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FABRICATION AND APPLICATIONS OF MULTIFUNCTIONAL NANOSTRUCTURED TiO2

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Abstract *Nanomaterials development is a rapidly emerging field of research with enormous potential for societal and economic benefits. In agro and food industries dimension-dependent properties or phenomena of nanomaterials may be used for various functional effects such as increased bioavailability or decreased toxicity of products, better detection of pathogens, improved food packaging materials, or improved delivery of nutrients. Since these effects may derive from altered or unique characteristics of materials in the nanoscale range that are not normally observed or expected in larger-scale materials with the same chemical composition, such changes raise questions about the safety, effectiveness, performance, quality or public health impact of nanotechnology products. In this article, we have reviewed the fabrication, properties, and selected applications of nanostructured TiO_2 based materials. Special attention has been paid to TiO_2 nanoparticles and nanotubes fabrication perspectives and applications in agriculture. We have shown that high photocatalytic disinfection and photobiological effects of nanostructured TiO_2 coupled with its low price, nontoxicity, and stable performance especially provide new approaches for solving environmental pollution and pesticide residue problems in agriculture.*

Keywords: *nanomaterials, nanoparticles, nanotubes, TiO_2*

1. INTRODUCTION

Nanotechnology and nanomaterials fabrication has great potential to positively impact the food sector through improvement of existing products and development of new ones. Agriculture may benefit from advances in nanotechnology which will not only develop new nanostructured biocatalysts in order to modify the agro-resources in the green chemistry context, but will also decrease and optimize the use of nanoparticles pesticides, increase the efficiency of nanostructure biodegradable materials, develop autonomous nanosensors for real-time monitoring and develop the smart delivery of nanosystems for prevention, improved diagnostics and treatment. One group of materials which have great potentials in this field is based on nanostructured TiO_2. Their application is closely related to their electrical, chemical and optical properties and depends on the TiO_2 crystal structure. TiO_2 crystallizes into three different polymorphs: anatase, rutile, and brookite. Rutile is generally considered to be the thermodynamically most stable bulk phase. Beside crystal structure and chemical composition, it has been established that, in order to achieve a maximum overall material's efficiency, it is crucial to maximizing the specific surface area of the material (which is, for example, obvious for any catalytic reaction). By diminishing dimensions to the nanoscale, not only the specific surface area increases significantly, but also the electronic properties may change considerably (owing for example to quantum size effects, a strong contribution of surface reconstruction, or surface curvature). These effects may also drastically improve the reaction/interaction between the material and the surrounding media, thereby making the system more effective or even allow entirely novel reaction pathways. For all nanomaterials, dimension-dependent and surface phenomena become more important compared to bulk phenomena, while quantum effects change the way how nanosystems work [1, 2]. A lot of methods were developed for fabrication nanoscale TiO_2. It has been established that by varying of processing parameters it is possible to obtain different dimensionality of TiO_2 based nanomaterials, such as 0D (nanoparticles and spheres), 1D (nanofibers, nanotubes and nanorods), 2D (sheet) and 3D (interconnected architecture). All these structural morphologies have certain advantages, for example, nanoparticles have the higher specific surface area, nanotubes and nanorods less charge carrier recombination, while sheets have a smooth surface and interconnected architectures have high carrier mobility [3]. Taking into account that 0D and 1D TiO_2 nanomaterials have great potential in agro and food industries, in this article TiO_2 nanoparticles and nanotubes fabrication perspectives and applications, have been analyzed.

2. FABRICATION OF NANOSTRUCTURED TIO_2 BASED MATERIALS

TiO_2 nanoparticles have all three dimensions under 100 nm and due to that specific surface state drastically increase, while pore volume and pore size rise up. Although a lot of techniques for synthesis of TiO_2 nanoparticles were developed, the most used are a sol-gel and hydrothermal method. In sol-gel method, in order to obtain TiO_2 nanoparticles, titanium precursor (Ti-alkoxides) and solvent with addition of water, acid or base are used to form a sol. After drying sol transfers into a gel, and the organic precursor is removed by calcination on a high temperature, forming nanoparticles at the end. By controlling composition, pH and temperature of the solution, it is possible to control size and morphology of the particles [4]. Synthesis of the monodispersed and highly homogenous TiO_2 nanoparticles is possible by using hydrothermal method in autoclave as well. Beside titanium precursor and water, in this method, it is necessary to use mineralizer such as NaOH, KOH, HNO_3, HCl, HCOOH, H_2SO_4. In order to obtain desired morphology, a lot of parameters which influence this type of synthesis: temperature, pressure, duration, pH of solution and solvent type, should be controlled [4]. Nanocrystalline TiO_2 can be also obtained by mechanical milling of Ti and CuO in a planetary ball mill with stainless steel balls. Using this process, it is possible to synthesize TiO_2 nanopowder with an average particle diameter less than 50 nm after 4 h of milling and powder with an average particle diameter under 20 nm after 12 h of milling [5]. More recently, TiO_2 nanoparticles and nanorods were prepared by using micelle templates of appropriate surfactants above their critical micelle concentration (the surfactant molecules aggregate and disperse in a liquid to give so-called spherical or rod-like micelles, which are used as a template for TiO_2 preparation). In this approach, nanotube formation is mostly carried out using water containing reverse micelles with a cylindrical exterior surface [6].

The hydrothermal method can be used to synthesize not only TiO_2 nanoparticles but nanotubes as well [7]. Because this method is template free, nanotubes form loose agglomerates and bundles. In order to obtain nanotubes on a substrate, Maiyalagan et al. [8] used alumina membrane as a template for the formation of TiO_2 nanotubes. At first, the template was dipped in a solution of Ti(IV)-isopropoxide and 2-propanol for a 2 min. For removing excess of solution, the vacuum was applied on the back side of the membrane. Then samples were dried at 30 °C and annealed at 600 °C. Finally, the template was removed by immersing each sample in 3M solution of NaOH and rising it with DI water. But one of the easiest and template-free methods for obtaining TiO_2 nanotubes (NTs) perpendicular to the substrate is electrochemical oxidative anodization. Although electrochemical anodization of the suitable metals has been conducted for almost a century for the creation of protective or decorative oxide layers on metal surfaces, self-organized oxide nanotube layers or ordered nanopore assembly have only recently been fabricated. It has been shown that TiO_2 NTAs, fabricated by anodic oxidation of Ti, have excellent biocompatibility, large surface area, good uniformity, and conformability over large areas and constitute a promising platform for protein and biomolecule immobilization and biosensing applications [9].

This process is generally carried out on a two-electrode configuration (Fig. 1). In general, the morphology and structure of the porous layers are affected by the electrochemical conditions, especially the anodizing voltage and solution parameters including the electrolyte composition, pH, and water content (Fig. 2) [10]

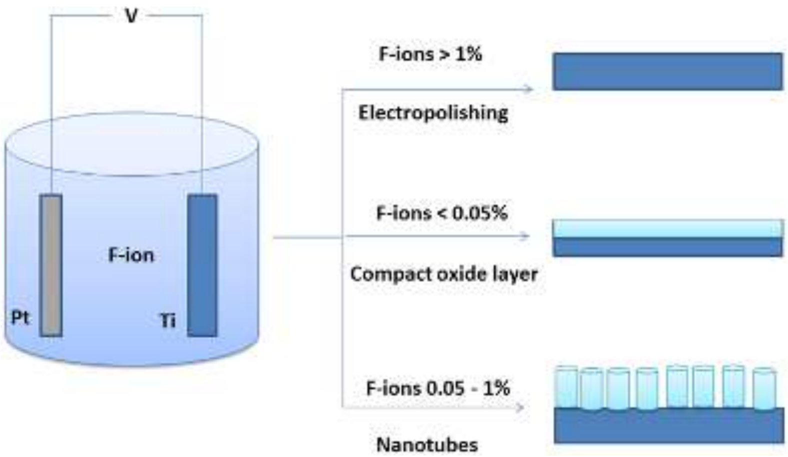

Fig. 1. Schematic illustration of set-up for anodization (left part of image) and influence of concentration F^{-}ion in electrolyte on formation oxide layer (right part of image).

It should be noticed that various advanced modifications in the tube geometry can be achieved by changing the anodization voltage during the tube growing process, and some examples are shown in Fig. 3. It has been established that the nanotubes produced in an aqueous electrolyte usually have a rough external surface and rings (ripples) on the walls because of current oscillation during anodization [11].

The as-anodized TiO_2 nanotubes are generally amorphous and the conductivity of native TiO_2 is very low, thus hampering many applications. Therefore, in recent years, many studies have focused on the modification of TiO_2 nanotubes to improve the electrical, chemical, and optical properties. The common modification methods include: (1) thermal treatment, (2) doping, (3) decoration or filling of TiO_2 NTs with other species, and (4) conversion of TiO_2 nanotubes into nanoporous $MTiO_3$ (M = Ba, Sr, Ca, Pb, Zn, etc.) or perovskite nanotubes [12].

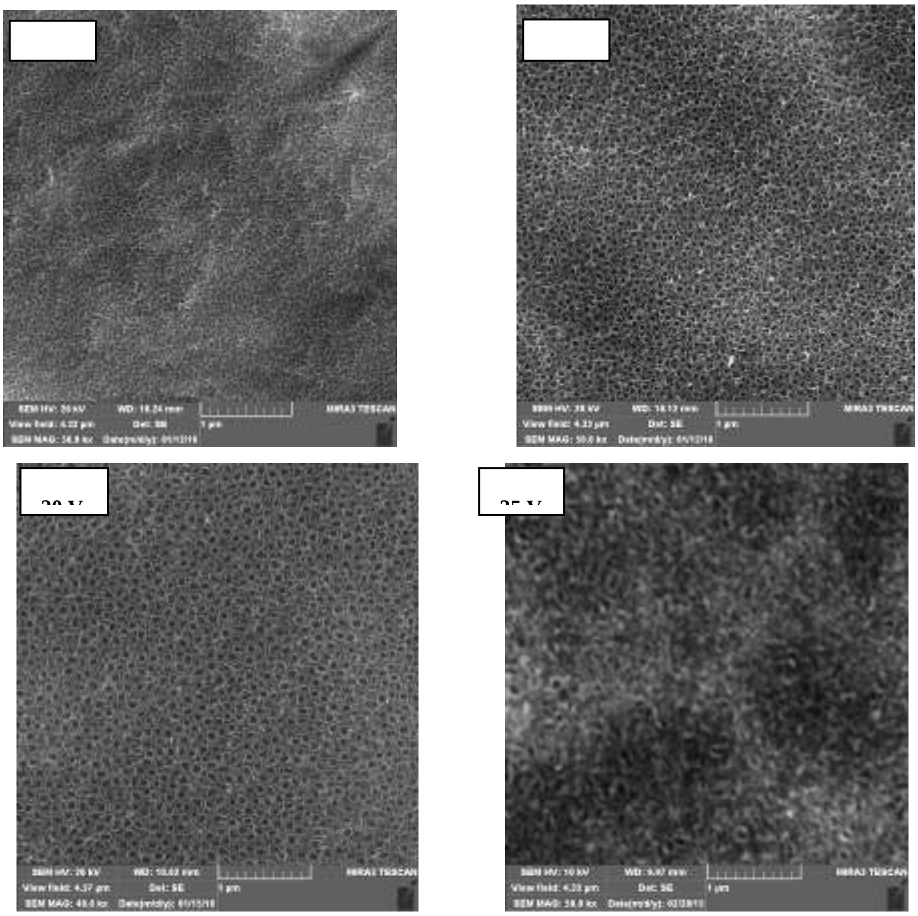

Fig. 2. SEM micrographs of influence applied voltage on diameter of nanotubes TiO_2.

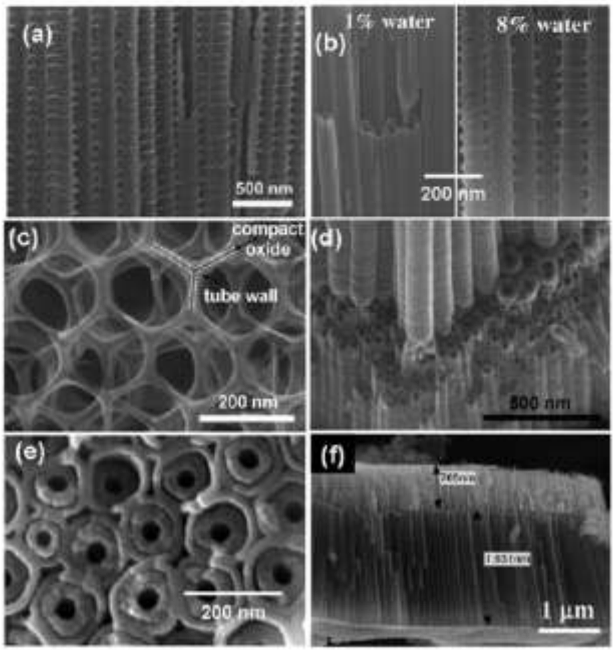

Fig. 3. Advanced TiO_2 nanotube morphologies: a) Bamboo nanotubes fabricated by alternating voltage anodization, b) smooth to bamboo-tube transition induced by variation of H_2O content in the electrolyte, c) nanolace, d) branched nanotubes by voltage stepping, e) double-walled nanotubes, f) amphiphilic double-layer tubes [11].

It is generally accepted that amorphous TiO_2 nanotubes can be fully converted into anatase TiO_2 nanotubes by using thermal treatment, at 450 °C. When the annealing temperature is higher than 500 °C, anatase and rutile phase of TiO_2 coexist. In order to improve the electrical, chemical, and optical properties of these materials, another method for modification of TiO_2 nanotubes can be used, including doping and decoration or filling of TiO_2 nanotubes with other materials. Asahi et al. reported that N-doped TiO_2 exhibited improved photoelectrochemical reactivity under visible light illumination [13]. Subsequently, other non-metals such as C, B, S, and P [14] and metals such as V, Cr, and Fe have been incorporated into TiO_2 [15]. These doped TiO_2 nanotubes usually exhibit enhanced visible light absorption and photoelectrochemical conversion efficiency or sensing performance. Typical methods for doped TiO_2 nanotubes preparation include: (1) thermal treatment of TiO_2 NTAs in a gas atmosphere containing the dopants, (2) plasma ion implantation or sputtering in an atmosphere with the doping species, and (3) Ti alloy anodization [16].

It should be mentioned that defined geometry (length and diameter) makes nanotube layers very interesting for membrane-type applications, such as filtration or microphotoreactors. The strategy to produce such membranes typically consists of the formation of a tube layer and its separation from the substrate which is followed by opening the tube bottoms. The atypical free-standing membrane is shown in Figure 4.

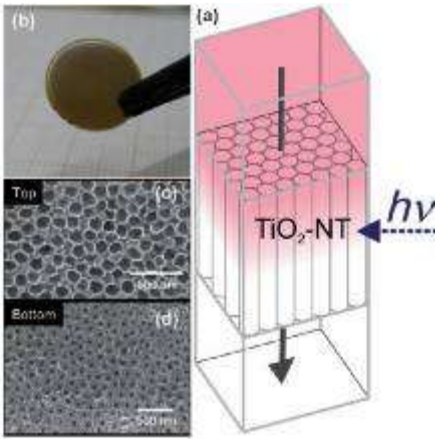

Fig. 4. TiO_2 nanotube freestanding membrane fabricated by anodization: a) flow through a membrane, b) optical image of membrane, c) SEM micrographs of membrane, top and bottom side [11].

3. NANOSTRUCTURED TiO_2 APPLICATIONS

Nanostructured TiO_2 can be used in numerous fields of agriculture, including pesticide decomposition, due to their photocatalytic properties. In the photocatalytic oxidation process, pesticides are destroyed in the presence of TiO_2 photocatalysts and a UV light source (Fig. 5).

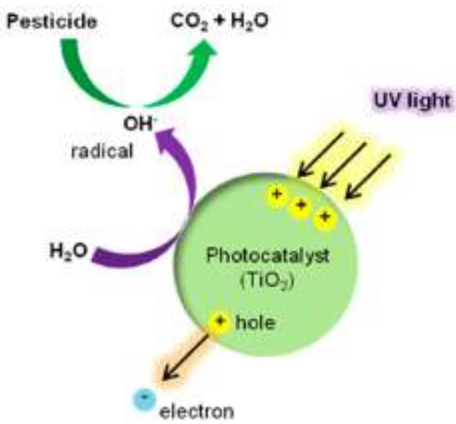

Fig. 5. Scheme of photocatalytic mechanism for pesticide degradation [19].

It was reported that a photocatalytic degradation of chlortoluron and cyproconazole pesticides on TiO_2-coated media is effective in degrading and mineralizing of pesticides

[17]. Furthermore Cedric et al. investigated the influence of TiO_2 nanotubes length on the degradation of paraquat in water. They found out that longer tubes have thinner walls and absorb on a longer distance, so pollutant has to diffuse longer, while for shorter tubes pollutant diffusion is ineffective. They reported that optimal length for photocatalysis is 7 μm [18]. Several approaches have been developed to improve the photocatalytic activity of TiO_2 nanomaterials for a wide range of applications. One effective method for improving the performance of TiO_2 nanomaterials is to increase their optical activity by shifting the response onset from the UV to the visible region by doping the TiO_2 nanomaterial with different metals or other elements.

Under light, TiO_2 nanomaterials can generate superoxide ion and hydroxyl radicals. Since it has been found that these active oxygen species are effective antimicrobial agents, the TiO_2 photocatalyst technique has a potential for crop disease control as well. Numerous investigations showed that photochemical disinfection of plant pathogens using TiO_2 thin films may offer an alternative method to conventional bactericidal methods that are used to protect plants against pathogens by applying chemical pesticides to the irrigation water. Furthermore, TiO_2 nanomaterials can be used as efficient eco-materials for water purification and heavy metal sorption. In this photocatalysis process, reactive species can be formed on the surface of a nano-TiO_2 photocatalyst that is exposed to UV radiation [19]. The complete degradation and mineralization of a large variety of organic contaminants can be achieved in most cases. TiO_2 nanoparticles have potential to be used for reducing metal uptake by agricultural crops as well. In order to minimize bioaccumulation of lead in rice, F.Cai et al. used four types of TiO_2 nanoparticles: anatase (NAnT), rutile (NRuT), rutile with a hydrophilic group (NLRuT) and hydrophobic group (NBRuT), and bulk TiO_2 (BT). Due to high sorption of NAnT, NRuT and NLRuT for Pb, it was observed that lead concentration decreases by 80% in root and by 77-97 % in the shoot, while NBRuT and BT reduce Pb for 45-61 % in roots and 11-38 % in shoots [20].

It has been also found that TiO_2 nanomaterials can induce active oxygen, including superoxide and hydroxide anions, in the photocatalytic process, which increases the seed stress resistance and water and oxygen intake [19]. As a result, these type of materials can be used for plant germination and growth. Hong et al. observed that after treating the spinach with rutile TiO_2, germination of the aged seeds is accelerated and its vigor increases. As a consequence, spinach grows faster and formation of chlorophyll is improved. Also, chloroplasts of spinach were treated with nanosized TiO_2 in order to protect chloroplasts from aging under light [21, 22]. It should be mentioned that although plants exposed to TiO_2 nanoparticles showed significant improvements in shoot length, root length, root area, and root nodules, they may be a possible threat to the terrestrial environment as well [23]. So far, toxicity testing of TiO_2 nanoparticles has been conducted on different levels of ecological complexity, from the cellular to the individual and the community level. Although most studies using TiO_2 nanoparticles have been performed in aqueous media, while only a few in the soil, changes in soil bacterial communities were found by Ge et al. and a reduction in total biomass and shifts in the community composition were shown [24]. Therefore, there is a great need for further investigation on how nanostructured TiO_2 based materials can be present in complex media, namely wheat roots, grains and the soil matrix.

Another important application of TiO_2 nanomaterials is their use for pesticide residue detection. In this field, there is an increasing interest in developing systems to sense, monitor, and remove pesticide residues, because they are toxic even at trace levels and because current pesticide detection methods based on liquid or gas chromatography coupled with mass spectrometric detection (HPLC-MS and GC-MS) require meticulous sample preparation and highly qualified technicians. Recently nano-TiO_2 semiconductors, which are efficient sorbents for enriching and detecting pesticides, have attracted significant attention in the photocatalytic and photoelectrochemical area, not only due to their nontoxicity, hydrophilicity, availability, and stability against photocorrosion, but also because of their high sensitivity, low detection limits and high selectivity [25, 26].

4. Conclusion

Future development of agro and food industries will benefit from advances of nanotechnology and nanomaterials development by increasing of soil fertility, improving crop quality and production and development of advanced multifunctional eco-materials for detection and degradation of various contaminants. In this review, we have shown potentials of nanostructured TiO_2 based materials for agricultural applications. The continuous breakthroughs in the fabrication and modifications of nanostructured TiO_2 have resulted in new properties and new agricultural applications including pesticide degradation, plant germination and growth, crop disease control, water purification, and pesticide residue detection.

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