Water Purification by Photocatalysis on Semiconductors

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Abstract

This paper describes the basics of photocatalysis on semiconductors, mainly on TiO_2 and the application of photocatalytic processes to water purification from organic matter. The second chapter is devoted to metal cocatalysts introduced in order to improve the photocatalytic action of titania. Finally, a short review of more interesting practical applications of the processes is presented.

Introduction

Advanced Oxidation Processes are among the newer chemical techniques used for water purification. Depending on the techniques used the AOP processes can be divided into two groups [1, 2]:

- abiotic degradation, e.g. thermal degradation (combustion), molten salt processes, wet oxidation, chemical oxidation, acid-base hydrolysis,
- photodegradation, e.g. H_2O_2/UV, O_3/UV or $O_3/H_2O_2/UV$ processes, solar photolysis, processes in vacuum ultraviolet and photocatalysis.

The processes of heterogeneous photocatalysis on semiconductors, developed during the last twenty years, were firstly regarded as potential methods for hydrogen photoproduction from water [3, 4]. However, even at the very beginning of their development, some papers appeared which dealt with photooxidation of organic and some inorganic (e.g. CN^- ions) compounds [5, 6]. For more than ten years the interest of scientists has turned into application of the heterogeneous photocatalytic methods to water detoxification. Until now hundreds of papers have been published, and many applications of the processes to water and air purification have been patented. In this article the basics of the heterogeneous photocatalysis on semiconductors, mainly on TiO_2, and applications of the methods to water purification are described.

Principles of Heterogeneous Photocatalysis and Water Purification Processes

According to the band theory, each solid can be characterised by two energetic bands: a valence one, V_B, which possesses lower energy, completely filled with electrons (at least at 0°K); and a conductivity one, CB, with higher energy, empty at 0°K. The energetic distance between them amounts to 0.7-3.5 eV for semiconductors and is called a forbidden band or a band gap, E_G. The distance between the valence and conductivity bands determines electronic properties of the solid, e.g. electric conductivity. For comparison, in metals V_B overlaps C_B, in isolators E_G amounts to 6-7 eV. Table 1 shows the values of band gaps of some semiconductors.

Band gap values also determine the colour of the semiconductor, because they absorb light having energy equal to or higher than E_G energy. Such light absorption

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Table 1. Forbidden bandwidths of some more popular semiconductors.

| Semiconductor	$E_g(eV)$
Si	1.1
Fe_2O_3	2.3
CdS	2.5
WO_3	2.8
TiO_2 (rutile)	3.0
TiO_2 (anatase)	3.2
ZnO	3.2
SnO_2	3.5

Fig. 1. Schematic representation of semiconductor energetic bands and a redox level of a solution before (A) and after contact in the dark (B) and under illumination (C). E_g - forbidden band; V_B - valence band; C_B - conduction band; E_F - semiconductor Fermi level; e^-, h^+ - photoexcited electron and hole, resp.

causes electron transfer from a valence band to a conductivity one. The energy of visible light lies in the region of 1.5 (red) - 3.0 eV (violet). Thus, the semiconductors having a narrow band gap of about 1.5 eV are black, those having a band gap of about 3.0 eV - white. WO_3 and CdS, which absorb part of the wavelength from the visible region, are yellow [7].

Some impurities or defects in the crystal lattice (e.g. presence of Ti^{3+} ions in TiO_2) are responsible for additional electronic levels (donor or acceptor ones) placed inside the forbidden gap of a semiconductor. The donor level (e.g. in TiO_2) is placed close to the conductivity band and supplies the band with electrons. Such semiconductor is called an electron-excess semiconductor or an n-type one. The empty acceptor level is placed near the valence band and can withdraw the valence band electrons, leaving behind an electronic hole. Such a semiconductor is called an electron-defect or a p-type one. A Fermi level, E_F, which represents the chemical potential of electrons in a semiconductor, is placed in the forbidden gap energetically. Its position depends on the presence of majority charge carriers in the semiconductor, i.e. on the presence of electrons or holes. In p-semiconductors E_F lies close to V_B, in n- ones - close to C_B. Note that E_F is not a level filled with electrons, but it only expresses an average chemical potential of electrons [3, 8, 9].

Photocatalytic properties, which are described below, refer to n-semiconductors exclusively. The n-type materials, mainly TiO_2 (both anatase and rutile) are generally used as photocatalytically active substances owing to their high chemical resistance. They also do not undergo photocorrosion (photogenerated holes can cause the oxidation of the semiconductor itself).

As mentioned above, the chemical potential of electrons in a semiconductor is expressed by the position of Fermi level. The chemical potential of electrons in a solution is determined by redox potentials of all dissolved substances, including the redox potential of the solvent itself, as well as their concentrations and standard potentials, $E°$. When a semiconductor is in contact with an electrolyte (e.g. when we have a suspension of TiO_2 in a water solution) electrons are transferred from the semiconductor to the electrolyte or *vice versa,* depending on their potentials in both phases, until the potentials are
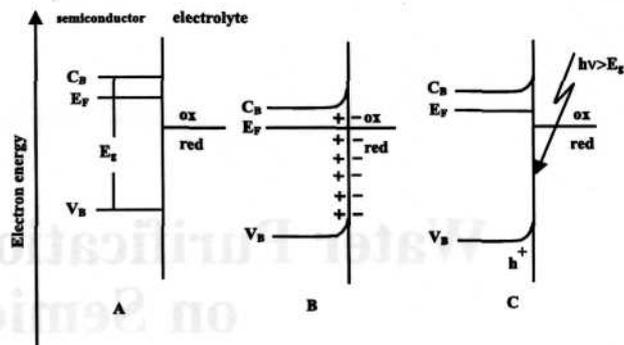
equilibrated. The situation, which is interesting from a point of view of n-semiconductor photocatalytic activity (e.g. TiO_2), is shown in Fig. 1 [3, 10, 11].

In the case represented in Fig. 1, electrons move from the semiconductor to the electrolyte. The loss of electrons causes positive charging of the semiconductor, negative - of the electrolyte. In the semiconductor the excess negative charge is located at the solid - liquid interface, in the depletion region, 50-2000 A from the surface. Thus, the electric field formed inside the semiconductor causes bending of the valence and conductivity bands (see Fig. 1B). Because of the direction of the field, each electronic hole in a valence band, formed after the electron transfer to the conduction band, moves to the surface. On the other hand, the electrons in the conductivity band move in the opposite direction, because the energy of C_B is lower inside the solid. To sum up, the electric field in the semiconductor results in the separation of photogenerated electron-hole pairs. This phenomenon allows construction of photocells possessing an n-semiconductor photoanode and a metal (usually platinum) cathode [3] (see Fig. 2).
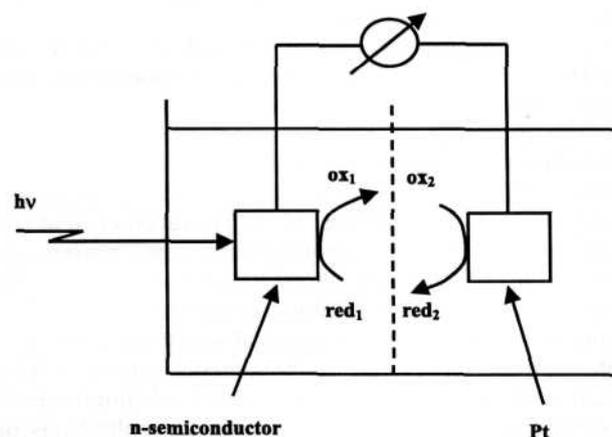

Fig. 2. Scheme of a photoelectrochemical cell with a semiconductor anode and a platinum cathode.

In the electrolyte (also at the solid-liquid interface) a layer of negatively charged ions is formed. This socalled Helmholtz layer has a thickness of less than 10 A. The equilibration of electron potential in the semiconductor and in the electrolyte and the formation of opposite charges prevent further electron transfer between the two phases - a Schottky barrier is formed at the semiconductor - the electrolyte interface.

If the semiconductor is illuminated with a light having an appropriate wavelength (hv > E_G), some electrons are excited from the valence to the conduction band. Thus, the equilibrium shown in Fig. 1B is altered - see Fig. 1C, making further electron transfer possible. In the photocell shown in Fig. 2 electric current is measured in the external circuit when the semiconductor anode is illuminated.

A photoactive semiconductor surface is generally regarded as a set of short-circuit microcells. A TiO_2 particle with surface platinum islands is usually given as an example. After titania absorbs light the photogenerated electrons move to the Pt islands charging them negatively (microcathodes), the holes remain at the bare TiO_2 surface. On the Pt/TiO_2 surface both oxidation and reduction reactions can occur. Suspensions of fine semiconductor powders in water solutions, when illuminated, can run chemical reactions similar to those which take place on separated electrodes in photoelectrochemical cells (Fig. 3). The particulate semiconductor photosystems are, however, much cheaper. The disadvantage of the systems is that oxidation and the reduction centres, formed due to light absorption, are very close. Thus, the probability of recombination of the photogenerated electrons and holes is high and, for this reason, a quantum yield of photocatalytic reactions diminishes. Besides, the products of photooxidation and photoreduction half-reactions can react easily with each other. For example, the products of water splitting on illuminated Pt/TiO_2, H_2 and O_2, recombine easily to a water molecule in the presence of dispersed platinum. On the basis of the assumption that particulate semiconductor photosystems operate like photoelectrochemical cells, Frank and Bard studied the photocatalytic oxidation of CN^- ions in a TiO_2 aqueous suspension over twenty years ago [5]. The practical importance of the process is obvious. In the study, light and titanium dioxide were used to catalyse the reaction of cyanide ions with oxygen. According to the authors, photogenerated electrons reduce oxygen dissolved in water, and the holes oxidise CN^-. The introduction of an additional cocatalyst (Pt) was not necessary because a bare TiO_2 surface could catalyse the reduction of oxygen. However, other photocatalytic reactions such as acetic acid decarboxylation (photo-Kolbe reaction), which leads to methane and carbon dioxide [6], or water photosplitting mentioned above, needed a cocatalyst besides TiO_2. In the last process the presence of platinum was necessary for both H^+ reduction and the recombination of atomic hydrogen into H_2 molecules.

A simplified scheme, which is often used as an illustration of the photocatalytic processes that occur in particulate semiconductor photosystems, is shown in Fig. 3. In the scheme the circle represents a spherical particle of the semiconductor. The energetic positions of both V_B and C_B are shown [11].
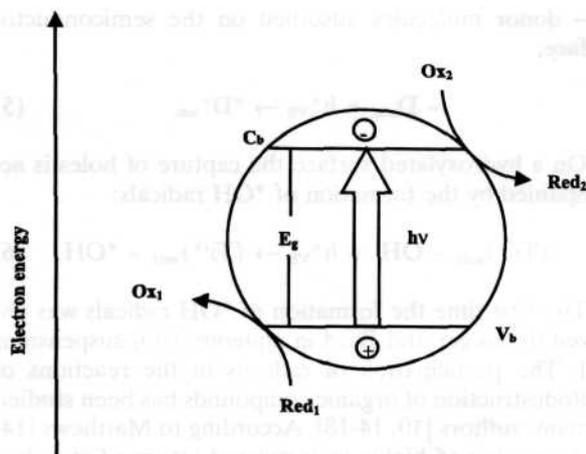

Fig. 3. Schematic representation of redox processes on an illuminated semiconductor particle. E_g - forbidden band; V_b, C_b - semiconductor valence and conductivity bands, resp; Ox, Red - oxidized and reduced forms, resp., of solution species.

A mechanism of the photocatalytic action of semiconductors is somewhat more complicated [10]. The absorption of photons causes the formation of an electron and a hole on the surface or near it. The e^- - h^+ pair quickly diffuses to the surface. Their recombination of $e^- + h^+$ -» heat occurs usually in several nanoseconds. Such a short lifetime would not allow the electrons and holes to participate in any chemical reaction. Therefore, the electrons and holes should be captured by any of chemical species which exist on the surface (ions, atoms, molecules, etc.), by the so-called surface traps. For TiO_2 the capture of an electron and hole is fast, below 20 picosecond. The lifetime of the trapped e^- and h^+ is long enough for their reaction with molecules present in the solution.

There are several traps for photogenerated electrons:
- surface Ti^{IV} ions:

$$\{Ti^{IV}\}_{surf.} + e^-_{CB} \text{-»} \{Ti^{III}\}_{surf.} \quad (1)$$
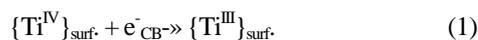
The formation of Ti^{3+} ions during the illumination of TiO_2 slurry was observed by Howe and Gratzel in ESR studies [12];
- adsorbed acceptor molecules:

$$A_{ads} + e^-_{CB} \text{-»} *A^-_{ads} \quad (2)$$
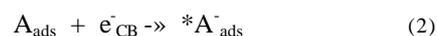
In an aqueous solution dissolved oxygen or oxygen adsorbed on the titania surface can serve as an electron acceptor:

$$O_{2,ads} + e^-_{CB} \to *O^-_{2\,ads} \quad (3)$$
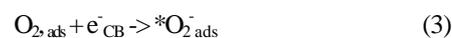
The role of oxygen in the process of water decontamination will be described below. The valence band holes can be captured by:
- O_2^- ions of the crystal lattice of TiO_2:

$$\{Ti^{IV} - O_2^- - Ti^{IV}\} + h^+_{VB} \to \{Ti^{IV} - *O^- - Ti^{IV}\} \quad (4)$$
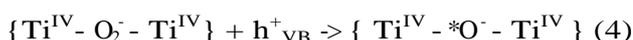
- donor molecules adsorbed on the semiconductor surface:

$$- D_{ads} + h^+{}_{VB} \twoheadrightarrow {}^*D^+{}_{ads} \qquad (5)$$
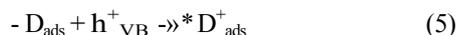
On a hydroxylated surface the capture of holes is accompanied by the formation of *OH radicals:

$$\{Ti^{IV}\}_{surf.} - OH^- + h^+{}_{VB} \twoheadrightarrow \{Ti^{IV}\}_{surf.} - {}^*OH \qquad (6)$$
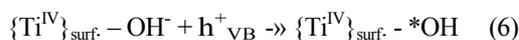
The first time the formation of *OH radicals was observed by Jaeger and Bard in aqueous TiO_2 suspensions [13]. The participation of radicals in the reactions of photodestruction of organic compounds has been studied by many authors [10,14-18]. According to Matthews [14] the formation of highly hydroxylated intermediates during the oxidation of organic compounds on illuminated titania can serve as evidence for the participation of *OH in the process. Such compounds were detected also in our laboratory using the GC-MS technique as the intermediates of phenol, 1,2-, 1,3- and 1,4-dihydroxybenzene photomineralisation on TiO_2 [19, 20]. However, another mechanism is also possible: direct oxidation by surface holes is favoured when the organic molecule is strongly adsorbed on the TiO_2 surface. Higher substrate concentration and hence higher substrate adsorption make the latter process more important. Stafford *et al.* [18] showed, on the basis of his studies of 4-chlorophenol photooxidation on titania, that both reactions were possible. The authors also found that the direct oxidation by holes did not lead to the formation of higher hydroxylated aromatics like 4-chloro-1,2-dihydroxybenzene (4-chlorocatechol) or 4-chloro-1,4-dihydroxybenzene (chlorohydroquinone).

AOP techniques of water purification base mainly on the generation of *OH radicals and their homogeneous attack on organic molecules. Similarly, Richard and Lemaire [21] stated, on the basis of the kinetic studies of furfuryl alcohol oxidation on irradiated n-ZnO, that firstly the hydroxyl radicals diffused from the surface to the bulk solution and reacted with organics in a homogeneous way. The diffusion of *OH from the TiO_2 surface was observed by Peterson *et al.* [22]. Turchi and Ollis [23] found that during the phenol photooxidation on TiO_2 the diffusion of *OH radicals was possible, up to several hundred angstroms, when the coverage of the surface with the substrate was small. At high phenol adsorption the reaction took place on the semiconductor surface, between the adsorbed species.

Kinetics of the photooxidation of organic water impurities on illuminated TiO_2 is generally regarded to be based on a Langmuir-Hinshelwood equation [23]:

$$r = -dc/dt = kKc/(1+Kc) \qquad (7)$$

where c is substrate concentration in water; k is a rate constant; K is a constant of adsorption equilibrium.

According to the above formula the reaction rate is directly proportional to surface coverage with substrate molecules, 0, which is a function of substrate concentration and adsorption equilibrium constant, K:

$$\Theta = Kc/(1+Kc) \qquad (8)$$

$$r = -dc/dt = k\Theta \qquad (9)$$

For the first order of reaction kinetics the dependence of 1/r on 1/c should be linear. Such dependence has been proved experimentally [24]. The magnitude of phenol adsorption on TiO_2 was also established and K for phenol adsorption was calculated both from adsorption and reaction kinetics studies. The Langmuir - Hinshelwood model is generally accepted for the photooxidation of organics on titanium dioxide [25-31]. However, Turchi and Ollis [23] showed that similar 1st order rate equation could be derived if one assumed that:

1. adsorbed radicals react with adsorbed phenol molecules, in accordance with the L-H model;
2. adsorbed phenol molecules react with *OH radicals from the bulk solution;
3. adsorbed *OH radicals react with soluble phenol molecules;
4. the reaction of both species takes place in the bulk solution.

This means that the kinetic calculations, which are based on the results of reaction rate studies, have no justified value.

On the basis of kinetic studies of phenol photodestruction on titanium dioxide, Okamoto *et al.* [32, 33] stated that the rate constant depends on the initial phenol concentration, the amount of the semiconductor powder, oxygen partial pressure and the intensity of incident light. They proposed a kinetic expression, which includes all the factors. According to the authors, below the light intensity of $1 \cdot 10^{-5}$ mole of quanta$\cdot m^{-2} \cdot s^{-1}$, the rate of the photoreaction is directly proportional to the intensity, above - to square root of the intensity. However, the light intensity is usually constant during the studies and is omitted in kinetic calculations. Moreover, the problems of oxygen partial pressure are not taken into account: its content in water is defined by solubility in saturation conditions and regarded to be constant. However, in course of the study of oxidation photocatalytic reactions in water, oxygen or air should be constantly supplied to the reaction environment to keep its content constant.

The reduction of oxygen molecules by photogenerated electrons in semiconductors leads primarily to hydrogen peroxide (partial reduction to O^-) and finally to O^{2-} (H_2O). According to Gerischer and Heller [34, 35], at a higher concentration of organic water contaminants and high light intensity the rate of oxidation by photogenerated holes is high. The overall reaction rate can be limited by the rate of reduction of dissolved oxygen by photogenerated electrons. Taking into account low oxygen solubility in water, 10 ppm or less and a low rate of oxygen reduction by C_B electrons, one can expect an accumulation of the electrons in a semiconductor. This accumulation enhances a rate of recombination of the photogenerated electrons and holes. Under these conditions the overall reaction rate is determined by a slow oxygen reduction as mentioned above. Gerischer and Heller stated [34, 35] that photogenerated electrons reacted *via* surface traps (reaction 1). The small density of the traps retards the process. To enhance the photoactivity the authors proposed a modification of TiO_2 surface by the introduction of metal additives, the best platinum group metals. Indeed, Wang *et al.* [36] observed the de-

polarisation of titanium dioxide particles after the deposition of Pd "islands". The introduction of palladium enhanced the rate of electron transfer from TiO_2 to dissolved oxygen, thus eliminating the excess negative charge of the semiconductor. The presence of Pd cocatalyst also increased a quantum yield of photocatalytic oxidation of 2,2-dichloropropionic acid.

The oxidation of organic compounds on the surface of illuminated TiO_2 proceeds *via* many steps, which make one-electron oxidation or reduction reactions. A full set of the reactions which take place (or are likely) on the surface of the semiconductor has been given by Gerischer and Heller [34]. The reactions explain in the best way the essence of the processes that occur on illuminated semiconductors; see below. A photooxidized organic molecule is represented as RH_2.

Photogenerated electrons and holes, if they do not recombine, react with organics or with water:

$$h^+ + RH_2 -> *RH + H^+ \qquad (10)$$

$$h^+ + H_2O -» *OH + H^+ \qquad (11)$$
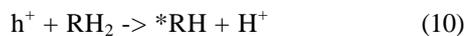
If the semiconductor surface is hydroxylated, OH^- groups can serve as hole traps:

$$h^+ + OH^- -» *OH_{ads} \qquad (12)$$

Thus formed, *OH radicals react with organic molecules:

$$RH_2 + *OH -* *RH + H_2O \qquad (13)$$
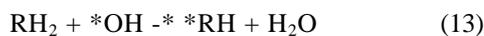
Note that energy of the captured hole is somewhat lower than V_B hole energy. Reaction (11) competes with reaction (10). The reaction with organic molecules (13) takes place when substrate concentration is high or when it is strongly adsorbed on the semiconductor surface.

If oxygen molecules, which have been dissolved in water are the only molecules of the acceptor , photogenerated electrons reduce them:

$$e + O_2 -» O_2^- \qquad (14)$$

Oxygen can be also reduced by captured electrons:

$${Ti^{III}} + O_2 -» {Ti^{IV}} + O_2^- \qquad (15)$$
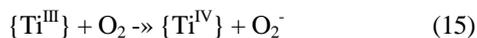
According to the authors [34], reaction (15) is more likely than reaction (14).

Both free and captured electrons and holes can recombine. As a result, the quantum efficiency of the photoprocess decreases.

The primary products of photooxidation and photoreduction (*OH radicals and O_2^- ions) can react further with electrons and holes, which are still being photoproduced:

$$h^+ + *RH_{ads} + H_2O -> HROH + H^+ \qquad (16)$$

$$e + O_2^- + H^+ -> HO_2 \qquad (17)$$

The thus formed peroxide ion, HO_2^-, can combine with proton. The product, H_2O_2, can undergo a further reaction:

$$HO_2^- + H^+ -» H_2O_2 \qquad (18)$$

$$H_2O_2 + e^- -> *OH + OH^- \qquad (19)$$
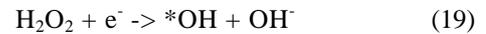
Radicals, usually the primary products, can react further, resulting in stable molecules. Dissolved oxygen or the products of its reduction can also participate in the processes:

$$*RH + O_2^- -> RO + OH^- \qquad (20)$$
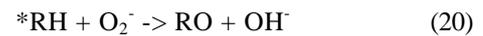
The dimerisation of *RH radicals is the other possible reaction, especially at a high concentration of the species:

$$2*RH -> (RH)_2 \qquad (21)$$

Stable organic molecules can be also formed *via* a reaction with *OH radicals:

$$*RH + *OH -> HROH \qquad (22)$$

The stable organic molecules are usually not final products of the photocatalytic reactions. On TiO_2, in the reactions with photogenerated holes or *OH radicals, many organics undergo total mineralisation, i.e. to CO_2 and H_2O.

Cocatalysts in Photocatalytic Water Decontamination in Semiconductor Suspensions

As mentioned above, the semiconductor surface with metal additives could be regarded as a set of "short circuit" electrochemical (or photoelectrochemical) cells. The metal "islands" play the role of microcathodes; anodic processes proceed on a bare titania surface. Such semiconductor particles having surface metal admixtures is shown schematically in Fig. 4. It is well known in electrochemistry that many substances catalyse electrode reactions. The phenomenon, termed electrocatalysis, consists of the reduction of an overpotential of electron transfer at the interface electrode - electrolyte. The reduction of the overpotential results from activation of molecules, which participate in the electrode process. The activation of some molecules is caused by their selective chemisorption at the electrode material. As a result, the electrode processes (oxidation or reduction) are considerably enhanced. In the case of physical adsorption of the substrate or in the lack of adsorption the rate of electrode processes depends on electrode material only to a little extent - potential distribution in an electrolyte double layer depends slightly on the electrode material. The differences in electrocatalytic properties of various substances are usually explained by the difference in stability of chemical bonds between the adsorbed molecule and the electrode.
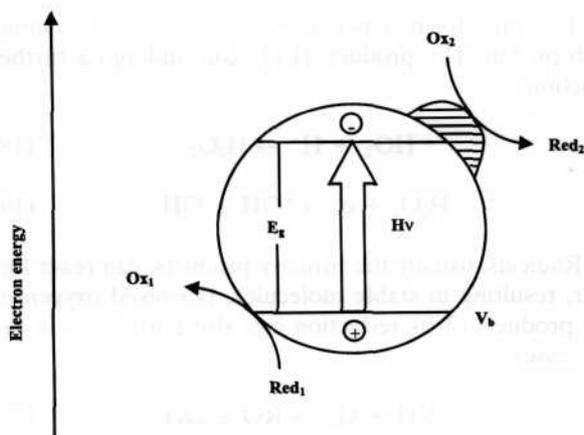
Fig. 4. Schematic representation of redox processes on an illuminated cocatalyst-on-semiconductor particle. E_g - forbidden band; V_b, Q, - semiconductor valence and conductivity bands, resp.; Ox, Red - oxidized and reduced forms, resp., of solution species.

The action of the metal islands on TiO_2 surface is similar to the processes of electrocatalysis. However, the processes described here are termed "photocatalytic" and, according to Wang *et al.* [36], the terms "cocatalysis" and "cocatalyst" are used in this paper.

The processes of hydrogen photogeneration from water were relatively efficient on TiO_2 (or other semiconductors) in the presence of additional cocatalysts. Many papers devoted to semiconductor-cocatalyst systems have been published. Many properties of the systems and their preparation methods have been described. The problems related to hydrogen evolution cocatalysts are the subject of a previous review [37]. This paper presents a short review of the cocatalyst-semiconductor systems used in water detoxification.

As mentioned above, in spite of an abundant literature devoted to water purification on illuminated semiconductors (mainly on TiO_2) only a few authors applied additional cocatalysts. This could be on account of high photocatalytic activity of titania itself, especially of widely used TiO_2 P25 fine powder produced by Degussa (a mixture of anatase and rutile). However, several authors have observed a pronounced effect of metal or other additives on the photoactivity of titanium dioxide in the destruction of water contaminants.

The first paper devoted to the photooxidation of benzene and some aliphatic hydrocarbons on Pt/TiO_2 was published by Izumi *et al.* in 1980 [38]. On the basis of electrochemical and photoelectrochemical studies the authors showed that the role of the platinum cocatalyst lies in lowering oxygen reduction overpotential. They also proved that the hydrocarbons, which were resistant to the attack of many strong oxidants, were oxidised to H_2O and CO_2 by *OH radicals formed on illuminated titanium dioxide.

The role of a metal (Pd) cocatalyst was studied by Wang *et al.* [36]. As mentioned above the authors observed the inhibition of quantum yield of photocatalytic reactions on TiO_2 caused by a slow rate of oxygen photoreduction. Owing to the slow reduction of oxygen by

photogenerated electrons (the reaction of organics with photogenerated hydroxyl radicals was much faster) an excess negative charge was accumulated on the semiconductor. The charge was totally eliminated after Pd-islands had been built on the titania surface. The metal additives also increased drastically a quantum yield of 2,2-dichloropropionate photooxidation - up to 7 times for Pd(2 wt.%)/TiO_2 in comparison to pure titania.

Liu and Gao [39] studied phenol photodegradation in water suspensions of TiO_2 and polyaniline. The polyaniline additive caused a twofold increase of titania photoactivity. Moreover, the system polyaniline/TiO_2 showed photoactivity under solar light illumination.

The photoactivity of titanium dioxide with gold additives was studied by Gao *et al.* [40]. The authors observed a 30% increase of titania (both P25 Degussa and a powder prepared in their laboratory) activity after deposition 1 at.% of gold on its surface. In other studies on gold-covered titanium dioxide more than twofold increase of phenol photodestruction was observed when 1 wt.% Au was photodeposited onto a titania surface [41]. Total phenol mineralisation to CO_2 and H_2O was much slower than phenol disappearance. Catechol, hydroquinone and p-benzoquinone were detected as the main reaction intermediates and were determined quantitatively.

Lee *et al.* [42] observed a 30% increase of TiO_2 photoactivity in 1,4-dichlorobenzene oxidation after deposition 1.5 at.% Ag. The Ag/TiO_2 photocatalysts were prepared by metal photoreduction (photogenerated in TiO_2 electrons firstly reduced silver, then oxygen dissolved in water) from nitrate and fluoride solutions. However, other studies showed more than threefold increase of titania activity in the presence of 0.5 wt.% Ag, photodeposited *in situ* (in the reaction cell) on a titanium dioxide surface [43].

The influence of surface Pd additives on the activity of titanium dioxide in 1,4-dichlorobenzene photodegradation was studied by Papp *et al.* [44]. The deposition of small islands of palladium was performed using two different methods: (1°) impregnation with $PdCl_2$ solution followed by thermal decomposition (400°C) and (2°) the photoreduction of the metal ions. The authors observed the existence of optimum metal loading on titania: 0.15 or 0.2 at.%, depending on the preparation method. For both methods of Pd/TiO_2 preparation approximately a 30% increase of titanium photoactivity was observed. The application of the palladium cocatalyst on thin titania films increased also the rate of salicylic acid photooxidation [44].

Additions of tungsten trioxide to titania increased the rate of 1,4-dichlorobenzene photodestruction [45] considerably. According to the authors, WO_3 operates similarly to the metal cocatalysts: E_F of tungsten trioxide has energy lower than that of titania and therefore WO_3 islands collect the electrons photogenerated in TiO_2. A catalytic action of the tungsten trioxide is related, in the author's opinion, to the ability of reduction and oxidation of lattice tungsten ions ($W^{+6} \iff W^{+5}$). The photoactivity of WO_3 itself in the reaction of 1,4-dichlorobenzene oxidation was shown to be negligible.

Crittenden *et al.* [46] studied the influence of surface admixtures of Pt, Ag and Fe_2O_3 on the photocatalytic

activity of TiO_2 in trichloroethylene and 1,4-dichlorobenzene destruction. They observed the enhancement of the reaction rate when Pt or Ag were deposited onto TiO_2 (Aldrich). The effect was more pronounced for platinum cocatalyst. The metal cocatalysts did not improve photoactivity of TiO_2 P25 Degussa considerably. For both metals optimum cocatalyst loading was observed. According to the authors, too high coverage of the surface with the metal cocatalyst makes a part of it not accessible to incident light (so called "screening effect"). Fe_2O3 admixture decreased strongly the photoactivity of titanium dioxide.

Chen *et al.* [47-49] studied the photodestruction of such compounds as methanol, ethanol, trichloromethane, trichloroethylene and dichloropropionic acid in water suspensions of TiO_2, Pt/TiO_2 and Pd/TiO_2. The platinum and palladium cocatalysts improved considerably titania photoactivity in the reactions of MeOH and EtOH photooxidation. The influence of Pt admixture was more pronounced. However, both cocatalysts decreased titania activity in the photodegradation of trichloromethane and trichloroethylene. In the case of dichloropropionic acid, the platinum cocatalyst slightly increased the photoactivity of TiO_2 in the dechlorination of the compound, and the palladium one decreased it. Pt did not have any influence and Pd strongly retarded the reaction of photodecarboxylation of the dichloropropionic acid. On the basis of SEM and electron microprobe analysis the authors also stated that at least a part of the metal admixture was placed inside the pores of titanium dioxide particles. According to the authors the reduction of oxygen by photogenerated electrons occurs on metal islands in the pores, whereas oxidation by holes takes place on an illuminated part of the surface.

Recent studies of phenol photodestruction on Cu/TiO_2 showed that photodeposition *in situ,* in the reaction vessel, of 0.025 wt.% Cu (the metal was photoreduced under neutral atmosphere), causing a seven-time increase of the reaction rate. Phenol total mineralization was also considerably fast. Catechol, hydroquinone and p-benzoquinone were the main reaction intermediates [50].

To sum up, some cocatalysts increase titania activity in the photodestruction of organic water pollutants. Their action depends on the type of cocatalyst used and on the method of preparation of the cocatalyst/TiO_2 systems. It also depends on the kind of organic compound that should be decomposed.

Application of Photocatalysis on Semiconductors in Water and Air Purification

Titanium dioxide, owing to its special properties, is the most frequently used photocatalyst in water and air purification processes. TiO_2 is relatively cheap, non-toxic, insoluble in water and very resistant to most chemicals. It shows also the highest photocatalytic activity and resistance to so-called anodic photocorrosion. Additionally, the photocatalytic processes on titanium dioxide can be also initiated by solar radiation.

The application of titanium dioxide in the form of a powder suspended in water to be purified requires, however, additional operations for separation of the two phases. To avoid this inconvenience, several solutions are proposed, which enable the photocatalyst to be immobilised. The deposition of fine TiO_2 powder on glass surfaces is the most common one. This can be accomplished by the simple coverage of the surface with suspension of titania fine powder in water and drying. The prepared film adheres strongly to the glass because of TiO_2 electrostatic charge (the glass surface is usually negatively charged) [51]. Titanium dioxide also shows very good adhesive properties to many other materials, thus allowing for the usage of such supports as glass fibres, plastics or even metals [52-56]. TiO_2 can be deposited directly onto the surface or can be bound using various binders as silica or alumina gels [57, 58], silicones, modified resins and other polymers [56, 59-61]. TiO_2 powder can also be built into some laminates, e.g. acrylic and fluoro-polymers, phenolic resins, polyurethanes and others [62-66].

The immobilised photocatalysts can be applied in various reactors; they are especially recommended for those working in a continuous mode. Several reactors have been described, e.g. tanks with suspended matter (in water or in air) [57], tanks with immobilised photocatalyst [52, 53, 67, 68], agitators [69, 70], tubes or pools [54]. Titanium dioxide layer can cover reactor walls [54, 68, 71, 72], surfaces of reactor packing [52, 53, 57, 68, 71, 72], outer surfaces of some exposure lamps [73] and rotors placed inside the reactors [69, 70].

The application of an immobilised film of photocatalysts does not need any additional processes for the solid-liquid separation. However, the immobilisation of the semiconductor powder reduces considerably a number of active sites on its surface. Therefore, many attempts have been undertaken to solve the problem. For example, after illumination the suspension can be separated on membranes [74] or on electrical or biological filters [75, 76]. What seems to be the most interesting is the combination of various unit processes such as:

- water purification on membranes with immobilised titania particles [77-81],
- filtration on filters with immobilised TiO_2 [82, 83],
- the adsorption of water impurities on active carbon mixed with titanium dioxide [84-86].

The utilisation of solar energy in photocatalytic water treatment makes the technique much cheaper. However, the process needs huge areas to be illuminated. In many cases a layer of the active semiconductor can be deposited on already existing surfaces exposed to the sun. TiO_2 particles mixed with building materials or paints can cover outer walls or roofs of houses [87, 88], and in the form of laminates or paints can be applied to light exposed parts of cars, ships, planes, etc. [66, 89, 90]. It can also be built onto ceramic plates, which cover walls of ponds [54], toilets [91], can cover furniture and walls of apartments or offices [62, 63, 92, 93].

The efficiency of water and air decontamination on illuminated TiO_2 depends on many factors, such as type, source and concentration of the impurity to be removed, applied photocatalytic technique, a source of light, etc.

Photocatalytic processes on TiO_2 can be applied to air

purification from nitrogen oxides, volatile hydrocarbons and chlorohydrocarbons, odorous compounds, microbes, fungi, etc. Hence some attempts have been made to use the photocatalytic techniques in places exposed to high emission of exhaust gases - at crossroads, roundabouts, also for deodorisation and detoxification-sterilisation purposes in hospitals, public toilets and others. The techniques based on TiO_2 are especially useful in removing impurities from industrial gases, the composition of which is well defined. The knowledge concerning compounds to be decomposed allows to apply an appropriate modification of the semiconductor or its surface. For example, the photocatalytic process on TiO_2 was economically most efficient in removing trichloroethylene from a gaseous extract of the compound from polluted soil [94]. Removing trichloroethylene by means of adsorption on active carbon or by means of burning was much more expensive. The photocatalytic method was also more efficient economically in removing dichloromethane, methanol, ethanol and other volatile substances from exhaust gases of some manufacturers [94].

Photocatalysis on TiO_2 can be applied for household wastes and dry-cleaner effluent purification, as well as for the detoxification of many dangerous compounds contained in industrial waste. It can be used for water purification, desinfection and sterilization: living matter like microorganisms, viruses and bacteria can be easily destroyed on illuminated titania. Besides, some metals can be removed from water using the photocatalytic method.

Matthews [51] found that potable water purification of many metals and other elements (Fe, Cu, Al., Zn, Mn, Mo, P) was much more efficient on illuminated TiO_2 film than on a standard Al_2O_3 filter. After it was used, the photocatalyst was regenerated by 1% HCl solution. The author also compared the costs of water purification of phenol additives by means of adsorption on commercial active carbon to the costs of purification by means of photooxidation in TiO_2 suspension, taking into account full mineralisation of the water pollutant. In the catalytic processes both UV lamps and solar radiation were used. The purification of 1000 1 of water from phenol (initial concentration - 100 ppm, the final one - 10 ppm) on active carbon amounted to about 6 Australian dollars. When photocatalysis on a semiconductor was used, the cost oscillated between 10 dollars (in rush hours) and 5.5 dollars (in other hours). The cost of lowering phenol concentration in water from 10 to 1 ppm in 1,000,000 litres of water amounted to 1200 dollars in the case of adsorption method. When solar radiation was applied, the price of photocatalytic phenol mineralisation was about 1375 dollars. The process on active carbon is still more economical. However, the fast development of the photocatalytic methods, as well as progress in semiconductor modification (e.g. the application of efficient cocatalysts of the process) can make the method more competitive.

Final Remarks

The methods and technologies applied universally, such as precipitation, sedimentation, adsorption or membrane separation are very efficient in potable and waste water purification. However, the application of these technologies does not solve the problem entirely. Separated impurities, in many cases very toxic ones, have to be stored, usually in special tanks, thus causing an additional threat to the environment. In other words the impurities are only moved in space, from water to the storage tanks. The entire problem of the impurities is also shifted in time - they will have to be utilised in the future. The AOP processes, including the photocatalytic method described here, belong to clean technologies - organic water pollutants are transformed into CO_2 and H_2O. If they are developed, they can be really competitive with the standard methods. If so, we will see in the future.

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