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Sol-Gel Prepared TiO_2 Photocatalyst

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Abstract. A brief overview of the latest advances in the preparation of nanostructured titanium dioxide and its application in photocatalysis and other fields are given. The data of scanning electron microscopy and X-ray diffraction analysis on the study of the dispersion, morphology, structure and phase composition of titanium dioxide nanopowders obtained by the sol-gel method are presented. The application of TiO_2 nanomaterials for the photocatalytic decomposition of organic pollutants is discussed. The high photocatalytic activity of the nanosized TiO_2 powder for the decomposition of methylene blue is demonstrated and supporting the advantages of using ultraviolet light for photocatalytic water purification.

1. INTRODUCTION

Titanium dioxide is widely used from the early twentieth century to our days in paints, sunscreens, toothpaste etc. [1]. In Ref. [2] Honda and Fujishima described photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (UV) light. Nowadays photocatalysis has found application in pollutant destruction, organic synthesis and hydrogen production [3]. The basic principles of this phenomenon are well detailed (e.g. see Ref. [4]). Semiconductors (TiO_2, CuO, ZnO, GaP, GdS etc.) can act as promoter for light-induced redox processes [5-8].

TiO_2 is an n-type semiconductor due to a deficiency of oxygen and has three main different crystal structure (anatase, rutile and brookite, which have different band gaps of 3.2, 3.0 and about 3.2 eV, respectively) [3,5]. Unfortunately, due to its wide bandgap, TiO_2 only works under UV light, which is less than 5% of sunlight, to fix these limitations, a lot of research has focused on modifying TiO_2 to improve charge separation and narrow its bandgap for efficient absorption of visible light. Bandgap excitation of TiO_2 causes charge separation followed by scavenging of electrons and holes by surface adsorbed species (Fig. 1), consequently the reaction that occurs is typically an oxidation reaction that results in the decomposition of the pollutant, by making use of the dissolved oxygen present in water [9,10].

One of the key parameters of TiO_2 photocatalytic activity is its phase composition. Refs. [11,12] report that the highest catalytic activity in such processes has shown by the anatase or a controlled mixture of crystalline TiO_2 phases. Other parameters: particle size, degree of crystallinity and developed specific surface area affect the catalytic activity. The ideal size of TiO_2 particles for photocatalytic processes in aqueous media is in the range from 15 to 110 nm [13]. Thus, variation of the phase composition, particle size, morphology, and elemental composition is an important factor for controlling the properties of the final photocatalyst material.

Improving the efficiency of using sunlight and increasing the quantum efficiency are important problems for the wide-spread industrial application of the TiO_2 photocatalyst. The modification of TiO_2 by changing the electrical properties and inducing bathochromic shift of the band gap is actively being carried out in order to increase the efficiency of using visible light and the

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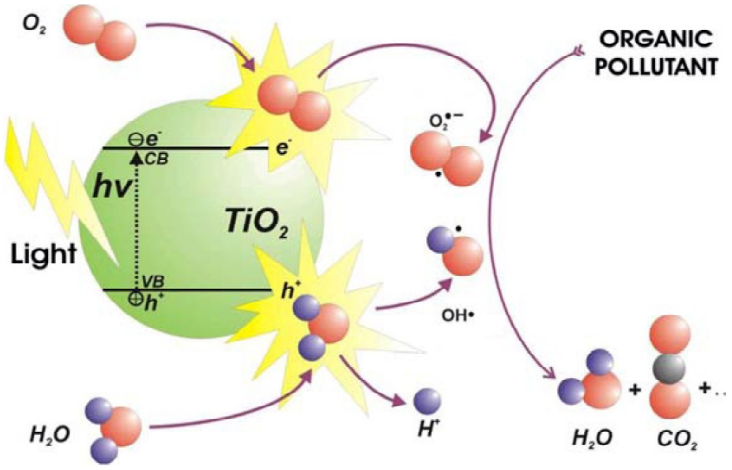

Fig. 1. Schematic diagram illustrating the principle of TiO_2 photocatalysis. Reprinted from Ref. [9] under the Creative Commons Attribution License.

photocatalytic quantum efficiency of TiO_2 [14]. According to Ref. [15], modifications of TiO_2 can be divided into three classes: doping, surface modification and sensitization.

Enormous efforts aimed at the study of titanium dioxide make it possible to use it not only as a photocatalyst for the decomposition of organic pollutants in the purification of water and air [16,17], but also in other areas, for example, in the production of lithium batteries [18,19], solar cells [20], hydrogen storage systems [21], sensors [22,23], etc.

This paper presents the application of photocatalysis with titanium dioxide, obtained by a simple method (which does not require additional modifications), for ecology by the example of water purification from the model pollutant methylene blue.

2. METHODS AND MATERIALS

2.1. Fabrication

To synthesize a nanosized TiO_2 powder 5.35 ml of titanium isopropoxide were slowly added to 50 ml of isopropyl alcohol and 50 ml of distilled water with constant stirring (all reagents were analytical grade and produced by Sigma-Aldrich). The resulting mixture was kept under stirring using the PE-6110 magnetic stirrer at a speed of $\omega \approx 500$ rpm for 30 minutes. Then the sol was aged, i.e. exposured at room temperature for about 4 hours. The sol was separated from the liquid by the Frontier FC5706 centrifuge, and slowly mixed with 20 ml of H_2O_2 until gelation was complete (resulting mixture became transparent and bright orange). Drying of the resulting mass was carried out at a temperature of 70-85 °C for 12 hours. The titanium dioxide powder fabricated by this method was in the amorphous phase. Then, the sample was mechanically crushed to obtain a homogeneous powder and subjected to annealing in the electric furnace SNOL 8.2/1100 in air at various temperatures (450, 700, 800 °C) for 4 hours to form a crystalline phase.

2.2. Characterization

The chemical composition was studied by energy-dispersive X-ray fluorescence spectrometry (Shimadzu EDX-8000). Structural analysis was performed on the Shimadzu XRD 7000 X-ray diffractometer. The particle size distribution and dispersion were determined using Shimadzu SALD-2300 laser analyzer. The morphology of nanoparticles was determined by field emission scanning electron microscope TESCAN Mira3.

2.3. Photocatalytic tests

The study of the photocatalytic activity of the synthesized TiO_2 powder was carried out using the organic model pollutant methylene blue (MB). Homemade classic capacitive reactor with UV radiation source (250 W medium pressure mercury lamp with radiation wavelength in the range from 200 to 400 nm) was used. Oxygen, which is part of the air mixture supplied by the bubbler into the reaction area, was used as an oxidizing agent. The photocatalyst was preliminarily dispersed in the test solution using an ultrasonic bath for 10 min. To achieve sorption equilibrium the exposure was carried out in a dark cabinet for 30 min, and then the radiation source was switched on to start the photocatalysis process. Samples were taken every half an hour. The MB concentration in the solution was determined by spectrophotometry method on Shimadzu UV-2600.

3. RESULTS

We investigated TiO_2 powders fabricated under various conditions of sol-gel synthesis as a photocatalyst (Table 1). The pH index of the reaction during the hy-

Table 1. Samples of TiO_2 fabricated under various synthesis conditions.

Samples	T-1	T-2	T-3	T-4	T-5
pH index	4	6	8	4	4
Annealing temperature, °C	450	450	450	700	850

drolysis stage affects the rate of the reaction and as result determines the particle size dispersion. In Refs. [13,24] it was noted that amorphous titanium dioxide obtained by the sol-gel method passes into the crystalline phase of anatase during thermal oxidation above 400 °C. In addition, at such temperatures, decomposition and removal of organic materials remaining after synthesis and washing occurs. To obtain the anatase phase, we chose the annealing temperature of amorphous TiO_2 equal to 450 °C. It should be noted a mixture of anatase and rutile phases forms at above 500 °C temperature, and pure rutile forms at above 800 °C.

As mentioned above, the most effective photocatalysts are powders with particle sizes in the nanometer range. Samples T-1, T-2, T-4, according to scanning electron microscopy (SEM) data, have particle sizes in range from 20 to 60 nm, which corresponds to the synthesis conditions at pH from 4 to 6 and annealing temperature up to 700 °C (morphology of the samples is shown in Fig. 2). SEM images show agglomerates of nanoparticles, which are easily broken when the powder is dispersed in an ultrasonic bath. Sample T-3 contains particles with fractions within the order of 1 μm and 100 nm. The average particle size for sample T-5 is about 200 nm, that agrees with the data obtained using the laser diffraction method.

The results of X-ray phase analysis showed that samples T-1, T-2, T-3 are in the structural modification of anatase. Sample T-4 contains a mixture of phases anatase and rutile with weight ratios of 33% and 67%, respectively. Sample T-5 has the rutile structural modification. Fig. 3 shows the typical diffraction patterns of samples T-1 and T-4.

The results of the photocatalytic activity of samples T-1, T-2, T-4, T-5 are shown in Fig. 4a as a dependence of the MB concentration on the time of photocatalysis. The most widely used commercial titanium dioxide powder Degussa P25 was chosen as a sample for comparison [10]. Degussa P25 consists of 80 % anatase phase and 20% rutile phase possess a band gap of 3.2 and 3.0 eV for both anatase and rutile phase respectively and it has an effective surface area of 50 m^2/g [24].

Sample T-3 showed very low photocatalytic efficiency; when it was used for 4 hours of photocatalysis MB concentration decreased by 12%, which is comparable to the results of the blank reaction (without photocatalyst). For sample T-5 with an average size of about 200 nm, the photocatalytic activity was 54% of MB decomposition in 3 hours of photocatalysis.

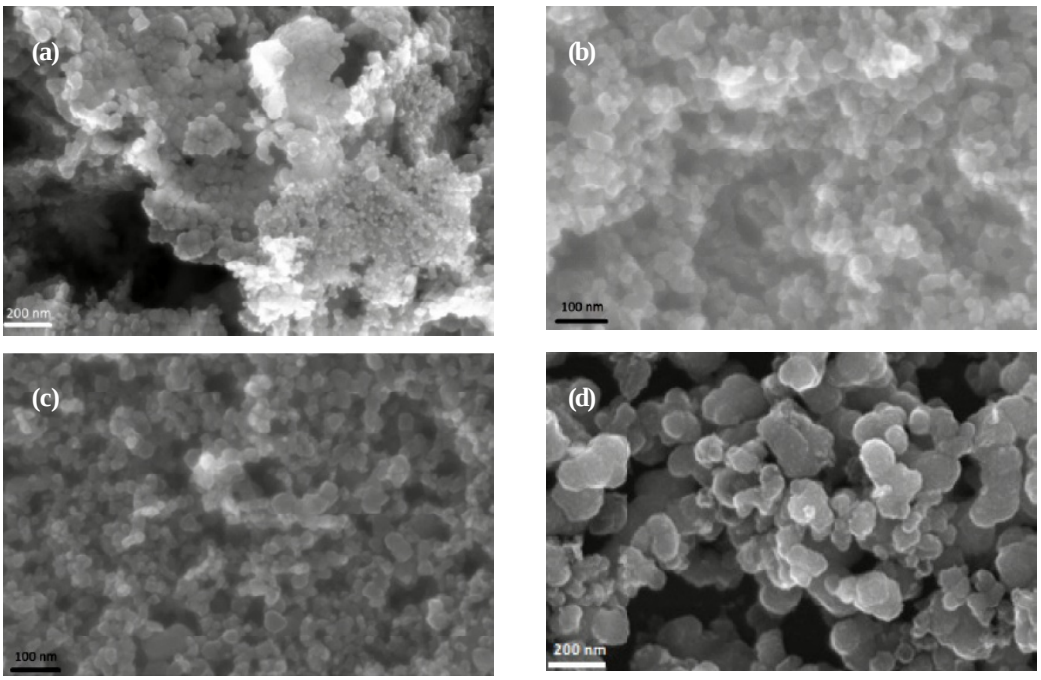

Fig. 2. Scanning electron microscope images of the sol-gel prepared TiO_2 powders: (a) sample T-1 synthesized at pH = 4 and annealing temperature (AT) 450 °C, (b) sample T-2 synthesized at pH = 6 and AT 450 °C, (c) sample T-4 synthesized at pH=4 and AT 700 °C, (d) sample T-5 synthesized at pH = 4 and AT 850 °C.

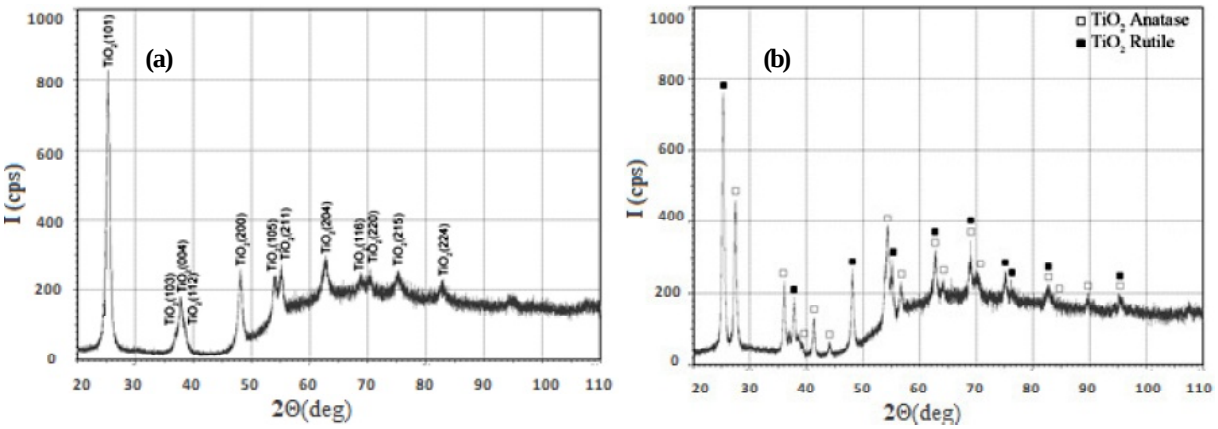

Fig. 3. X-ray diffraction data obtained for sol-gel prepared TiO_2 powders: sample T-1 (a) and sample T-4 (b).

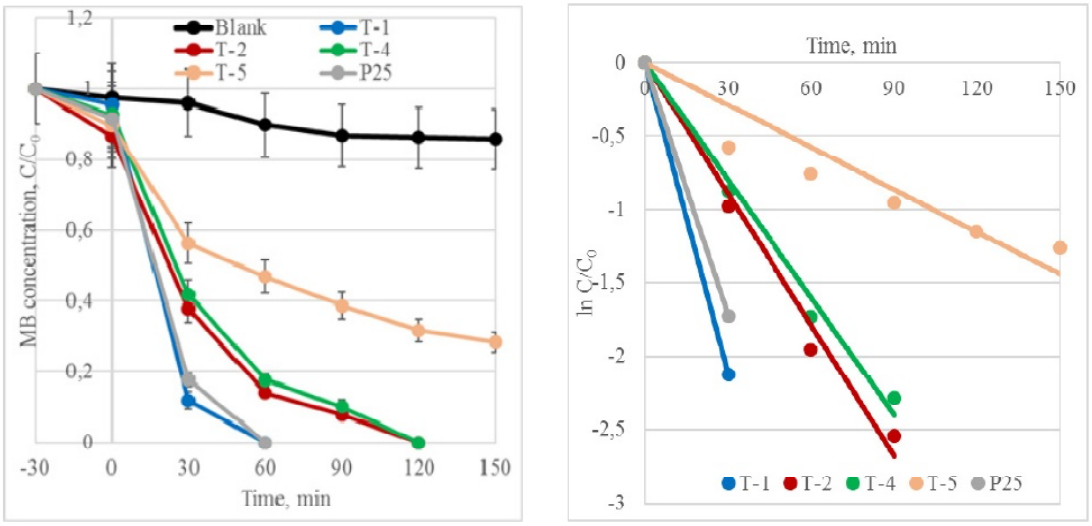

Fig. 4. Photocatalytic destruction (a) of methylene blue (initial concentration C_0 of 10 mg/L) and kinetic (b) of the process.

According to the results of spectrophotometric analysis of the best efficiency sample T-1 with an average particle size of 20 nm in the anatase modification, the time for complete decomposition of MB was 2 hours. The time of complete decomposition for samples T-2 and T-4 was 3 hours, which is more time consuming compared to using sample T-1.

4. DISCUSSION

Let us consider kinetic of photocatalytic MB destruction. The decrease of MB concentration (C) during the photocatalysis time (t) is described by the pseudo first-order kinetics based on equation [26]:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = kC, \tag{1}$$

where k is the rate constant of reaction.

To simplify the heterogeneous photocatalytic process the initial concentration of MB C_0 was kept constant. The apparent pseudo first-order rate constant (min^{-1}) k_1 was obtained by approximating the experimental data using the following equation:

$$-\ln\frac{C}{C_0} = k_1 t, \tag{2}$$

The linear regressions (Fig. 4b) obtained by plotting $\ln(C/C_0)$ vs. time were used for the evaluation of k_1. The apparent rate constant of the catalyst per mass units (k_w) was estimated from Eq. (3) [27]:

$$k_w = \frac{k_1}{C_{ph}V}, \tag{3}$$

where C_{ph} is the concentration of the photocatalysts and V – the reactor volume (500 cm^3).

Half-life value was calculated by following equation:

$$k_{1/2} \cong \frac{0.693}{k_1}. \tag{4}$$

Table 2. Kinetic parameters of photocatalytic methylene blue destruction.

Samples	k_1,10^{-2} min^{-1}	R^2	k_w,10^{-2} $min^{-1}g^{-1}$	$t_{1/2}$,min
T-1	7.09	n/a	14.18	9.78
T-2	2.98	0.985	5.96	23.26
T-4	2.67	0.988	5.34	25.96
T-5	0.96	0.851	1.92	72.20
P25	5.75	n/a	11.50	12.05

Pseudo first-ordered reaction rate constants (k_1) per gram of catalyst (k_w) of the photocatalytic oxidation of MB and coefficients of determination (R^2) of linear fitting are presented in Table 2.

The photocatalysis study results revealed T-1 sample is more effective in photocatalytic destruction of MB than reference Degussa P25. As well the span between less effective T-2, T-4 samples and P25 is characterized by a factor of around two.

5. CONCLUSIONS

As a result of the conducted studies of the effect of pH on the TiO_2 particle size, it was noted that at pH index of 4 to 8 particles with sizes from 10 to 60 nm were obtained. In hydrolysis process the rate of the process depends on the pH value and process is quite intensively with the rapid formation of a suspension. At the stage of gelation, reordering of atoms and adhesion of intersecting linear chains can occur, which affects the process of grain growth during heat treatment. As a result, rather large agglomerates can form. Thus, the optimal conditions for the synthesis of TiO_2 photocatalysts by the sol-gel method are pH index of about 4 and an annealing temperature of 450 to 700 °C.

The fabricated TiO_2 nanomaterials have good photocatalytic activity in the decomposition of organic pollutants in UV light. Doping TiO_2 with other elements makes it possible to shift the photocatalytic activity of these materials to the visible region of the spectrum. However, in a number of cases, for example, when purifying water or air, the usage of ultraviolet radiation allows the destruction of viruses and bacteria in addition to purification, i.e. in one technological cycle two operations can be combined: cleaning and disinfection.

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REFERENCES

[1] X. Chen and S.S. Mao, *Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications*, Chem. Rev., 2007, vol. 10, no. 7, pp. 2891-2959. https://doi.org/10.1021/cr0500535

[2] A. Fujishima and K. Honda, *Electrochemical Photolysis of Water at a Semiconductor Electrode*, Nature, 1972, vol. 238, no. 5358, pp. 37-38. https://doi.org/10.1038/238037a0

[3] R. Ratshiedana, A.T. Kuvarega and A.K. Mishra, *Titanium Dioxide and Graphitic Carbon Nitride–based Nanocomposites and Nanofibres for the Degradation of Organic Pollutants In Water: A Review*, Environ. Sci. Pollut. Res., 2021. https://doi.org/10.1007/s11356-020-11987-3

[4] A. Fujishima, *photocatalytic and self-cleaning functions of TiO_2 coatings*, In: *Proceedings of the Third Asia-Pacific Conference on Sustainable Energy and Environmental Technologies* (APCSEET '2000), ed. by: X. Hu and P.L. Yue (Hong Kong University of Science and Technology, 2000), pp. 1-5. https://doi.org/10.1142/9789812791924_0001

[5] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco and W. Gernjak, *Decontamination and Disinfection of Water by Solar Photocatalysis: Recent Overview and Trends*, Catal. Today, 2009, vol. 147, no. 1, pp. 1-59. https://doi.org/10.1016/j.cattod.2009.06.018

[6] M. Dorogov, A. Kalmykov, L. Sorokin, A. Kozlov, A. Myasoedov, D. Kirilenko, N. Chirkunova, A. Priezzheva, A. Romanov and E.C. Aifantis, *CuO Nanowhiskers: Preparation, Structure Features, Properties, and Applications*, Mater. Sci. Technol., 2018, vol. 34, no. 17, pp. 2126-2135. https://doi.org/10.1080/02670836.2018.1514706

[7] I.M. Sosnin, S. Vlassov, E.G. Akimov, V.I. Agenkov and L.M. Dorogin, *Transparent ZnO-coated Polydimethylsiloxane-Based Material for Photocatalytic Purification Applications*, J. Coatings Technol. Res., 2020, vol. 17, no. 2, pp.

573-579. https://doi.org/10.1007/s11998-019-00314-2

[8] L.M. Dorogin, M.V. Dorogov, S. Vlassov, A.A. Vikarchuk and A.E. Romanov, *Whisker Growth and Cavity Formation at the Microscale*, Rev. Adv. Mater. Tech., 2020, vol. 2, no. 1, pp. 1-31. https://doi.org/10.17586/2687-0568-2020-2-1-1-31

[9] A. Ibhadon and P. Fitzpatrick, *Heterogeneous Photocatalysis: Recent Advances and Applications*, Catalysts, 2013, vol. 3, no. 1, pp. 189-218. https://doi.org/10.3390/catal3010189

[10] K.P. Gopinath, N.V. Madhav, A. Krishnan, R. Malolan and G. Rangarajan, *Present Applications of Titanium Dioxide for the Photocatalytic Removal of Pollutants from Water: A Review*, J. Environ. Manage., 2020, vol. 270, art. 110906. https://doi.org/10.1016/j.jenvman.2020.110906

[11] D. Li, H. Huang, X. Chen, Z. Chen, W. Li, D. Ye and X. Fu, *New Synthesis of Excellent Visible-Light $TiO_{2-x}N_x$ Photocatalyst Using a Very Simple Method* , J. Solid State Chem., 2007, vol. 180, no. 9, pp. 2630-2634. https://doi.org/10.1016/j.jssc.2007.07.009

[12] V.S. Smitha, K.A. Manjumol, K.V. Baiju, S. Ghosh, P. Perumal and K.G.K. Warrier, *Sol–Gel Route to Synthesize Titania-Silica Nano Precursors for Photoactive Particulates and Coatings*, J. Sol-Gel Sci. Technol., 2010, vol. 54, no. 2, pp. 203-211. https://doi.org/10.1007/s10971-010-2178-9

[13] S.M. Gupta and M. Tripathi, A Review of TiO_2 Nanoparticle // Chinese Sci. Bull. vol. 56(16) (2011) 1639-1657; DOI: https://doi.org/10.1007/s11434-011-4476-1

[14] K. Lv, Q. Xiang and J. Yu, *Effect of Calcination Temperature on Morphology and Photocatalytic Activity of Anatase TiO_2 Nanosheets With Exposed {001} Facets*, Appl. Catal. B Environ., 2011, vol. 104, no. 3–4, pp. 275-281. https://doi.org/10.1016/j.apcatb.2011.03.019.

[15] H. Zangeneh, A.A.L. Zinatizadeh, M. Habibi, M. Akia and M. Hasnain Isa, *Photocatalytic Oxidation of Organic Dyes and Pollutants in Wastewater Using Different Modified Titanium Dioxides: A Comparative Review*, J. Ind. Eng. Chem., 2015, vol. 26, pp. 1-36. https://doi.org/10.1016/j.jiec.2014.10.043.

[16] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, *Photocatalytic Degradation Pathway of Methylene Blue in Water*, Appl. Catal. B Environ., 2001, vol. 31, no. 2, pp. 145-157. https://doi.org/10.1016/S0926-3373(00)00276-9

[17] H. Zhan and Y. Jiang, *Metal Oxide Nanomaterials for the Photodegradation of Phenol*, Anal. Lett., 2016, vol. 49, no. 6, pp. 855-866. https://doi.org/10.1080/00032719.2015.1079211

[18] G.-N. Zhu, Y.-G. Wang and Y.-Y. Xia, *Ti-Based Compounds as Anode Materials for Li-Ion Batteries*, Energy Environ. Sci., 2012, vol. 5, no. 5, pp. 6652-6667. https://doi.org/10.1039/C2EE03410G

[19] N.P. Benehkohal, M.J. Sussman, H. Chiu, M. Uceda, R. Gauvin and G.P. Demopoulos, *Enabling Green Fabrication of Li-Ion Battery Electrodes by Electrophoretic Deposition: Growth of Thick Binder-Free Mesoporous TiO_2-Carbon Anode Films*, J. Electrochem. Soc., 2015, vol. 162, no. 11, pp. D3013-D3018. https://doi.org/10.1149/2.0111511jes

[20] T. Lindgren, J.M. Mwabora, E. Avendaño, J. Jonsson, A. Hoel, C.-G. Granqvist and S.-E. Lindquistet, *Photoelectrochemical and Optical Properties of Nitrogen Doped Titanium Dioxide Films Prepared by Reactive DC Magnetron Sputtering*, J. Phys. Chem. B, 2003, vol. 107, no. 24, pp. 5709-5716. https://doi.org/10.1021/jp027345j

[21] D.V. Bavykin, A.A. Lapkin, P.K. Plucinski, J.M. Friedrich and F.C. Walsh, *Reversible Storage of Molecular Hydrogen by Sorption into Multilayered TiO_2 Nanotubes*, J. Phys. Chem. B, 2005, vol. 109, no. 41, pp. 19422-19427. https://doi.org/10.1021/jp0536394

[22] W. Maziarz, A. Kusior and A. Trenczek-Zajac, *Nanostructured TiO_2-Based Gas Sensors with Enhanced Sensitivity to Reducing Gases*. Beilstein J. Nanotechnol., 2016, vol. **7,** pp. 1718-1726. https://doi.org/10.3762/bjnano.7.164

[23] Y. Wang, T. Wu, Y. Zhou, C. Meng, W. Zhu and L. Liu, *TiO_2-Based Nanoheterostructures for Promoting Gas Sensitivity Performance: Designs, Developments, and Prospects*, Sensors, 2017, vol. 17, no. 9, art. 1971. https://doi.org/10.3390/s17091971

[24] A. Kirkey, J. Li and T.K. Sham, *Low Temperature Amorphous to Anatase Phase Transition of Titanium Oxide Nanotubes*, Surf. Sci., 2019, vol. 680, pp. 68-74. https://doi.org/10.1016/j.susc.2018.10.012

[25] A. Das, M. Patra, R.R. Wary, P. Gupta and R.G. Nair, *Photocatalytic Performance Analysis of Degussa P25 Under Various Laboratory Conditions*, IOP Conf. Ser. Mater. Sci. Eng., 2018, vol. 377, art. 012101. https://doi.org/10.1088/1757-899X/377/1/012101

[26] J.-M. Herrmann, *Photocatalysis Fundamentals Revisited to Avoid Several Misconceptions*, Appl. Catal. B Environ., 2010, vol. 99, no. 3-4, pp. 461-468. https://doi.org/10.1016/j.apcatb.2010.05.012

[27] B. Czech and K. Rubinowska, *TiO_2-Assisted Photocatalytic Degradation of Diclofenac, Metoprolol, Estrone and Chloramphenicol as Endocrine Disruptors in Water*, Adsorption, 2013, vol. 19, no. 2-4, pp. 619-630. https://doi.org/10.1007/s10450-013-9485-8