

C.I. TARCEA¹, C.M. PANTILIMON¹, G. COMAN^{1*}, A.A. TURCANU¹,
A.M. PREDESCU¹, E. MATEI¹, A.C. BERBECARU¹, C. PREDESCU^{1*}

PHOTOCATALYTIC TiO₂ NANOSTRUCTURES DEVELOPED ON THE GRADE 2 Ti MATERIAL

The research focused on TiO₂ nanostructures environmental applications due to the special characteristics that displayed degradation of the organic compounds into environmentally friendly products through exposure to UV light. The protocol behind obtaining the nanostructures involved the use of a Ti material exposed to alkaline treatment and advanced oxidation using NaOH solution and acetone. These studied nanostructures were analyzed extensively by using methods such as scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) for characterizing the elements, compounds and morphological properties of the material. These differences in morphology is attributed to different NaOH solution concentrations. The Ti sheets were immersed into NaOH and acetone mixed solutions for 72 hours. The best results were recorded by using 30% NaOH solution. After obtaining the 3D structures, which improve specific surface and contact area with the environment, the samples were tested under UV light in order to degrade methylene blue in order to determine their photocatalytic performance.

Keyword: Ti material; nanostructures; photocatalytic activity; alkaline treatment; advanced oxidation

1. Introduction

In the universe of the oxide metals, TiO₂ nanostructures with unique physical and chemical characteristics have attracted special attention. In fact, after the discovery of TiO₂ in 1972 by Fujishima and Honda, it was considered an extraordinary nanomaterial with a promising capacity in the catalytic field [1]. As a photocatalyst, TiO₂ can completely and rapidly photodegrade various toxic compounds into CO₂, H₂O and other non-toxic substances [2]. All these positive results regarding the use of TiO₂ in the photocatalytic applications are due to the fact that TiO₂ compared to other photocatalysts has hydrophilicity, long-term stability and high photo-reactivity, along with lower costs and non-toxicity [3,4].

Lately, nano-TiO₂ has attracted attention through its various nanostructured forms that provide an improvement in photocatalytic performance [5-8]. Although, in the processes of photodegradation, TiO₂ is used in powder form being considered a viable alternative, in practice, the efficiency of the photocatalytic process varies quite a lot, depending on the material used, as well as the environmental factors in which the process takes place. It is known that in photocatalytic applications, TiO₂ is intensively studied in powder form due to its specific surface area, but at the

same time disadvantages such as formation of aggregates, limitation of UV light due to strong absorption of catalyst particles and organic species and loss of photocatalyst after each cycle causes limitations. In this context, the researchers turned their attention to other types of nanostructures that would offer not only chemical stability but also superior photocatalytic properties [9].

Syed Z.J. Zaidi and al. were obtained TiO₂ nanotubes on reticulated vitreous carbon (RVC) by anodic electrophoresis [10]. Up to now, various methods have been used to obtain nanotubes, such as templating sol-gel method [11], synthesis method [12], anodization method [13], hydrothermal method [14] and alkaline treatment method [15]. Among them, the alkaline treatment method has the advantages of low reaction temperature and is easy to obtain, thus becoming a development perspective in obtaining the different nanostructures. According to the studies, the main substrate for the preparation of TiO₂ nanomaterials were glass, absorbent (activated carbon, silica gel, etc.) and metal [16-18]. However, when the glass is used as a substrate, there is poor compatibility with TiO₂, which leads to easy separation of TiO₂ from the substrate. To overcome the disadvantages of these substrates, the metal can be used as a precursor and substrate to obtain TiO₂ nanomaterials. The advantages of using metal are excellent conductivity and strength.

¹ UNIVERSITY POLITEHNICA OF BUCHAREST, FACULTY OF MATERIALS SCIENCE AND ENGINEERING, DEPARTMENT OF MATERIALS PROCESSING AND ECOMETALLURGY, 313 SPLAIUL INDEPENDENTEL, 060042, BUCHAREST, ROMANIA

* Corresponding authors: George.coman@upb.ro, Cristian.predescu@upb.ro



2. Experiment

TiO₂ nanostructures obtained

TiO₂ nanostructures were obtained on a fixed support using using a grade 2 Ti material. In order to obtain a homogeneous reaction surface, the discs with a diameter of 2.5 cm were obtained by cutting which were subsequently mechanically processed. The discs were prepared by successive mechanical grinding with abrasive paper with granules between 180-300 μm and by polishing with colloidal solutions with dimensions between 0.1-9 μm, in order to obtain a homogeneous surface, with a roughness below 0.1 μm which allows the further development of nanostructures on the surfaces thus prepared. The requirement for such a low roughness of the surface exists because the solution which attacks the titanium surface and oxidizes it needs to have a uniform plane in order to obtain the correct types of nanostructures and to maintain a homogeneous nature across the material. The sanded samples were washed and rinsed with distilled water and then dried in an oven at 80°C for 1 hour. The mechanically prepared surface was subsequently chemically treated to obtain dense TiO₂ nanostructures acicular and spherical. The chemical treatment consisted in the application of an alkaline treatment using NaOH aqueous solution, followed by advanced oxidation, using acetone as oxygen source. Thus, the samples with a diameter of 2.5 cm were immersed in NaOH solutions with different concentrations of 10, 20, 30 and 40% (noted P1, P2, P3, P4) over which acetone was added. In order to intensify the process, the samples were kept in the dark for 72 hours, after which they were washed with deionized water and ethanol to remove possible traces of impurities, and then subjected to heat treatment at a temperature of 550°C for 1 hour, with a temperature rise rate of 2°C/min (Fig. 1). The samples subjected to chemical treatment developed, after 72 hours, nanostructures validated by structural and morphological investigations, presenting structures acicular and spherical appearance.

Characterization

The morpho-structural characterization of the obtained nanomaterials was performed by a wide range of measurements depending on the main factors that influence their structure and texture. The evaluation of the performances of the obtained

materials was performed by tests on structure and morphology, using X-ray diffraction measurements (XRD) and scanning electron microscopy (SEM). Thus, the structural characterization was performed with an X'Pert PRO MPD X-ray diffractometer, PANalytical equipped with an X-ray tube with copper anode (wavelength of 1.54Å rays), linear and point focusing and with the help of the electron microscope scan (FEI Model: QUANTA 450 FEG) information was provided on the size and shape.

Photodegradation and kinetic study

Methylene blue (MB) synthetic dye was used in the photodegradation processes. Photodegradation experiments were performed at laboratory scale, at room temperature, reaction volume of 50 mL and pH 5 conditions, as close as possible to that of most solutions in the textile industry, without any corrections. In order to ensure a good reaction and to improve the concentration of dissolved oxygen in the solution, the whole system was connected to a compressed air filter. For the photocatalysis experiments, a UV-A lamp equipped with 4 tubes of 15 W each Philips ($\lambda_{\text{max}} = 365 \text{ nm}$) was used as light source. In the process of photodegradation under UV-A light, samples were taken from the reaction systems at regular intervals, from 15 in 15 minutes.

During the photodegradation process, the MB concentrations were measured using the UV-VIS Spectrometer, Cintra 220. The photodegradation efficiency was calculated using the following Eq. (1):

$$\text{Efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t (mg/L⁻¹) are the initial and final concentrations of MB in solution, respectively.

The kinetics of the photodegradation rate of MB was determined using the Langmuir-Hinshelwood kinetics model, as given in the following equation:

$$\ln \frac{C_0}{C_t} = k_{app} t \quad (2)$$

The pseudo-first-order rate constant, k_{app} (min⁻¹), was calculated from the slope of $\ln \frac{C_0}{C_t}$ versus irradiation time t .

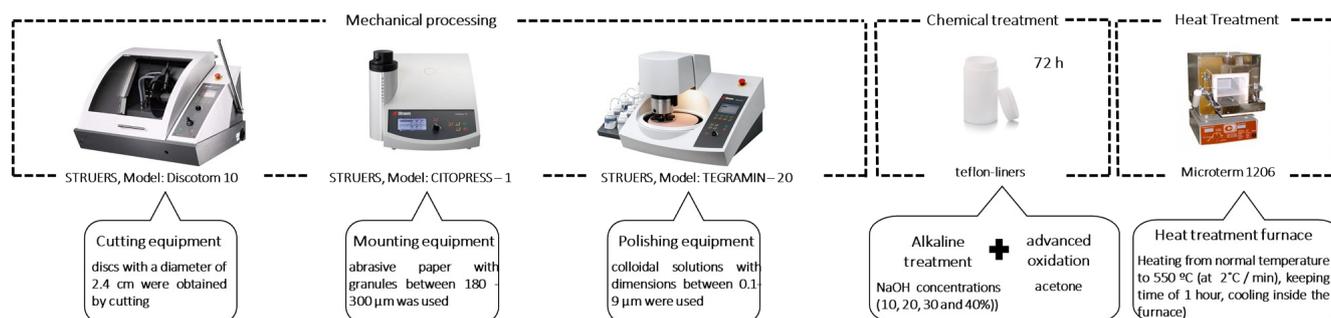


Fig. 1. Sample preparation and experimental procedure for obtaining TiO₂ nanostructures

3. Results and Discussion

Characterization of TiO₂ nanostructures

TiO₂ nanostructures obtained by alkaline treatment followed by advanced oxidation showed different morphology and structures, depending on the concentrations of NaOH used. The results obtained by the X-ray diffraction test show the following results regarding the purity and crystalline phases identified. Regardless of the NaOH concentration used, the diffractogram highlights the appearance of specific maxima for pure Ti, as seen in Fig. 2. This indicates that the Ti substrate exists for all samples. The X-ray diffraction indexing was done using the ICDD database, and the Ti element corresponds to PDF file no. 01-089-2762, from which it can be seen that the diffraction angles (2θ) correspond to planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively. With the increase of the NaOH concentration, from the X-ray diffraction analyzes, it can be observed that besides the presence of Ti, in the structure of the samples the crystalline compound of TiO₂ is formed, which according to the PDF file no. 01-085-5943 indicates the crystalline phase of the anatase type. Therefore, a different degree of crystallization was observed depending on the NaOH concentrations used.

Comparing the 4 samples, Ti material treated with 30% NaOH (noted P3) shows the most diffraction peaks at (2θ) of 25.3°; 37.79°; 55.06°; 62.69° and 75.05°, angles corresponding to planes (101), (004), (211), (204) and (215), according to the

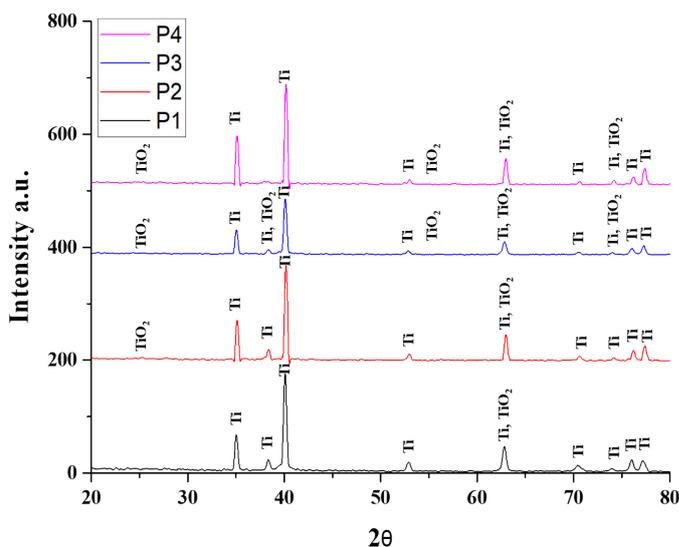


Fig. 2. X-ray diffractograms of TiO₂ nanostructures obtained using different concentrations of NaOH 10%, 20%, 30% and 40% noted P1, P2, P3 and P4

ICCD file, PDF no. 01-085-5943, specific to the anatase phase, reason for which the photocatalytic response is expected to be better for this structure obtained.

The morphological aspect corresponding to the 2 nanostructures developed on the surface of the Ti material using different NaOH solution concentrations of 10%, 20%, 30% and 40% respectively are presented in Fig. 3.

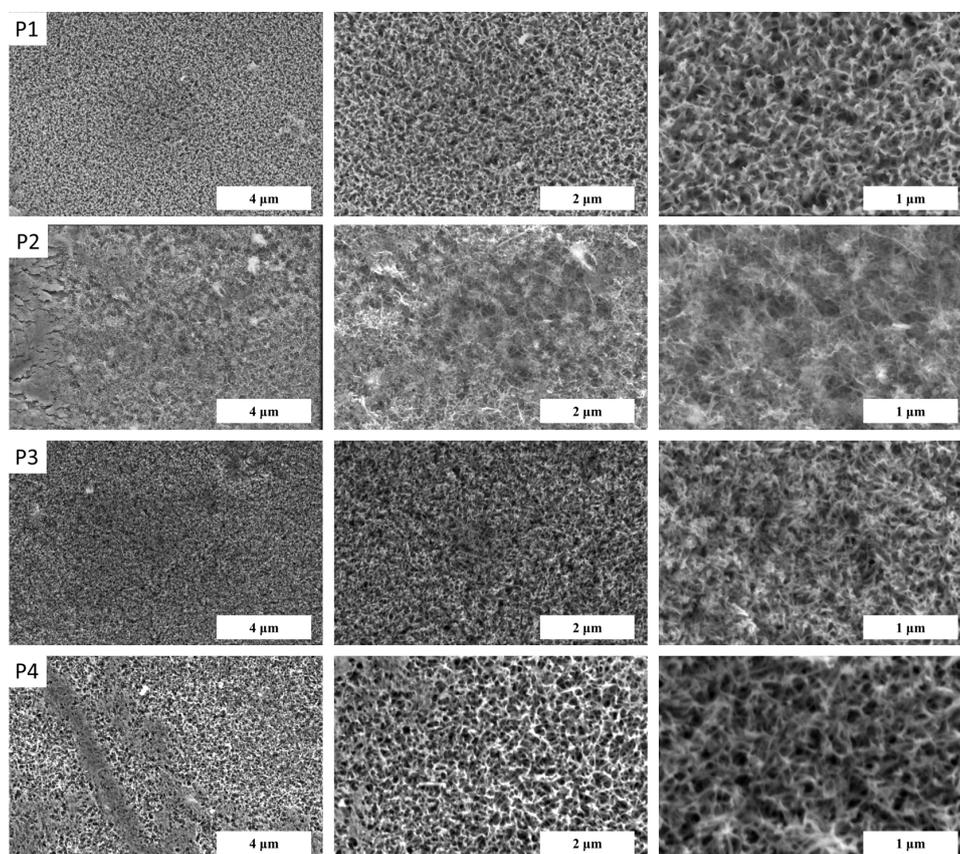


Fig. 3. SEM images at different magnifications ($M = 30,000\times, 60,000\times, 120,000\times$) of samples P1, P2, P3 and P4 treated on the Ti material with 10%, 20%, 30% and 40% NaOH solutions

The analyses were performed at different magnifications to highlight the uniform and homogeneous structure of the surface, as well as to determine the average pore size formed after treatment. It can be seen that for each sample treated with different concentrations of NaOH, nanodimensional structures were obtained, with a different profile depending on the concentrations used. At a low concentration of 10% NaOH there is a superficial reaction on the surface, while for 20% NaOH the structures formed begin to show fragility. This tendency disappears at a concentration of 30% NaOH, in this case appearing on the surface, nanodimensional structures acicular and spherical. When the surface has been treated with a solution of 40% NaOH, it is found that the structures formed begin to destroy starting to form voids. Although these structures would favor the photodegradation process, the fact that they do not show homogeneity on the entire surface, leads to the decrease of the specific active surface necessary for the degradation of dyes.

Photodegradation performance of TiO₂ nanostructures

The photocatalytic activity of TiO₂ nanostructures obtained using different concentrations of NaOH solutions was studied by photocatalytic degradation of Methylene Blue dye, using the optimal concentration of 1 mg/L MB (Fig. 4).

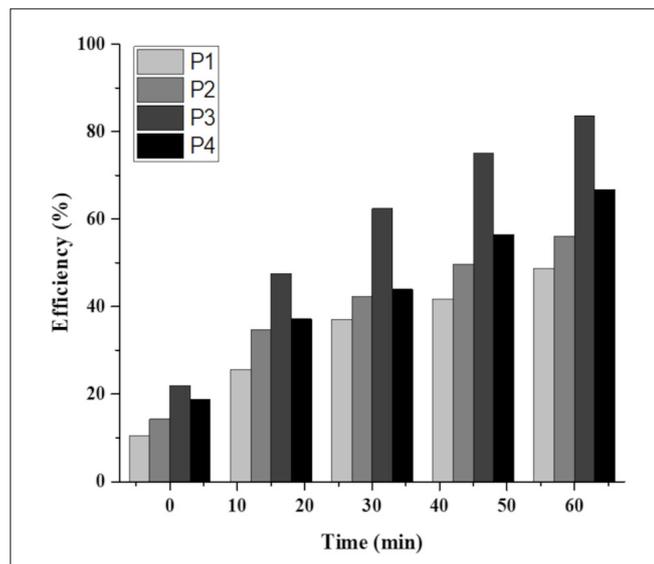


Fig. 4. Efficiency of photodegradation of MB in the presence of photocatalysts obtained on samples P1, P2, P3 and P4 treated on the Ti material with 10%, 20%, 30% and 40% NaOH solutions (1 mg/L MB, solution volume of 50 mL, irradiation time of 60 min)

After the irradiation time of 60 minutes, the maximum photodegradation of MB was observed for the P3 sample and decreasing in the following order: 83% (P3) > 60% (P4) > 49% (P2) > 40% (P1). This result is supported by the anatase crystalline phase and 3D structures which improve specific surface and contact area.

These values are consistent with Langmuir-Hinshelwood model by plotting $\ln(C_0/C_t)$ against the irradiation time (t) according to the correlation coefficients R^2 . The pseudo-first order rate constants for each TiO₂ nanostructure obtained using different concentrations of NaOH solutions, k_{app} (min⁻¹), were calculated from the slope of the plots and are shown in Fig. 5.

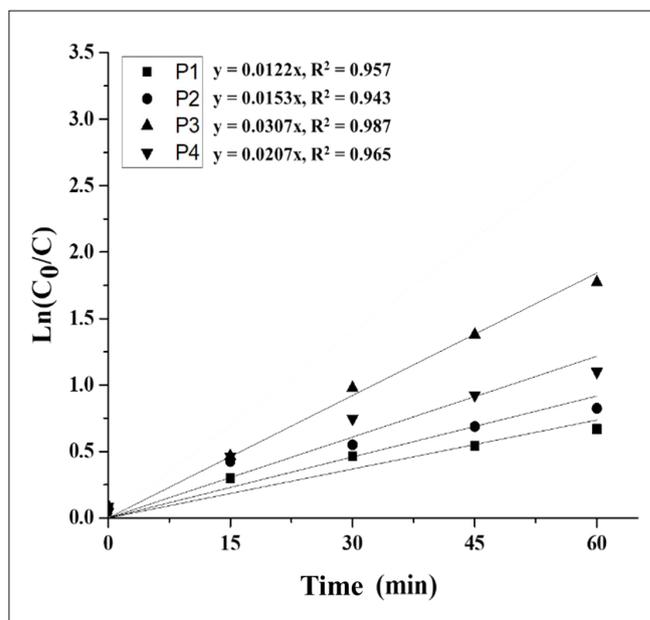


Fig. 5. First order kinetics of MB photocatalytic degradation for the photocatalysts obtained on Ti material

The results obtained from the slope of the lines represent the pseudo-first order rates constants (k_{app}) associated with the photodegradation efficiencies in the case of MB in contact with samples P1, P2, P3, P4. The variation of the NaOH concentration from 10 to 40%, used in obtaining TiO₂ nanostructures on Ti material influences the performance of the photodegradation process, observing an increase of the first order constant, the maximum being registered in the case of the P3 sample.

TiO₂ nanostructures stability

TiO₂ nanostructures (P3) re-usability were examined by cycling experiments in the same reaction conditions. This process is important because has an economic necessity. TiO₂ nanostructures were used in more cycles of photocatalytic process to investigate the durability of them. TiO₂ nanostructures were washed several times with deionized water and then dried in air after each process, in order to reuse it in other experiments. The photodegradation efficiency of TiO₂ nanostructures remained stable during the first three cycles, then decreased to 25% in the last cycle, as shown in Fig. 6.

This decrease in photodegradation efficiency can be explained by the occupation of the organic molecules of the active sites on the surface of the photocatalyst.

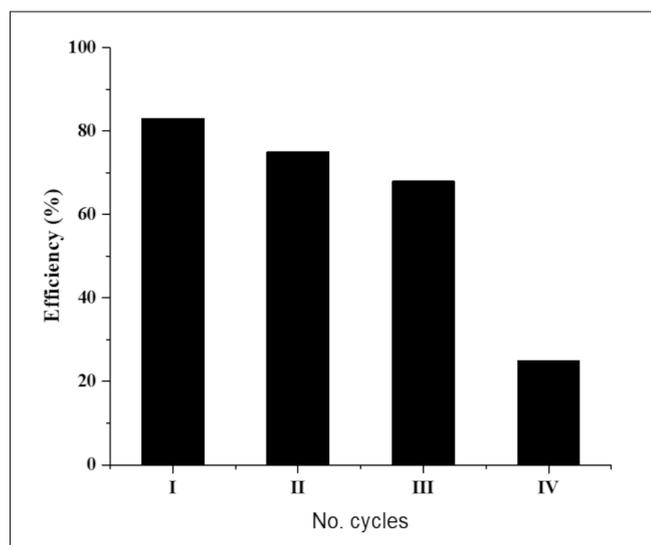


Fig. 6. Stability of TiO₂ nanostructures obtained on sample P3 for the photodegradation of MB at initial concentration 1 mg/L, solution volume of 50 mL, irradiation time of 60 min

4. Conclusions

In this study, anatase TiO₂ nanostructures were obtained using alkaline treatment method on the surface of Ti material. Thus, it has been demonstrated that (1) TiO₂ nanostructures are obtained directly on the Ti material surface using alkaline treatment method with excellent photodegradation performance of methylene blue synthetic dye; (2) TiO₂ nanostructures and Ti material are connected facilitating reusing the nanostructures in more cycles; (3) the effect of NaOH concentration on TiO₂ nanostructures morphology and properties has been demonstrated.

The effect of the concentration of NaOH on the formation of TiO₂ nanostructures on the surface of Ti material using alkaline treatment and advanced oxidation reaction was reported. The varying NaOH concentrations lead to different formations of 3D nanostructures. Furthermore, the photodegradation of methylene blue show that TiO₂ nanostructures obtained using 30% NaOH concentration might be potential catalyst for the degradation the dye due to the presence of crystalline phase of the anatase type and 3D nanostructures.

The stability studies showed that the photodegradation efficiency of MB using TiO₂ nanostructures remained stable under the experimental conditions studied during 3 cycles.

REFERENCES

- [1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* **238** (5358), 37-38 (1972). DOI: <https://doi.org/10.1038/238037A0>
- [2] M. Yao, J. Zhao, S. Lv, K. Lu, Preparation and hydrogenation of urchin-like titania using a one-step hydrothermal method, *Ceramics International* **43**, 6925-6931 (2017). DOI: <https://doi.org/10.1016/j.ceramint.2017.02.115>
- [3] J. Tolia, M. Chakraborty, Z. Murthy, Photocatalytic degradation of malachite green dye using doped and undoped ZnS nanoparticles, *Polish Journal of Chemical Technology* **14**, 16-21 (2012). DOI: <https://doi.org/10.2478/v10026-012-0065-6>
- [4] M.B. Mukhlis, F. Najnin, M.M. Rahman, M. Uddin, Photocatalytic degradation of different dyes using TiO₂ with high surface area: a kinetic study, *Journal of Scientific Research* **5**, 301-314 (2013). DOI: <https://doi.org/10.3329/jsr.v5i2.11641>
- [5] Y.J. Hwang, C. Hahn, B. Liu, P. Yang, Photoelectrochemical properties of TiO₂ nanowire arrays: a study of the dependence on length and atomic layer deposition coating, *ACS Nano* **6**, 5060-5069 (2012). DOI: <https://doi.org/10.1021/nn300679d>
- [6] H. Zhang, X. Liu, Y. Li, Q. Sun, Y. Wang, B.J. Wood, Vertically aligned nanorod-like rutile TiO₂ single crystal nanowire bundles with superior electron transport and photoelectrocatalytic properties, *Journal of Materials Chemistry* **22**, 2465-2472 (2012). DOI: <https://doi.org/10.1021/nl802096a>
- [7] A. Kusior, K. Kollbek, K. Kowalski, M. Borysiewicz, T. Wojciechowski, A. Adamczyk, Sn and Cu oxide nanoparticles deposited on TiO₂ nanoflower 3D substrates by Inert Gas Condensation technique, *Applied Surface Science* **380**, 193-202 (2016). DOI: <https://doi.org/10.1016/j.apsusc.2016.01.204>
- [8] N.C. Jeong, O.K. Farha, J.T. Hupp, A convenient route to high area, nanoparticulate TiO₂ photoelectrodes suitable for high-efficiency energy conversion in dye-sensitized solar cells, *Langmuir* **27**, 1996-1999 (2011). DOI: <https://doi.org/10.1021/la104297s>
- [9] S.Z. Zaidi, C. Harito, D.V. Bavykin, A.S. Martins, B. Yulianto, F.C. Walsh, Photocatalytic degradation of methylene blue dye on reticulated vitreous carbon decorated with electrophoretically deposited TiO₂ nanotubes, *Diamond and Related Materials* **109**, 108001 (2020). DOI: <https://doi.org/10.1016/j.diamond.2020.108001>
- [10] S.Z., Zaidi, C. Harito, D.V. Bavykin, A.S. Martins, B. Yulianto, F.C. Walsh, C. Ponce de León, Photocatalytic degradation of methylene blue dye on reticulated vitreous carbon decorated with electrophoretically deposited TiO₂ nanotubes, *Diamond and Related Materials* **109**, 108001 (2020). DOI: <https://doi.org/10.1016/j.diamond.2020.108001>
- [11] A.S. Attar, S. Mirdamadi, F. Hajiesmaeilbaigi, M.S. Ghamsari, Growth of TiO₂ nanorods by sol-gel template process, *Journal of Materials Science and Technology* **23** (5), 611-613 (2007).
- [12] S. Dong, H. Wang, L. Gu, X. Zhou, Z. Liu, P. Han, Rutile TiO₂ nanorod arrays directly grown on Ti foil substrates towards lithium-ion micro-batteries, *Thin Solid Films* **519**, 5978-5982 (2011). DOI: <https://doi.org/10.1016/j.tsf.2011.03.048>
- [13] L. Qin, Q. Chen, R. Lan, R. Jiang, X. Quan, B. Xu, Effect of anodization parameters on morphology and photocatalysis properties of TiO₂ nanotube arrays, *Journal of Materials Science & Technology* **31**, 1059-1064 (2015). DOI: <https://doi.org/10.1016/j.jmst.2015.07.012>
- [14] Z.-H. Liu, X.-J. Su, G.-L. Hou, S. Bi, Z. Xiao, H.-P. Jia, Hierarchical TiO₂ nanorod array for dye-sensitized solar cells, *Materials Letters* **89**, 309-311 (2013).

- [15] L.B. Arruda, C.M. Santos, M.O. Orlandi, W.H. Schreiner, P.N. Lisboa-Filho, Formation and evolution of TiO₂ nanotubes in alkaline synthesis, *Ceramics International* **41**, 2884-2891 (2015). DOI: <https://doi.org/10.1016/j.ceramint.2014.10.113>
- [16] A. Fernandez, G. Lassaletta, V. Jimenez, A. Justo, A. Gonzalez-Elipe, J.-M. Herrmann, Preparation and characterization of TiO₂ photocatalysts supported on various rigid supports (glass, quartz and stainless steel), Comparative studies of photocatalytic activity in water purification. *Applied Catalysis B: Environmental* **7**, 49-63 (1995). DOI: [https://doi.org/10.1016/0926-3373\(95\)00026-7](https://doi.org/10.1016/0926-3373(95)00026-7)
- [17] J. Matos, J. Laine, J.-M. Herrmann, D. Uzcategui, J. Brito, Influence of activated carbon upon titania on aqueous photocatalytic consecutive runs of phenol photodegradation, *Applied Catalysis B: Environmental* **70**, 461-469 (2007). DOI: <https://doi.org/10.1016/j.apcatb.2005.10.040>
- [18] Y. Chen, K. Wang, L. Lou, Photodegradation of dye pollutants on silica gel supported TiO₂ particles under visible light irradiation, *Journal of Photochemistry and Photobiology A: Chemistry* **163**, 281-287 (2004). DOI: <https://doi.org/10.1016/j.jphotochem.2003.12.012>