Study of photocatalytic systems based on immobilized excitable species

final report
(project nr.: OTKA K 101141)

Abstract

New ruthenium(II)-polypyridine complexes as well as water-soluble metalloporphyrins with planar and pre-distorted ligands were synthesized and characterized by photophysical and –chemical properties in homogeneous solutions. They were immobilized on solid supports and applied for degradation of organic compounds. The action spectrum of TiO_2 was extended into the visible range by a ruthenium(II) complex as a sensitizer for photocatalytic degradation of amino acids.

Pure TiO_2 was applied for photocatalytic oxidative degradation of various organic compounds (environmentally dangerous drug, anionic and non-ionic detergents). The mechanisms of these processes were revealed, focusing on the roles of oxidizing agents (hydroxyl, hydroperoxyl radicals and singlet oxygen) and intermediates formed in the photoinduced reactions.

TiO_2-based photocatalysis, using both untreated and surface-modified (by deposition of noble metals) catalysts, was combined with other advanced oxidation procedures, mainly ozonation, for enhancing the degradation efficiency. Synergistic effects were achieved in mineralization of aromatic surfactants.

In situ prepared TiO_2 was immobilized on various supports. Their photocatalytic efficiency was studied by degradation of anionic and non-ionic detergents. After suitable thermal and photochemical pre-treatments, the poly(vinyl alcohol)-TiO_2 composite proved to be efficient and durable through several cycles, proving the practical applicability of this method.

1. Introduction

In the frame of this project, various photoactive compounds were studied, which could serve as basis for photocatalytic systems, mostly for oxidative degradation of organic pollutants and, to a minor extent, for reductive systems. In the first part of this study, various metal complexes were synthesized and characterized in homogeneous aqueous solutions, mostly in photophysical and photochemical respects. Besides, photocatalytic degradation of different organic compounds was investigated by application of titanium dioxide based heterogeneous systems alone and combined with other advanced oxidation procedures like ozonation. In the second part of the project, the prepared metal complexes were utilized as sensitizers extending the action spectrum of the titanium dioxide into the visible range, as well as original (independent) photocatalysts immobilized on various solid supports such as graphene or clay minerals. Titanium dioxide was also immobilized on/in different supports, e.g., glass or poly(vinyl alcohol), for oxidative decomposition of different surfactants as potential pollutants. The results achieved are described in the following sections, according to the previously mentioned order.

2. Investigation of potential photocatalysts in homogeneous aqueous solutions

Photophysical and photochemical properties of two types of coordination compounds were studied in this stage of the project; various water-soluble metalloporphyrins and mixed-ligand cyano-diimino ruthenium(II) complexes.

2.1. Water-soluble metalloporphyrins

Two main types of metalloporphyrins can be distinguished on the basis of their structure; in-plane and out-of-plane (or sitting-atop) ones. In the case of the previous group, the metal center fits into the cavity of the porphyrin, thus, it is located within the plane of this ligand, forming a kinetically inert complex. If the diameter of the metal ion is too big for the core of the porphyrin, it is located out-of the ligand plane, distorting its structure [5]. Such complexes are labile, existing only in equilibria. Several metalloporphyrins of both types were synthesized and thoroughly studied from photophysical and photochemical points of view [2, 37], beside the investigation of their formation kinetics and equilibria. Between the two categories mentioned above, a few border-line cases were also studied. On the basis of our results, we have complemented the categorization introduced by Barnes and Dorough for the metalloporphyrins. According to our observations, also in metalloporphyrins, the distortion, i.e., the planarity or nonplanarity of the macrocycle, is basically responsible for the spectral characteristics, while the electronic structure of the metal center is a secondary factor, with a considerable importance mainly in the in-plane complexes [8]. The type of complexes can be spectrophotometrically determined on the basis of their UV-Vis absorption and fluorescence spectra. Beside the spectral and photophysical effects of metalation, also those of the structural distortions were studied, which can originate from metalation, protonation, or overcrowded peripheral substitution of the free-base porphyrins, as well as from the axial ligation of metalloporphyrins.

2.1.1. Out-of-plane metalloporphyrins

In the case of anionic lanthanide(III) porphyrins, being of out-of-plane type, the composition and structure of the complexes strongly depend on their axial ligands; the relatively strongly connecting acetato ligands hinder the coordination of further metal ions, while in the case of weakly binding chloro ligands trinuclear sandwich type complexes can also be formed [4]. These compounds, deviating from the corresponding mononuclear complexes, do not display any fluorescence, and undergo a relatively efficient photodissociation, beside the photoinduced ligand-to-metal charge transfer (LMCT) reactions, which are characteristic of the out-of-plane metalloporphyrins [9].

Our further results regarding the formation, structural and photoinduced properties of metalloporphyrins indicated that lanthanides as hard Lewis acids can coordinate to peripheral substituents possessing similarly hard O-donor atom (e.g. sulfonatophenyl), resulting in the formation of tai-to-tail oligomers [15]. This is manifested in the detectable fluorescence, deviating from the head-to-head sandwich complexes, which are formed only at higher temperature. The photoinduced LMCT reaction of these kinetically labile metalloporphyrins was promoted by increasing ionic strength, which was favorable for charge separation.

2.1.2. In-plane metalloporphyrins

Photocatalytic redox cycles based on kinetically inert (in-plane) cationic manganese(III) porphyrins, in the presence of suitable electron donor and acceptor compounds were investigated in homogeneous solutions and micellar systems. Cationic micelles promoted, while anionic ones hindered the photocatalytic process transferring electron from triethanol amine to methylviologen [22, 30].

Photocatalytic degradation of 4-*(*2-pyridylazo*)*-resorcinol (PAR) was also studied in the presence of anionic and cationic manganese(III) porphyrins and the corresponding free bases. This substrate is a typical representative of the azo dyes, which cause considerable pollution, one of the major hazards to our environment. According to our results, both the metalation of these free-base porphyrins and the charge of these macrocycles strongly affected the efficiency of the photocatalytic degradation of PAR in the presence of hydrogen peroxide. The process of degradation was followed by spectrophotometric and chromatographic methods. Both free-base porphyrins and their manganese(III) complexes can catalyze the oxidative decomposition of PAR in homogeneous system, however, the process is much more efficient in the case of free ligands. Besides, the mechanisms of the decomposition are considerably different in the two cases as indicated by the results of FT-IR and Raman spectroscopic measurements. The hydroxylation of the aromatic rings is favorable in the presence of manganese(III) complex, while breaking of the N=N bond is the main reaction path when free-base porphyrin catalyzes the reaction [22, 31, 32].

2.2.Ruthenium(II)-polypyridine complexes

Three different LL ligands (LL: dmdpq = 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline; 2,5-bppz = 2,5-bis(2-pyridyl)-pyrazine és phendo = 1,10-phenantroline-5,6-dione) were used for preparation of $K_2[Ru(LL)(CN)_4]$ complexes. These LL ligands can also play the role of abridge. Accordingly, during the synthesis of the complexes involving 2,5-bppz, three different products were obtained, which were identified as $K_2[Ru(2,5\text{-bppz})(CN)_4]$, $[Ru(2,5\text{-bppz}_{)2}(CN)_2]$, using spectroscopic analysis. The third, minor product was a multinuclear complex. The basic photophysical properties of the mononuclear complexes were determined. The phendo derivative alone displayed long-lived phosphorescence (originated from triplet MLCT excited state) at room temperature [11]. Hence, it was chosen as a sensitizer for the immobilization on the surface of TiO_2 (see in section 4.1.1.)

3. Investigation of TiO_2-based photocatalysis in colloidal systems

TiO_2 was applied for photocatalytic oxidative degradation of various organic compounds (such as environmentally dangerous drug, anionic and non-ionic detergents). The mechanisms of these processes were revealed, focusing on the roles of oxidizing agents (hydroxyl, hydroperoxyl radicals and singlet oxygen) and intermediates formed in the photoinduced reactions. In order to enhance the photocatalytic efficiency of this catalyst, surface modifications were applied by deposition of noble metals (silver, gold, and platinum). Such catalysts were utilized for both oxidative decomposition of different organic compounds as potential contaminants and reductive hydrogen generation in aqueous systems.

TiO_2-based photocatalysis, using both untreated and surface-modified catalysts, was combined with other advanced oxidation procedures (AOPs), mainly ozonation, for enhancing the degradation efficiency.

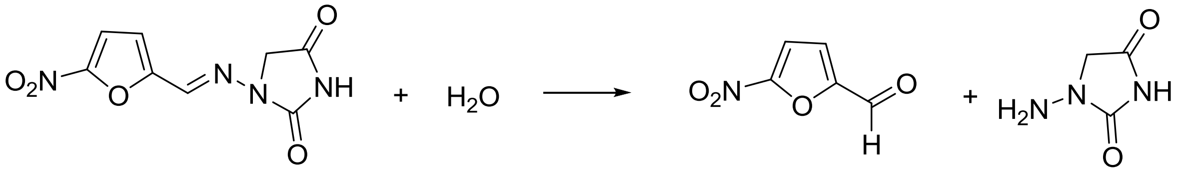
3.1. Photocatalytic oxidative degradation of various organic pollutants – mechanistic studies

3.1.1. Application of untreated titanium dioxide photocatalyst

Degradation of 4-hydroxybenzenesulfonic acid (4-HBS, a key intermediate of the decomposition of benzenesulfonic acid) was thoroughly studied by application of heterogeneous photocatalysis with untreated TiO_2. For elucidation of the degradation mechanism, the formation rate of hydroxyl radical was determined in various procedures applied by utilization of coumarin as an $HO^\bullet$ scavenger. According to our results, the order of the degradation steps of 4-HBS is the following: hydroxylation, desulfonation and finally, cleavage of the benzene ring. In the last one photogenerated oxidative agents other than $HO^\bullet$ play key roles.

TiO_2-mediated photocatalytic degradation of a non-ionic, alkylphenyl polyethoxylate type detergent, Triton X-100 was also realized and characterized. (Notably, this detergent can hardly be degraded by biological treatments.) The degradation mechanism was elucidated, based on various analytical measurements. The mineralization of this surfactant was monitored by following the TOC and pH values, as well as the absorption and emission spectra of the reaction mixture. An ultra-high-performance liquid chromatography (UHPLC) method was developed and optimized for monitoring the degradation of Triton X-100. Intermediates were also detected by GC-MS analysis and followed during the photocatalysis, contributing to the elucidation of the degradation mechanism [25, 26]. Deviating from the ionic surfactants studied earlier, no hydroxylation of the aromatic rings took place in this case. Instead, the polyethoxylate chain was fragmented in the early stage of the photocatalytic process, the alkyl part of the tensid molecules was mineralized much slower. This mechanism also explains why combination of the heterogeneous photocatalysis with other advanced oxidation procedures such as ozonation or treatment with peroxydisulfate did not increase the degradation or mineralization rate of this tensid.

Besides surfactants, a pharmaceutical belonging to the widely applied nitrofuran antibiotics, nitrofurantoin (NFT) was also photocatalytically degraded by using titanium dioxide in aqueous system upon irradiation with a solar simulator. Beside this drug itself, the photocatalytic degradation of its primary decomposition products, nitrofuraldehyde (NFA) and aminohydantoin (AHD), was investigated and compared to their photolysis in aerobic systems. UV-vis spectrophotometry, pH, IC, and HPLC measurements were applied to follow the changes in the systems during the irradiations and, subsequently, keeping them in the dark. After a fast *anti→syn* (or *trans→cis*) photoisomerization of NFT (giving i-NFT), a slower photohydrolysis of both isomers took place in both systems upon UV irradiation, leading to the formation of NFA and AHD (Scheme 1).



Scheme 1. Photoinduced hydrolysis of NFT.

i-NFT underwent hydrolysis in the dark, too – interestingly, in the photocatalyzed system significantly faster. While photolysis could not totally transfer NFT and i-NFT within 120 min, they disappeared within 90 min during the photocatalysis under the same irradiation conditions, along with the degradation of NFA and AHD and the accumulation of a rather stable intermediate. The fast photolysis of NFA gave two characteristic intermediates, which very slowly decomposed, while almost disappeared during photocatalysis. Direct irradiation could not convert AHD, while photocatalysis led to its significant degradation in aerobic system. Scavenging experiments demonstrated that $HO^•$ radicals played a determining role in the generation of NO_2^- from NO originated from NFT and NFA. Methanol, an efficient $HO^•$ scavenger, strongly depressed the nitrite formation in the photocatalytic system, while benzoquinone and sodium azide as scavengers of $O_2^{•-}$ and $^1O_2$, respectively, enhanced the accumulation of nitrite, indicating their important roles in the oxidation of NO_2^- to NO_3^- [19, 20, 27-29, 39]. All of these results clearly indicate that TiO_2-based photocatalysis is suitable for the decomposition and mineralization of NFT and their photoderivatives.

3.1.2. Application of surface-modified titanium dioxide photocatalysts

The efficiency for the formation of hydroxyl radicals was also determined on titanium dioxide photocatalysts, the surface of which was modified by deposition of silver or gold clusters. Both coumarin in slightly acidic medium and terephthalic acid in basic solution were applied as radical scavengers, utilizing luminsecence measurements. Our results confirmed that in the degradation of both formic and oxalic acids the main oxidizing agent was hydroxyl radical. The efficiencies of their mineralization were enhanced by any of these metals, however, the formation of $HO^•$ radicals was only promoted by gold clusters, while silver deposition hindered this reaction [3]. Just the opposite effects were observed for the photocatalytic degradation of benzenesulfonic acid. Deposition of silver on the TiO_2 catalyst increased the rate for the conversion of the initial surfactant via hydroxylation, while it decreased the mineralization rate (i.e., decrease of TOC), compared to the corresponding values achieved with pure titanium dioxide. These results indicated that modification of the surface of TiO_2 with silver promoted the production of $HO^\bullet$ radicals, but decreased the formation of oxidative radicals ($O_2^{\bullet-}/HO_2^\bullet$, $O_2(^1\Delta g)$) responsible for the ring-opening [36].

Surface modification of titanium dioxide was also realized by silver- and/or platinum-deposition. While Ag was deposited by a photochemical way, for the reduction of Pt a thermal reaction with borohydride was utilized. Diffuse reflectance measurements indicated that the threshold of the excitation energy of the photocatalyst was shifted from 3.2 eV (387 nm) to 2.0 eV (620 nm) for Ag-, 2.4 eV (517 nm) for Pt-, and 1.7 eV (729 nm) for Ag/Pt-deposited titanium dioxide. These photocatalysts were applied for hydrogen generation from water containing various carboxylic acids (as sacrificial electron donors) upon irradiation with solar simulator. The best quantum yield (exceeding 3%) was achieved with the Ag-TiO_2/Pt catalyst in the presence of formic acid at pH 3. Comparisons of the acid consumption with the H_2 evolution indicated that carboxylic acids functioned not only as hole scavengers but, although to a lesser extent, they could also be reduced by the conduction-band electrons (manuscript in preaparation).

3.2. Combination of TiO_2-based photocatalys with other AOPs, mainly ozonation

Both untreated and metal-deposited titanium dioxides were applied for photocatalysis in combination with other AOPs involving ozone or peroxodisulfate. While ozonation enhanced the degradation efficiency in most cases (especially regarding the mineralization of aromatic surfactants), peroxodisulfate did not increase, moreover, in some cases, decreased the efficiency of the photocatalysis. Hence, combinations with ozonation were studied in details.

3.2.1. Application of photocatalysis including untreated TiO_2 combined with other AOPs

Heterogeneous photocatalytic degradation of benzenesulfonate combined with ozonation displayed a synergistic effect (i.e., the mineralization efficiency was significantly higher the the sum of the efficiencies regarding the individual procedures applied separately). The rate of the mineralization showed a maximum at pH 5-6. The predominant intermediate was the meta-hydroxy derivative, in accordance with the effect of the sulfo group [1, 6, 18, 23, 35].

In the case of naphthalenesulfonates, the presence of peroxodisulfate slightly hindered the degradation, while ozonation resulted in a synergistic effect significantly increasing the efficiency of mineralization [7]. The latter result was in good accordance with our earlier observations regarding the degradation of benzenesulfonate (BS). Our investigation of the pH effect indicated that an increase of pH accelerated the conversion of the starting material in the aerated system faster than in the ozonated one. This effect can be explained by the hindrance of the $HO^\bullet$ formation from ozone via protonated ozonide ion. A reversed relation was observed regarding the mineralization (TOC decrease), which can be attributed to the key role of superoxide radical anion in the cleavage of the benzene ring. Synergistic effect of ozonation was also observed in the photocatalytic degradation of hydroxylated derivatives of BS and of industrial detergents such as alkylbenzene sulfonates and alkyl ether sulfates [16, 17]. Efficient combinations of heterogeneous photocatalyis with biological treatments were also demonstrated with purification of industrial wastewaters [13].

3.2.2. Application of metal-deposited TiO_2 and ozonation

The effect of silver-deposition on the surface of the TiO_2 particles was also studied in combination with ozonation for the degradation of 4-hydroxy-benzenesulfonate and 2,5-

dihydroxy-benzenesulfonate as key intermediates of the mineralization of benzenesulfonate. Similarly to the parent tensid, the first step of the mineralization of these derivatives is hydroxylation followed by desulfonation, then ring-cleavage. The latter step needs reactive oxygen-based species, possibly hydroperoxyl radical or singlet oxygen molecule, but not hydroxyl radical [33, 34]. Silver deposition on the catalyst surface increased the rate of the formation of $HO^\bullet$ radicals (monitored by application of coumarin), hence it accelerated the hydroxylation of the substrates to be degraded. However, the formation of other oxygen-based species needed for the ring-cleavage was not speeded up, accordingly, this surface modification did not increase the mineralization rates. Combination with ozonation, however, caused synergistic effect for the mineralization of these derivatives, similarly to the case of the parent compound, indicating the enhanced formation of the oxygen-based species needed for the ring-cleavage (manuscript in preparation).

4. Immobilization of photocatalyst on various supports

Both metal complexes, which can be applied as sensitizers and independent photocatalyts as well, and titanium dioxide as a heterogeneous photocatalyst were immobilized on/in various supports for realization mostly of oxidative degradation of different organic pollutants.

4.1. Immobilization of metal complexes

4.1.1. $K_2[Ru(phendo)(CN)_4$ (phendo = 1,10-phenantroline-5,6-dione)

As it was indicated in section 2.2., from the viewpoint of sensitization, only the phendo complex proved to be promising from the prepared $K_2[Ru(LL)(CN)_4$ coordination compounds, due to its long-lived triplet excited state. Accordingly, it was immobilized on the surface of TiO_2 (Degussa P25) in the pH range of 3.0-11.5 via adsorption. The presence of strongly adsorbing acetate or phosphate ions efficiently hindered the immobilization of this complex. Besides, neither in the presence of (non-coordinating) perchlorate ions occured its adsorption in basic solutions. However, in acidic solutions the efficiency of the adsorption of this ruthenium(II) complex was significantly enhanced, increasing the pH up to 4. The adsorption efficiency reached its maximum (90%) at pH =3.7, and no further increase was observed at stronger acidification. The adsorption rate was also measured, and 2 min time and pH 3.5 were chosen as optimum conditions along with the concentration of 4×10^{-5} mol/dm^3 for the complex and1 g/l for TiO_2. Visible light-excitation (λ>410 nm) of this sensitized photocatalyst led to the formation of conduction-band electron scavenged by methylviologen. However, no hydroxyl radical was formed, indicating that the electron was injected into the conduction band from the excited ruthenium(II) complex, not from the valence band of the photocatalyst. Hence, this sensitized TiO_2 could be used for the degradation of electron-acceptor type organic compounds, e.g., amino acids such as phenylalanine, due to the amine groups in these compounds. Non-sensitized titanium dioxide (Degussa P25) was not photoactive upon visible-light irradiation. Drying and re-suspendation of the sensitized catalyst decreased its efficiency, due to the agglomeration as proved by the analysis of particle size. The diffuse reflectance spectrum of the sensitized catalyst confirmed the extension of its absorption, making its excitation possible even with 500-520-nm light [10, 14, 21]. X-ray photoelectron spectroscopy (XPS) analysis of this sensitized photocatalyst delivered evidences for its surface modification; as a consequence of which the chemical environment around the O atoms was changed compared to the case of the pure titanium dioxide. Besides, both the binding energies and the ratios of the Ru, N, and C components on the catalyst surface gave unambiguous proofs for the coating with this metal complex. These observations are in good agreement with the results of the successful, visible light-driven photocatalytic degradation of phenylalanine achieved (manuscript in preparation).

4.1.2. Metalloporphyrins and free porphyrin ligands

Athough most of the immobilized photocatalysts studied in this project were applied for degradation of organic contaminants, some experiments were also carried out to compile photocatalytic reductive systems, similarly to those working in homogeneous and micellar solutions (see in section 2.2.2.). Graphene powder was chosen as a support because it very efficiently adsorbed (practically 100 % of the) metalloporphyrins. However, at the same time, it totally impeded the photoinduced electron transfer – probably due to its high electric conductivity. This effect could not be eliminated by application of apolar organic compounds as potential insulators adsorbed on the graphene surface. Nevertheless, graphene could be an efficient support of metalloporphyrins for oxidative photocatalysis, but such systems were not studied in this project.

For oxidative photocatalysis involving porphyrins, exfoliated kaolinite (consisting of nanotubes and nanosheets) was applied, also in order to investigate the reaction mechanisms and the effect of the support. Both manganese(III) porphyrins (anionic and cationic as well) and the corresponding free-base ligands were immobilized and tested as photocatalysts. In these experiments visible light-driven photocatalytic degradation of 4-(2-pyridylazo)-resorcinol (PAR), a widely used azo dye as a typical pollutant was studied, similarly to the experiments with the corresponding homogeneous systems (see section 2.1.2.). According to our results, immobilization strongly affected the efficacy of the photocatalytic decomposition of PAR in the presence of hydrogen peroxide. As NMR, Raman, and IR spectroscopic as well as and HPLC-DAD analyses indicated, the hydroxylation of the aromatic rings is favorable with manganese(III) complexes, while breaking of the N=N bond is the main reaction path when free-base porphyrins catalyze the reaction. Photoinduced formation of singlet oxygen is the key step in the case of the free bases, while activation of the axially coordinated peroxide plays the determining role in the mechanisms. Immobilization on the exfoliated kaolinite increased the efficiency of the photocatalytic degradation especially in the case of the free-base porphyrins [22, 31, 32] (manuscript in preparation).

4.2. Immobilization of titanium dioxide

The suspensions of titanium dioxide photocatalysts, both pure and surface-modified (by silver-deposition), were layered on glass plates by dip coating. Both types of suspensions were prepared in situ by sol-gel technique. The coating, after drying and 4-hour treatment at 150°C, proved to be mechanically stable, but its activity in photocatalytic degradation of benzenesulfonate was rather modest. Further experiments was carried out with thin (60-140 nm) mesoporous layers of pure or surface-modified TiO_2 also prepared by sol-gel technique, utilizing a cationic surfactant (cetyltrimethylammonium bromide). These coatings were treated at 450 °C. Silver was deposited on the surface of the pores by dipping the coated glass plates into $AgNO_3$ solutions of various concentrations. The surface-modified catalysts prepared in this way proved to be much more efficient than that containing silver in the whole cross-section of the particles prepared by sol-gel technique [12].

Immobilization of titanium dioxide photocatalyst was also carried out by application of polyvinyl alcohol (PVA). The PVA-TiO_2 composite catalyst was prepared from a PVA with 146 000-186 000 molecular weight and 99+% hydrolysis degree and Degussa P25 TiO_2. The water solubility of the polymer in the composite was decreased with a heat treatment causing a coloration from white to brown. Upon stirring with distilled water and irradiation in a reactor, the colour of the composite catalyst gradually bleached, and the organic carbon content significantly increased in the liquid phase. Unsaturated alcohols, aldehydes, and carboxylic acids were identified by GC-MS in the liquid phase. The activity of the catalyst immobilized in PVA film was tested by degradation of Triton X-100 surfactant as model compound, irradiating with a solar simulator. The photocatalytic efficiency could be sustained through several cycles.

Moreover, it increased then levelled off, due to the decomposition of the top of the polymer layer [24, 38].

5. Summary and conclusions

Comparing the content of the detailed final report to the original (planned) program, the main goals have been achieved: new photoactive metal complexes (of two types) were synthesized and thoroughly characterized, they were applied in photocatalytic systems in both homogeneous solutions and immobilized forms (also as sensitizer); semiconductor-based heterogeneous photocatalysis utilizing pure and surface-modified titanium dioxide was applied mostly for oxidative degradation of various organic pollutants and, to a minor extent, for hydrogen generation in aqueous systems. The previous task was also efficiently fulfilled with combination of heterogeneous photocatalysis with ozonation. In situ prepared, immobilized TiO_2 photocatalysts were successfully utilized, too, for decomposition of environmentally dangerous contaminants. These works involved comprehensive mechanistic studies, too. Hence, our achievements in this project can considerably contribute to the development of the photocatalytic water treatment procedures.

Our results have so far been published in 8 papers in internationally respected journals and one has been submitted also to a high-impact one. (This number is in accordance with the planned one.) The accepted manuscriptsalong with the submitted one have been uploaded in the repository of the library of the Hungarian Academy of Sciences (the corresponding URLs are given at the references). As indicated in this report, at least 4 further publications are in preparation, regarding the sensitized TiO_2, the immobilized porphyrins, the photocatalytic hydrogen generation, and the role of the oxidative intermediates formed by application of metal-deposited titanium dioxide.

The results of this project serve as bases for two PhD dissertations to be compiled by Orsolya Fónagy and Péter Hegedűs, not to mention some diploma works, scientific compositions and conference presentations of our students. Thus, the realization of this project successfully contributed to the development of several young, talented researchers. Notably, for the presentation of his results in this topic, Péter Hegedűs reached 1st place at the National Scientific Students' Association Conference, besides for his diploma thesis he received Lászlóffy Woldemár Award (1st place in MSc category) and Soós Ernő Young Researcher Award (in MSc category).

Besides, international cooperations were also involved by the realization of this project. Colleagues from Zagreb took part in the heterogeneous photocatalytic degradation of a widely used drug, nitrofurantoin, while scientists from Graz contributed to the characterization of water-soluble metalloporphyrins.

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