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TiO₂ based nanomaterials and nanostructures for green convergent technologies and environmental protection

ABSTRACT

Taking into account the importance of development of the advanced nanomaterials for the environmental protection, in this article the application of TiO₂ based nanomaterials and nanostructures in the fields of renewable energy, chemical and bio decontamination has been presented. The role of TiO₂ in formation of composite hybrid structures for solar energy harvesting has been explained, as well as the use of various antimicrobial TiO₂ based nanomaterials for photocatalytic degradation of pollutants. Special attention has been paid to structure and properties of TiO₂ nanotubes obtained by electrochemical anodization and their application in bio decontamination.

Keywords: TiO₂, convergent technologies, environmental protection, nanomaterials.

1. INTRODUCTION

Nowadays, maintaining and restoring the quality of the environment (water, air and soil) are immensely important, due to pollution, global ecological problems and environmental changes [1]. It is expected that by 2025, 15% of all materials used in the European economy should be reused, while the green and environmentally friendly industries will transform almost all the industry sectors [2]. Recently launched European Green Deal is a new European Union development strategy to tackle the problem of progressive environmental degradation and climate change [3-5]. This strategy promotes innovation in cleaner technologies, products and services that reduce environmental risk and minimise pollution. It requires numerous structural changes on all policy levels in order to break up unsustainable industry structures, build up sustainable ones and to give the right mid- to long-term orientation towards development of more efficient circular and bioeconomies. The concept of sustainability is composed of three pillars (economic environmental, and social) and focuses

on meeting the needs of the present without compromising the ability of future generations to meet their needs. It is generally recognized that convergent technologies are one of the key drivers for building a framework for a transition to more resource-efficient, more sustainable circular economy societies. The term 'converging technologies' is frequently used for groups of technologies, such as nano-, bio- and information technologies, with potential links between them and resultant synergies and benefits [6]. There is a common agreement that the convergence of these diverse technologies is based on the understanding of complex hierarchical structures and systems, as well as on the material unity at the nanoscale and on technology integration from that scale. Development of advanced ecomaterials is especially important in the field of green convergent technologies, since their processing should enable selection of materials of less environmental load, their better flexibility for DfE (Design for the Environment) and connection with other industries from the viewpoint of industrial ecology and environmental protection. While enhancing the environmental improvement throughout the whole life cycle, these materials should exhibit energy saving ability, resource saving ability, reusability, recyclability, structural reliability, chemical stability, biological safety ability, substitutability, amenity and cleanability [7] (Figure 1).

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Figure 1. Conceptual model of eco-materials and their properties

Slika 1. Konceptualni model eko materijala i njihovih svojstava

It has been found that TiO₂ based materials and nanostructures have great potentials in the field of green convergent technologies due to their green resource profile, minimal environmental impact during the material manufacturing process, high productivity in use, high recyclability, and high

environmental purification efficiency (Figure 2). As an environment-friendly and energy-creating base material, TiO₂ has been used as a photocatalyst for water and air purification, in hydrogen/oxygen generation, as well as an antibacterial coating, and in gas sensors.

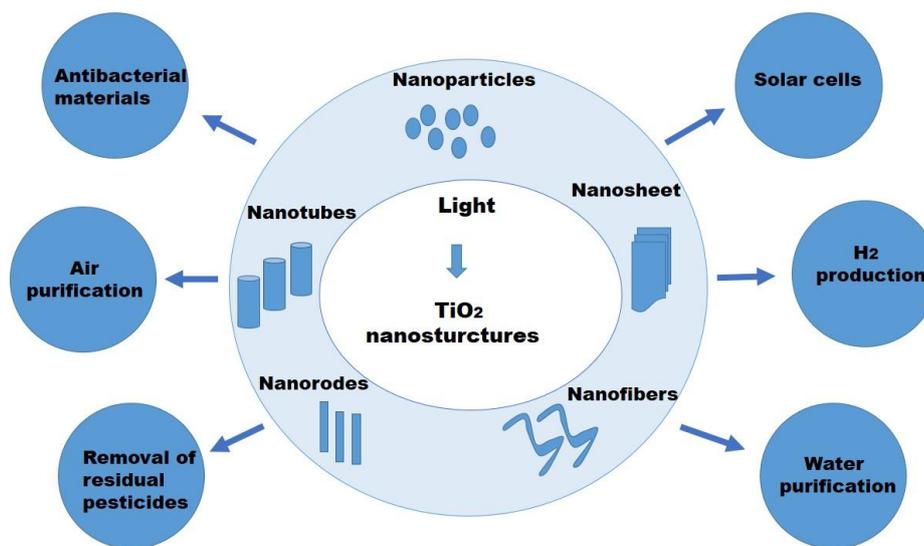


Figure 2. The use of TiO₂ nanomaterials in green convergent technologies and environmental protection

Slika 2. Primena TiO₂ nanomaterijala u zelenim konvergentnim tehnologijama i zaštiti prirodne okoline

The applications of TiO₂ based materials and nanostructures are closely related to their electrical, chemical and optical properties and depend on three different TiO₂ crystalline forms (anatase, rutile and brookite) [8]. It has been found that by diminishing dimensions to the nanoscale, not only the specific surface area of these materials increase significantly, but also the electronic properties may change considerably due to

quantum size effects, strong contribution of surface reconstruction, or surface curvature. These effects may also drastically improve the reaction/interaction between material and the surrounding media, thus influencing the application of these materials in the various fields of environmental protection. Having this in mind the aim of this article is to present the application of these materials in the fields of solar energy harvesting, chemical and bio decontamination.

2. THE APPLICATION OF TiO₂ IN ADVANCED NANOCOMPOSITES FOR SOLAR ENERGY HARVESTING

Development of novel, efficient and cheap devices for solar energy harvesting is one of the main targets of numerous renewable energy strategies. It has been shown that photoactive TiO₂ based materials are highly perspective materials which can be used in this field, despite the fact that their application might be limited due to TiO₂ absorption edge at 387 nm [9]. Therefore, numerous investigations are performing in order to develop TiO₂ based materials and structures with absorption in visible part. This includes decoration of the TiO₂ surface with other species [10], doping TiO₂ with transition metal [11,12] or nonmetal [13-16], photosensitization [17] and heterojunction preparation [18]. Although sensitization of TiO₂ surface can be achieved by numerous methods, the use organometallic salts [19], with the band gap of 1.5-1.65 eV, lately attracted much attention, since they can be used for sensors, light-emitting diode, photodetector and solar cell.

As a result the photovoltaic market, which is currently dominated by crystalline Si solar cells with efficiencies close to 20%, is constantly challenged with alternative "third generation" solar cells such as organic photovoltaics (OPVs), dye sensitized solar cells (DSs), quantum dot solar cells (QDSCs) and organic-inorganic halide perovskite solar cells. They promise low cost solar power and development of novel photovoltaic devices with unique functionalities and superior performances.

Layered organic-inorganic perovskites are extensively studied due their advantageous properties which include: high mobilities for thin-film transistors, strong excitonic properties for light emitting diodes, large nonlinearities with ultrafast responses and polariton emission in 2D perovskite-based microcavities. It has been established that perovskite crystallization from solution may produce large morphological variations and incomplete filling of the mesoporous oxide scaffold, resulting in an unwanted deterioration of the photovoltaic performances.

Structure control in solution-processed hybrid perovskites is crucial for designing and fabrication of highly efficient solar cells. Initial structure of perovskite solar cells arose as an evolution of the solid-state dye sensitized solar cell architecture. Solid-state dye sensitized solar cells can be fabricated by dye sensitized mesoporous film of TiO₂ filled with a solid hole-conducting material such as p-type semiconductors or organic hole conducting material.

Typical schematic of layered sandwich-type device architecture of inorganic-organic hybrid hetero junction solar cells containing perovskite compound and polymeric hole conductors is presented on Fig 3. In this type of structures the HTM and FTO electrode can form ohmic contacts, which may lead to recombination of charge carriers. Therefore, in order to reduce this recombination, the introduction of a compact TiO₂ layer (CL) between FTO electrode and TiO₂ nanoparticle layer has been proposed [20]

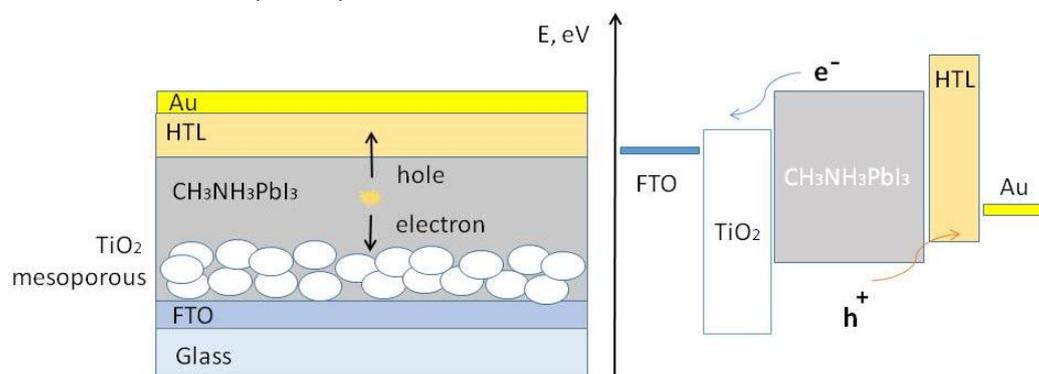


Figure 3. Typical layered sandwich-type architecture of inorganic-organic CH₃NH₃PbI₃ perovskite hybrid solar cell with mesoporous TiO₂

Slika 3. Tipična slojevita sendvič struktura organsko-neorganske CH₃NH₃PbI₃ perovskitne hibridne solarne ćelije sa mezoporoznim TiO₂

Various investigations have shown that doped TiO₂ electrode may increase the photoelectric conversion efficiency in the cell. Also, increased efficiency can be achieved by increasing the interfacial surface area between the organic and

the inorganic part of the cell and by controlling the nanoscale lengths and periodicity of each structure so that charges are allowed to separate and move toward the appropriate electrode without recombining. Following the solid-state dye

sensitized solar cell architecture, a common device configuration for hybrid perovskites solar cell consists of compact TiO₂ hole blocking layer, TiO₂ mesoporous layer and deposited perovskite film. Although TiO₂ nanoparticles are most commonly used in the mesoporous layer, various others TiO₂ nanostructures like nanosheets, nanorods, nanofibers have been exploited in order to modify composite structure of the perovskite solar cell. It has been found that TiO₂ nanotubes can be used to enhance the electrons transfer, since their electrons transfer is 30 times faster under UV light and the electron energy loss is reduced compared to TiO₂ nanoparticles [21]. Furthermore, by varying

the different synthesis parameters, it is easy to control and to predict the characteristics of the TiO₂ nanotubes which can be used as a substrate for the deposition of perovskite sensitizer and for the formation of the photodiode. Our recent research on the application of TiO₂ nanotubes as substrates for the deposition of perovskite sensitizer and for the formation of the photodiodes, have shown that beside the TiO₂ nanotube morphology, dopant amount and the nature of its incorporation into TiO₂ nanotube arrays can significantly influence the optical response and photodetection area of perovskite based photodiodes [22].

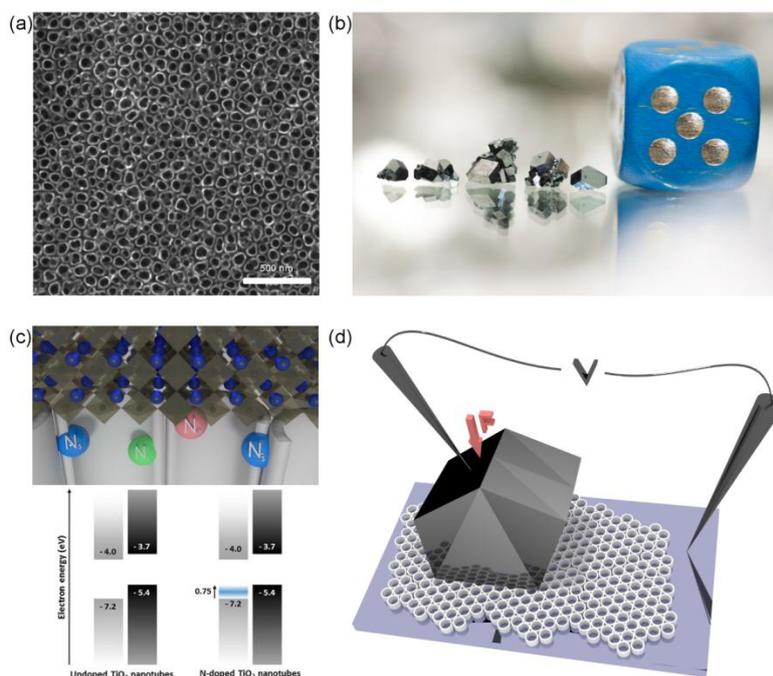


Figure 4. Schematic illustration of the TiO₂ nanotube array and CH₃NH₃PbI₃ single crystal junction
 a) SEM micrograph of TiO₂ nanotubes, b) image of CH₃NH₃PbI₃, c) Schematic illustration of junction N-doped TiO₂ nanotubes and Perovskite, d) Schematic illustration of heterojunction of TiO₂ nanotubes and perovskite [22]

Slika 4. Shematski prikaz TiO₂ nanotuba i spoja sa CH₃NH₃PbI₃ kristalom a) SEM mikrografija TiO₂ nanotuba, b) CH₃NH₃PbI₃ c) shematska ilustracija spoja TiO₂ dopiranog azotom i perovskita, d) shematska ilustracija heterospoja TiO₂ nanotuba i perovskita [22]

Despite the rapid progress in organic–inorganic perovskite solar cells, a clear understanding of the charge generation and transport mechanisms in perovskite solar cells is still severely lacking. There is a still open question whether electron collection is more efficient through the mesoporous TiO₂ or within the perovskite itself and which pathway results in higher extraction efficiency in perovskite solar cell.

3. THE USE OF TiO₂ FOR CHEMICAL AND BIO DECONTAMINATION

Materials based on TiO₂ are often used for chemical and bio decontamination due to their photocatalytic ability to oxidize organic contaminants and antimicrobial properties [23]. Photocatalytic degradation of pollutants is typically attributed to the reactions involving reactive oxygen species (ROS), although direct participation of

photogenerated carriers in the photocatalytic reactions is also possible [24]. Antibacterial activity of these materials is also commonly attributed to the production of ROS, which are non-selective microbicides [25]. Although TiO₂ may exist in amorphous and three natural crystalline forms (anatase, rutile, and brookite), only TiO₂ materials in the form of anatase and rutile are photocatalytically active. Since the anatase phase shows an indirect optical band gap of 3.2 eV, while the rutile phase has a direct bandgap of 3.06 eV and an indirect one of 3.10 eV, the photocatalytic generation of ROS and the efficient antibacterial properties TiO₂ generally occur under UV illumination. Despite the fact that anatase has more negative potential on the edge of the conductive band, and is more active as a photocatalyst than rutile, it has been found that a mixture of anatase and rutile may increase

photocatalytic activity of those materials, making them more commonly used for photocatalysis. Since the conduction band of anatase lies 0.2 eV above that of rutile, the band alignment which favours the transfer of photogenerated electrons from anatase to rutile, and the transfer of holes from rutile to anatase at a clean interface is considered to be a dominant factor of superior photocatalytic activities of these biphasic TiO₂ materials [26] (Fig. 5). Unfortunately, the application of TiO₂ as a photocatalyst for visible light-induced chemical reactions is hampered by its large band-gap energy and is limited by the fast charge-carrier recombination and low interfacial transfer rates of charge carriers. Therefore in order to reduce the band-gap energy to the visible light range, numerous research in the field of bandgap-engineering has been performed.

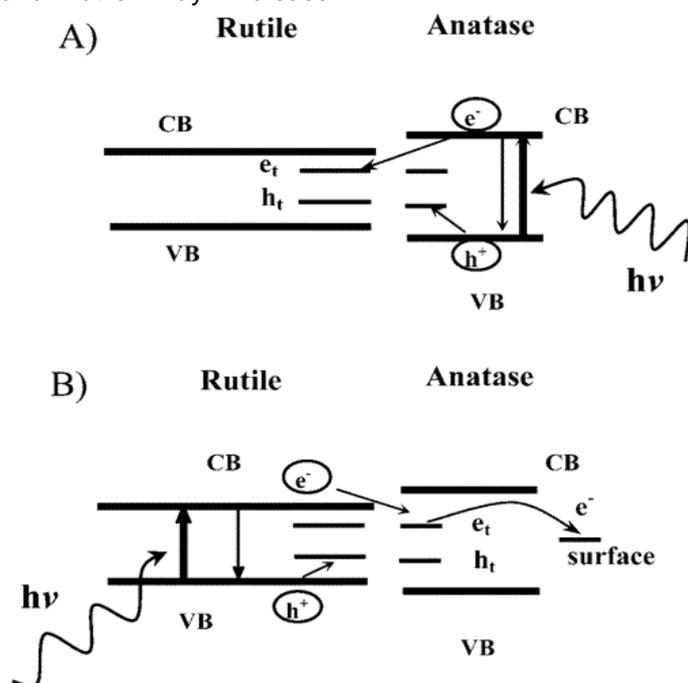


Figure. 5 Two valence and conduction band alignment mechanisms for the anatase/rutile interface. **a**, Type-II (rutile). **b**, Type-II (anatase)

Slika 5. Shematski prikaz dva modela za mehanizam poravnjavanja valentne i provodne zone na anatas-rutilnom spoju a) Tip-II (rutil), b) Tip-II (anatas)

It has been established that by diminishing dimensions to the nanoscale, not only the specific surface area increases significantly but also, due to quantum size effects, the strong contribution of surface reconstruction, or surface curvature, photocatalytic properties may change considerably. Our recent research in this field indicated that mechanical activation may appear as a powerful method not only for obtaining TiO₂ nanoparticles, but also for tailoring their photocatalytic and antimicrobial properties. We have shown that mechanical activation can dramatically enhance

the antimicrobial activity of TiO₂, due to the impact on the structure, morphology and phase composition of the starting material [27]. As a result these materials can be used to prevent the spread of contaminations such as bioaerosols in facilities with common ventilation systems, transportation, and in private homes. It is important to notice that, beside particle size, a number of other factors, such as surface area, the ratio of polymorphs, type of dopants, defect concentration, synthesis method, and phase purity, strongly affect the antimicrobial activity of TiO₂.

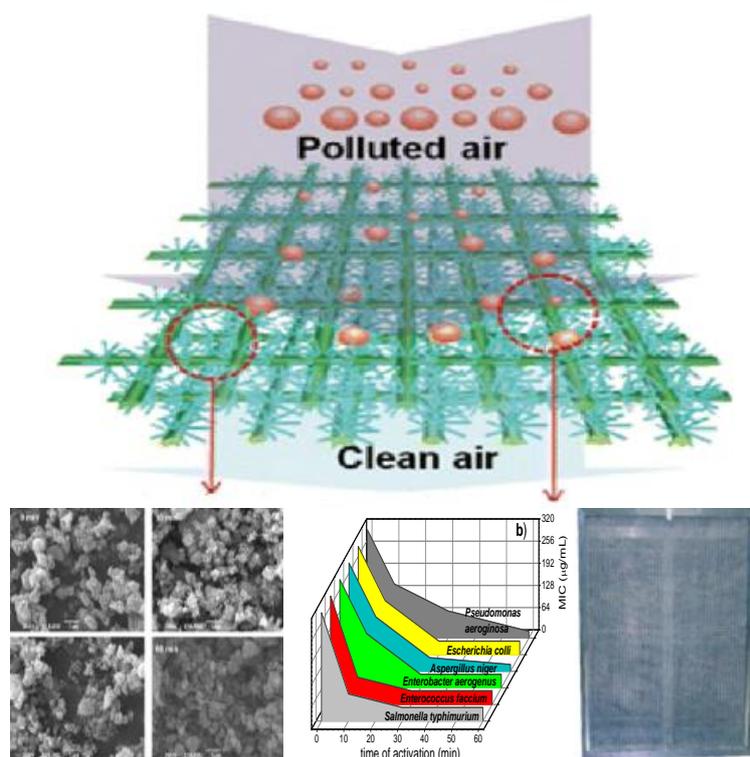


Figure 6. TiO₂ eco materials for Air Filtration Technologies

Slika 6. TiO₂ eko materijali u tehnologijama za filtraciju vazduha

The antibacterial mechanisms are complex, including charge repulsion, membrane stretching, and surface roughness variation. These antibacterial mechanisms, such as membrane stretching and surface roughness, are closely related to the dimensions and morphology of TiO₂ nanostructures. It has been found that formation of TiO₂ nanotubes (TNT) can be associated with stronger antibacterial ability of these materials. Several studies have shown that an increasing diameter is associated with stronger antibacterial ability. Peng et al. [28] claimed that TNTs with a diameter of 80 nm exhibited better bactericidal ability than TNTs with a diameter of 30 nm. Simi and Rajendran produced TNTs with various diameters by controlling the contents of the electrolyte [29]. They concluded that increasing TNT diameters lead to increasing hydrophilicity, thus enhancing the antibacterial ability. However, some studies yielded contradictory results. Radtke et al [30] reported that TNTs prepared at 5 V with smaller diameters exerted a stronger antibacterial effect than other TNTs, while Lewandowska et al [31] claimed that the 20–30 nm TNT prepared at 4 V demonstrated stronger antibacterial ability against various strains of *S. aureus* than other TNTs with larger diameters.

These discrepancies are attributed to the inability to precisely control variables during the experiments. Apart from the diameter, factors such as length, wall thickness, gaps between walls and crystal forms also influence the morphology of TNTs. Considering the limitations of the TNT fabrication methods, precisely controlling other variables to determine the impact of one parameter on the antibacterial property of TNTs is not possible.

Although TiO₂ nanotubes with different sizes and geometrical shapes could be prepared using various physical and chemical synthesis routes such as: templating growth, hydrothermal process, electrochemical anodization is the simplest and most straight-forward approaches that lead to ordered nanotubular/nanoporous structures of TiO₂ [32,33]. Anodization usually takes place in an electrochemical cell (Fig 7 a). The system is powered by a direct current power supply. The anode is the titanium sheet to be anodized, and the inert metal (eg, platinum) is usually the cathode. Both of the electrodes are immersed in the electrolyte, which usually contains fluoride ions. The essence of TNT fabrication is the competition and equilibrium between electrochemical oxidation and chemical dissolution. According to the current-time curve, the reaction process can be

divided into three stages, namely the initial decrease (oxidation dominance), the subsequent increase (chemical dissolution dominance), and the

final steady stage (equilibrium between chemical dissolution and oxidation).

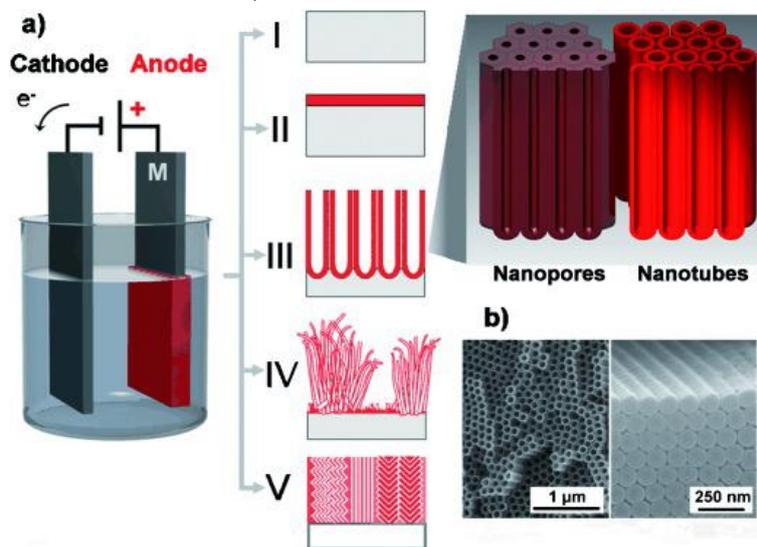


Figure 7. The electrochemical anodization process and possible anodic morphologies: metal electropolishing, II) formation of compact anodic oxides, III) self-ordered oxides (nanotubes or nanopores), IV) rapid (disorganized) oxide nanotube formation, V) ordered nanoporous layers a) and b) SEM micrographs of top and bottom view of TiO₂ nanotubes [34]

Slika 7. Proces elektrohemijske anodizacije i moguće morfologije: elektropoliranje metalnog substrata, II) formiranje kompaktnih anodnih oksida, III) samouređenje oksida (nanotube i nanopore), IV) ubrzano (neorganizovano) formiranje oksidnih nanotuba V) uređeni nanoporozni slojevi, a) i b) SEM mikrofografije TiO₂ nanotuba viđene odgore i od dole [34]

Advantage of anodization is ability to achieve the desired dimensions of nanotubes by manipulating electrolyte components, the pH value, voltage, temperature, and reaction time. Consequently, it was developed different form of nanotubes. First TiO₂ nanotube arrays was grown in HF electrolytes or acidic HF mixtures [34]; an example of the typical morphology is shown in Fig. 1c. These layers showed a limited thickness that would not exceed 500–600 nm. By using buffered neutral electrolytes containing NaF or NH₄F instead of HF and taking into account the importance of the pH gradient within the tube, it was shown that self-organized nanotube TiO₂ layers with thicknesses

higher than 2 μm could be grown [35]. The third generation nanotubes were grown in (almost) water free electrolytes.

The anodization process allows for many variations in the tube geometry and several approaches were reported that allow the formation of more sophisticated nanotube geometries and morphologies. In general, these approaches are based on changing the electrochemical conditions during anodization. By two-step anodization stacked tube layers and branched tubes can be fabricated on Ti (some examples are shown in Figure 8) [36].

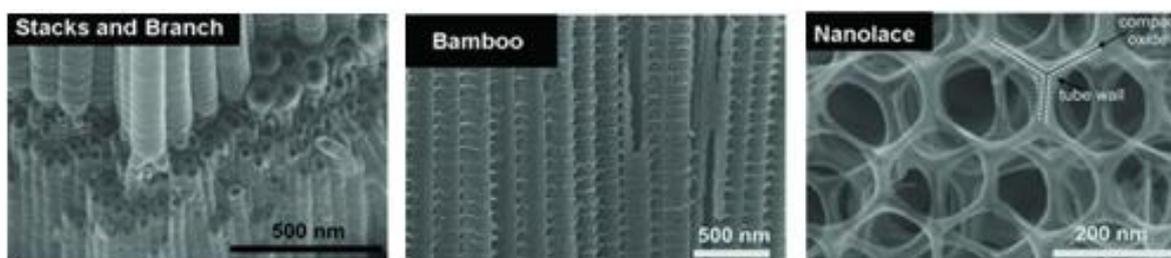


Figure 8. SEM and STEM images showing advanced morphologies of TiO₂ nanotubes based morphologies: tube-stacks and branching of tubes, bamboo type of nanotubes and nanolace [36]

Slika 8. SEM i STEM slike naprednih morfologija TiO₂ nanotuba a) Nagomilane i granajuće tube, bambusolike tube i nanočipke [36]

Chan et al. have been prepared TiO₂ nanotubes by anodization of titanium foil and their antibacterial activities have been tested against Gram-positive bacteria (*Bacillus atrophaeus*) [37]. They found out that temperature of annealing influenced on antibacterial activities of TiO₂ nanotubes. The nanotube samples exhibited excellent antibacterial activity for all annealing temperatures except for the samples annealed at 850 °C. Koklic et al. synthesized copper doped TiO₂ nanotubes [38]. They observed that Cu-TiO₂ nanotubes produce about five times more OH radicals as compared to undoped TiO₂ nanotubes and that effective surface disinfection can be achieved even at low intensity UVA light of 30 μW/cm². The nanotubes can be deposited on a preformed surface at room temperature, resulting in a stable deposition resistant to multiple washings. Up to 10³ microorganisms per cm² can be inactivated in 24 hours, including resistant strains such as *Methicillin-resistant Staphylococcus aureus* (MRSA) and *Extended-spectrum beta-lactamase Escherichia coli* (E. coli ESBL). Moon et al. were deposited the Au and Pt nanoparticles (NPs) on anodized 100 nm TiO₂ NTs by ion plasma sputtering [39].

From the results of antibacterial activity test, Au and Pt NPs that were deposited on TiO₂ NTs showed excellent antibacterial activity under 470 nm visible light irradiation due to the plasmonic photocatalysis based on the localized surface plasmon resonance effect of the Au and Pt NPs. Hajjaji et al. investigated the effect of the diameter of TiO₂ nanotubes and silver decorated nanotubes on optical properties and photocatalytic inactivation of *Escherichia coli* under visible light. The TiO₂ nanotubes (TiO₂-NTs) were prepared using the electrochemical method varying the anodization potential starting from 20 V until 70 V [40]. The Ag nanoparticles were carried out using the photoreduction process. Bacteria were seen to adhere on TiO₂-NTs in the dark; however, under light the bacteria were killed before they establish a strong contact with the TiO₂-NTs and Ag/TiO₂-NTs surfaces. Bacterial inactivation kinetics were faster when the anodizing potential of the NTs-preparation increases. A total bacterial inactivation was obtained on 100 nm nanotubes diameter within 90 min. TiO₂ nanotubes on Ti substrate were fabricated by electrochemical anodization. Ag nanoparticles were deposited on the TiO₂ nanotubes by a silver mirror reaction. Antibacterial activity of the nanotubes with different structural features was evaluated by a culture test with *Escherichia coli* bacteria. The anatase nanotubes showed the highest antibacterial activity among two crystal phases including anatase, rutile, including amorphous titania. The diameters of the nanotubes

affected the antibacterial activity. The two nanotubes with 200 nm and 50 nm diameters had higher antibacterial rate than those with other diameters.

4. CONCLUSIONS

In this article an overview on application of TiO₂ based nanomaterials and nanostructures in the fields of green convergent technologies and environmental protection has been presented. The applications of TiO₂ in advanced nanocomposites for solar energy harvesting and for chemical and bio decontamination has been analysed. Their importance in the formation of solid-state dye sensitized solar cells has been stressed. An importance on formation of various TiO₂ nanostructures has been emphasized. Special attention has been paid to the application of TiO₂ nanotubes synthesized by electrochemical anodization. It has been explained why the application of TiO₂ as a photocatalyst for visible light-induced chemical reactions is hampered and what investigations are carried out in order to be able to further develop TiO₂ coatings, films and nanocomposites for green convergent technologies and environmental protection.

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IZVOD

NANOMATERIJALI I NANOSTRUKTURE NA BAZI TiO₂ ZA ZELENE KONVERGENTNE TEHNOLOGIJE I ZAŠTITU PRIRODNE OKOLINE

Imajući u vidu značaj razvoja naprednih nanomaterijala za zaštitu prirodne okoline, u ovome radu su prezentovane primene nanomaterijala i nanostruktura na bazi TiO₂ u oblastima obnovljivih izvora energije, hemijske i bio dekontaminacije. Objašnjena je uloga TiO₂ u formiranju kompozitnih hibridnih struktura za prikupljanje solarne energije, kao i primena različitih antimikrobnih materijala na bazi TiO₂ koji se koriste za fotokatalitičko uklanjanje polutanata. Naročita pažnja je posvećena strukturi i svojstvima titan dioksidnih nanotuba dobijenih primenom metode elektrohemijske anodizacije i njihova primena u bio dekontaminaciji.

Ključne reči: TiO₂, konvergentne tehnologije, zaštita prirodne okoline, nanomaterijali.

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