Journal of Engineering Science *Vol. XXVIII, no. 1 (2021), pp. 23 - 30*
Fascicle *Industrial Engineering* *ISSN 2587-3474*
Topic *Materials Science and New Technologies* *eISSN 2587-3482*

https://doi.org/10.52326/jes.utm.2021.28(1).01
UDC 621.357.8:546.824-31

TiO_2 NANOTUBES FOR PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE

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Received: 12. 08. 2020
Accepted: 02. 18. 2021

Abstract. Titanium dioxide remains one of the most studied semiconductor for photocatalytic applications due to its low cost production, reduced toxicity, ability to break down the organic pollutants and possibility to achieve complete mineralization. In this work, we report on results of the photocatalytic activity of titanium dioxide nanotubes fabricated by electrochemical anodization technique in an electrolyte solution containing a mixture of hydrofluoric acid, ethylene glycol and phosphoric acid. The morphology and crystallinity of the obtained nanotubes were investigated by means of electron microscopy and it was found that nanotubes have a constant outer diameter of 200 nm and an internal conical shape where the diameter gradually decreases from 120 nm at the wide end to 50 nm at the narrow end. The transmission electron microscopy investigation defined two different phases of titanium dioxide obtained after annealing of amorphous TiO_2 in air at 650 °C and 850 °C. Photocatalytic activity of the samples have been evaluated in methylene blue solution in the presence of dispersed nanotubes under visible and UV irradiation by means of UV/Vis spectroscopy. Anatase phase TiO_2 shows the best performance degrading 85 % of dye in 25 min under UV illumination, while rutile phase with anatase inclusions shows the best results with a 50 % decay of dye concentration in 25 min under visible light illumination.

Keywords: *Methylene Blue degradation, electrochemical anodization, photocatalysis, TiO_2 nanotubes, TiO_2 plasma etching.*

Introduction

Among the metal oxide semiconductors, titanium dioxide (titania, TiO_2) nanomaterials have attracted much attention in the last decades. TiO_2 is considered a semiconductor with high potential applications due to its advantageous optical and electronic properties, structural and chemical stability, non-toxicity and photocatalytic activity. These properties make titania an excellent material for solar energy conversion [1], applications in dye functionalized solar cells [2, 3], biomedicine [4, 5], microengines [6] and in other fields [7, 8]. Comparing with other forms of TiO_2, unidimensional nanostructures like nanotubes are the most suitable structures for solar energy conversion and

photocatalysis due to inherent high scattering of light and related optical absorption and high surface to volume ratio. Different techniques were applied by researchers to increase the material performances like doping, combination with other materials or inducing structural changes. For instance, doping with non-metal elements has demonstrated a decrease of material bandgap and its possibility for optical applications in the visible range. The anodic oxidation technique is one of the most effective way to fabricate titania nanotubes due to its simplicity, self-ordering and low cost process [9]. This technique has the disadvantage because one end of nanotubes at interface with the Ti foil is closed. Therefore, the nanotube membranes have limitation for some applications and an additional opening process is necessary.

Water pollution has become a serious concern nowadays. Pollution can cause many diseases to human body such as cancers, tumors or skin irritation [10]. Different techniques for water purification were investigated in order to remove the dyes from wastewaters such as chemical precipitation [11], reverse osmosis [12], electrochemical oxidation [13], chemical coagulation-flocculation and bio-oxidation [14] as well as membrane filtration [15]. In recent years, the photocatalytic degradation of organic pollutants from residual waters has attracted much attention. Semiconducting oxide photocatalysts have an enormous potential for air and water treatment of organic contaminants. There are many studies on semiconducting materials for photocatalysis such as TiO_2 [16], ZnS [17], CdS [18], Fe_2O_3 [19], ZnO [20], GaN/ZnO compound [21]. Among these materials, TiO_2 is the most studied because of its ability to break down the organic pollutants and possibility to achieve complete mineralization. Due to its low-cost production, reduced toxicity, high reactivity and hydrophobicity, TiO_2 remains close to an ideal catalyst. In this work, we demonstrate the fabrication of titania nanotubes with both ends opened for photocatalytic degradation of Methylene Blue (MB) in water-based solution. The MB was selected as the dye for the experiments because it represents one of the most stable pollutant [22]. The anatase and anatase-rutile mixture phases of TiO_2 nanotubes were investigated.

Methods

Preparation of TiO_2 nanotubes

TiO_2 nanotubes were fabricated using electrochemical anodization of Ti foils purchased from Sigma-Aldrich with the thickness of 0.25 mm and purity >99,7%. Before anodization, the Ti foil was cleaned in acetone in an ultrasonic bath, rinsed with distilled water and dried under nitrogen flow. An electrolyte consisting of ethylene glycol (99.8%), hydrofluoric acid (48 wt%) and H_3PO_3 (85 wt%) was used. The anodization was realized in a two-electrode system with a Pt mesh as counter electrode. The electrolyte temperature was maintained at 25 °C during the anodization process. The applied voltage was increased gradually to 120 V, with a step of 1 V/sec and then kept constant for 1 h. After anodization, the samples were cleaned in acetone and DI water and then the formed oxide was mechanically separated from the Ti foil. The constituent nanotubes of membranes have the bottom ends closed because of the formation of a barrier oxide layer at the interface with the Ti foil. In order to open the bottom ends of the nanotubes, a Plasma Etching process was applied. The process took place in a PlasmaLab System 100-ICP Deep Reactive Ion Etching System in a mixture of Ar and SF_6 gases at ratio 5:1 for 5 min.

The obtained TiO_2 nanotubes were annealed at different temperatures in order to modify their crystallinity. The samples were treated at 650 °C and 850 °C in air in order to

obtain anatase and anatase - rutile phases, respectively. In order to separate individual nanotubes in the solution, the membrane consisting of nanotubes was sonicated for 30 sec.

Photocatalytic Tests

The organic contaminant solution was prepared by using 10 μM MB solution diluted in deionized water (DI). 20 mg of TiO_2 nanotubes of anatase and anatase - rutile mixture phases were added to 50 ml contaminant solution in a transparent glass beaker and kept under stirring conditions at 600 rpm using a magnetic stirrer. The mixture was irradiated from the top using a 100 W Blak Ray Hg lamp with the main intensity peak at 365 nm and a 150 W Halogen lamp with power density of 100 $mW \bullet cm^{-2}$ for investigation of MB degradation in UV and visible range, respectively. During the experiment, 3 ml solution was collected each 10 min and analyzed at UV/Vis spectrometer. The experiment on photocatalytic degradation continued until the solution becomes colorless, the minimum time being 80 min. The collected solution was centrifuged at 20,000 rpm for 15 min in order to sediment the micro/nanoparticles and then the liquid is transferred into a cuvette for UV/Vis spectroscopy. The absorption spectra were collected in the region 450 – 750 nm.

Characterization Techniques

The morphology and structural investigations of TiO_2 nanotubes were realized using electron microscopy (SEM Zeiss Gemini Ultra55 Plus, TEM JEOL JEM-2100). To monitor the degradation of MB, the optical absorption spectra were recorded with Perkin Elmer Lambda 750 UV/Vis spectrometer.

Results and Discussions

Morphology study

TiO_2 nanotubes have been fabricated by electrochemical anodization technique of Ti sheets. By using this method, it is possible to obtain huge amounts of nanotubes on a small surface of material. The images from the Figure 1 illustrates the top, cross section view and the bottom part of the TiO_2 nanotubes membrane detached from the Ti substrate before and after dry etching step.

The results of the morphology characterization of samples clearly demonstrate the tubular shape along both faces of the membrane, with a constant outer diameter of 200 nm and a variable inner diameter, which gradually decreases from 120 nm at the wide end to 50 nm at the narrow end. The length of the nanotubes can be easily tuned from tens of nm to hundreds of μm by adjusting the anodization conditions.

TEM Structural Study

It was reported previously that titania anatase-rutile phase transformation starts at approximately 600 °C [23,24]. Hence, to obtain anatase phase nanotubes the initial amorphous sample was treated at 650 °C, while treatment at temperature as high as 850 °C was applied to obtain anatase - rutile phase sample.

The results of TEM (Transmission Electron Microscopy) investigations presented in Figure 2 suggest that both TiO_2 nanotube samples, calcinated at 650 °C and 850 °C, are polycrystalline.

Polycrystalline electron diffraction (ED) patterns were analyzed by Rotational Average method which calculates a medium intensity of the electron reflection at certain distance from the ED central spot. To all the meaningful reflections were attributed corresponding crystal planes, referred as the *d*-values of the intensity peaks.

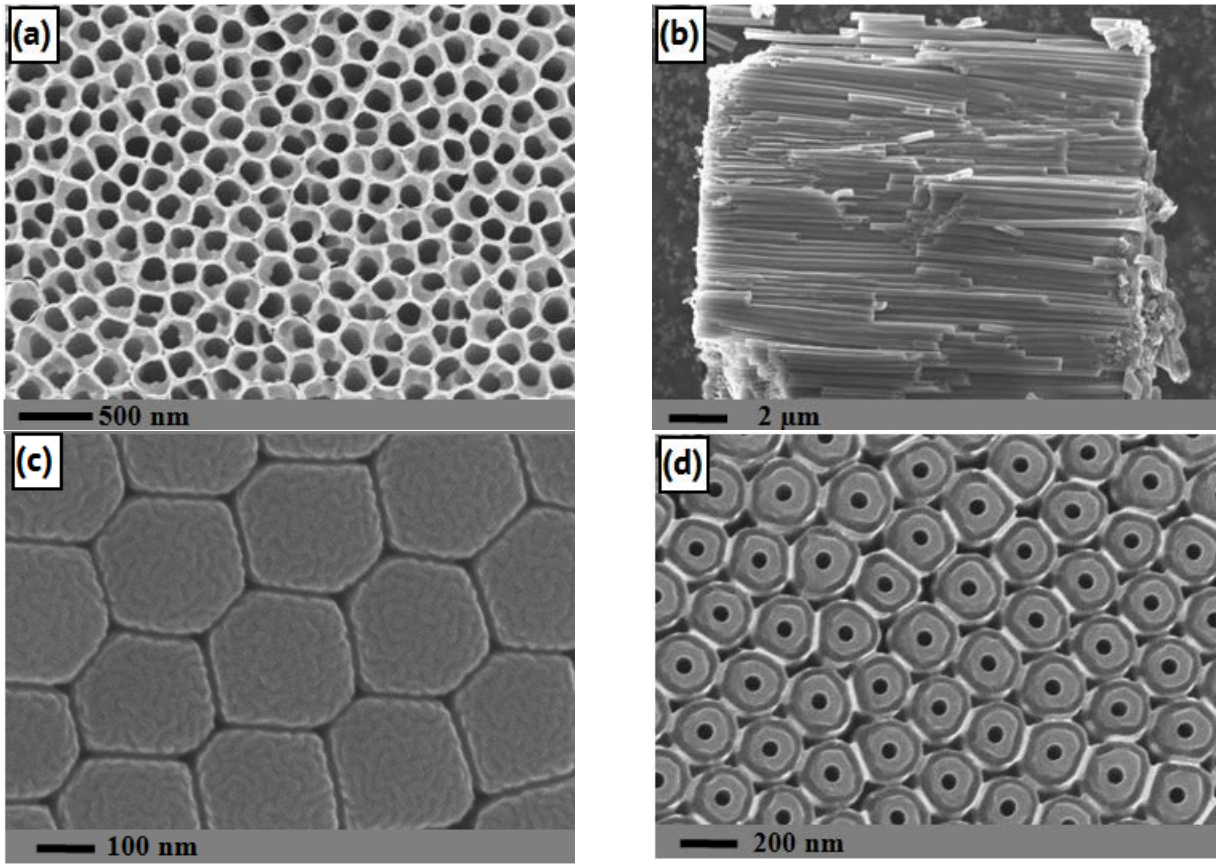

Figure 1. SEM images of TiO_2 membrane: (a) top part, (b) side view, (c) bottom part before dry etching step, (d) bottom part after dry etching showing opened nanotubes.

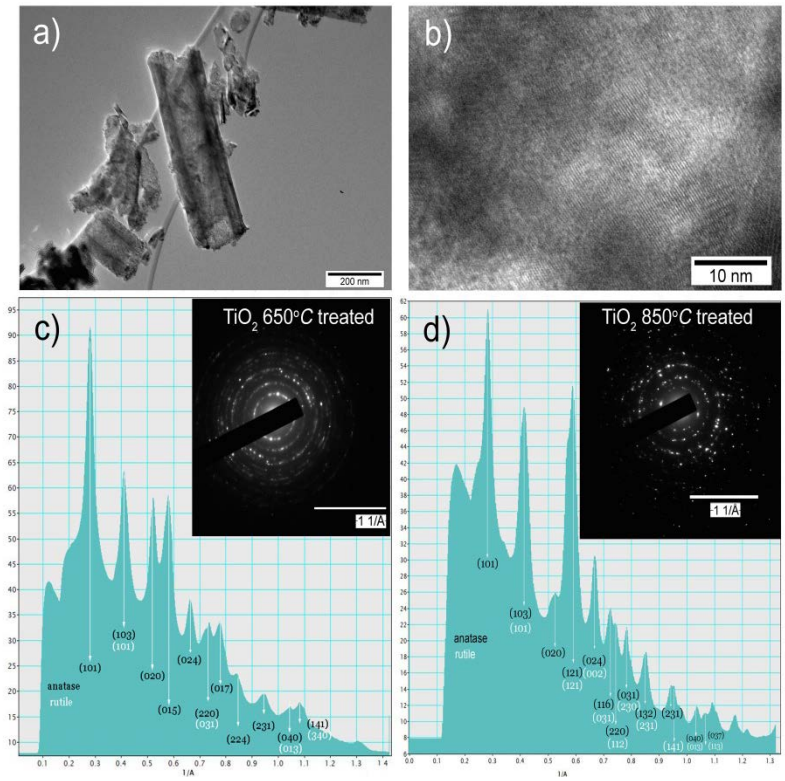

Figure 2. TEM analysis of TiO_2 nanotubes: (a) an overview image of nanotubes; (b) high resolution image of nanotube wall; selected area electron diffractogram and rotational average diagram of TiO_2 nanotubes treated at (c) 650 °C, and (d) 850 °C.

Almost all observed reflections can be attributed to rutile and anatase phases. The results correlate well with the data reported in previous publications in which the concentration of phases is changing at applied calcination regimes [25]. Some ambiguity in phase distinction between anatase *I4/amd* and rutile *P42/mnm* phases of titania comes from the fact that they both are of tetragonal space group and big part of their *d*-values coincides. Both crystal structures consist of TiO_6 octahedra, sharing four edges in anatase and two in rutile [26 – 29]. Polyhedral models of TiO_2 simulated in Diamond (Crystal Impact) software are presented in Figure 3.

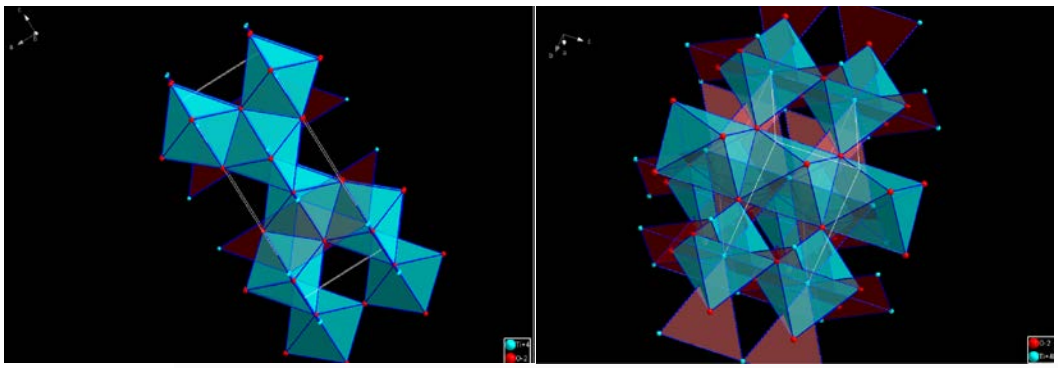

Figure 3. Three-dimensional representation of TiO_6 octahedra arrangement in anatase and rutile crystalline phases.

MB Photodegradation

Two types of titania nanotubes were investigated for photocatalytic degradation of MB. The first sample was subjected to thermal treatment in air at 650 °C and represented the anatase phase, while the sample treated at 850 °C represented a mixture of anatase and rutile phases of TiO_2. Depending on the annealing temperatures, the bandgap of TiO_2 is changing from 3.2 eV for anatase to 3.0 eV for rutile phase. Because of the band-to-band transitions identified in the UV region at 375 - 410 nm and deep defects in the material [30], it can be used as a photocatalytic material in both UV and visible regions. According to ref. 6, the opened TiO_2 nanotubes will increase the photocatalytic activity compared to one side closed nanotubes, the chemical reactions in this case take place on the inner and outer side of the nanotube surface. The formation of oxygen bubbles as a result of chemical reactions will result in motion of nanotubes in the liquid, the permanent liquid exchange inside the nanotubes will favor the occurrence of the reactions. Mixed-phase photocatalysts with rutile–anatase compositions have been reported to exhibit enhanced photoactivity relative to single-phase titania [28, 31 – 33]. Comparing to stable rutile phase, anatase modification has wider bandgap and lower recombination rate facilitating the efficient photocatalytic reactions [29]. At the same time higher surface free energy of rutile enhances its hydrophilicity [34, 35] . It is also expected that in case of residual anatase phase remaining in titania transformed into rutile at 850 °C similarly to the mixture of two types of particles the electron transfer between two phases may enhance the efficiency of photo-oxidative reactions [28, 36].

The photodegradation process of MB using TiO_2 nanotubes under visible and UV light is illustrated in Figure 4, where the concentration C_t (%) of remained MB is measured every 10 min during 80 min. The initial concentration of 10 μM of MB and pure water were took as 100 % and 0 % and it is used for elaboration of calibration curve.

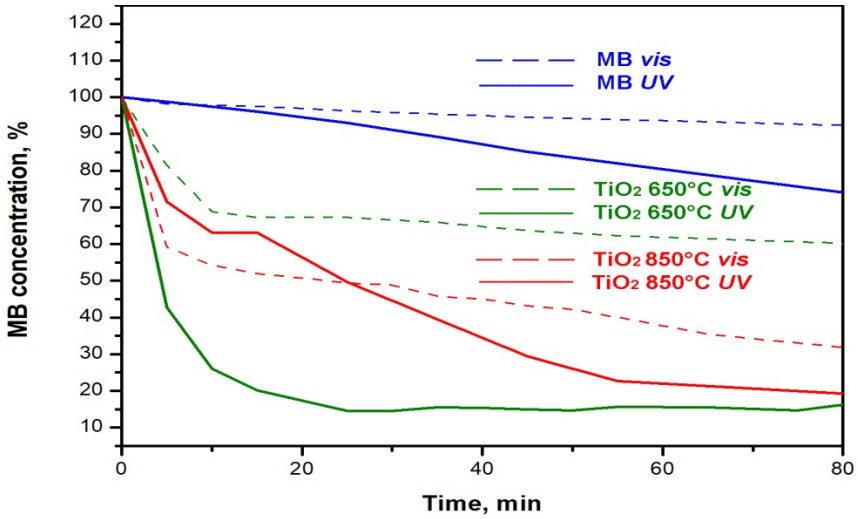

Figure 4. MB concentration decay in time in presence of 20 mg of TiO_2 nanotubes.

The dye concentration in the analyzed solution was calculated from Beer-Lambert law (Eq(1)):

$$A=\varepsilon lc \quad (1)$$

where ***A*** is the measured absorption value,

ε - absorptivity of the solution at certain wavelength ***(λ)***,

l - optical pathway during the measurement expressed in cm,

c - solution concentration.

The ***ε*** value was calculated by a calibration absorption plot measured for 100 % concentrated MB solution at 664 nm.

Photocatalytic degradation under visible light was found to be the most efficient for TiO_2 with higher concentration of the rutile phase, degrading the dye till ~ 30 % concentration compared to the mixed phase of TiO_2 degrading the MB to 60 % during 80 min. Better photocatalytic activity of TiO_2 nanotubes under visible light irradiation is related to the high density of electronic defects as observed in the PL spectrum [30]. Under UV illumination, best photodegradation of MB is performed by TiO_2 anatase phase with 15 % dye remaining in water after only 25 min compared to 50 % for the sample with more concentration of rutile phase.

Conclusions

It was found that both TiO_2 nanotubes annealed at 650 °C and 850 °C can degrade MB under UV and visible light irradiation. According to TEM analysis, the TiO_2 tends to transform from anatase to rutile phase with increasing the annealing temperature. The higher photocatalytic activity in the visible range was observed on samples treated at 850 °C where the rutile phase predominates, however the sample annealed at 650 °C exhibits higher photocatalytic activity under UV illumination. Because of its bandgap near visible range and the possibility to modulate it with different techniques, the TiO_2 nanotubes have a great potential to be used in industry for water treatment.

Acknowledgments. The authors acknowledge the funding from European Commission under the Grant #810652 "NanoMedTwin" and from the Ministry of Education, Culture and Research of the Republic of Moldova under the Grant #20.80009.50007.20.

References

1. Asghar M.I., Miettunen K., Halme J., Vahermaa P., Toivola M., Aitola K., Lund P. Review of stability for advanced dye solar cells. In: *Energy and Environmental Science*, 2010, 3(4), pp:418–426.
2. Zhu K., Neale N.R., Miedaner A., Frank A.J. Enhanced Charge-Collection Efficiencies and Light Scattering in Dye-Sensitized Solar Cells Using Oriented TiO2 Nanotubes Arrays. In: *Nano Letters*, 2007, 45(1), pp:10623–10631.
3. Qu Y., Zhou W., Pan K., Tian C., Ren Z., Dong Y., Fu H. Hierarchical anatase TiO2 porous nanopillars with high crystallinity and controlled length: An effective candidate for dye-sensitized solar-cells. In: *Physical Chemistry Chemical Physics*, 2010, 12(32), pp:9205–9212.
4. Grosjean R., Delacroix S., Gouget G., Beaunier P., Ersen O., Ihiawakrim D., Kurakevych O., Portehault D. Progress in TiO2 nanotube coatings for biomedical applications: A review. In: *Journal of Materials Chemistry B*, 2018, 13(23), pp:1862–1886.
5. Shrestha N.K., Macak J.M., Schmidt-Stein F., Hahn R., Mierke C.T., Fabry B., Schmuki P. Magnetically guided titania nanotubes for site-selective photocatalysis and drug release. In: *Angewandte Chemie - International Edition*, 2009, 48(5), pp:969–972.
6. Enachi M., Guix M., Postolache V., Ciobanu V., Fomin V.M., Schmidt O.G., Tiginyanu I. Light-Induced Motion of Microengines Based on Microarrays of TiO2 Nanotubes. In: *Small*, 2016, 12(39), pp:5497–5505.
7. Li Z., Zhang H., Zheng W., Wang W., Huang H., Wang C., MacDiarmid A.G., Wei Y. Highly sensitive and stable humidity nanosensors based on LiCl doped TiO2 electrospun nanofibers. In: *Journal of the American Chemical Society*, 2008, 130(15), pp:5036–5037.
8. Jiang Z., Yang F., Luo N., Chu B.T.T., Sun D., Shi H., Xiao T., Edwards P.P. Solvothermal synthesis of N-doped TiO2 nanotubes for visible-light-responsive photocatalysis. In: *Chemical Communications*, 2008, 1(47), pp:6372–6374.
9. Enachi M., Guix M., Braniste T., Postolache V., Ciobanu V., Ursaki V., Schmidt O.G., Tiginyanu I. Photocatalytic properties of TiO2 nanotubes doped with Ag, Au and Pt or covered by Ag, Au and Pt nanodots. In: *Surface Engineering and Applied Electrochemistry*, 2015, 51(1), pp:3–8.
10. Vakili M., Rafatullah M., Salamatinia B., Abdullah A.Z., Ibrahim M.H., Tan K.B., Gholami Z., Amouzgar P. Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review. In: *Carbohydrate Polymers*, 2014, 113, pp:115–130.
11. Pan Y., Wang J., Sun C., Liu X., Zhang H. Fabrication of highly hydrophobic organic-inorganic hybrid magnetic polysulfone microcapsules: A lab-scale feasibility study for removal of oil and organic dyes from environmental aqueous samples. In: *Journal of Hazardous Materials*, 2016, 309, pp:65–76.
12. Zheng L., Wang X., Wang X. Reuse of reverse osmosis concentrate in textile and dyeing industry by combined process of persulfate oxidation and lime-soda softening. In: *Journal of Cleaner Production*, 2015, 108, pp:525–533.
13. Chatzisymeon E., Xekoukoulotakis N.P., Coz A., Kalogerakis N., Mantzavinos D. Electrochemical treatment of textile dyes and dyehouse effluents. In: *Journal of Hazardous Materials*, 2006, 137(2), pp:998–1007.
14. Manekar P., Patkar G., Aswale P., Mahure M., Nandy T. Detoxifying of high strength textile effluent through chemical and bio-oxidation processes. In: *Bioresource Technology*, 2014, 157, pp:44–51.
15. Guo J., Zhang Q., Cai Z., Zhao K. Preparation and dye filtration property of electrospun polyhydroxybutyrate–calcium alginate/carbon nanotubes composite nanofibrous filtration membrane. In: *Separation and Purification Technology*, 2016, 161, pp:69–79.
16. Nakata K., Fujishima A. TiO 2 photocatalysis: Design and applications. In: *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 2012, 13(3), pp:169–189.
17. Lee G.J., Wu J.J. Recent developments in ZnS photocatalysts from synthesis to photocatalytic applications — A review. In: *Powder Technology*, 2017, 318, pp:8–22.
18. Cheng L., Xiang Q., Liao Y., Zhang H. CdS-Based photocatalysts. In: *Energy and Environmental Science*, 2018, 11(6), pp:1362–1391.
19. Mishra M., Chun D.M. α-Fe2O3 as a photocatalytic material: A review. In: *Applied Catalysis A: General*, 2015, 498, pp:126–141.
20. Widiyandari H., Ketut Umiati N.A., Dwi Herdianti R. Synthesis and photocatalytic property of Zinc Oxide (ZnO) fine particle using flame spray pyrolysis method. In: *Journal of Physics: Conference Series*, 2018, 1025(1).
21. Wolff N., Ciobanu V., Enachi M., Kamp M., Braniste T., Duppel V., Shree S., Raevschi S., Medina-Sánchez M., Adelung R., Schmidt O.G., Kienle L., Tiginyanu I. Advanced Hybrid GaN/ZnO Nanoarchitectured Microtubes

for Fluorescent Micromotors Driven by UV Light. In: *Small*, 2020, 16(2), pp:1–10.
22. Hou C., Hu B., Zhu J. Photocatalytic degradation of methylene blue over TiO2 pretreated with varying concentrations of NaOH. In: *Catalysts*, 2018, 8(12).
23. Ghosh T.B., Dhabal S., Datta A.K. On crystallite size dependence of phase stability of nanocrystalline TiO2. In: *Journal of Applied Physics*, 2003, 94(7), pp:4577–4582.
24. Li G., Li L., Boerio-Goates J., Woodfield B.F. High purity anatase TiO2 nanocrystals: Near room-temperature synthesis, grain growth kinetics, and surface hydration chemistry. In: *Journal of the American Chemical Society*, 2005, 127(24), pp:8659–8666.
25. Enachi M., Lupan O., Braniste T., Sarua A., Chow L., Mishra Y.K., Gedamu D., Adelung R., Tiginyanu I. Integration of individual TiO2 nanotube on the chip : Nanodevice for hydrogen sensing pss. In: *Physica Status Solidi - Rapid Research Letters*, 2015, 174(3), pp:171–174.
26. Hadjiivanov K.I., Klissurski D.G. Surface chemistry of titania (anatase) and titania-supported catalysts. In: *Chemical Society Reviews*, 1996, 25(1), pp:61–69.
27. Beltrán A., Gracia L., Andrés J. Density functional theory study of the brookite surfaces and phase transitions between natural titania polymorphs. In: *Journal of Physical Chemistry B*, 2006, 110(46), pp:23417–23423.
28. Hanaor D.A.H., Sorrell C.C. Review of the anatase to rutile phase transformation. In: *Journal of Materials Science*, 2011, 46(4), pp:855–874.
29. Muscat J., Swamy V., Harrison N.M. First-principles calculations of the phase stability of TiO2. In: *Physical Review B - Condensed Matter and Materials Physics*, 2002, 65(22), pp:2241121–22411215.
30. Pallotti D.K., Passoni L., Maddalena P., Di Fonzo F., Lettieri S. Photoluminescence Mechanisms in Anatase and Rutile TiO2. In: *Journal of Physical Chemistry C*, 2017, 121(16), pp:9011–9021.
31. Huang S.Y., Schlichthörl G., Nozik A.J., Grätzel M., Frank A.J. Charge recombination in dye-sensitized nanocrystalline TiO2 solar cells. In: *Journal of Physical Chemistry B*, 1997, 101(14), pp:2576–2582.
32. Bacsa R., Kiwi J. Effect of rutile phase on the photocatalytic properties of nanocrystalline titania during the degradation of p-coumaric acid. In: *Applied Catalysis B: Environmental*, 1998, 16(1), pp:19–29.
33. Bickley R.I., Gonzalez-Carreno T., Lees J.S., Palmisano L., Tilley R.J.D. A structural investigation of titanium dioxide photocatalysts. In: *Journal of Solid State Chemistry*, 1991, 92(1), pp:178–190.
34. Banfield J.F., Zhang H. Thermodynamic analysis of phase stability of nanocrystalline titania. In: *Journal of Materials Chemistry*, 1998, 8(9), pp:2073–2076.
35. Rupp F., Scheideier L., Olshanska N., De Wild M., Wieland M., Geis-Gerstorfer J. Enhancing surface free energy and hydrophilicity through chemical modification of microstructured titanium implant surfaces. In: *Journal of Biomedical Materials Research - Part A*, 2006, 76(2), pp:323–334.
36. Ohno T., Tokieda K., Higashida S., Matsumura M. Synergism between rutile and anatase TiO2 particles in photocatalytic oxidation of naphthalene. In: *Applied Catalysis A: General*, 2003, 244(2), pp:383–391.