

Doctoral (PhD) theses

TiO₂-based photocatalysts and photoreactive coatings for water and
air cleaning

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1. INTRODUCTION AND OBJECTIVE

Pollution of water and air due to intensive human activity is undoubtedly a major concern worldwide. This challenge urges the scientific community to look for sustainable, green solutions to obtain the purity of these media without imposing more strain on the environment. Using materials which can be activated by renewable energy sources – such as sunlight – could be an ideal solution for that. TiO_2 is a semiconductor material which is capable of generating electron – hole pairs under UV light irradiation. These evolved charge carriers then can react with the surrounding water and oxygen molecules to generate reactive radicals which can thus induce photo-degradation of various pollutants, toxic substances or even viruses, bacteria thus TiO_2 is suitable for the purification and detoxification of air and water. The major limitations of this compound to be applied as a purifying agent in commercial use is its low quantum efficiency due to the fast recombination rate of charge carriers and the large band gap (3.2 eV for anatase and 3.0 eV for rutile) which fundamentally determines the minimum photon energy of the irradiating light for the charge separation to occur. The ideal case would be if TiO_2 was able to be “activated” by visible light with high quantum efficiency thus a vast amount of light coming from the Sun could be harvested and cleaning of air or water media by means of photocatalysis would finally be solved under large scale conditions, utilising the largest renewable energy source.

This work aimed to investigate possible approaches to increase the photocatalytic activity of TiO_2 -based photocatalysts and photocatalytic coatings. A few methods were tried which could contribute to better electron – hole separation to result in higher photocatalytic activity, namely, modification of TiO_2 with noble metal nanoparticles (NPs) and engineering the structural properties of TiO_2 . Once considering the application of TiO_2 in practical use, one has to make sure that the recovery of this solid is meticulously executed both for economic and environmental reasons. Given this challenge, I was motivated to study possible alternatives to separate and reuse TiO_2 . Finally, functionality of Ag- TiO_2 , embedded in polymer matrix, was coated inside a photocatalytic reactor constructed as a prototype of an indoor air purification device for VOC removal.

2. EXPERIMENTAL

Preparation of photocatalysts and nanocomposites

To prepare Ag- or Au-modified TiO₂, required amounts of AgNO₃ or HAuCl₄, were added P25 TiO₂ suspended in water/2-propanol mixture. After that NaBH₄ was added to the suspension as a reducing agent and the suspension was stirred for 1 hr. The modified TiO₂ was washed 3 times then separated from the aqueous medium by centrifugation and finally dried in oven at 60°C.

TiO₂ samples with various crystal phases and morphologies were prepared by acidic hydrothermal post treatment (HPT) of hydrogen titanate nanofibres (H-TNFs) using nitric acid. The TiO₂ samples were prepared in Teflon-lined autoclaves at 180°C in 24 hrs using 0.05; 0.1; 0.5; 1; 2; 4 mol/L HNO₃ as reaction medium. The samples were washed with a large amount of water then separated and dried in oven at 60°C.

TiO₂- graphene oxide (TiGO) nanocomposites, containing 1 – 5 wt% of graphene oxide (GO), were prepared by heterocoagulation and. Briefly 0.04- 0.2 g of GO nanosheets exfoliated in 1.6 L highly alkali solution (pH = 8.3 ± 0.3) was rapidly dispersed in 0.4 L of 9.5 – 9.9 g/L TiO₂ suspension (pH = 5). The colloids were stirred for a few minutes then sedimented and separated from the medium. The sediment was dried at 50°C then ground into fine powder in a mortar. The nanocomposites were named as TiGO-1; TiGO-2; TiGO-5 and TiGO-10, referring to the wt% of GO content of the sample.

The nanocomposite films were prepared using TiO₂, Ag-TiO₂ as photocatalysts and inorganic supports, such as ZrO₂ and Na-hectorite (Na_{0.3}(Mg,Li)₃Si₄O₁₀(OH)₂), hereafter Hect, or organic binder, poly-ethyl-acrylate-co-methyl-metacrylate [poly(EA-co-MMA)]. All nanocomposite films were prepared by homogeneously spraying aqueous suspensions (10 wt%) of the selected compounds on glass slides and dried.

2.1. Characterisation and study of photocatalytic activity

X-ray diffraction (XRD) measurements of the TiO₂ samples prepared by acidic hydrothermal treatment of hydrogen titanate nanofibres were carried out on a *Bruker D8* diffractometer (Bruker-AXS GmbH, Karlsruhe, Germany).

X-ray photoelectron spectra (XPS) of the Ag-modified TiO₂ and TiGO samples were recorded with a *Specs* instrument equipped with a *Phoibos 150 MCD 9* hemispherical electron energy analyser operating in the FAT mode. The excitation source was a K α radiation of a magnesium anode (h ν = 1253.6 eV).

A *Philips CM 100* transmission electron microscope (TEM) was used at the University of Szeged, Hungary, and a *Technai TF20 Super Twin* microscope was used in ICES, Singapore to take images of the Ag-TiO₂ sample and the HPT samples, respectively.

Scanning Electron Microscopy (SEM) images were taken on a Hitachi S-4700 SEM device.

A *Biorad FTS-60A* Fourier Transformation Infrared (FTIR) spectrometer equipped with Attenuated Total Reflection crystal detector was used to record the spectra of the nanocomposite films. The scans were recorded in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹.

Advancing and receding contact angles (CAs) on the photocatalyst/polymer nanocomposite films were measured using a drop shape analysis system (*EasyDrop*, Krüss GmbH, Hamburg, Germany).

The electric conductivity measurement of TiGO was assessed using a *Keithley 2400* source meter at room temperature in a two-wire direct current configuration. Conductance was determined as the slope of current-voltage characteristics determined in the voltage range of 1-50 V. An aqueous suspension (c= 0.1 m/V%) of TiGO-2 was dispersed and dried on an interdigitated gold electrode, which was irradiated by a UV-rich light source (*Original Hanau*, Q81, P= 70 W, $\lambda = 310\text{-}590$ nm) both in dry air and in water saturated atmosphere.

The photocatalytic activity of the TiGO nanocomposites were determined at room temperature (25 ± 2 °C) in 1 mmol/L phenol solution. The photodegradation of phenol was followed by *Knauer* HPLC on a C-18 column using acetonitrile/water mixture as eluent. Photocatalytic activity of other photocatalysts and photocatalyst – organic/inorganic nanocomposite films was studied in a flat film photoreactor (volume, ca. 0.165 L) at room temperature by following the photodegradation of ethanol vapour. The light source was low-pressure mercury lamps (GCL303T5/4 type, *Light-Tech*, Hungary; P= 15 W, $\lambda = 254\text{-}612$ nm). The ethanol concentration was determined by gas chromatograph GC (*Shimadzu* GC-14B) equipped with a thermal conductive detector (TCD) and with a flame ionization detector (FID). The initial concentration of ethanol vapour was 0,36 mmol/L.

3. NOVEL SCIENTIFIC RESULTS

3.1. TiO₂- GO (TiGO) nanocomposites

TiGO nanocomposites were prepared by heterocoagulation of exfoliated graphene oxide (GO) lamellae and TiO₂ NPs. Unlike pure TiO₂, TiGO nanocomposites showed accelerated sedimentation rates in a wide pH range which makes these materials very attractive

from a practical point of view. The GO support in the nanocomposite network is converted into a graphene-like material (rGO) due to UV-irradiation. Despite the chemical transformation of the support, it held TiO₂ anchored on its surface and the nanocomposite of a more hydrophobic character showed a faster sedimentation kinetics. TiGO-2 was reused 4 times for the photocatalytic degradation of phenol solution without observable loss of photocatalytic activity [1].

3.1.1. TiGO nanocomposites were prepared with 1-5 wt% of GO content. Due to the high surface charge density and the several micrometre large lateral dimension, the GO sheets were found to be ideal catalyst support to hold nearly 100 times more TiO₂ than that of their own weight. The nanocomposites were probed as photocatalysts for the photooxidation reaction of phenol solution (c = 1 mmol/L). Surprisingly, introduction of GO to TiO₂ seemed to have an adverse effect on the photocatalytic activity which was found to be less pronounced as the GO content was increased. The phenomenon was associated with the optical shading of GO lamellae and with the decreased amount of available active sites on TiO₂ due to anchoring. 4 consecutive photocatalytic cycles were conducted using TiGO-2. All photocatalytic kinetic curves were found to be almost identical (within experimental accuracy: $\pm 0.3\%$) implying that the nanocomposite was suitable for repeated use without any decrease in the photocatalytic efficiency.

3.1.2. It was observed that all TiGO nanocomposites, which were originally light grey, became darker and eventually black under UV-irradiation during the photocatalytic experiments which was the first, obvious sign of the chemical reduction of GO into a graphene-like carbonic compound (rGO). The phenomenon was then evidenced by XPS and electric conductivity measurements. XPS results indicated the loss of epoxy and hydroxyl groups which was suggested by the decrease of photoemission peak intensity at 287 eV and simultaneous relative increase of peak area at ~ 285 eV. This latter referred to the aromatic (graphitic) carbon rings of graphene platform. However, the carbonyl and carboxyl groups were found to remain intact upon UV-irradiation as their indicative XPS peak at ~ 289 eV showed rather insignificant change ($\sim 3\%$). It was concluded that the full restoration of the polyaromatic graphene structure was not complete after one photocatalytic cycle. A charge-induced shift (0.5 eV) of peak position at ~ 285 eV towards lower binding energies also indicated the formation of rGO with higher electric conductivity. This latter was also proved on the TiGO-2 sample by electric conductivity measurements under 2 hrs of UV-irradiation (UV-B-C). The GO-graphene transformation was indicated to be more efficient in moist air, because the increase of electric

conductivity was 100-fold in saturated water vapour atmosphere, while it was only 25-fold under ambient conditions.

3.1.3. It was found that the nanocomposites showed strikingly different settling behaviour than pure TiO_2 in aqueous suspensions. TiO_2 showed high kinetic stability at most pH values, except at around the isoelectric p.z.c. (pH=6.6), where the surface charge of primary particles was negligible which led to aggregation and slow sedimentation of the solid. The supernatant became clear only after 24 hrs of settling and only in a narrow pH range (pH = 6-8). In contrast to that of TiO_2 , the settling velocity of TiGO nanocomposites was significantly higher in the examined pH range and showed the typical settling behaviour of a highly destabilised disperse system containing large aggregates, forming easily re-dispersible, voluminous sediments after settling with a sharp settling interface. All nanocomposites showed faster sedimentation than TiO_2 , however, the settling rate was inversely proportional with the GO content because the sedimentation was slightly hindered by the presence of large, anisometric GO sheets.

3.1.4. The chemical transformation of GO into rGO, due to UV-irradiation, also affected the settling properties of the nanocomposites as the reduced compound became more hydrophobic with the loss of functional groups. The terminal settling velocity (TSV) of TiGO-5 irradiated for 80 min increased from 2 to 10 cm/min. Despite the chemical transformation, the rGO lamellae held the TiO_2 nanoparticles attached on their surface as it was evidenced by turbidity measurements. It has to be noted that the pH of the reaction medium decreased from ~6.5 to 4.5 by the end of photocatalytic cycle which obviously affects the electrostatic forces between GO and TiO_2 particles. At this pH the surface charge of GO lamellae is negligible. This implies that the TiO_2 NPs were primarily attached to the GO sheets by weak van der Waals adhesion forces, instead of electrostatic attraction or through hydrogen bonds. The attachment of particles in the TiGO network could be reversed by strong mechanical (sonication), however the reversibility of the process is indicated by the recollection of TiO_2 particles on the GO lamellae by gentle shaking of the dispersions.

3.2. Nanocomposite coatings

Nanocomposite films were prepared using TiO_2 and inorganic (ZrO_2 and Hect) and organic p(EA-co-MMA) supports. Hect is a great adsorbent of organic pollutants therefore it can readily contribute to the photocatalytic process as a support [1]. High-energy UV-B irradiation triggers simultaneous processes when p(EA-co-MMA) is used as a photocatalyst binder: decrease of mechanical stability but at the same time increase of photocatalytic activity of the film owing to partial degradation of the polymer matrix [2]. Small amount (10 wt%) of

Hect added into the polymer successfully preserved the coherence of the polymer matrix and slow down its degradation which is encountered due to the presence of generated (reactive oxygen species) ROS. The addition of Hect did not decrease the mechanical stability of the nanocomposite.

3.2.1. The added inorganic supports ($\text{ZrO}_2\text{:Hekt}=9:1$) were optically transparent in the UV-Vis region thus they allowed free penetration of the light into the deeper layers of the films which is necessary to induce photocatalytic reactions on TiO_2 . Besides preventing TiO_2 from aggregation, Hect, present in a small amount (0-10 wt%), apparently increased the processability of the nanocomposite suspensions when preparing the layers, i.e., the prepared films were more homogeneous and easy to spray on the glass slides. Moreover, due to the relatively high surface area ($305.0 \text{ m}^2/\text{g}$) and high adsorption capacity of the layer silicate, the adsorption of ethanol was higher on the nanocomposite film compared to pure TiO_2 . Owing to a highly dispersed arrangement of the photocatalyst in the nanocomposite and the good adsorption properties of the layered silicate, the nanocomposite layers having 40-80 wt% of photocatalyst showed comparable photocatalytic efficiency to the pure TiO_2 film. This implies that less amount of photocatalyst is enough to obtain similar photocatalytic performance than pure TiO_2 with same film thickness.

3.2.2. The photocatalytic activity of nanocomposite films, containing Hect and p(EA-co-MMA) polymer as supporting materials, were contrasted. The nanocomposite films contained 60 wt% of photocatalyst and 40 wt% of support. While photocatalytic activity of Hect-supported film was comparable to that of pure TiO_2 film (Table 1 1st and 2nd rows); the polymer matrix significantly decreased the photocatalytic activity (Table 1 3rd row). The significant increase in photocatalytic activity was owing to that the polymer thoroughly enwrapped the photocatalyst NPs, hindering any photochemical reactions between TiO_2 and the model pollutant. However, it was found that the deteriorating effect of the polymer binder can be reversed by irradiating the nanocomposite film with high-energy ($\lambda_{\text{max}} = 254 \text{ nm}$) UV-photons (Table 1; 3-4th rows). As a result of 24 hrs pre-treatment, 34.7% increase of EtOH conversion was registered which was associated with partial degradation of the polymer matrix and increased amount of free TiO_2 active sites in the nanocomposite structure.

Table 1 Photocatalytic activity of nanocomposite films supported by Hect and p(EA-co-MMA)

Nr	Film ID	Conversion (%)	Δm_{EtOH} (mg)	Δm_{EtOH} (mg /g kat)	k (1/min)
1	TiO ₂	58.64	1.27	22.6	0.0107
2	60% TiO ₂ /40% Hect	52.5	0.60	16.3	0.0128
3	60% TiO ₂ /40% p(EAcoMMA) before UV-treatment	23.8	0.60	17.3	0.0044
4	60% TiO ₂ /40% p(EAcoMMA) after 24 hrs of UV treatment	58.5	1.37	39.4	0.0145

3.2.3. Nanocomposite films were prepared using TiO₂ or Ag-TiO₂ as photocatalyst and p(EA-co-MMA) polymer as binding agent [3] and the effect of UV-irradiation was further examined. The as-prepared nanocomposite films were irradiated UV-light ($\lambda_{\text{max}} = 254 \text{ nm}$) for different periods of time (0; 1; 4; 24 and 48 hrs). Photochemical degradation of pure polymer upon UV-irradiation with and without photocatalyst was proved by FTIR measurements. The characteristic IR vibration regions representing the chemical structure of the p(EA-co-MMA) showed decreasing intensities for all samples as the irradiation time was increased. Faster degradation kinetics of the polymer was observed in the presence of catalyst NPs, because besides the UV-initiated photolysis, the generated ROS contributed to the degradation mechanism. The polymer was represented by the symmetric and asymmetric bending vibrations of CH₃-groups at 1382 and at 1447 cm⁻¹, respectively; the stretching vibrations of C–H region at 3100- 2800 cm⁻¹; and finally the stretching vibrations of C – O and C = O at 1157 and at 1725 cm⁻¹, respectively. Decreasing absorbance of these vibrations indicated the degradation of polymer, i.e. breaking of chains and detachment of functional groups. It was also observed that the intensity of broad IR absorption band at around 3000 cm⁻¹, was increased referring to increasing amount of O – H bonds, indicating the formation of surface – OH groups on the photocatalyst NPs due to irradiation or the presence of increasing amount of adsorbed water on the surface. This latter was confirmed by the presence of very weak vibration band at 1624 cm⁻¹ for the nanocomposites irradiated for 24-48 hrs.

3.2.4. Contact angle measurements were performed on the pure polymer film and on TiO₂- and Ag-TiO₂-containing nanocomposite films after given periods of UV irradiation (0-2 hrs). Equilibrium contact angles and surface free energy were calculated from the measured advancing and receding contact angle values. While the equilibrium contact angle and calculated surface free energy did not change for the pure polymer film, rapid decrease of contact angle values were observed on the nanocomposite films which in direct correlation with the increase of surface free energy. This phenomenon was a result i) manifestation of UV-induced super-hydrophilic property of TiO₂, presented already by FTIR measurements. and ii) increased relative photocatalyst content consequently resulting in a higher surface free energy of the nanocomposite film. These effects were so pronounced on the TiO₂-containing film that after one hr of irradiation the contact angle decreased to 0°. Obviously, under the short irradiation time not much of the polymer matrix could be degraded therefore it is suggested that the first process had a priority importance of the resulted decrease in contact angle values. Surprisingly, the contact angle decreased much slower on the Ag-TiO₂/polymer nanocomposite film under UV-irradiation, however the accelerated rate of polymer degradation on this composite compared to the TiO₂-containing counterpart has already been shown by FTIR measurements. With other words, the formation of surface –OH groups on the Ag-TiO₂ was slightly limited compared to that of TiO₂-containing counterpart. According to our speculation, the nucleation of Ag NPs, formed on the TiO₂ surface, started at the high energy active sites of TiO₂ that hindered the formation of – OH groups when it was exposed to UV photons.

3.2.5. Mechanical stability of the irradiated nanocomposite films was probed by the adhesive tape test. The adhesive tape was applied to the surface of the non-irradiated and irradiated films then it was removed by a quick pull. The higher number of removed NPs and polymer fragments indicated the process of polymer degradation and reversed mechanical stability of the nanocomposite film. The deteriorating effect of UV on the polymer matrix could already be seen by after 4 hrs of irradiation, but it was very much pronounced after 24-48 hrs.

3.2.6. The structural and morphological changes were also represented by the SEM images taken on the TiO₂/polymer layer before and after 24 hrs of UV-irradiation. While the non-irradiated film showed that the polymer covers the photocatalyst NPs and the film therefore displays a rather smooth surface, the nanocomposite layer after 24 hrs of UV irradiation displayed mostly uncovered TiO₂ NPs with a rougher surface.

3.2.7. Although high-energy UV-irradiation had an adverse effect on the mechanical stability of the nanocomposite film, it significantly improved the photocatalytic activity. After 24-48 hrs of irradiation, the nanocomposite films performed similarly than pure TiO₂ and Ag-TiO₂ films.

3.2.8. The polymer served as an excellent binding material, but at the same time its long-term durability was not assured for our purposes, thus 10 wt% Hect as an inorganic binder, resistant to UV and ROS, was added to the nanocomposite while keeping 60 wt% catalyst content in the nanocomposite. After 0-24 hrs of preliminary UV-irradiation, photocatalytic activity of nanocomposite films with and without Hect in the matrix, were contrasted. Photocatalytic activity of nanocomposite film without Hect showed significantly accelerated reaction rates of ethanol decomposition reaction as the duration of UV-treatment proceeded. On the contrary, nanocomposite films containing 10% Hect showed nearly steady reaction rates, irrespectively of the preliminary UV-irradiation and the photocatalytic activity showed only a slight increase. This indicates that the inorganic Hect, lamellar structured clay mineral, slowed down the photodegenerative processes induced by the generated ROS.

3.3. Ag_x(O)-TiO₂ heterostructures

Interconversion of Ag(0) – Ag (I)O on TiO₂ surface can be reversibly triggered by varying the wavelength of irradiation source. Photocatalytic activity of Ag-TiO₂, prepared by in situ chemical deposition of Ag NPs, was studied and contrasted to samples, prepared by different methods and containing the same amount of Ag but with different states of oxidation [3]. It was found that the preparation method and the oxidation state of Ag did not affect significantly the photocatalytic activity.

3.3.1. Ag-modified TiO₂ (wt_{Ag} % = 0.5) prepared by chemical reduction of Ag⁺ ions, showed a broad absorption band in the UV-Vis spectrum in the Vis range at $\lambda_{\max} = 455$ nm indicating the presence of plasmonic Ag NPs. However, slow, but gradual bleaching of the brown coloured Ag-TiO₂ film occurred when it was kept in dark and the same process was observed, but slightly faster under natural light conditions. The change of the colour indicated the spontaneous oxidation of Ag(0) on TiO₂ surface which was accelerated under Vis light. The process was followed by UV-DR measurements under UV- ($\lambda_{\max} = 254$ nm) and under Vis-light ($\lambda_{\max} = 450$ nm) irradiation to qualitatively describe the phenomenon. UV-rich light facilitated the formation of Ag(0) on the surface, which was indicated by the brownish colour, while Vis-light resulted in formation of Ag₂O which was indicated by the gradual change of colour.

3.3.2. Photocatalytic conversion of ethanol on TiO₂ was increased from 59% to 82% due to addition of Ag NPs. Further silver modified samples were prepared using different silver oxides

(Ag₂O és AgO). Surprisingly, neither the state of oxidation, nor the preparation method (in situ deposition or physical mixing) resulted in significant difference in the photocatalytic efficiency ($\pm 2.5\%$ difference in conversion).

3.4. TiO₂ samples prepared by acidic hydrothermal treatment of H-titanate nanofibers (H-TNFs)

Changing one parameter, the HNO₃ concentration of the hydrothermal reaction resulted in TiO₂ samples with various structural, optical and morphological properties. The bi-crystalline anatase-brookite nanofibers generated high concentration of charge carriers and at the same time showed stable photoelectrochemical response under repeated cycles. These results correlated well with the photocatalytic experimental data as this sample had the highest rate of fotooxidation of ethanol. The enhanced photoelectrochemical and photocatalytic activity was attributed to the retarded electron-hole pair recombination compared to other samples which was owing to the advantageous crystal composition and 1D morphology [4].

3.4.1. TiO₂ samples were prepared by acidic HPT of H-TNFs. By changing the concentration of HNO₃ ($c=0.05-4$ mol/L) in the reaction medium, TiO₂ NPs with various crystalline phase compositions could be obtained, i.e. anatase-, brookite-, and finally rutile-rich samples. The crystal phase compositions and average crystallite sizes of the obtained TiO₂ NPs are shown in Table 2. The crystal structure of the obtained NPs fundamentally determined the morphology thus anatase-rich nanofibres, brookite-rich rhomboid NPs and rutile-rich flower-like assemblies of nanorods were formed. The optical properties, i.e. the band gap energies, which were obtained from the Tauc-plot, correlated well with the crystal phase compositions: band gap energies of anatase- and rutile-rich samples were found to be ~ 3.2 eV and ~ 3.0 eV, respectively.

Table 2 Crystal phase composition of the TiO₂ samples

Nr	c _{HNO3} (mol/L)	Crystal phase composition (%)			Crystallite size (nm)		
		Anatase	Brookite	Rutile	Anatase	Brookite	Rutile
1	0.05	100	-	-	9.5 ± 2.0	-	-
2	0.1	93.2 ± 1.2	6.8 ± 1.2	0	9.2 ± 3.1	37.0 ± 11	-
3	0.5	49.2 ± 2.9	47.7 ± 2.9	3.05 ± 2.9	8.0 ± 3.9	53.1 ± 3.7	47.0 ± 1.4
4	1	34.4 ± 2.6	55.7 ± 2.7	9.9 ± 1.0	7.9 ± 5.4	50.3 ± 2.8	63.4 ± 7.3

5	2	-	74.8 ± 1.1	25.2 ± 1.1	-	33.9 ± 0.5	49.7 ± 1.4
6	4	-	27.5 ± 1.5	72.5 ± 1.5	-	15.9 ± 0.5	24.0 ± 0.3

3.4.2. Linear sweep photo-voltammetry under periodically interrupted UV-irradiation provided information about the photoelectrochemical properties of the TiO₂ samples. It was revealed that samples with high brookite content, were able to generate high photocurrents indicating that a large amount of charge carriers had been created. Furthermore, as the rutile content was increased in the sample, the generated photocurrents dropped as rutile.

3.4.3. Repeated PEC scans, registered in a potential range from -0.8 to + 1.5 V, in 0.1 mol/L Na₂SO₄ electrolyte solution revealed the differences between the PEC stability of the samples. The pure anatase nanofibres and the rutile-rich samples showed notable stability, but not the brookite-rich rhomboid NPs. It was found that despite the ability to generate high photocurrents, they showed poor stability of the PEC response, which was reflected by the decrease of the photocurrents in the series of the voltammetric scans.

3.4.4. Two aspects of PEC properties are identified with high importance: one is the ability to generate adequate amount of viable charge carriers and the other is the stability of the PEC response. The photocatalytic properties of a material are closely related to these features, because they carry information on the ability of the solid to generate viable charge carriers. It is found that although a high concentration of brookite crystal phase in the samples can generate high rate of charge carriers, the photoresponse is not stable for these samples. On the other hand, the suitable proportion of 93.2% anatase and 6.8% brookite endowed the sample with good capability for generating charge carriers while having a stable photoresponse, leading to its highest photocatalytic activity. It is assumed that the elongated shape and the bi-crystalline nature hinders the recombination which is undoubtedly closely related to the photocatalytic activity.

3.5. Air cleaning device designed for indoor air purification

The air cleaning device is practically a photoreactor which works with Vis-LED light sources therefore its operation is very economical. Ag-TiO₂ was used as a photocatalyst, immobilised in p(EA-co-MMA) polymer matrix. Based on the standard ethanol degradation tests, it was found that the device is suitable to degrade Volatile Organic Compounds (VOCs) in a

concentration more than three times higher than the average total VOC concentration in an average indoor environment.

3.5.1. A photocatalytic reactor was designed for indoor air purification operating with Vis ($\lambda_{\max} = 405$ nm) light emitting diodes (LEDs). LEDs provide long term durability and low operation costs for the photoreactor because their electric power consumption is low ($P_{\text{total}} = 25$ W/hr). The photocatalyst, Ag-TiO₂ (wt%_{Ag}=0.5) in p(EA-co-MMA) matrix ($m_{\text{Ag-TiO}_2} = 70$ wt%), was evenly sprayed on both sides of the catalyst support, which was a waved aluminium cylinder ($A = 880$ cm²). The cylinder was irradiated on both sides: 12 LEDs were circularly arranged around the cylinder and 6 LEDs were attached to a 3-sided column (2 LEDs on each side), in the middle of the photoreactor. A ventilator provided continuous circulation of the reaction medium.

3.5.2. The photocatalytic reactions were run in a sealed vessel. The initial average concentration of ethanol was 3.15 mg/L. Total VOC content (TVOC) of indoor air is considered to be good $< 0.6 \cdot 10^{-3}$ mg/L and according to a study in Hong Kong, the average TVOC concentration in a typical room in residential homes is $0.5 \cdot 10^{-3}$ mg/L, but a few exceed $25 \cdot 10^{-3}$ mg/L [5]. In our case the initial ethanol concentration was more than three orders of magnitude higher than that. After a 24 hrs of UV-treatment ($\lambda_{\max} = 254$ nm), three consecutive photocatalytic cycles were performed with an ethanol conversion of 89 %; 76% and then 64 %., referring to degradation rates of 1.8; 1.6 and 1.4 mg/L/hr, respectively. It was found that the photocatalyst coating can be re-activated with a 24 hrs of high-energy UV-irradiation (for the reason, please refer to *Point 3.2*) to obtain 96%; 87% and 68 % conversion of ethanol. This finding suggests that the air cleaning device is suitable to efficiently eliminate VOCs in an average indoor environment with low operation costs.

4. REFERENCES

- [1] T. Szabó, Á. Veres, E. Cho, J. Khim, N. Varga, I. Dékány; Photocatalyst separation from water using graphene oxide/TiO₂ nanocomposites; *Coll. Surf. A* 433 (2013) 230– 239.; DOI: 10.1016/j.colsurfa.2013.04.063
- [2] Á. Veres, T. Rica, L. Janovák, M. Dömök, N. Buzás, V. Zollmer, T. Seemann, A. Richardt, I. Dékány; Silver and gold modified plasmonic TiO₂ hybrid films for photocatalytic decomposition of ethanol under visible light; *Catal. Today* 181 (2012) 156– 162.; DOI:10.1016/j.cattod.2011.05.028

[3] Á. Veres, J. Ménesi, Á. Juhász, O. Berkesi, N. Ábrahám, G. Bohus, A. Oszkó, G. Pótári, N. Buzás, L. Janovák, I. Dékány; Photocatalytic performance of silver-modified TiO₂ embedded in poly(ethyl-acrylate-co methyl metacrylate) matrix; *Coll. Polym. Sci.* 292 (2014) 207–217.; DOI 10.1007/s00396-013-3063-1

[4] Á. Veres, J. Ménesi, C. Janáky, G. F. Samu, M. K. Schreyer, Q. Xu, F. Salahioglu, M.V. Garland, I. Dékány, Z. Zhong; New insights into the relationship between structure and photocatalytic properties of TiO₂ catalysts; *RSC Adv.* 5 (2015) 2421-2428.; DOI: 10.1039/C4RA11489B

[5] H. Guo, N. H. Kwok, H. R. Cheng, S. C. Lee, W. T. Hung, Y. S. Li Formaldehyde and volatile organic compounds in Hong Kong homes: concentrations and impact factors; *Indoor Air* 19 (2009) 206–217. DOI:10.1111/j.1600-0668.2008.00580.x

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Publications

Publications closely related to the dissertation:

1. Á. Veres, T. Rica, L. Janovák, M. Dömök, N. Buzás, V. Zollmer, T. Seemann, A. Richardt, I. Dékány; Silver and gold modified plasmonic TiO₂ hybrid films for photocatalytic decomposition of ethanol under visible light; *Catal. Today* 181 (2012) 156– 162.; DOI:10.1016/j.cattod.2011.05.028; IF: 4.03 (5 yrs)

2. Á. Veres, J. Ménesi, Á. Juhász, O. Berkesi, N. Ábrahám, G. Bohus, A. Oszkó, G. Pótári, N. Buzás, L. Janovák, I. Dékány; Photocatalytic performance of silver-modified TiO₂ embedded in poly(ethyl-acrylate-co methyl metacrylate) matrix; *Coll. Polym. Sci.* 292 (2014) 207–217.; DOI 10.1007/s00396-013-3063-1; IF: 2.280 (5 yrs)

3. T. Szabó, Á. Veres, E. Cho, J. Khim, N. Varga, I. Dékány; Photocatalyst separation from water using graphene oxide/TiO₂ nanocomposites; *Coll. Surf. A* 433 (2013) 230– 239.; DOI: 10.1016/j.colsurfa.2013.04.063; IF: 2.832 (5 yrs)

4. Á. Veres, J. Ménesi, C. Janáky, G. F. Samu, M. K. Schreyer, Q. Xu, F. Salahioglu, M.V. Garland, I. Dékány, Z. Zhong; New insights into the relationship between structure and photocatalytic properties of TiO₂ catalysts; *RSC Adv.* 5 (2015) 2421-2428.; DOI: 10.1039/C4RA11489B; IF: 3.708 (5 yrs)

$$\sum_{\text{IF}} = 12.85$$

Other publications:

5. Á. Veres, L. Janovák, T. Bujdosó, T. Rica, E. Fodor, S. Tallósy, N. Buzás, E. Nagy, I. Dékány; Silver and phosphate functionalized reactive TiO₂/polymer composite films for destructions of resistant bacteria using visible light *J. Adv. Oxid. Technol.* 15 (2012) 205-216.

IF: 0.700 (5 yrs)

Cumulative IF: 13.55

PRESENTATIONS

Oral presentation:

Á. Veres, L. Janovák, I. Dékány; TiO₂-based photocatalysts in water and air cleaning; Kémia Más Megvilágításban, Szeged, 15th June 2015.

Posters:

1. Á. Veres, L. Janovák, I. Dékány, T. Seemann, V. Zöllmer, A. Richardt; Photocatalytic Degradation of Ethanol on TiO₂ Thin Hybrid Films Supported by Inorganic Materials; Solar Chemistry and Photocatalysis: Environmental Applications 6th (SPEA6), Prague, Czech Republic, 13-16th June, 2010.

2. Á. Veres, T. Rica, T. Seemann, V. Zöllmer, A. Richardt, I. Dékány; Effect of silver-modification on TiO₂ for photocatalytic degradation of thio-di-glycol on photocatalyst/polymer composite films; 11th International Symposium "Interdisciplinary Regional Research" (ISIRR11) Szeged, Hungary, 13-15th October, 2010.

3. Á. Veres, T. Rica, T. Seemann, V. Zöllmer, A. Richardt, I. Dékány; Self-cleaning reactive surfaces for photocatalytic degradation of organic pollutants using visible light, Euronanoforum; Budapest, Hungary, 30th May- 01st June 2011.

4. Á. Veres, I. Dékány, Z. Zhong; Ag and Au@TiO₂ nanostructures for photocatalytic applications; 6th Singapore Catalysis Forum, Singapore, 17th May 2013.

5. Á. Veres, J. Ménesi, C. Janáky, G. F. Samu, M. Schreyer, Q. Xu, F. Salahioglu, P. Gunawan, M. Garland, I. Dékány, Z. Zhong; The role of crystal structure and morphology on the photocatalytic activity of TiO₂; 7th Singapore Catalysis Forum, Singapore, 23rd May 2014.

6. Á. Veres, J. Ménesi, C. Janáky, G. F. Samu, M. K. Schreyer, Q. Xu, F. Salahioglu, M. V. Garland, I. Dékány, Z. Zhong; The role of crystal structure and morphology on the

photocatalytic activity of TiO₂; 7th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT7), Kyoto, Japan, 1-6th June 2014.

7. Á. Veres, J. Ménesi, C. Janáky, G. F. Samu, M. K. Schreyer, Q. Xu, F. Salahioglu M. V. Garland, I. Dékány, Z. Zhong; Various TiO₂ nanostructures derived from acidic hydrothermal treatment of hydrogen titanate nanofibres: Structural characterisation and photocatalytic property; 6th Szeged International Workshop on Advances in Nanoscience (SIWAN6), Szeged, Hungary, 15-18th October, 2014.