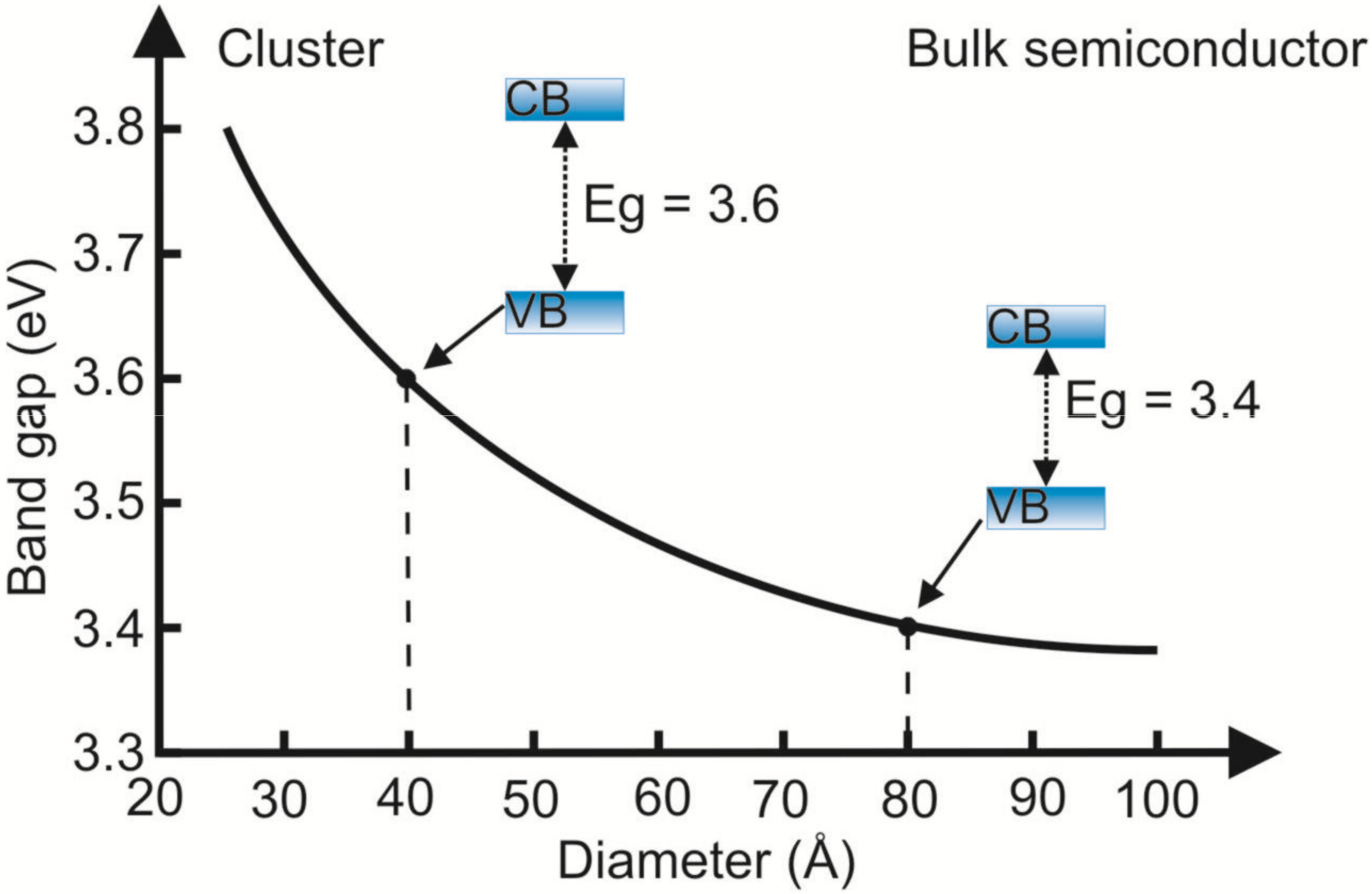

**Mechanisms of enhancement of photocatalytic efficiency under UV and visible light irradiation after deposition of a noble metal on $TiO_2$: (a) bandgap-excitation state, (b) LSPR state, (c) dual-excitation state, (d) separate-excitation state**

**Wzbudzenie półprzewodnika modyfikowanego nanocząstką metalu szlachetnego**



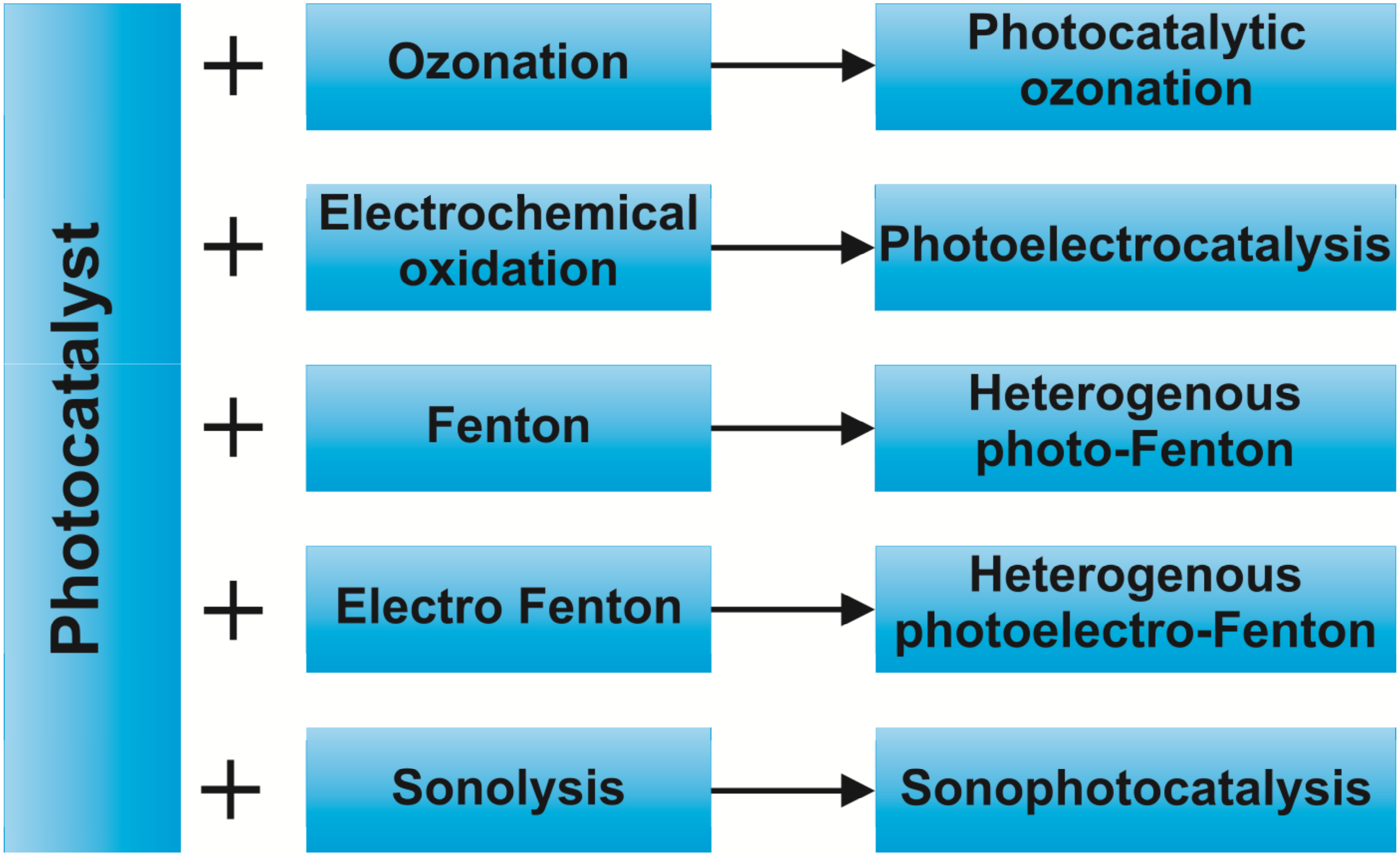

# Fotokataliza heterogeniczna: szybkość reakcji

# Przerwa wzbroniona a wielkość cząstki



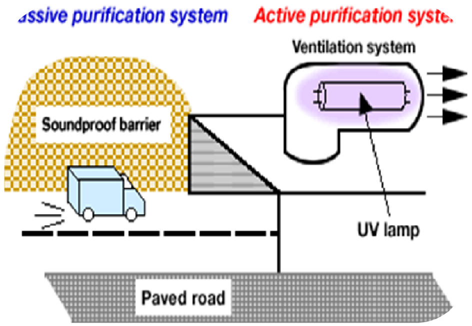

Quantum size effect on semiconductor bandgap (for ZnO)

# Fotokataliza heterogeniczna sprzęgana z innymi technikami



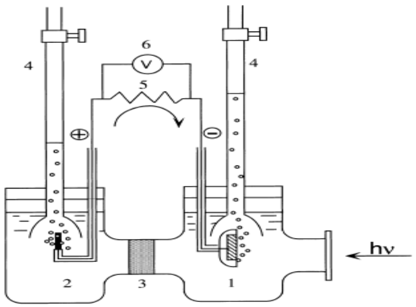
# Zastosowanie fotokatalizy heterogenicznej w ochronie środowiska

Oczyszczanie wód i ścieków

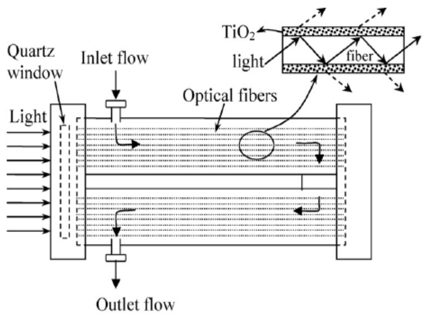



Oczyszczanie powietrza

Powierzchnie samoczyszczące




Rozkład wody

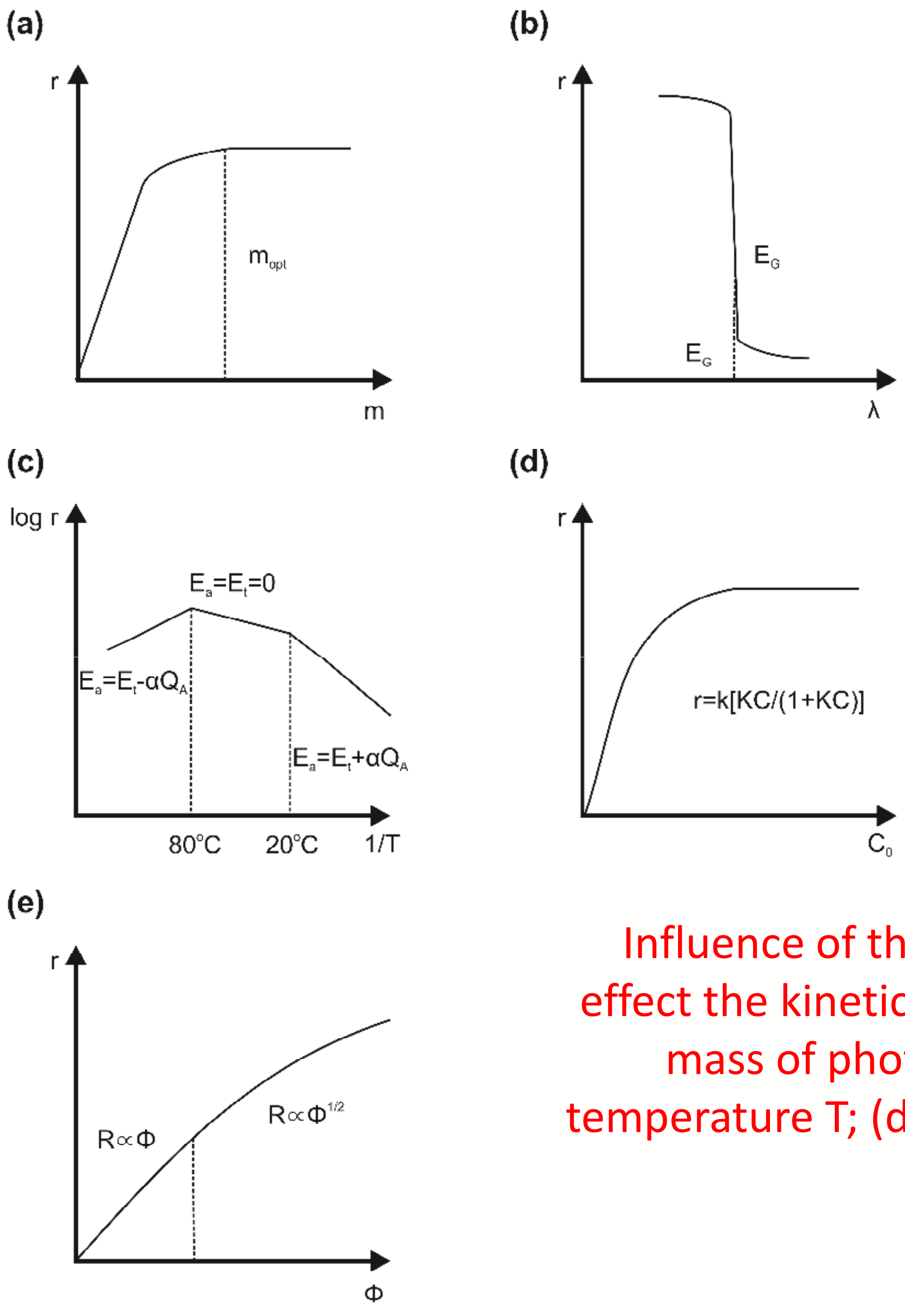



Fotokonwersja $CO_2$

# Efektywność degradacji zanieczyszczeń

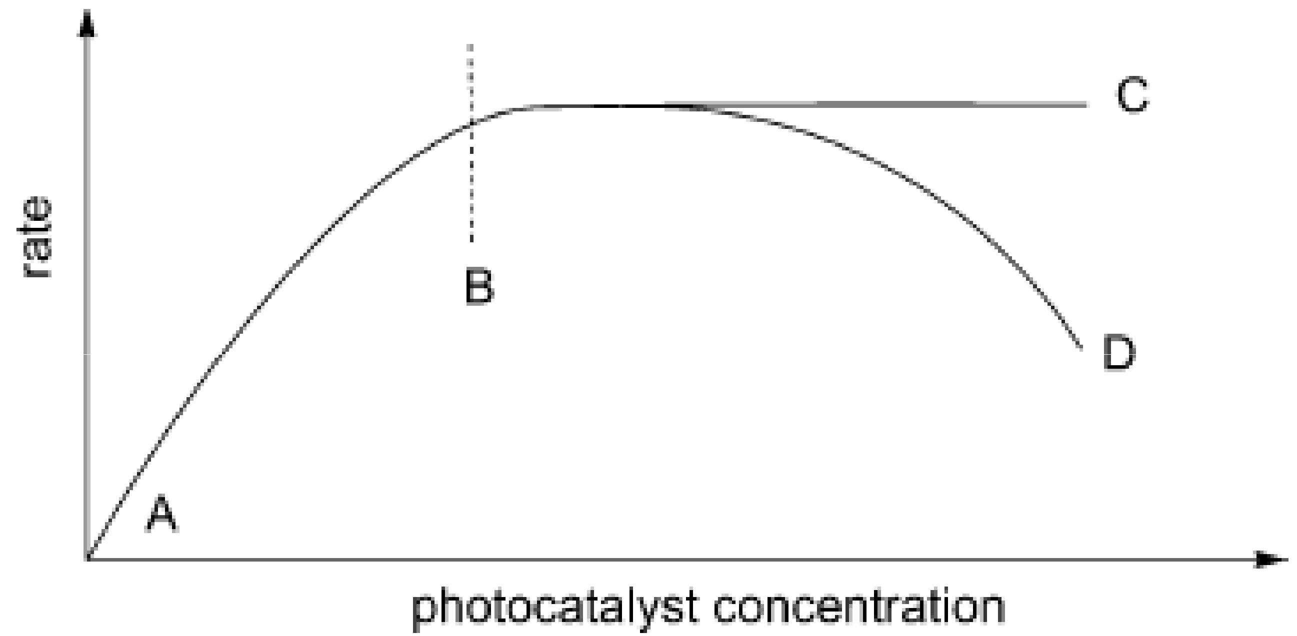
- ❑ **Budowa i stężenie zanieczyszczeń**
- ❑ **Intensywność promieniowania**
- ❑ **Zawartość $TiO_2$ oraz $O_2$**
- ❑ **Medium reakcyjne (faza gazowa/ ciekła)**
- ❑ **Właściwości $TiO_2$:**
    - ❖Powierzchnia właściwa
    - ❖Odmiana krystaliczna (anataz/ rutyl)
    - ❖Obecność domieszek

# Efektywność degradacji zanieczyszczeń - wpływ parametrów reakcji




Influence of the different physical parameters that effect the kinetics of photocatalysis, reaction rate *r*: (a) mass of photocatalyst *m*; (b) wavelength λ; (c) temperature T; (d) initial concentration *c* of reactant; (e) radiant flux *Φ*.

# Efektywność degradacji zanieczyszczeń




Wpływ zawartości fotokatalizatora na szybkość reakcji

*Angew. Chem. Int. Ed.* **2013**, 52, 812–847

# Fotokataliza - zastosowanie

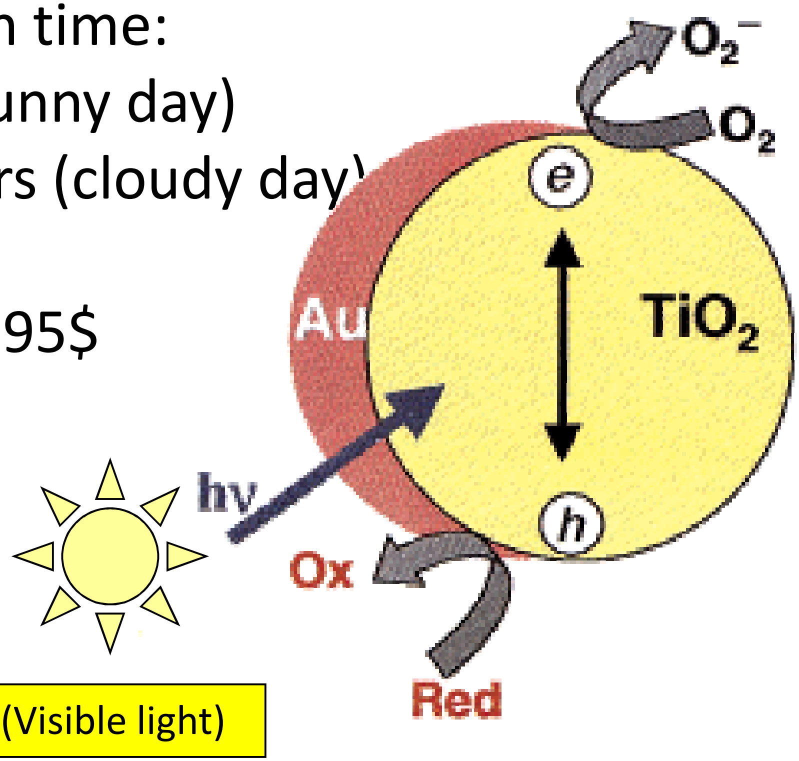
## *Portable photoreactors for water treatment and disinfection*


SolarBag®

Purification time:

- ❑ 2-3 h (sunny day)
- ❑ 4-6 hours (cloudy day)

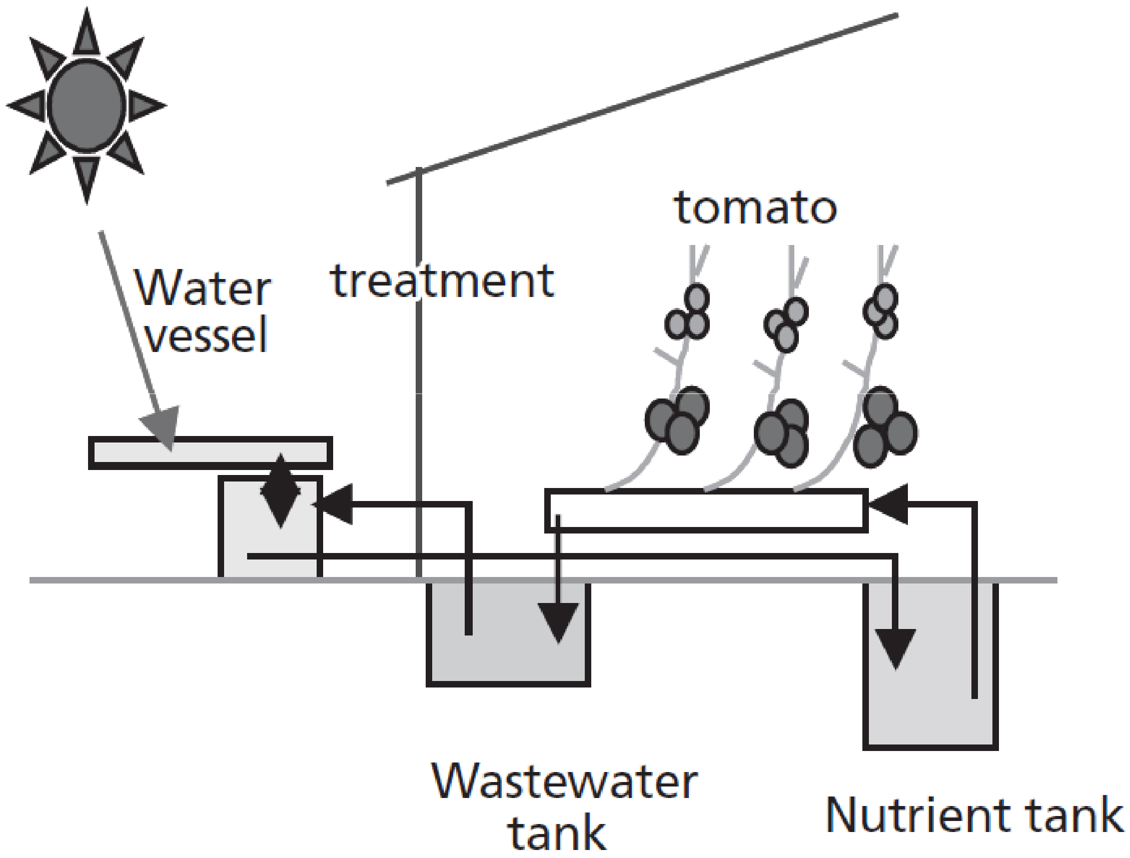
1 bag – 99.95$




*Puralytics®*

# Fotokataliza - zastosowanie

**Water treatment**

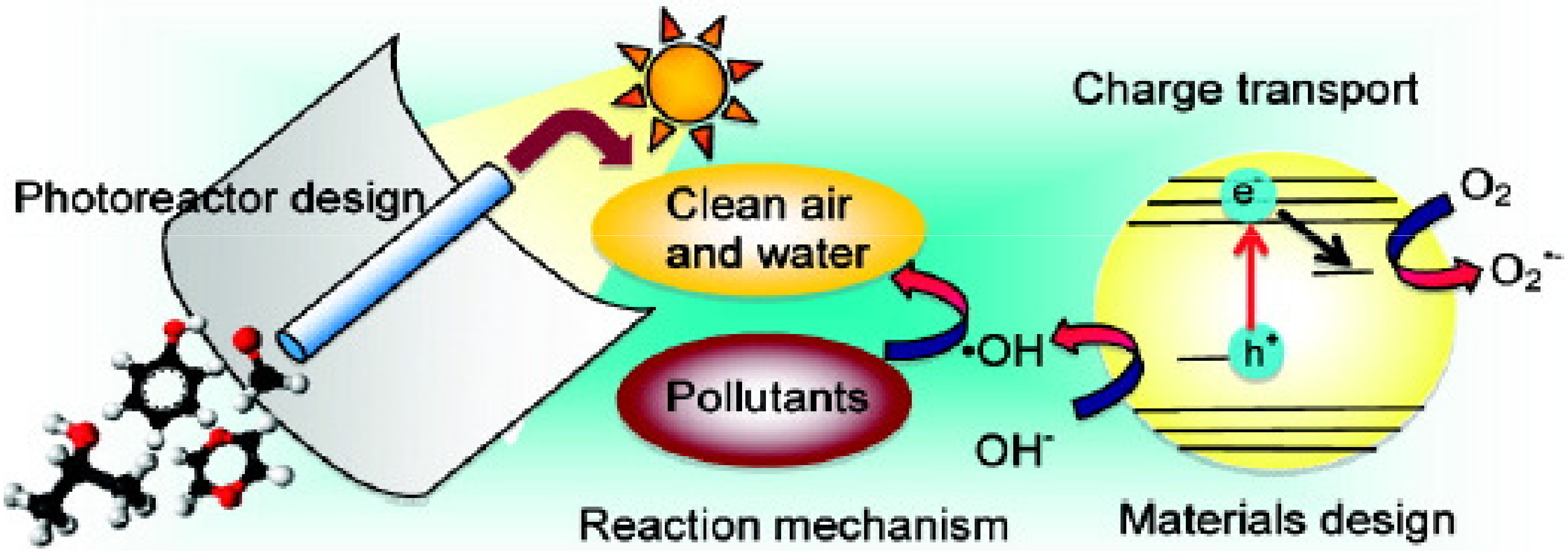



**Novel photocatalytic water recycling system of tomato hydroponic culture**

*K. Hashimoto et al.. / Jap. J. Appl. Phys. A. 44 (2005) 8269-8285*

# Instalacje ćwierć-techniczne

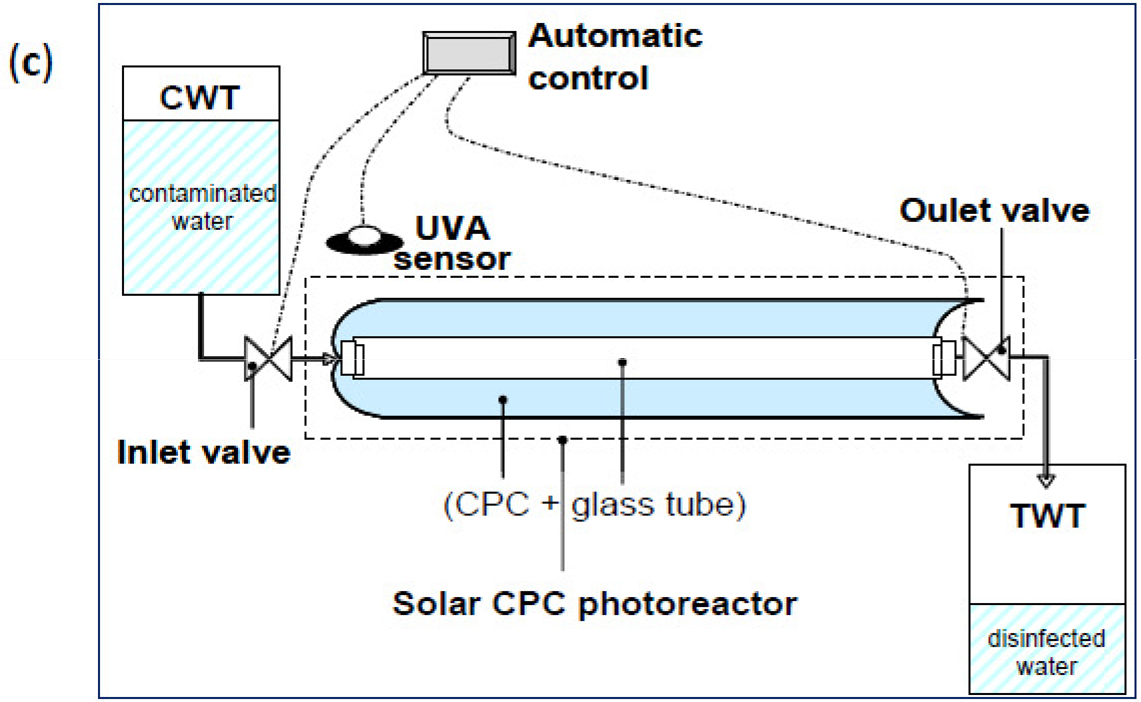
**Water and air treatment/disinfection**




**Schematic of the interplay of photocatalytic treatment**

# Instalacje ćwierć-techniczne

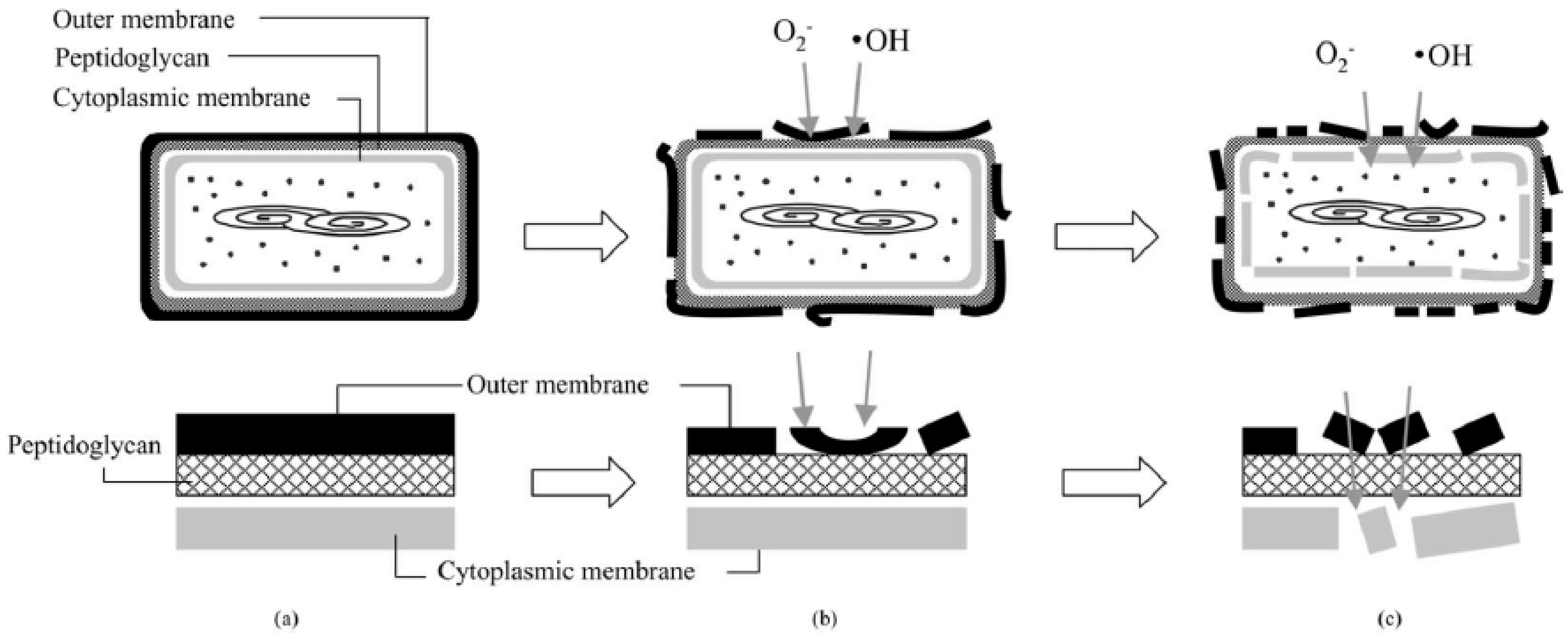
## Water treatment/disinfection




**Batch reactor for solar water treatment**

*E. coli, S. aures, Psedomonas aeruginosa, E. faecium, C. albicans*

# Inaktywacja mikroorganizmów




**Schematic illustration of the process of *E. coli* inactivation on photo-excited $TiO_2$**

*K. Sunada et al.. / J. Photochem. Photobiol. A. 3 (2003) 227-233*

# Inaktywacja mikroorganizmów

**Waterborne microbial species known to be inactivated by solar disinfection**

| Microbe | Species |
|---|---|
| Bacteria | *Campylobacter jejuni* |
| | *Enterococcus* sp. |
| | Enteropathogenic *E. coli* |
| | *Mycobacterium avium* |
| | *Mycobacterium intracellulare* |
| | *Pseudomonas aeruginosa* |
| | *Salmonella typhi* |
| | *Salmonella typhimurium* |
| | *Shigella dysenteriae type 1* |
| | *Shigella flexneri* |
| | *Streptococcus faecalis* |
| | *Staphylococcus epidermidis* |
| | *Vibrio cholerae* |
| | *Yersinia enterocolitica* |
| Viruses | Bacteriophage f2 |
| | Encephalomyocarditis virus |
| | Polio virus |
| | Rotavirus |
| | Coxsackie virus A/B |
| | Hepatitis A |
| Protozoa | *Acanthamoeba polyphaga* (cyst ) |
| | *Cryptosporidium parvum* (oocyst) |
| | *Entamoeba* sp. (cysts) |
| | *Giardia* sp. (cysts) |
| | *Naegleria* sp. |

*A.O. Ibhadon and F. Fitzpatrick / Catalysis 3 (2013) 189-218*

# Fotokataliza - zastosowanie

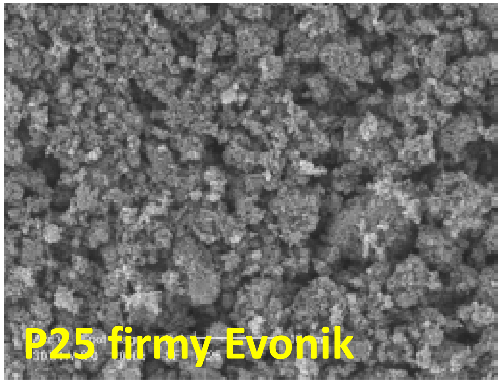
**What could we remove from water using heterogeneous photocatalysis?**

- ***Microorganisms***
- ***Organic compounds:*** alcohols, carboxylic acids, phenolic derivatives, chlorinated aromatics, pesticides, etc.
- ***Inorganic compounds:*** azide, halide ions, cyanide ($CN^-$, thiocyanide ($SCN^-$), ammonia ($NH_3$), nitrates ($NO_3^-$)and nitrides ($NO_2^-$)
- ***Natural organic matter:*** (e.g. humic substances)
- ***Trace metals:*** Hg, Pd, Cr, Cd, As, Ni, Cu, etc.

*C.C. Kaan et al.. / Heterogeneous Photocatalytic Oxidation as an Effective Tool for Wastewater Treatment (2012)*

# Cechy idealnego fotokatalizatora

- ❑ ***Stability and sustained photoactivity***
- ❑ ***Biologically and chemically inert, non toxic***
- ❑ ***Low cost***
- ❑ ***Suitability toward visible or near UV light***
- ❑ ***High conversion efficiency and high quantum yield***
- ❑ ***Can be react with wide range of substrates and high adaptability to various environment***
- ❑ ***Good absorption of solar spectrum***




*C.C. Kaan et al.. / Heterogeneous Photocatalytic Oxidation as an Effective Tool for Wastewater Treatment (2012)*

# AOP – jakie ścieki?

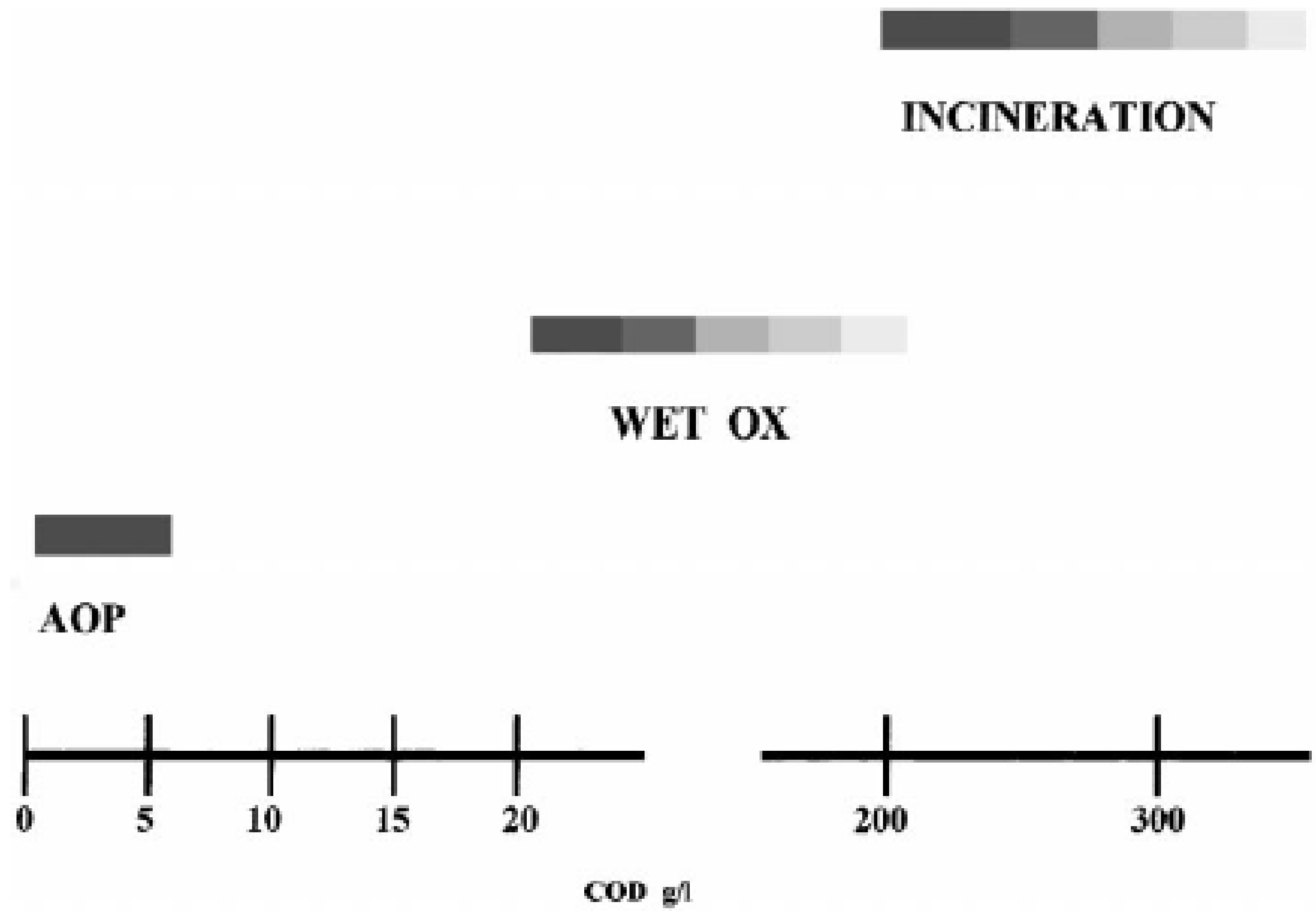



Fig. 2. Suitability of water treatment technologies according to COD contents.

*R. Andreozzi et al. / Catalysis Today 53 (1999) 51–59*

# Fotokataliza - podsumowanie

| Photochemical Process | Characteristics | Applications |
|---|---|---|
| Ozone and UV radiation ($O_3$/UV) | Generation of $HO^•$ radicals through photolysis of $O_3$ by singlet oxygen ($\lambda$ < 310 nm)<br>$O_3 + h\nu \rightarrow O_2 + O(^1D)$<br>$O(^1D) + H_2O \rightarrow 2HO^•$<br>Molar extinction coefficient of $O_3$ at 254 nm: 3300 $mol^{-1}$ $cm^{-1}$<br>Disadvantages: high operating costs | Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water. |
| Hydrogen peroxide and UV radiation ($H_2O_2$/UV) | Generation of $HO^•$ radicals through photolysis of $H_2O_2$ ($\lambda$ < 300 nm)<br>$H_2O_2 + h\nu \rightarrow 2HO^•$<br>Elevated photolysis at higher pH<br>Disadvantages: elevated costs, low radical formation velocity through low molar extinction coefficient of $H_2O_2$: 18.7 $mol^{-1}$ $cm^{-1}$ at 254 nm | Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water. Taste and odour elimination. Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate.<br>Industrial applications. |

# Fotokataliza - podsumowanie

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|---|---|---|
| Ozone, hydrogen peroxide and UV radiation ($O_3/H_2O_2/UV$) | Generation of $HO^{\bullet}$ radicals through photolysis of $H_2O_2$ ($\lambda < 310$ nm)<br>$O_3 + H_2O_2 + h\nu \rightarrow O_2 + HO^{\bullet} + HO_2^{\bullet}$<br>Disadvantages: elevated costs | Elimination of organic contaminants in water. Disinfection of effluent waters. Disinfection and treatment of potable water. Taste and odour elimination Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate, etc. Industrial applications. |
| Photo-Fenton ($Fe^{2+}/H_2O_2/UV$) | Photocatalytic system. Generation of $HO^{\bullet}$ radicals, photocatalytic regeneration of $Fe^{2+}$<br>$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-}$<br>$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^{+}$<br>Disadvantages: low pH (2.8-3) and elimination of Fe necessary | Elimination of organic contaminants in water. Treatment of industrial waste waters: textiles, agriculture, pharmaceuticals, leachate, etc. Industrial applications |