# Application of $TiO_2$ and its derivatives for alternative energetic sources

V. Bozhilov, S. Kozhukharov, E. Bubev, M. Machkova, V. Kozhukharov

***Abstract:*** *Nowadays, the continuous rise of the population in the world emerges diversification of the energetic sources, for reliable energy supply. Furthermore, the sustainable development of the modern communities relies to environmentally friendly energy production equipment. In this aspect the present work has attention to overview some applications of $TiO_2$ as effective material for alternative energetic sources..*

***Key words:*** *Titanium dioxide, Energy source, Photovoltaic cells, Water-splitting electrolysers, SOFC,*

## INTRODUCTION

In nature $TiO_2$ exists in three basic polymorphic modifications: rutile, anatase and brookite, as is well described in ref. [1]. Nevertheless, various solid $TiO_2$- containing materials can be produced in artificial conditions, (i.e. industrial plants or laboratories). Furthermore, the respective $TiO_2$–based solids find large variety of applications for elaboration and production of different devices and equipment.

The purpose of the present brief review is to describe the main fields of $TiO_2$ application, remarking the potential abilities in the energy generation sources.

## FIELDS OF APPLICATION

Titanium dioxide is well known as a photocatalyst and it is widely used for photocatalysed decomposition of various organic substances [2 - 5]. Recently, it has found various fields of application - for sensor elements, [6 - 10], water purification [11 - 12] and photodisinfection [11,12] systems, photoelectrochromic devices [13], electronic components [14, 15] and even for corrosion protection [16]. Furthermore, the beneficial properties of $TiO_2$ could be enhanced by its modification [17, 19]. Recently, this material has found effective for even medical applications, as medical implants [20 – 24] or medicine carriers and for gradual release of active substances [25 – 27], too. Due to its photo-activity, this oxide possesses a great potential for application for alternative energy sources. It could be used as layer in Dye Sensitized Solar Cells (DSSC) [28 - 32], Solid Oxide Fuel cells (SOFC) [33 - 35], or light induced water splitting devices [36 - 38]. The fields of application of $TiO_2$ containing materials are summarized in Fig. 1.

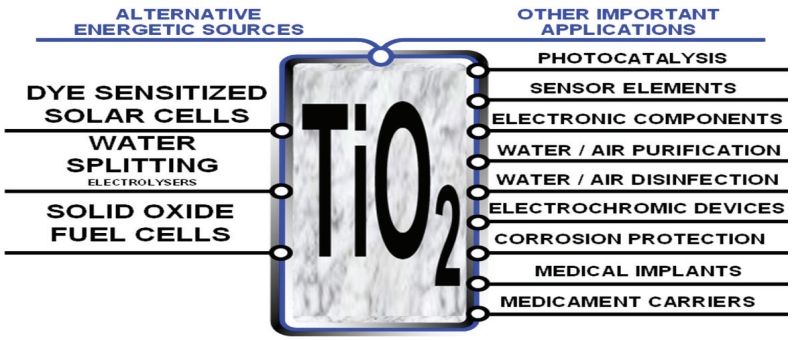


Figure 1. Fields of application of titanium dioxide solids

Undoubtedly, the characteristics of the $TiO_2$ containing devices depends on its structure, as well as on its form of application. This oxide could be obtained from large variety of solids with different structures and forms, according to the method and conditions applied for its synthesis. Examples of transparent, mesoporous anatase $TiO_2$

monoliths [39], highly dispersive powders [40 - 43], nanomaterials of $TiO_2$ with controlled porosity [44], dense [45 - 48] or porous [49 - 52] thin film coatings and others are found and a selection is presented here. The basic natural and artificial forms are illustrated in Fig. 2. Nanosize $TiO_2$ is not shown, since the field is too broad, innovative one and presents a separate object of overview and discussion.

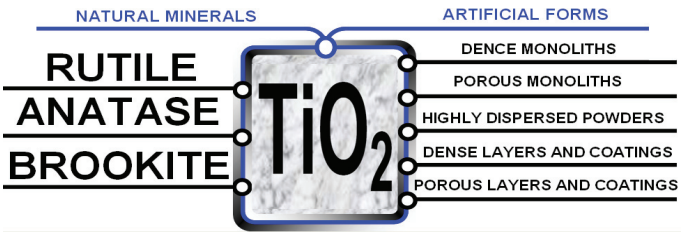


Figure 2. Natural and artificial titanium dioxide solids

## CONCLUSIONS

The literature analysis for the present brief review enables to achieve the following conclusions:

1. Besides its use for alternative energy sources, $TiO_2$ has really extended fields of application, e.g. in the chemical industry, automation, electronics, environmental technologies, and medicine.
2. It could be produced in different forms, according to the methods and conditions, applied for its synthesis.
3. The authors of almost all of the articles, cited in the present brief review, have employed the sol-gel method, in order to obtain $TiO_2$ – based materials in various forms and with desirable properties. This fact reveals the significant versatility of the sol-gel approach of synthesis.
4. The spray pyrolysis techniques are also appropriated for $TiO_2$ powder production or film deposition, regardless the fact that the high temperatures required may cause polymorphic transitions during synthesis.

**Akcnowledgements:** The authors appreciate the support of this work accomplished in the 7fp of EC, contract N° 286605, “FABRIGEN”.

## REFERENCES

[1] Educational materials Colorado University, http://ruby.colorado.edu/~smyth/min/tio2.html

[2] C. Jwo, H. Chang, M. Kao, C. Lin, “Photodecomposition of volatile organic compounds using TiO2 nanoparticles”, J. Nanosci, Nanotechnol. 7, (6), (2007), 1947-1952.

[3] X. Duan, D. Sun, Z. Zhu, X. Chen,P. Shi, “Photocatalytic decomposition of toluene by $TiO_2$ film as photocatalyst”, J. Environ. Sci. Health, A-37, (2002), 679-692.

[4] Y. Ku, J-S. Chen, H-W. Chen, “Decomposition of Benzene and Toluene in Air Streams in Fixed-Film Photoreactors Coated with $TiO_2$ Catalyst”, J. Air & Waste Manage. Assoc., 57, (2007), 279–285.

[5] A. Rezaee, Gh. H. Pourtaghi, A. Khavanin, R. S. Mamoory, M. T. Ghanean, H. Godini, “Photocatalytic decomposition of gaseous toluene by $TiO_2$ nanoparticles coated on activites carbon”, Iranian J. Environ. Sci. Eng., 5, (2008), 305-310.

[6] S. Kozhukharov, Z. Nenova T. Nenov, S. Ivanov, “Influence of dopants on the performance of humidity sensitive elements, prepared by deposition of $TiO_2$ via sol-gel method” Proccedings, “Angel Kanchev” University of Ruse, 49, (2010), 33 – 35.

[7] M. Okuya, K. Shiozaki, N. Horikawa, T. Kosugi, A.G.R. Kumara, J. Madarasz, S. Kaneko, G.Pokol, "Porous $TiO_2$ thin films prepared by spray pyrolysis deposition (SPD) technique and their application to UV sensors", Solid State Ionics, 172, (2004), 527–53.

[8] S. Kozhukharov, T. Nenov, Z. Nenova, M. Machkova, "Impact of Dopants on the Characteristics of Thin-Film Humidity Sensor Elements", Proceed. SENSOR+TEST Conference 7. – 9.6.2011, Nuernberg, (Germany), paper: P – 3.5.

[9] A. Trinchi, Y. X. Li, W. Wlodarsky, S. Kaciulis, L. Pandoufi, S. Viticoli, E. Comini, "Investigation of sol–gel prepared $CeO_2$–$TiO_2$ thin films for oxygen gas sensing", Sensors and Actuators, B 95, (2003), 145-150.

[10] J. Ryu, W. Choi, "Substrate-Specific Photocatalytic Activities of $TiO_2$ and Multiactivity Test for Water Treatment Application", Environ. Sci. Technol. 42, (2008), 294–300.

[11] M. Chong, B. Jin, Christopher P. Saint, "Bacterial inactivation kinetics of a photo-disinfection system using novel titania-impregnated kaolinite photocatalyst", Chem. Eng. Journal, 171, (2011), 16–23.

[12] C. Karanukaran, A. Vijabalan, G. Manikandan, "Photocatalytic bacteria inactivation by polyethylene glycol-assisted sol-gel synthesised Cd-doped $TiO_2$ under visible light", Res. Chem. Intermed. DOI 10.1007/s11164-012-0700-0.

[13] G. Leftheriotis, G. Syrrokostas, P. Yianoulis, "Electrochemical processes in photoelectrochromic devices", Proceedings "9th European Symposium on Electrochemical Engineering", (9- ESEE), 19 – 23 June 2011, Chania, (Greece), paper: A1.2.4.

[14] A. M. Cruz, Y. Reyes, B. Gallego, D. Fernandez-Hevia, M. Pietado, "Control of microstructure in $TiO_2$-doped ceramic varistors based on ZnO-$Bi_2O_3$-$Sb_2O_3$ system", Bol. Soc. Esp. Ceram. Vidrio, 51, (1), (2012), 61-66.

[15] S. Bernik, N. Daneu, A. Recnik, "Inversion Boundary induced grain growth in $TiO_2$ or $Sb_2O_3$ doped ZnO-based varistor ceramics" J. Eur. Ceram. Soc., 24, (2004), 3703-3708.

[16] O. Zubillaga, F. G. Cano, I. Azkarate, I. S. Molchan, G. E. Thompson, P. Skeldon, "Synthesis of anodic films in the presence of aniline and $TiO_2$ nanoparticles on AA2024-T3 aluminium alloy", Thin Solid Films, 517, (2009), 6742-6746.

[17] D. Li, H. Haneda, S. Hishita, N. Ohashi, N. K. Labhsetwar, "Fluorine-doped TiO powders prepared by spray pyrolysis and their improved photocatalytic activity for decomposition of gas-phase acetaldehyde", Jour. Fluor. Chem., 126, (2005), 69–77.

[18] S.J. Cho, C-K. Junk, Y-H. Song, J-H. Boo, "Synthesis of N-doperd $TiO_2$ photocatalytic thin films with controlled nitrogen partial pressure and study on their catalytic activity", Proceedings "First international conference on materials for energy" – 4-8 July 2010, Karlsruhe, (Germany), B-1121.

[19] D. Crisan, N. Dragan, M. Crisan, M. Raileanu, A. Braileanu, A. Ianculescu, D. Mardare, D. Luca, A. Nastuta, "Sol-Gel Au/$TiO_2$ films from nanopowders – structural study", Proceedings, "4th. Balkan Conference on glass science and technology & 16th conference on glass and ceramics", 27 September – 01 October, 2011, Varna (Bulgaria), Volume 2, "Ceramics", 138-144.

[20] S-H. Lee, H.-W. Kim, E-J. Lee, L.-Hao Li, H-E. Kim, "Hydroxyapatite-$TiO_2$ Hybrid Coating on Ti Implants" J. Biomater. Appl. 20, (2006), 195-208.

[21] A. Kar, K.S. Raja, M. Misra, "Electrodeposition of hydroxyapatite onto nanotubular $TiO_2$ for implant applications", Surf. Coat. Technol., 201, (6), (2006), 3723-3731.

[22] K. Shiraishi, H. Koseki, T. Tsurumoto, K. Baba, M. Naito, K. Nakayama, H. Shindo, "Antibacterial metal implant with a $TiO_2$-conferred photocatalytic bactericidal effect against Staphylococcus aureus", Surface & Interface Analysis, 41, (1), (2009), 17-22.

[23] K. Gotfredsen, A. Wennerberg, C. Johansson, L. T. Skovgaard, E. Hjørting-Hansen, "Anchorage of $TiO_2$-blasted, HA-coated, and machined implants: an experimental study with rabbits", J. Biomed. Mater. Res., 29, (10), (1995), 1223-1231.

[24] S. Oh, C. Daraio, L-H. Chen, T. R. Pisanic, R. R. Fiñones, Sungho Jin, "Significantly accelerated osteoblast cell growth on aligned $TiO_2$ nanotubes", J. Biomed. Mater. Res., Part A, (2006), 97-103.

[25] H. Jiang, T. Wang, L. Wang, C Sun, T. Jiang, G. Cheng, S. Wang, "Development of an amorphous mesoporous $TiO_2$ nanosphere as a novel carrier for poorly water-soluble drugs: Effect of different crystal forms of $TiO_2$ carriers on drug loading and release behaviors", Microporous and Mesoporous Materials, 153, (2012), 124-130.

[26] Y. Qin, L. Sun, X. Li, Q. Cao, H. Wang, X. Tang, L. Ye, "Highly water-dispersible TiO2 nanoparticles for doxorubicin delivery: effect of loading mode on therapeutic efficacy" J. Mater. Chem., 21, (2011), 18003-18010.

[27] Hong Peng, S. Feng, X. Zhang, Y. Li, X. Zhang, "Adsorption of norfloxacin onto titanium oxide: Effect of drug carrier and dissolved humic acid", Science of The Total Environment, 438, (2012), 66-71.

[28] J. Krueger, U. Bach, M. Gratzel, "High efficiency solid-state photovoltaic device due to inhibition of interface charge recombination", Appl. Phys. Res., 79, (2001), 2085–2087.

[29] L. I. Halaoui, N. M. Abrams, T. Mallouk, "Increasing the conversion efficiency of Dye-sensitized photoelectrochemical cells by coupling to photonic crystals", J. Phys. Chem. B 109, (2005), 6334-6342.

[30] Y-C. Liu, Y-F. Lu, Y-Z. Zeng, C-H. Liao, J-C. Chung, T-Y. Wei, "Nanostructured mesoporous titanium dioxide film prepared by sol-gel method for Dye-sensitized solar cell", Int. Jour. Photoenergy – 2011, Article ID: 619069.

[31] S-S. Kim, J-H. Yum, Y-E. Sung, "Improved performance of a dye-sensitized solar cell using a $TiO_2$/ZnO/Eosin Y electrode", Solar Energy & Solar cells, 79, (2003), 495-505.

[32] J. Szeifert, D. Fattakhova, J.Feckl, D. Georgiadou, V. Kalousek, J. Ratousky, D. Kuang, S. Zakeeruddin, M. Gratzel, T. Bein, "Highly crystalline mesoporous titania films for photovoltaic applications based on self-assembled nanocrystalline building blocks" Proceedings "First international conference on materials for energy" – 4-8 July 2010, Karlsruhe (Germany), paper: A-449.

[33] P. Nikolopoulos, X. Mantzouris, F. Tietz, "Physical Characterization of $Y_2O_3$-$CeO_2$-$TiO_2$ (YCT) Mixed Oxides and Ni/YCT Cermets as Anode Electrodes in Solid Oxide Fuel Cells", Proceedings, "10th International Conference and Exhibition of the European Ceramic Society (ECerS-10)", June 17-21, 2007, Berlin, (Germany).

[34] V.Kozhukharov, Y. Tsvetkova, "Synthesis and study of Ti-O based materials for SOFC anode applications", Proceedings, "10 $^{th}$ International Symposium on Solid Oxide Fuel Cells (SOFC-X), Nara, Japan, 2007; Vol. 7, Issue 1, pp. 1631-1638.

[35] P. Nikolopoulos, X. Mantzouris, F. Tietz, "Physical Characterisation of Y-Ce-Ti Oxides as Mixed Conducting Anode Materials in Solid Oxide Fuel Cells", 7th European Solid Oxide Fuel Cell Forum, 3-7 July 2006,Lucerne, (Switzerland),(2006) paper:P0701-034.

[36] A. Delic, E. Vanhaecke, M. Ronning, "$TiO_2$ on aligned CNF substrates for photocatalytic water splitting", Proceedings "First international conference on materials for energy" – 4-8 July 2010, Karlsruhe (Germany), (2010) paper: A-477 - 478.

[37] A. J. Cowan, J. Tang, W. Leng, J. R. Durrant, D. R. Klug, "Water Splitting by Nanocrystalline $TiO_2$ in a Complete Photoelectrochemical Cell Exhibits Efficiencies Limited by Charge Recombination", Phys. Chem. C, 114, (9), (2010), 4208–4214.

[38] Z. Zhang, P. Wang, "Optimization of photoelectrochemical water splitting performance on hierarchical $TiO_2$ nanotube arrays", Energy Environ. Sci., 5, (2012), 6506-6512.

[39] B. Yao, L. Zhang, "Preparation and characterization of mesoporous titania gel-monolith", J. Mater. Sci., 34, (1999), 5983 – 5987.

[40] M. Crisan, M. Raileanu, A. Braileanu, M. Crisan, N. Dragan, I. Nitoi, A. Ianculescu, "Sol-Gel pure and S-doped $TiO_2$ with ecological applicatrions", Proceedings, "4th. Balkan Conference on glass science and technology & 16th conference on glass and ceramics", 27 September – 01 October, 2011, Varna (Bulgaria), Volume 2, "Ceramics", pp. 151-155.

[41] V. J. Nagpal, R. M. Davis, S. B. Desu. "Novel thin films of titanium dioxide particles synthesized by a sol-gel process", J. Mater. Res, 10, (12), (1996), p. 3068.

[42] N. Dragan, D. Crisan, M. Crisan, M. Raileanu, A. Braileanu, A. Ianculescu, V. Teodorescu, "Sol-Gel Au/$TiO_2$ films from nanopowders – structural study", Proceedings, "4th. Balkan Conference on glass science and technology & 16th conference on glass and ceramics", 27 September – 01 October, 2011, Varna, (Bulgaria), Volume 2, "Ceramics", 145-150.

[43] H. Kochkar, M. Triki, K. Jabou, G. Berhault, A. Ghorbel, "Novel synthesis route to titanium oxides nanomaterials using soluble starch", J. Sol-Gel Sci. Technol., 42, (2007), 27–33.

[44] M. Jensen, P. Fuierer, "Low-temperature preparation of nanocrystalline anatase films through a sol-gel route", J. Sol-Gel Sci. Technol, 39, (2006), 229–233.

[45] V. Kozhukharov, Ch. Trapalis, B. Samuneva, "Sol-gel processing of titanium-containing thin coatings. Part III properties", J. Mater. Sci, 28, (1993), 1283 – 1288.

[46] M. Mallak, M. Bockmeyer, P. Löbmann, "Liquid phase deposition of $TiO_2$ on glass: Systematic comparison to films prepared by sol–gel processing", Thin Solid Films, 515 (2007), 8072–8077.

[47] M-C. Carotta, M. Ferroni, V. Guidi, G. Martinelli, "Preparation and Characterization of Nanostructured Titania Thick Films", Adv. Mater. 11, (11), (1999), 943 – 946.

[48] E.Cazzanelli, N. Scaramuzza, G. Strangi, C. Versace, R. Ceccato, G. Carturan, "Sol-Gel Synthesis and Characterization of $TiO_2$ and $TiO_2$–$V_2O_5$ films for Electrodes in Assimetric Liquid Crystal Cells", Proceedings "Meeting of the Italian Liquid Crystal Society", 24.05.2000 - Calabria, (Italy); pp. 305-320.

[49] I. Truijen, M. K. Van Bael, H. Van den Rul, J. D'Haen, J. Mullens, "Preparation of nanocrystalline titania films with different porosity by water-based chemical solution deposition", J. Sol-Gel Sci. Technol., 43, (2007), 291–297.

[50] Z. Liu, Z. Jin, X. Liu, Y. FU, G. Liu. ''Fabrication of Ordered $TiO_2$ Porous Thin Films by Sol-Dipping PS Template Method", J. of Sol-Gel Sci. and Technol. 38, (2006),73–78.

[51] X. Liu, Z. Jin, S. Bu, T. Yin, "Influences of Solvent on Properties of $TiO_2$ Porous Films Prepared by a Sol-Gel Method from the System Containing PEG", J. of Sol-Gel Sci. Technol. 36, (2005), 103–111.

[52] G. Q. Liu, · Z. G. Jin, · X. X. Liu, · T. Wang, · Z. F. Liu, "Anatase $TiO_2$ porous thin films prepared by sol-gel method using CTAB surfactant", J. Sol-Gel Sci. Technol. 41 (2007), 49–55.

**About the autors:**

Valentin Bozhilov, M. Eng. University of Chemical Technology and Metallurgy - Sofia, (Bulgaria), email: valentin_kitov@abv.bg, mobile:+359878787851

**The paper is reviewed.**