

Activity of phthalocyanine-sensitized TiO₂-anatase in photooxidation of sulfite ions

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Hybrid catalysts based on the TiO₂ matrix impregnated with Nd, Eu and Yb diphthalocyanines proved effective in oxidation of sulfite ions under irradiation with light from the UV-visible range. Micro- and nano-crystalline anatase powders were used in preparation of the photocatalysts, which were applied in the form of a suspension in the water phase. The reaction yield was found to depend on the phthalocyanine sensitizer used and the conditions of TiO₂ impregnation. The best results were obtained when micro-anatase impregnated with Yb-diphthalocyanine was used.

Keywords: TiO₂, anatase, phthalocyanine sensitizer, photooxidation, hybrid photocatalysts.

INTRODUCTION

Titanium dioxide has become one of the most popular and promising inorganic materials during the last decades of the XX century. Commonly used in production of pigments, cosmetics and pharmaceuticals, TiO₂ was re-discovered for much more sophisticated applications, such as semiconductors or capacitors for electronics, photoactive elements for solar cells, catalysts and photocatalysts¹⁻³. As a chemically very stable and non-toxic solid material, titanium dioxide offers a range of important optoelectronic properties, i.a. semi-conductivity⁴⁻⁶, photocatalytic activity^{4,7} and considerable photostability^{8,9}. From among its three natural polymorphs only rutile and anatase have been considered for wide industrial application. Although rutile has proved thermodynamically more stable, however it is anatase which has displayed better photocatalytic activity and hence has received much more attention as a matrix for diverse catalytic systems than rutile does^{1,4,6}.

The band gap energy of anatase (3.2 eV) falls into the UV range of photonic energy and for this reason ultraviolet irradiation is necessary to (photo)activate its electronic system to create the reactive electron-hole pairs (e^- , h^+). Practically, photons of $\lambda > 400$ nm are not absorbed by TiO₂ and to enhance its light harvesting ability over the visual range some modifications must be introduced into the anatase matrix¹⁰. The most

simple way to extend the absorption range is to prepare TiO₂-dye composites, and there is a rich literature reporting on such systems. In the recent years novel anatase-based photocatalysts were developed involving phthalocyanine and porphyrin sensitizers^{7, 11-16}. These interesting hybrid systems proved effective in photodegradation of 4-nitrophenol, 2-propanol, polyethylene and polystyrene^{9, 11-15, 17-20}. It is believed they may be very useful both in industrial catalysis as well as important components of environment control systems.

Titanium dioxide (anatase) has become a commercial product and an abundance of its varieties has been made available, as far as grain size and activity are concerned. However, for the reasons of dedicated research projects (e.g. photocatalysis) it is usually synthesized in laboratory scale according to the methods reported elsewhere^{1-3, 5-7, 21-24}. Practically, most of the TiO₂ syntheses are carried out using the methods based on the sol-gel technique^{1-3, 24}.

Phthalocyanines, MPc (M is a metal ion, Pc = C₃₂H₁₆N₈ is the phthalocyanine ligand) represent a group of interesting heteromacrocyclic dye-sensitizers particularly valued for their significant photochemical activity both in the UV and visible range¹². These compounds can be appropriately chemically modified so that one can tune their light absorption spectrum in a wide range (Fig. 1).

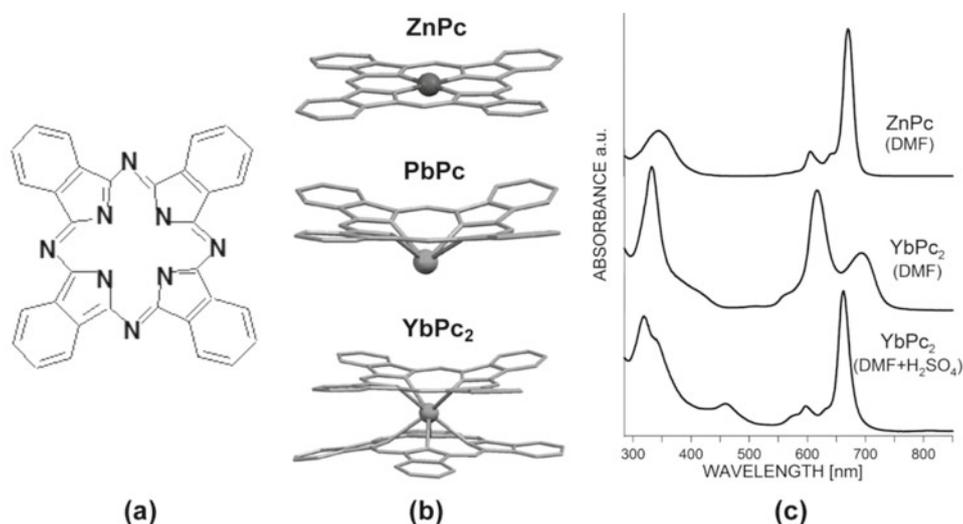


Figure 1. Molecular and spectral properties of phthalocyanines. (a) Phthalocyanine macrocycle (Pc = C₃₂H₁₆N₈); (b) Metal complexes of phthalocyanine (MPc); (c) Electronic absorption spectra (UV-Vis)

In dye-sensitized photocatalysis the matrix of a solid semiconductor catalyst has been impregnated with a properly chosen colorant to enhance the light absorption performance and hence improve the photoactivity of such a system. In fact, there are two photosystems operating simultaneously, that of the matrix and the other one of the sensitizer. The efficiency of such hybrid photocatalyst depends on how far these two photosystems may “cooperate” in electron transfer throughout the matrix, thus effectively extending the lifetime of the electron-hole pairs (e^- , h^+)^{12, 25}. The principle of the cooperative mechanism in a TiO_2 -phthalocyanine hybrid catalyst system has been presented in Figure 2.

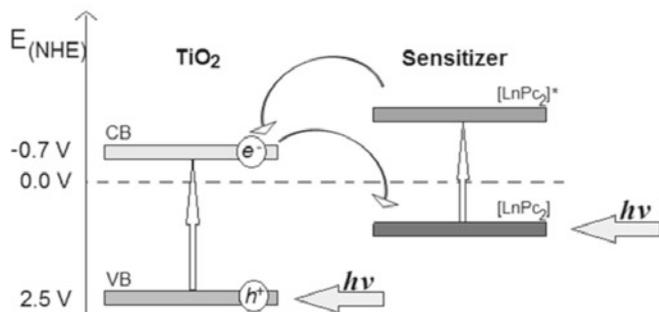


Figure 2. The cooperative mechanism principle in a phthalocyanine-sensitized TiO_2 (anatase) based hybrid photocatalytic system

In previous reports dedicated to porphyrin and/or phthalocyanine impregnated anatase composites, the lanthanide diphthalocyanines (Fig. 1b), LnPc_2 (where Ln is a lanthanide metal 3+ ion), were found particularly effective as sensitizers of the TiO_2 matrix^{12, 26}. On the other hand, in these hybrid systems, the microstructure of the anatase substrate was found to favor the microcrystalline TiO_2 over the nano-structured one, which would have emphasized the relevance of proper component selection in preparation of dye-sensitized semiconductor-based photocatalysts²⁶.

Effectiveness of diverse anatase- LnPc_2 composites applied in the form of suspension in water was confirmed in photooxidation of 4-nitrophenol and 2-propanol^{12, 18}, and preliminary tests had pointed at the potential of these photocatalysts also in photoactivated degradation of other chemicals, including sulfur compounds. Therefore, in this work we report on our recent results regarding the activity of some chosen anatase- LnPc_2 hybrid catalysts in photooxidation of sodium sulfite (Na_2SO_3). A homogeneous (not photo-activated) process involving a water-soluble Co-tetrasulfophthalocyanine catalyst in which the sulfite ions (SO_3^{2-}) were effectively converted into sulfate (SO_4^{2-}) ions was demonstrated elsewhere²⁷. Since under normal aerobic and dark conditions sulfite ions are relatively easy oxidized by water-dissolved oxygen, the principal objective of this study was to find out how much this reaction could be accelerated in a photocatalyzed process. On the other hand, this work was designed to demonstrate the general effectiveness of the anatase- LnPc_2 composites and the relevance of the search for similar hybrid systems.

EXPERIMENTAL

Commercial anatase (Tioxide Huntsman, 8 m^2/g BET, grain size range 0.15–0.5 μm) and home-prepared nanocrystalline anatase (grain size 15–40 nm) were used in preparations of the hybrid catalysts. The “nano” modification was synthesized from titanium tetra-isopropoxide by the sol-gel technique, following the literature reported procedure²². The product was characterized by X-ray powder diffractometry (XRD) and scanning electron microscopy (SEM). X’Pert Pro Panalytical diffractometer and JEOL JSM-5400 microscope were used to accomplish these analyses. Results have been presented in Figure 3.

The diphthalocyanines of Nd, Eu and Yb were synthesized in our laboratory (Faculty of Chemistry, Opole University) according to own method¹². Dichloromethane (DCM) and dimethylformamide (DMF), both of analytical grade, were purchased at Sigma-Aldrich, and used as supplied.

Optimum composition of the hybrid photocatalyst was determined based on a series of preliminary tests, and it was found similar to the value reported in a previous work²⁴. The anatase substrate was impregnated according to the procedure used there. For this reason a portion of 1.8 μmol (ca. 2 mg) of LnPc_2 was dissolved in 15 ml of DMF and/or dichloromethane in a round bottom flask and 1 g of TiO_2 was added. The mix was stirred for 5 h and afterwards the solvent was vacuum-evaporated and the solid residue, *i.e.* the TiO_2 - LnPc_2 composite, was left to dry in air at room temperature. The green form of YbPc_2 in DMF (see Fig. 1c) was obtained by addition of 2 drops of concentrated H_2SO_4 directly into the solution yet before mixing with TiO_2 . The studied samples were labeled as shown in Table 1.

Photoactivity of the catalysts was tested using a thermostated glass photoreactor ($V = 15 \text{ cm}^3$) presented in Figure 4. The hybrid catalyst (2.5–5.0 mg) was suspended in 10 cm^3 of $1 \times 10^{-3} \text{ M}$ Na_2SO_3 water solution, and the mixture was irradiated under continuous stirring. Sanolux HRC 300–280 xenon arc lamp was used to illuminate the content of the photoreactor from a distance of 50 cm. The emission spectrum of the radiation source has been shown in Figure 5 and the estimated irradiance (mW/cm^2) of the sample determined at the quartz window of the photoreactor (2 cm above the suspension) was 0.18 for UV-B (280–315 nm), 1.1 for UV-A (315–400 nm) and 3.9 for the visible radiation (380–780 nm). Periodically, 2 ml of the suspension was taken, filtered and analyzed for the content of SO_3^{2-} . Classical iodometric analysis was applied for SO_3^{2-} concentration greater than $1 \times 10^{-4} \text{ mol}/\text{dm}^3$ and smaller quantities were determined spectrophotometrically²⁸. The effectiveness of the tested

Table 1. Sample labeling mode

Sample label	Sample description
S	Na_2SO_3 (no catalyst added)
T-1	micro- TiO_2
T-2	nano- TiO_2
Nd-1	NdPc_2 (blue form in DMF)
Nd-2	NdPc_2 (green form in DCM)
Eu-1	EuPc_2 (blue form in DMF)
Eu-2	EuPc_2 (green form in DCM)
Yb-1	YbPc_2 (blue form in DMF)
Yb-2	YbPc_2 (green form in DCM)
Yb-3	YbPc_2 (green form in DMF)

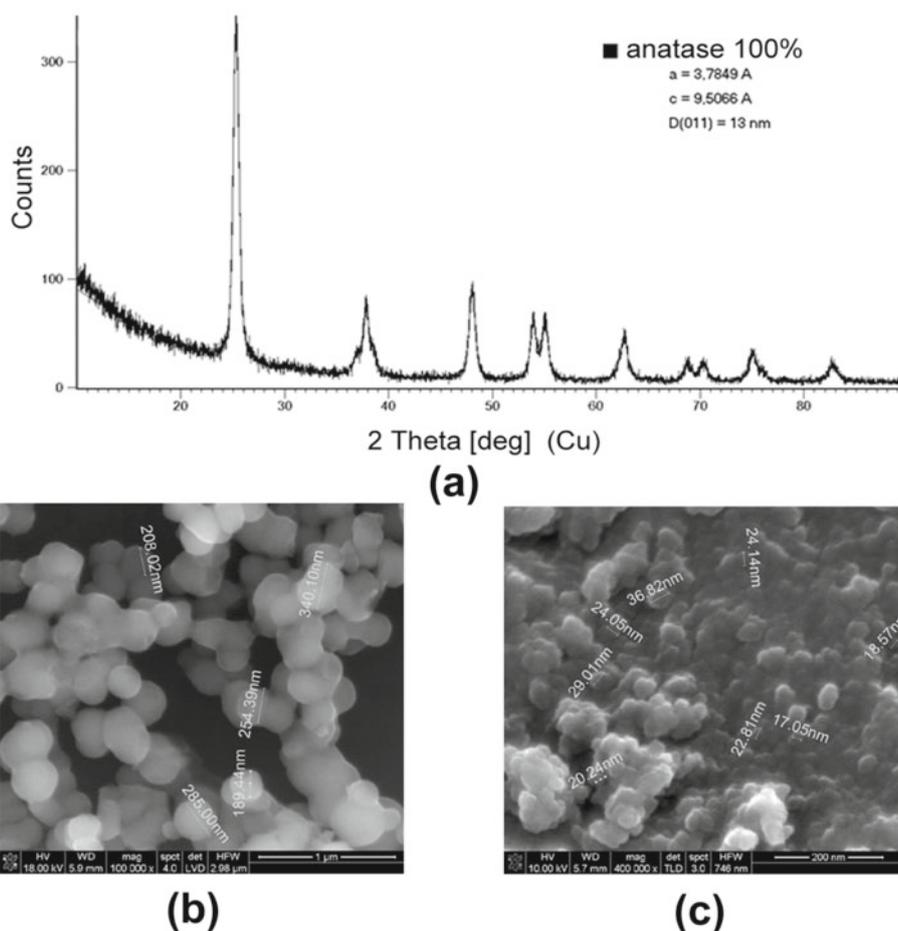


Figure 3. (a) X-ray powder diffraction pattern of the synthesized nano-anatase modification and SEM micrographs featuring the (b) micro- and (c) nano-anatase substrates

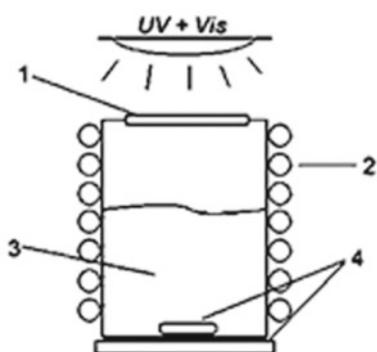


Figure 4. Scheme of the photoreactor setup; 1 – quartz glass window, 2 – thermostated cooler, 3 – suspension of the catalyst, 4 – magnetic stirrer

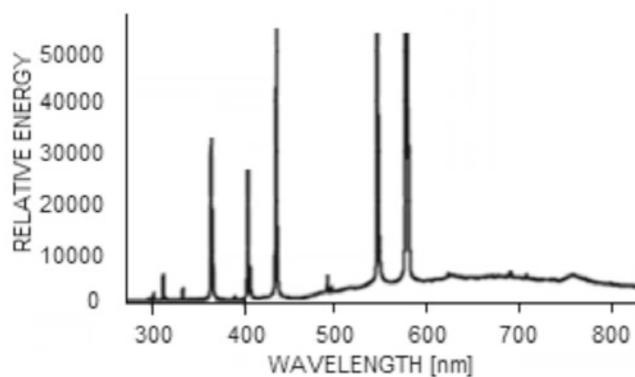


Figure 5. Emission spectrum of the Sanolux HRC 300–280 xenon arc lamp

hybrid photocatalyst was evaluated from the amount of sulfite ions remaining in the photoreactor after a fixed period of illumination.

RESULTS AND DISCUSSION

Under dark conditions, the sulfite ions have been oxidized only by molecular oxygen originally present in the water phase and addition of the bare TiO_2 substrates did not result in a faster reaction progress, Figure 6. The same was observed for the $\text{TiO}_2\text{-LnPc}_2$ composites (not shown). Moreover, the catalyst-free system appeared only slightly sensitive to the applied radiation. Both the micro- and nano-anatase bare substrates similarly showed some increased yield in sulfite oxidation upon irradiation, however this had become apparent only after longer illumination periods.

After impregnation with the LnPc_2 sensitizer, photoactivity of the micro- TiO_2 matrix increased considerably, as reported in Figure 7, whereas the nano-anatase composites revealed no catalytic activity (compared to the catalyst-free system). Similar observation was made while studying the photooxidation of 4-nitrophenol in water, although in this case the nano- TiO_2 hybrid catalysts clearly showed some enhanced activity²⁶. Evidently, the nano- TiO_2 matrix may not be sufficiently activated by the sensitizer to catalyze the photooxidation of Na_2SO_3 . Instead, the micro-anatase based hybrids appeared very effective here, and this fact would have indicated for the relevance of the sensitizer choice. As follows from

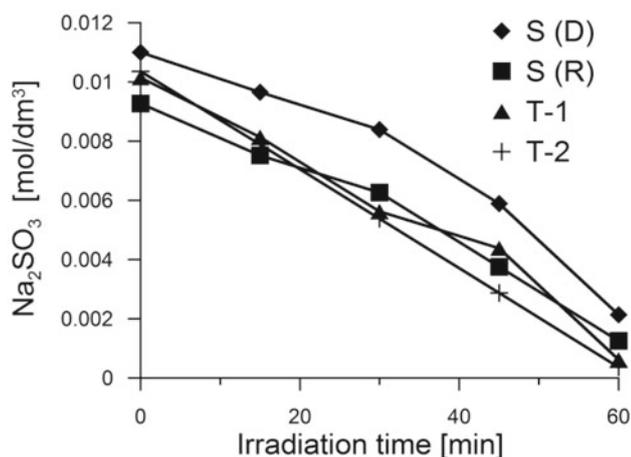


Figure 6. The effect of irradiation on the process of Na_2SO_3 oxidation in water. D – dark conditions, R – radiation conditions; T-1 and T-2 refer to R conditions only, since in dark they were very similar to S (D) and hence have not been shown

Figures 8 and 9, the most pronounced photocatalytic effect was achieved when the micro-anatase matrix was impregnated with YbPc_2 .

The proper amount of the catalyst used to compose the suspension (10 ml) in the photoreactor was determined as 5.0 mg per feed, under the applied reaction conditions. When less catalyst was added (2.5 mg) the reaction run

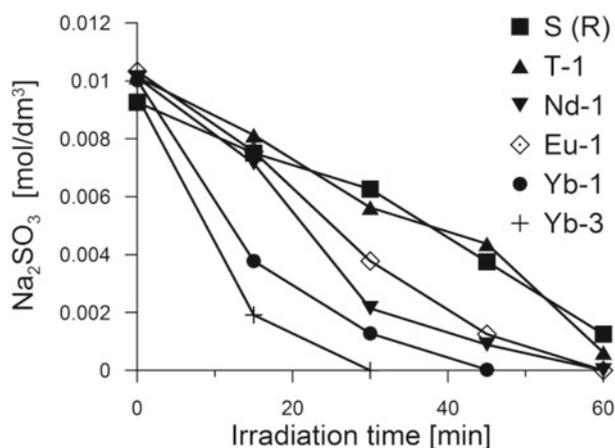


Figure 7. The effect of impregnation on the activity of the micro- TiO_2 (anatase) matrix in photooxidation of Na_2SO_3 in water (note, that impregnation was carried out in DMF)

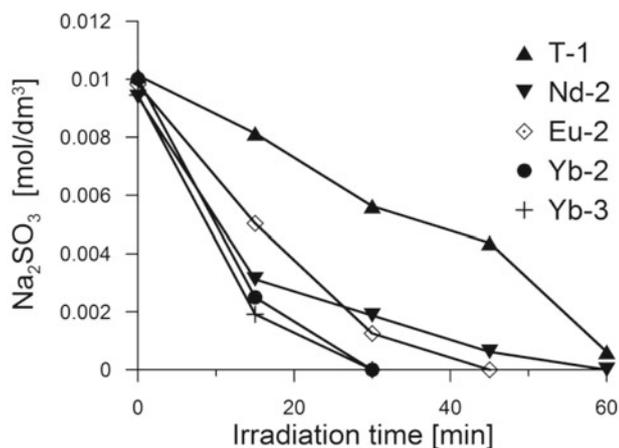


Figure 8. Impact of the LnPc_2 sensitizer type on the activity of the micro- TiO_2 (anatase) matrix in photooxidation of Na_2SO_3 in water

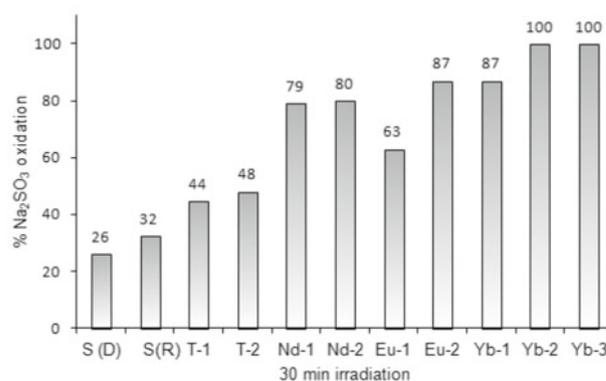
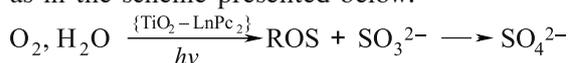


Figure 9. Comparison of the photooxidation degree of Na_2SO_3 in water achieved in the studied systems after 30 min of irradiation

definitely slower, depending on the system, however no simple relation was found. As follows from the graph presented in Figures 8 and 9, the way of preparation of the hybrid catalyst may also be important. Namely, the best results were obtained always when the catalyst was obtained in DCM and for YbPc_2 also in acidified DMF (see Table 1). This may be related to the formation of the so-called green form of the LnPc_2 complex, which has been considered more photoactive as the blue- LnPc_2 compound^{12,28}. The green modification is typically formed by LnPc_2 complexes when dissolved in DCM and also in DMF containing some amount of acid, which is featured in their UV-Vis spectra (Fig. 1c). However, in the latter case only compounds of the heavier lanthanide metals (Sm-Lu) are sufficiently stable. Hence in our study, the green form in DMF was represented only by YbPc_2 .

According to the published research, the mechanism of photooxidation by using TiO_2 -phthalocyanine composites is based on the concept of conversion of molecular oxygen and water molecules present in the reaction system into *reactive oxygen species* (ROS) by the photoexcited TiO_2 matrix and the MPc sensitizer. These are primarily free radicals and ions, e.g. $\text{O}_2^{\cdot-}$, $\text{O}_2^{2\cdot-}$, HO^{\cdot} , $\text{HO}_2^{\cdot-}$, however due to the peculiar photochemical activity of the phthalocyanine component generation of singlet oxygen, $^1\text{O}_2(^1\Delta_g)$, may also be possible¹⁵. In the explored systems, formation of ROS may be concluded from the comparison of the dark experimental results with those collected after irradiation. It can be seen, that there was only a little difference in the reaction rate between samples S (D) and S (R), whereas addition only of the bare TiO_2 catalysts distinctly accelerated the photooxidation of sulfite ions, Figures 6 and 9. On the other hand, the considerable rise in photocatalytic oxidation yield demonstrated by the TiO_2 - LnPc_2 loaded suspensions (Figs. 7–9) evidently complies with the co-operative mechanism proposed for such hybrid systems, not excluding the part of singlet oxygen species. Obviously, the only possible reaction product of sulfite photooxidation have been sulfate ions (SO_4^{2-}) as followed from the analyses carried out during the photochemical experiments, and the studied process involving hybrid TiO_2 - LnPc_2 may hence be summarized as in the scheme presented below.



CONCLUSIONS

Lanthanide diphthalocyanines (LnPc₂) effectively enhance the photochemical activity of the TiO₂(anatase) matrix. Based on the results collected so far one may assume, that such systems bear a great potential to be practically applied as photocatalysts in diverse oxidation reactions. Their catalytic efficiency was proved in some important photo-activated processes. However, the data reported here for sulfite photooxidation emphasize the peculiar feature of the TiO₂-LnPc₂ hybrids to considerably accelerate even a reaction, which under aerobic conditions proceeds rather fast by itself, without a catalyst. In summary, our results would point at the effectiveness of the explored photocatalysts particularly in photo-mediated oxidation processes, involving electron acceptor sulfur species, as well as other compounds of this kind.

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LITERATURE CITED

- Vadivel Murugan, A., Samuel, V. & Ravi, V. (2006). Synthesis of nanocrystalline anatase TiO₂ by microwave hydrothermal method. *Mater. Lett.* 60, 479–480. DOI: 10.1016/j.matlet.2005.09.017.
- Figgemeier, E., Kylberg, W. & Constable, E. (2007). Titanium dioxide nanoparticles prepared by laser pyrolysis: synthesis and photocatalytic properties. *Appl. Surf. Sci.* 254, 1037–1041. DOI: 10.1016/j.apsusc.2007.08.036.
- Su, C., Hong, B.Y. & Tseng, C.M. (2004). Sol-gel preparation and photocatalysis of titanium dioxide. *Catal. Today* 96, 119–126. DOI: 10.1016/j.cattod.2004.06.132.
- Li, Y., White, T.J. & Lim, S.H. (2004). Low-temperature synthesis and microstructural control of titania nanoparticles. *J. Solid State Chem.* 177, 1372–1381. DOI: 10.1016/j.jssc.2003.11.016.
- Billik, P. & Plesch, G. (2007). Mechanochemical synthesis of anatase and rutile nanopowders from TiOSO₄. *Mater. Lett.* 61, 1183–1186. DOI: 10.1016/j.matlet.2006.06.080.
- Ying, L., Hon, L.S., White, T., Withers, R. & Hai, L.B. (2003). Controlled Nanophase Development in Photocatalytic Titania. *Mater. Trans.* 44 (7), 1328–1332. DOI: 10.2320/matertrans.44.1328.
- Qamar, M., Yoon, C.R., Park, K., Kim, D.H., Lee, K.S., Lee, W.J. & Kim, S.J. (2008). Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide. *Catal. Today* 131, 3–14. DOI: 10.1016/j.cattod.2007.10.015.
- Al-Salim, N.I., Bagshaw, S.A., Bittar, A., Kemmit, T., McQuillan, A.J., Mills, A.M. & Ryan, M.J. (2000). Characterization and activity of sol-gel-prepared TiO₂ photocatalysts modified with Ca, Sr or Ba ion additives. *J. Mater. Chem.* 10, 2358–2363. DOI: 10.1039/B004384M.
- Ito, S., Inoue, S., Kawada, H., Hara, M., Iwasaki, M. & Tada, H. (1999). Low-Temperature Synthesis of Nanometer-Sized Crystalline TiO₂ Particles and Their Photoinduced Decomposition of Formic Acid. *J. Colloid Interface Sci.* 216, 59–64. DOI: 10.1006/jcis.1999.6275.
- Colmenares, J.C., Aramend, M.A., Marinas, A. & Urbano, F.J. (2006). Synthesis, characterization and photocatalytic activity of different metal-doped titania systems. *Appl. Catal. A: Gen.* 306, 120–127. DOI: 10.1016/j.apcata.2006.03.046.
- Mele, G., del Sole, R., Vasapollo, G., Garcia-Lopez, E., Palmisano, L., Jun, L., Słota, R. & Dyrda, G. (2007). TiO₂-based photocatalysts impregnated with metallo-porphyrins employed for degradation of 4-nitrophenol in aqueous solutions: Role of metal and macrocycle. *Res. Chem. Intermed.* 33, 443–448. DOI: 10.1163/156856707779238649.
- Mele, G., Garcia-Lopez, E., Palmisano, L., Dyrda, G. & Słota, R. (2007). Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO₂ impregnated with lanthanide double-decker phthalocyanine complexes. *J. Phys. Chem. C* 111, 6581–6588. DOI: 10.1021/jp070529j.
- Zhao, X., Li, Z., Chen, Y., Shi, L. & Zhu, Y. (2008). Enhancement of photocatalytic degradation of polyethylene plastic with CuPc modified TiO₂ photocatalyst under solar light irradiation. *Appl. Surf. Sci.* 254, 1825–1829. DOI: 10.1016/j.apsusc.2007.07.154.
- Fa, W. & Zan, L. (2008). Solid-phase photocatalytic degradation of polystyrene with TiO₂ modified by iron (II) phthalocyanine. *Appl. Catal. B: Environ.* 79, 216–223. DOI: 10.1016/j.apcatb.2007.10.018.
- Mele, G., del Sole, R., Vasapollo, G., Garcia-Lopez, E., Palmisano, L. & Schiavello, M. (2003). Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO₂ impregnated with functionalized Cu(II)-porphyrin or Cu(II)-phthalocyanine. *J. Catal.* 217, 334–342. DOI: 10.1016/S0021-9517(03)00040-X.
- Zuo, P. & Li, C. (2006). Mechanism of squarylium cyanine and Ru(dcbpy)₂(NCS)₂ co-sensitization of colloidal TiO₂. *J. Photochem. Photobiol. A: Chem.* 183, 138–145. DOI: 10.1016/j.jphotochem.2006.03.007.
- Słota, R., Dyrda, G., Galbas, M. & Mele, G. (2014). Hybrid photocatalysts with a TiO₂ matrix sensitized with lanthanide phthalocyanines. *Chemik* 68 (4), 385–390.
- Marcí, G., García-López, E., Mele, G., Palmisano, L., Dyrda, G. & Słota, R. (2009). Comparison of the photocatalytic degradation of 2-propanol in gas-solid and liquid-solid systems by using TiO₂-LnPc₂ hybrid powders. *Catal. Today* 143, 203–210. DOI: 10.1016/j.cattod.2008.12.029.
- Wang, C., Li, J., Mele, G., Yang, G.M., Zhang, F.X., Palmisano, L. & Vasapollo, G. (2007). Efficient degradation of 4-nitrophenol by using functionalized porphyrin-TiO₂ photocatalysts under visible irradiation. *Appl. Catal. B-Environ.* 76, 218–226. DOI: 10.1016/j.apcatb.2007.05.028.
- Duan, M.V., Li, J., Mele, G., Wang, C., Lu, X.F., Vasapollo, G. & Zhang, F.X. (2010). Photocatalytic Activity of Novel Tin Porphyrin/TiO₂ Based Composites. *J. Phys. Chem. C* 114, 7857–7862. DOI: 10.1021/jp911744a.
- Wetchakun, N. & Phanichphant, S. (2008). Effect of temperature on the degree of anatase-rutile transformation in titanium dioxide nanoparticles synthesized by the modified sol-gel method. *Curr. Appl. Phys.* 8, 343–346. DOI: 10.1016/j.cap.2007.10.028.
- Park, S.D., Cho, Y.H., Kim, W.W. & Kim, S. (1999). Understanding of Homogeneous Spontaneous Precipitation for Monodispersed TiO₂ Ultrafine Powders with Rutile Phase around Room Temperature. *J. Solid State Chem.* 146, 230–236. DOI: 10.1006/jssc.1999.8342.
- Wang, X.H., Li, J.G. & Kamiyama, H. (2006). Fe-doped TiO₂ nanopowders by oxidative pyrolysis of organometallic precursors in induction thermal plasma: synthesis and structural characterization. *Thin Solid Films* 506/507, 278–282. DOI: 10.1016/j.tsf.2005.08.069.
- Mishra, P.R. & Srivastava, O.N. (2008 June). On the synthesis, characterization and photocatalytic applications of nanostructured TiO₂. *Bull. Mater. Sci.* 31 (3), 545–550. DOI: 10.1007/s12034-008-0085-2.
- Mele, G., Ciccarella, G., Vasapollo, G., García-López, E., Palmisano, L. & Schiavello, M. (2002). Photocatalytic degradation of 4-nitrophenol in aqueous suspension by using polycrystalline TiO₂ samples impregnated with Cu(II)-phthalocyanine. *Appl. Catal. B.* 38, 309–319. DOI: 10.1016/S0926-3373(02)00060-7.

26. Słota, R., Dyrda, G., Szczegot, K., Mele, G. & Pio, I. (2011). Photocatalytic activity of nano and microcrystalline TiO₂ hybrid systems involving phthalocyanine or porphyrin sensitizers. *Photochem. Photobiol. Sci.* 10, 361–366. DOI: 10.1039/c0pp00160k.

27. Iliev, V. & Ilieva, A. (1995). Oxidation and photooxidation of sulfur-containing compounds in the presence of water soluble phthalocyanine complexes. *J. Mol. Cat. A* 103, 147–153. DOI: 10.1016/1381-1169(95)00139-5.

28. Słota, R., Dyrda, G. & Szczegot, K. (2008). Sulfur dioxide oxidation catalyzed by photosensitized ytterbium diphthalocyanine. *Catal. Lett.* 126, 247–252. DOI: 10.1007/s10562-008-9609-z.