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Methods of Titanium Dioxide Synthesis (Review)

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TiO_2-based nanomaterials are attracting much attention in many areas, such as photocatalysis, photoelectricity, probing, electrochromism, photochromism, etc. They are widely used in paints, polymers, sunscreens, and toothpaste. There are various ways of synthesis that affect the size, shape, and crystallinity of TiO_2 nanoparticles. The main methods of obtaining titanium dioxide (with the structure of anatase, rutile or brookite) in the form of spheres, rods, fibers, and tubes include: sol-gel technology, hydrothermal and solvothermal methods, microwave method involving high-frequency electromagnetic waves, template method, electrodeposition, a sonochemical method using ultrasound, chemical and physical vapor deposition, "green" methods, etc. This literature review presents modern scientific results on the production of TiO_2 nanoparticles by various methods.

Key words: titanium dioxide, sol-gel method, hydrothermal method, aquacomplex precursor, "green" synthesis, anatase, rutile, brookite, template.

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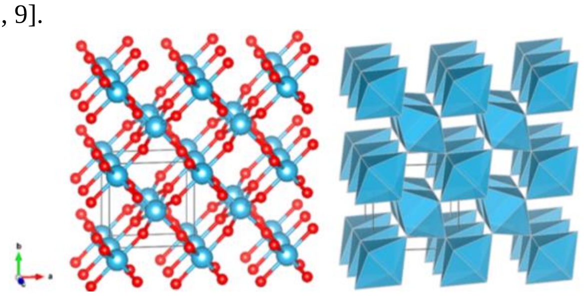
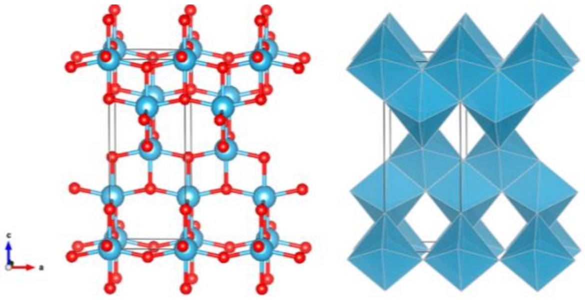
Introduction

Since Fujishima and Honda [1] in 1972 reported the photocatalytic activity of titanium dioxide (TiO_2) under the influence of UV light in water splitting reactions, TiO_2 has become one of the most effective and widely used materials in the photocatalysis [2, 3]. This discovery gave impetus to an in-depth study of the physicochemical properties of titanium dioxide, the development of methods for production of powder materials with nanosized particles, and to the search of new areas of its use [4]. TiO_2 -based nanomaterials have been widely studied in recent decades. They are widely used as pigments in paints and polymers, dental toothpaste, protection from ultraviolet radiation (sunscreen cosmetics), as well as in the photocatalysis, photoelectricity, probing, electrochromism, photochromism, etc. [5-7].

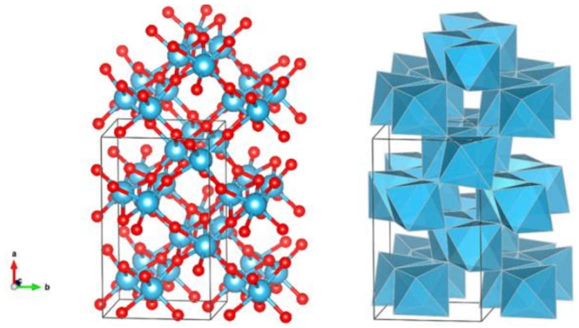
TiO_2 is a very important nanomaterial that attracts a lot of attention due to its unique properties. It has huge advantages in the transmission of solar energy, the production of hydrogen from water via photochemical reactions, and as photocatalyst for toxic compounds degradation. The strong oxidizing ability of photogenerated holes, chemical inertness, and non-toxicity of TiO_2 made it an excellent photocatalyst [5]. Titanium dioxide exists in three main polymorphic modifications: anatase, rutile, and brookite (Fig. 1 [8]). The phase stability under different conditions (temperature, pressure, and medium) is a key to the use of titanium dioxide-based materials [8]. The physical and chemical properties of the material may be completely different for different crystalline forms of TiO_2. The phase of brookite is practically not favorable for various applications. It is unstable at room temperature, but it can exist at low temperatures. The rutile is the most stable phase of titanium dioxide and the most commonly used form, in particular as a white pigment in paint. TiO_2, which is used as a photocatalyst, mainly has a crystalline structure of the anatase type (the band gap is 3.2 eV) [5, 8, 9].



Rutile



Anatase



Brookite

Fig. 1. Structural modifications of TiO_2 [8].

There are a large number of synthesis methods of nanostructured titanium dioxide: sol-gel, hydrothermal, solvothermal, liquid-phase low-temperature, microwave, template, chemical vapor deposition, sonochemical, electrodeposition, etc. Therefore, the aim of this article was to study and summarize the modern scientific results in the field of titanium dioxide by various methods.

I. Sol-gel method

The sol-gel method is a universal process used in the production of various ceramic materials. In a typical sol-gel process, a colloidal suspension or sol is formed by hydrolysis of precursors and their polymerization. The precursors usually are salts of inorganic metals or metallic organic compounds, such as metal alkoxides. Complete polymerization and loss of solvent lead to the transition of the liquid sol into the solid gel. Thin films can be made on a piece of the substrate by squeezing or dipping. The wet gel is formed when the sol is cast into a mold, then it turns into a dense ceramic with subsequent drying and heat treatment. A material with high porosity and extremely low density is called an aerogel. It can be obtained if the solvent in the wet gel is removed below the supercritical state. Ultrathin and homogeneous ceramic powders are formed by precipitation, spray pyrolysis, or emulsion method [9].

The sol-gel method of titanium dioxide obtaining combines the processes of chemical conversion of titanium salts or organotitanium substances solutions into monomeric titanium hydroxide $Ti(OH)_4$ and its subsequent polycondensation with the formation of colloidal particles [10-17]. In comparison with other methods, sol-gel technologies make it possible to influence the structure and morphology of TiO_2 particles, optimize energy costs, as well as use simple and affordable technological equipment [4].

At the stage of structural ordering and primary particles growing, the coagulation processes take place. They leads to the agglomeration and aggregation of primary particles. The speed of these processes affects the dispersion of particles, their morphology, and the texture of the whole material. The rate of nucleation and formation of nucleuses exceeds the rate of particles growth if there is a supersaturation of the reaction medium. Under such conditions, a metastable, insufficiently structured material with a large number of small particles is formed. When the gel is dried by evaporation, its volume decreases by an amount corresponding to the volume of removed water. The compression of the gel is accompanied by its restructuring mainly due to the reduction of the large pores volume. This causes significant stresses in the gel volume and its cracking. To prevent cracking the extraction of water from the gel volume is carried out, for example, by freezing (sublimation) or in supercritical conditions, because under such conditions the surface tension of water disappears [4].

In [11], the optical properties and structural characteristics of the synthesized TiO_2 nanocomposite, decorated with multiwall carbon nanotubes, are studied. The anatase TiO_2 nanoparticles were synthesized by the sol-gel method. First, 20 ml of titanium isopropoxide was added to 40 ml of acetic acid and stirred on a magnetic stirrer for 15 minutes to obtain a homogeneous solution. Then 120 ml of deionized water was added to the solution dropwise and stirred for 2 hours. The gel was formed when the solution was placed in an oven at 90 °C for 12 hours. The yellow powder was obtained by drying the gel at a temperature of 200 °C for 2 hours. Then the powder was ground in a porcelain mortar and calcined at 400 °C for 4 hours. For the synthesis of TiO_2 nanocomposite decorated with carbon nanotubes, 20 ml of deionized water was added to 0.01 g of multiwall carbon nanotubes and placed under ultrasonic waves for 30 minutes. Separately, 0.04 g of TiO_2 nanoparticles were added to 20 ml of deionized water and stirred with a magnetic stirrer for 15 minutes, and then added to the

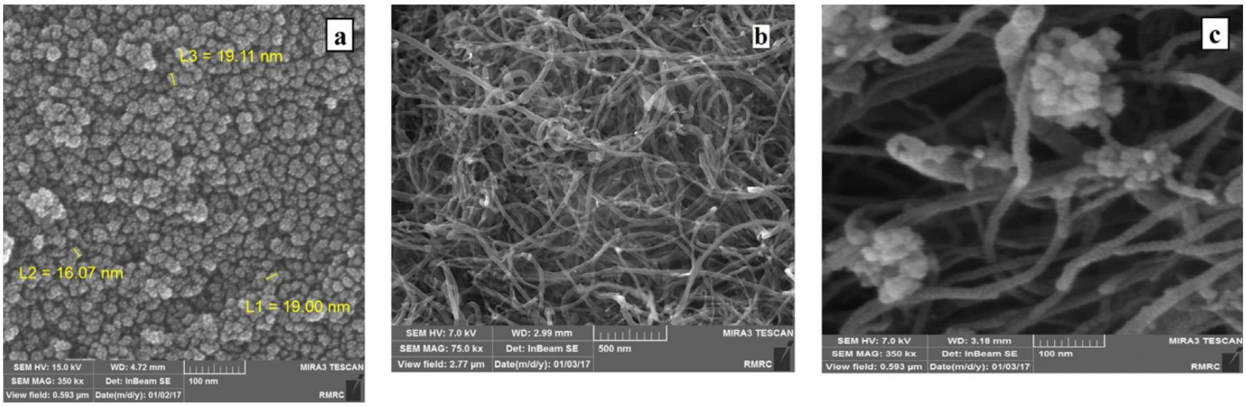


Fig. 2. FESEM-image of TiO_2 nanoparticles (a), pure carbon nanotubes (b) and TiO_2 nanocomposite decorated with carbon nanotubes (c) [11].

solution of carbon nanotubes under ultrasound for 15 minutes. Finally, the mixture was stirred with a magnetic stirrer for 18 hours, then centrifuged and the precipitate was dried in an oven at 50 °C for 2 hours. Fig. 2 shows the FESEM-images of the synthesized samples.

The authors of work [12] used a sol-gel method in order to synthesize samples of nanosized titanium dioxide at different pH (pH = 3; 7; 8; 9 and 10). Titanium tetrabutoxide $Ti(C_4H_9O)_4$, ethanol (95%), and distilled water in a volume ratio of 1:1:4 were used as precursors. The pH is controlled by HCl and NH_4OH addition. The TiO_2 synthesis was carried out according to the following scheme: $Ti(C4H_9O)_4$ was mixed with ethanol to a homogeneous state in a mixing device for 10 minutes, then distilled water was added and stirred again for 10 minutes. Then NH_4OH was added in the amount required to achieve the desired pH, followed by stirring for 60 minutes. The parameters of PE-6300 M at all stages were the same: substrate temperature 60 °C, power 80 W, rotation speed 26 rpm. The resulting gel was dried in a SNOL oven for 60 minutes for temperatures of 8 °C. The synthesized TiO_2 powders were annealed in a SNOL muffle furnace for 4 hours for temperatures of 350 °C. X-ray diffraction patterns showed the crystal structure of anatase in an acidic medium even without annealing and an amorphous structure in neutral and alkaline media. The particle size was in the range from 7 to 49 nm.

In work [13], the effect of annealing temperature on the structural and electronic properties of TiO_2-based films was investigated. Pure anatase TiO_2 was obtained by sol-gel method with the addition of Pluronic F127 at pH 3. The follow precursors have been used for the synthesis: $TiCl_4$, Pluronic F127 - (PEO) 100 (PPO) 65 (PEO) 100, and ethanol. 6 g of Pluronic F127 was dissolved in 76 ml of ethanol, then 3.5 ml of $TiCl_4$ was added to obtain a molar ratio of Pluronic F127:ethanol:$TiCl_4$ = 1.0:0.41:21.7 to obtain a pH = 3. The solution was heated at 40 °C for 7 days for the aging process to obtain a gel. The reaction was carried out at room temperature with stirring. The large amount of Cl_2 and HCl gases are formed during the reaction. The gel was then calcined at 500 °C, 550 °C, and 600 °C for 4 hours at a heating rate of 5 °C/min. It was found that the higher the calcination temperature, the larger the size of anatase crystallites is formed (up to 15 nm).

In a study [15], anatase TiO_2 nanopowder was synthesized by a simple sol-gel method. Titanium tetraisopropoxide – $Ti(C_3H_7O)_4$ was used as a precursor. An acidic aqueous ethanol solution (pH~1.6) of titanium tetraisopropoxide was prepared by adjusting the pH with HCl. 5 ml of the titanium precursor was added dropwise to 30 ml of ethanol over 15 minutes with stirring. The resulting solution was stirred for 2 hours at room temperature. Next, the temperature was raised to 125 °C and kept at 125 °C for one hour. The prepared sol-gel was heated at 300 °C for 2 hours in the air. After annealing, white TiO_2 nanocrystals were obtained. The average size of the crystallites was 7.5 nm. SEM images (Fig. 3) showed a particle size of 35 - 40 nm.

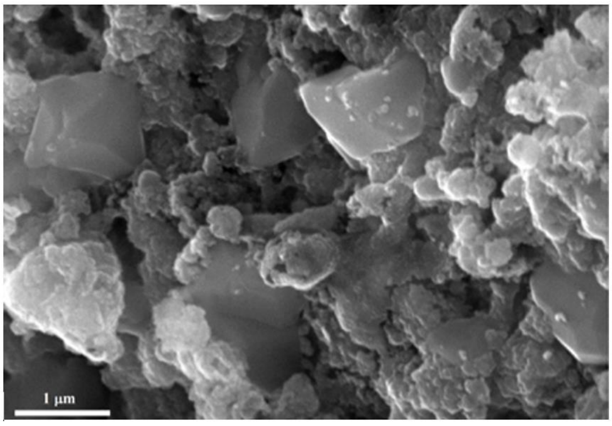


Fig. 3. SEM images of TiO_2 nanoparticles [15].

The authors of work [16] synthesized titanium dioxide thin films by the sol-gel method. Titanium tetraisopropoxide $Ti(OCH(CH_3)_2)_4$, ethanol and nitric acid were used as precursors. 10 ml of a titanium precursor was added to 40 ml of ethanol and stirred constantly under heating. In another beaker, 10 ml of HNO_3 solution and 40 ml of double-distilled water were prepared and stored with constant stirring at 80 °C. After 1 hour, the diluted HNO_3 solution was added dropwise to the precursor solution (1 drop for 3 s) and kept under constant stirring at 60 °C for 6 hours. A very viscous gel was obtained, which was washed with ethanol up to 3 - 4 times. The obtained product was kept at a temperature of 150 °C for 24 hours in an oven, which led to the

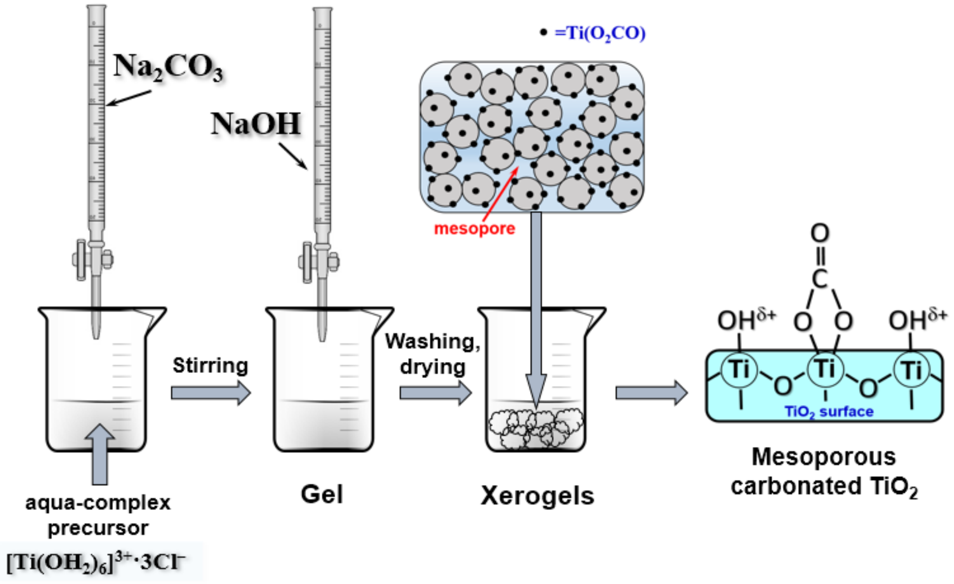


Fig. 4. Schematic diagram of the synthesis of carbonate TiO_2 with mesoporous structure [20].

formation of solid white agglomerations. They were further ground in order to obtain a fine powder. The powder was then calcined at 450°C for 2 hours to form a nanocrystalline TiO_2 powder. The average crystallite size is 10.56 nm.

The authors in [18-20] obtained anatase TiO_2 NPs with a mesoporous structure, modified by arsenate [18], phosphate [19] and carbonate [20] groups. The liquid-phase low-temperature method (modified sol-gel method) was used for the synthesis. Titanium aquacomplex precursor $[Ti(OH_2)_6]^{3+}\cdot 3Cl^-$ was obtained from titanium tetrachloride $TiCl_4$ and concentrated hydrochloric acid. The cooled to a $0 \div -5$ °C hydrochloric acid was poured in small portions into $TiCl_4$ under continuous stirring. The mass ratio between $TiCl_4$ and acid was 1.4:1.0. The formation of titanium aquacomplex precursor occurs by the reaction: $TiCl_4 + 6H_2O = [Ti(OH_2)_6]^{3+}\cdot 3Cl^- + ½\ Cl_2$. The originality of this study lies in the use of the aquacomplex of titanium $[Ti(H_2O)_6]^{3+}\cdot 3Cl^-$ as a precursor, which allows to obtain TiO_2 nanoparticles by liquid phase with unique physicochemical properties. The introduction of the modifier Na_3PO_4 [19], Na_2CO_3 [20], or Na_3AsO_4 [18] in the aquacomplex precursor changes the reaction equilibrium and causes the oxidation of Ti^{3+} cations. The amount of modifying component (Na_3AsO_4, Na_3PO_4, or Na_2CO_3) was 2, 4, and 8 % (wt.). Its peculiarity of the process of TiO_2 particles growth is that the chemisorbed groups are oriented on the primary particles surface. Due to that, the pores are formed between the particles and the surface area and pore volume in TiO_2 adsorbents increase. It was found that the introduction of 4 % (wt.) of PO_4^{3-}, CO_3^{2-}, AsO_4^{3-} anions in TiO_2 led to an increase in the mesopores number in the titanium oxide adsorbent. This increases the binding efficiency of heavy metal ions, in particular strontium ions, and increase the adsorption potential of the surface-active centers. The schematic diagram of the synthesis of TiO_2 with chemisorbed carbonate groups is shown in Fig. 4.

The synthesized phosphated TiO_2 adsorbents showed S_{BET} = 396 – 410 $m^2\cdot g^{-1}$ and the volume of mesopores were 0.262 - 0.275 $cm^3\cdot g^{-1}$. Arsenated TiO_2 samples have a large specific surface area up to 405 m^2/g and a pore volume of up to 0.26 cm^3/g with the main contribution of mesopores. The adsorption of Sr(II) on the modified samples 2P-TiO_2, 4P-TiO_2, and 8P-TiO_2 was found to be 94.1, 172.5, 128.9 mg/g, respectively. The adsorption capacity of the modified samples 2C-TiO_2, 4C-TiO_2 and 8C-TiO_2 was 170.4, 204.4, 190.8 mg/g, respectively, while for unmodified TiO_2 it was 70.9 mg/g. The maximum adsorption capacity of modified TiO_2 with arsenate groups of 4% (wt.) is equal 262.9 mg of Sr(II) ions per 1 g of the adsorbent. It has been experimentally proven that mesoporous materials based on modified titanium dioxide have a significant adsorption activity due to the high content of Bronsted surface acid centers. It has been shown that phosphate groups $=Ti(O_2POOH)$ and $\equiv TiOH^{\delta+}$ groups are active centers in Sr(II) binding. They transformed into negatively charged centers $=Ti(O_2POO^-)$ and $\equiv TiO^-$ in the medium with $pH>pH_{PZC}$. The results confirmed that an increase in the number of chemisorbed groups leads to an increase in the TiO_2 activity towads to strontium adsorption. Synthesized TiO_2 adsorbents can be used in sorption technologies for radioactive waste concentrating at nuclear power plants, for purification of artesian water from strontium ions, uranium, and transuranic elements.

II. Hydrothermal method

Hydrothermal synthesis is usually carried out in aqueous solutions at controlled temperature and/or pressure in steel vessels, called autoclaves. The temperature can be raised above the boiling point of water, reaching the vapor saturation pressure. The temperature and amount of solution added to the autoclave largely determine the internal pressure. This method is widely used for the production of fine particles in the ceramic industry [5]. Many researchers use the hydrothermal method to produce TiO_2 nanoparticles [21-27].

In work [21], titanium dioxide was synthesized by hydrothermal treatment of the glycolate-oxo-peroxo-titanium (IV) complex. 20 mmol of titanium metal powder was dissolved in a mixture of 40 ml of hydrogen peroxide solution and 10 ml of ammonia solution in an ice bath under ambient conditions. The titanium powder was completely dissolved after 2 hours and a yellow solution of the peroxo-titanium complex was formed. Then immediately added 30 mmol of glycolic acid and the solution was heated at 353 K to enhance complexation and remove excess of hydrogen peroxide and ammonia until the solution turned into an orange gel-like substance. It was dissolved in distilled water in order to obtain an aqueous solution of ammonium salt of glycolate-oxo-peroxo-titanium (IV) complex. In the next step, 40 cm^3 of titanium solutions with a concentration of Ti = 12.5, 25.0, 50.0, 75.0, and 100 mM were prepared using 2, 4, 8, 12, and 16 cm^3 of stock solution and the appropriate amount of distilled water. The solution was transferred into a vessel (50 cm^3), which was closed in a stainless steel casing and heated in an oven at a temperature of 473 K for 1 - 168 hours The autoclaves were then cooled to room temperature. The resulting precipitate was separated by centrifugation and washed three times with distilled water. The sample was obtained after drying overnight in an oven at 353 K. Table 1 shows the particle sizes of TiO_2 polymorphs in the samples, obtained from a Ti complex solution with a concentration of 50.0 mM depending on process duration.

Table 1

Particle sizes of TiO_2 polymorphs [21]

Processing time, hours	Crystal size, nm		
	anatase	brookite	rutile
2	4.9	7.7	29.1
3	5.7	9.7	34.8
12	8.6	14.0	51.7
24	10.0	15.6	57.4
72	12.9	19.8	63.7
168	16.6	23.5	67.2

In a study [23], the authors successfully grew nanocrystalline TiO_2 nanorods using a hydrothermal process. The tetrabutyl orthotitanate was mixed with the same amount of acetylacetone to slow hydrolysis and condensation. After that, 40 ml of water was slowly added to the solution and stirred for 5 minutes at room temperature. After constant stirring, 30 ml of aqueous ammonia solution (28 - 30 %) was slowly added dropwise to the solution. The solution was then transferred to a 250 ml stainless steel autoclave and placed in a silicone oil bath. Next, the precursor solution was heated to a temperature of 170 °C and kept for 24 hours with stirring at the same temperature. The autoclave was then cooled naturally to room temperature. The resulting product was washed thoroughly with aqueous HCl, 2-propanol, and water for several times, followed by drying at 120 °C for 12 hours. Finally, the obtained samples were calcined at 450 °C for 1 hour in a high-temperature furnace. X-ray analysis of the samples confirmed a larger proportion of the anatase nanorods with a specific surface area of approximately 34.82 m^2/g and an average pore width of 3.1 nm.

Using the same technology in another study [24], the authors synthesized TiO_2 nanorods/nanoparticles by the hydrothermal method in order to improve the charge transport properties. The specific surface area of the synthesized nanoparticles was 84.83 m^2/g and the pore width was 5.7 nm.

III. Solvothermal method

The solvothermal method is a hydrothermal process in the presence of a non-aqueous solvent. Therefore, in the solvothermal process, organic solvents that have high boiling points can be selected. In such processes, the temperature can be raised much higher than in hydrothermal methods [5]. The solvothermal method can be used to control the size, shape, and crystallinity of TiO_2 nanoparticles [28-32].

In work [28], the titanium dioxide nanoparticles with different morphology were obtained by the solvothermal method at 180 °C. Acetic acid and oleylamine were used as surfactants. Titanium isopropoxide was added to a mixture of acetic acid and absolute ethanol and stirred for 1 hour at room temperature. The suspension was converted (transmuted) in a stainless steel autoclave. The reaction was carried out at a temperature of 180 °C for 24 hours to obtain a monodisperse titanium dioxide powder, which was cooled under ambient conditions. The solution was then centrifuged at 12,000 rpm/min and washed three times with ethanol. The resulting precipitate was dried under ambient conditions and very finely ground. Finally, the dried TiO_2 powder was calcined at 550 and 950 °C for 18 and 24 hours, respectively. The physical and structural properties of the synthesized mesoporous TiO_2 nanoparticles are shown in Table 2.

Table 2

Physical and structural properties of TiO_2 nanoparticles synthesized using acetic acid and oleylamine as surfactants [28]

Temperature (°C)	Phase	The average size of the crystallite (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
unannealed	anatase	15	192.08	0.43	4.46
550	anatase	25	103.63	0.33	6.30
950	rutile	35	35.37	0.18	10.02

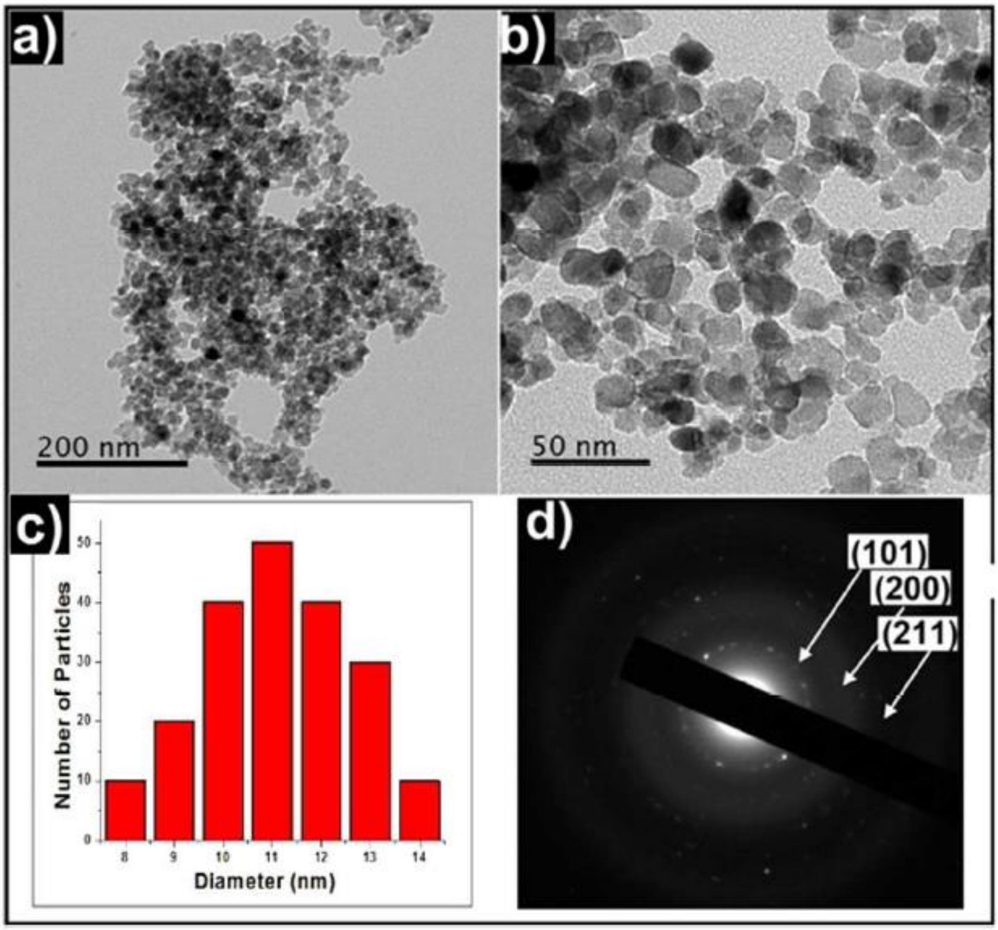


Fig. 5. TEM image (a, b), particle size distribution (c) and SAED (d) of TiO_2 NPs [31].

The authors [29] obtained TiO_2 powders by the solvothermal method. Samples were prepared using titanium(IV) n-butoxide and ethyl acetoacetate. The isopropyl alcohol was used as a solvent. Two samples were prepared, with and without ethyl acetoacetate, denoting THC and THN, respectively. First, an amount of 0.1 mol (13.1 g) ethyl acetoacetate (THC sample only) was added to 0.5 mol (30.4 g) of solvent. Then 0.1 mol (35.1 g) of titanium (IV) n-butoxide was dissolved in a solution of solvent/ ethyl acetoacetate. Titanium (IV) n-butoxide was added to the solution using a syringe to minimize the effects of humidity. The mixture was stirred in a closed reactor at room temperature. After 1 hour, a solution consisting of 0.2 mol (12.1 g) of isopropanol and 0.5 mol (9.0 g) of water was added dropwise to the mixture and further stirred for 1 hour in a closed reactor at room temperature. The mixture was then transferred to a stainless steel autoclave and sealed when the reaction proceeded at a temperature of 150 °C. After 24 hours, the autoclave was cooled to room temperature and the synthesized powders were separated by decantation and dried at room temperature. The anatase crystallites' size was less than 10 nm.

In another study [31], the solvothermal synthesis of a thermoresistance photocatalyst TiO_2 was performed using titanium(IV) butoxide as a precursor and dimethyl sulfoxide (DMSO) as a solvent. For the synthesis of TiO_2 NPs, the 5 ml of titanium (IV) butoxide was dissolved in 50 ml of dimethyl sulfoxide, heated to 190 °C and kept at this temperature for 2 hours with mechanical stirring. After completion of the reaction, the precipitate was centrifuged, washed several times with ethanol/acetone (2:1) solution, and then dried in vacuum at 50 °C for 12 hours. The resulting white dry TiO_2 powder was calcined at 400 °C. Subsequent annealing of TiO_2 NPs after solvothermal treatment induces crystallinity and completely removes solvent molecules that are trapped inside the particles. The results showed that monodisperse quasi-spherical TiO_2 NPs (average size 11 nm) (Fig. 5) consisted of a pure anatase phase.

IV. Microwave method

The dielectric material can be processed by the high-frequency electromagnetic energy. The frequencies of microwave heating are between 900 and 2450 MHz. At lower microwave frequencies, the current, flowing inside the material due to the movement of ionic components, can transmit energy from the microwave field to the material. At higher microwave frequencies, the energy absorption occurs primarily due to dipole molecules, which are reoriented under the influence of a microwave electric field [5]. The microwave synthesis method is used to obtain various TiO_2 NPs [33, 34].

Fig. 6. Scheme of the microwave synthesis of rutile TiO_2 [34].

In [34], the rutile TiO_2 powder was prepared from titanium slags by microwave activation (Fig. 6), and the effect of Na_2CO_3 additive on crystallinity, phase transformation, surface functional groups and surface microstructure of the calcined product was studied. The composition of titanium slag is the follow: 75.34 % TiO_2, 9.72 % Fe, 5.87 % Al_2O_3, 5.23 % SiO_2, 1.23 % MgO, 1.81 % CaO and other minor elements, such as S and P. In order to increase the specific surface area of the slag, the sample was first ground into powder by a planetary ball mill (model: QM-3_{SP}4) for 180 minutes Then, 100 g of the prepared titanium slag sample was equally separated into five parts, which were separately mixed with Na_2CO_3 in an agate mortar for 10 minutes. The mass ratio of Na_2CO_3 to titanium slag for mixtures was 0.2, 0.3, 0.4, 0.5, and 0.6, respectively. The mixture was then placed in a corundum crucible for high temperature roasting in a microwave box reactor at 850 °C for 30 minutes with a microwave heating power of 1 kW. 10 g of calcined slag was leached at a temperature of 92 - 95 °C for 4 hours using 20% HCl (mass ratio of liquid/solid – 4:1) using a magnetic stirrer. The residue after leaching was collected after washing three times with water and placed in a corundum crucible for high-temperature annealing in a microwave box reactor at 900 °C for 60 minutes with a microwave heating power of 1 kW. After that, the calcined product was cooled and used for analysis. The results showed that the optimal mass ratio of Na_2CO_3 was 0.4, at which the crystallinity of rutile TiO_2 reached highest value (99.21 %), and the average crystallites size was 43.5 nm.

V. Template method

The template method applies for the production of titanium dioxide in the form of nanorods, nanotubes, or porous materials with one-dimensional pores, oriented in one direction. The synthesis of such materials is carried out in the pore volume of template, which has a porous structure, using liquid-phase sol-gel technology for the TiO_2 deposition [4, 35-40].

In the work [36], the mesoporous TiO_2 nanoparticles were synthesized using a soft template method from titanium isopropoxide. Various molecules of cationic surfactants, such as CTAB (cetyl trimethylammonium bromide), SDS (sodium dodecyl sulfate), and DTAB (dodecyl trimethylammonium bromide), were used as templates. P25, a commercial TiO_2 powder with a crystallite size of 21 nm, was used as reference. The determined mass of CTAB (3.64 g) was dissolved in deionized water/ethanol mixture in a volume ratio of 4:1. The 14.31 ml of titanium isopropoxide was continuously added dropwise to this solution and stirred vigorously. Then the resulting gel was stirred continuously for several hours. The precipitate was separated by centrifugation. The resulting powder was calcined for 2 hours at 450 °C to remove the soft template and to increase the crosslinking of the inorganic base. The same procedure was followed for the mesoporous TiO_2 synthesis with SDS and DTAB as templates. The size of the synthesized nanoparticles of TiO_2 was 10 - 14 nm (Fig. 7).

The hollow fibers of titanium dioxide were synthesized by the template method using natural kapok fibers as a template in [37]. Titanium (IV) butoxide (3 ml) was slowly added to 150 ml of ethanol with vigorous stirring. The mixture was stirred for 1 hour at room temperature. The dried kapok fibers (1 g) were immersed in the mixture for 3 hours and then dried at room temperature for 24 hours. It was then calcined to remove the template and convert the titanium precursor, adsorbed on the hood surface, into TiO_2. The calcination temperature was 450 °C, 550 °C, 650 °C and 750 °C for 2 hours and then the samples were naturally cooled to room temperature. SEM images of the synthesized hollow fibers are shown in Fig. 8.

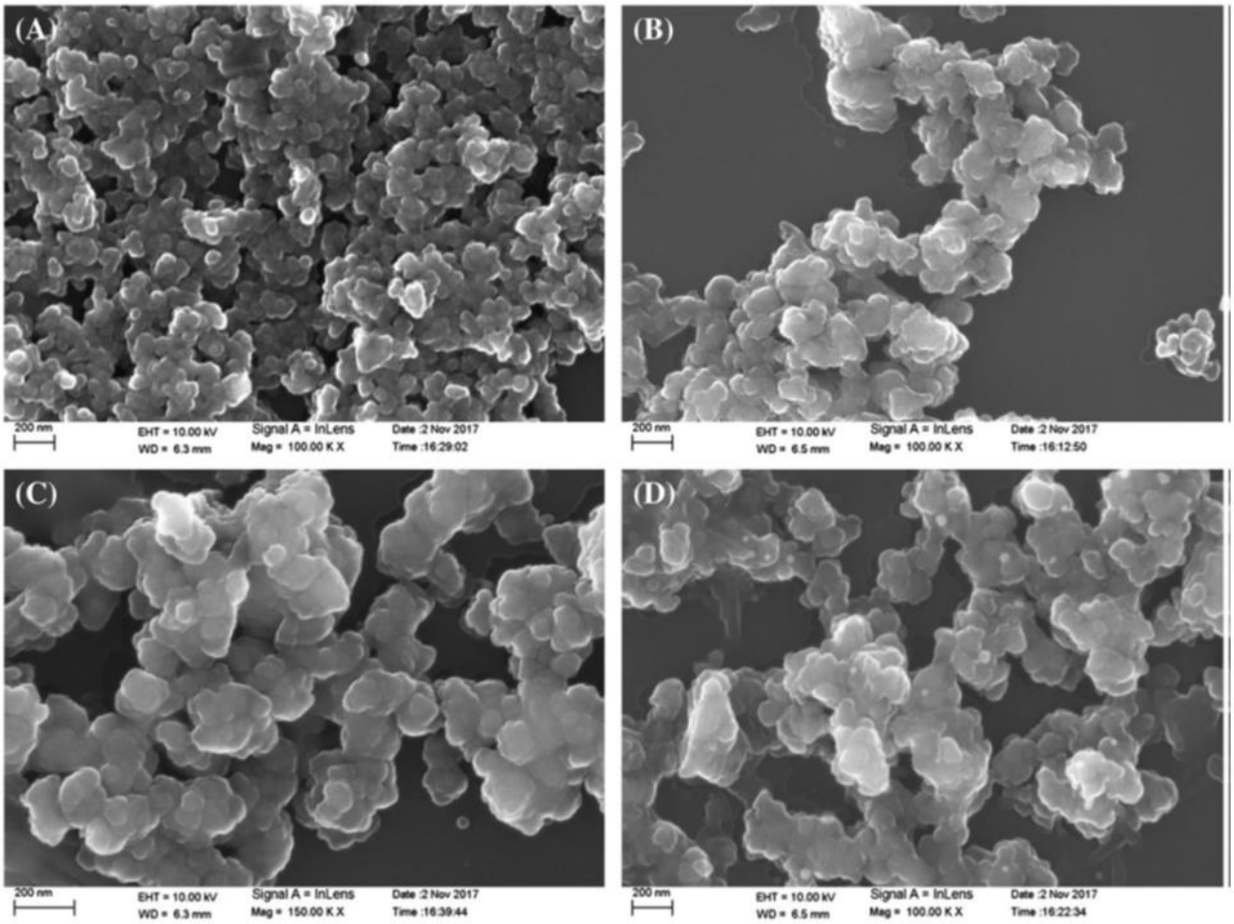


Fig. 7. FESEM-image of mesoporous TiO_2 nanoparticles: a) P25; b) P25+CTAB; c) P25+SDS; d) P25+DTAB [36].

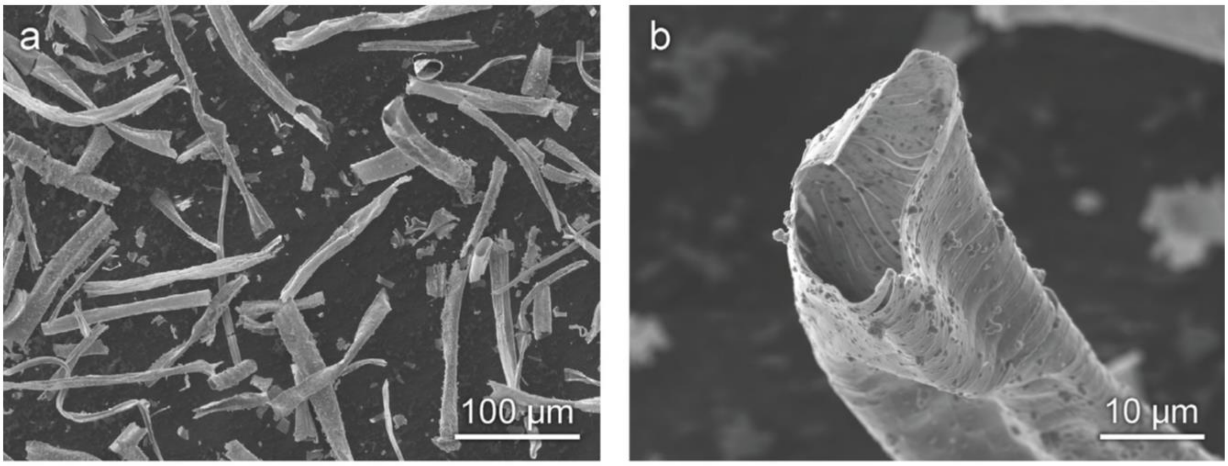


Fig. 8. SEM image of hollow TiO_2 fibers calcined at 450 °C [37].

In work [40], the monodisperse-porous magnetic microspheres of titanium dioxide (Fig. 9) with a size of 5.5 µm were obtained by the sol-gel template method using poly(HPMA-Cl-co-EDMA) magnetic microspheres as a template. In the first stage, the $TiO_2{\cdot}nH_2O$ nanoparticles were obtained by hydrolysis of the $TiCl_4$ precursor in an aqueous medium (60 ml, 0.1 M). Then the magnetic microspheres of polymethacrylate (0.4 g) were dispersed in the precursor solution and mechanically stirred at 250 rpm/min at room temperature for 24 hours. The magnetic microspheres of polymethacrylate, in which $TiO_2{\cdot}nH_2O$ nanoparticles were adsorbed, were washed with distilled deionized water. In the second stage, the magnetic microspheres were treated with a ammonia solution (60 ml, 1 M) containing hexadecyltrimethylammonium bromide (0.3 g), by mechanical stirring at 250 rpm/min at room temperature for 6 hours. $TiO_2{\cdot}nH_2O$ nanoparticles were deposited in the pores of the polymethacrylate magnetic microspheres, forming magnetic titanium-polymer

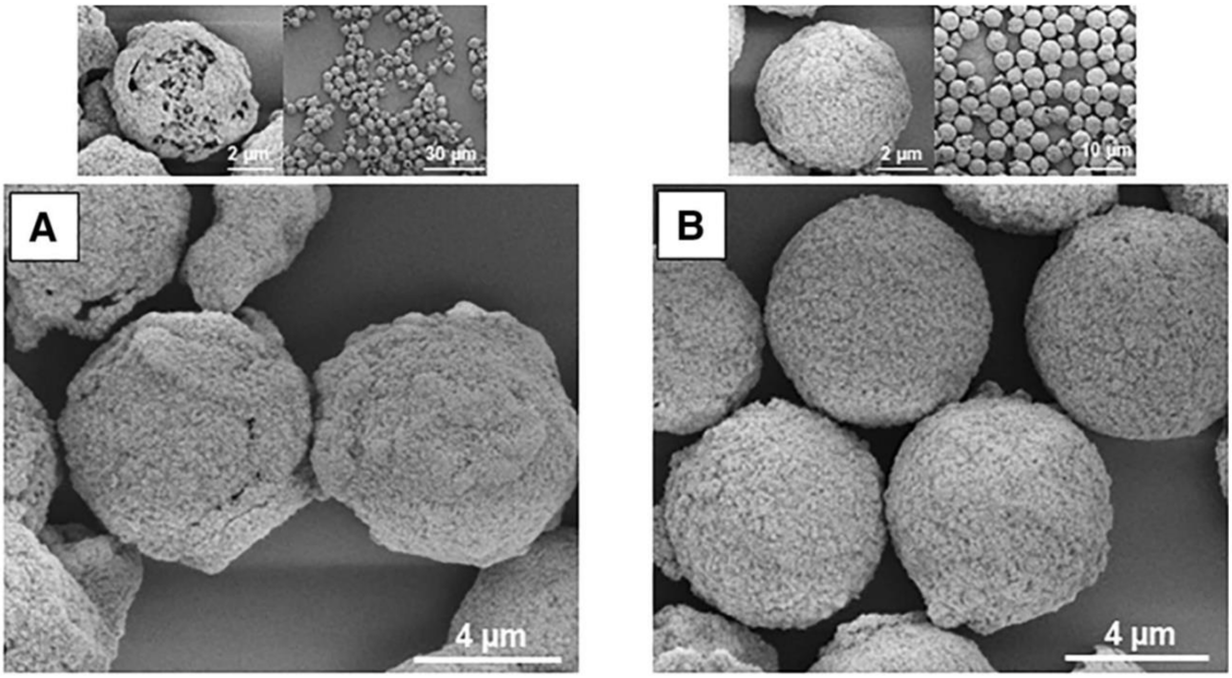


Fig. 9. SEM-image of TiO_2 magnetic microspheres with magnetization of 16.3 emu/g (a) and 5.3 emu/g (b) [40].

composite microspheres. The composite microspheres were washed with distilled deionized water in order to remove the excess of chloride ions. Then samples were dried at a temperature of 70 °C in vacuum for 12 hours and then the polymer template was removed by calcination at 450 °C.

VI. Chemical vapor deposition method

The vapor deposition method refers to any process in which materials in the vapor state is condensed to form a solid material. These processes are usually used to form coatings in order to change the mechanical, electrical, thermal, and optical properties, corrosion resistance, and wear resistance of various substrates [5]. Recently, these methods are widely studied for the production of various TiO_2-based nanomaterials. The vapor deposition processes usually take place inside the vacuum chamber. If there is no chemical reaction, this process is called physical vapor deposition (PVD). Otherwise, it is called chemical vapor deposition (CVD) [41-45].

In work [41], the CVD-method was used to synthesize the pure anatase on glass substrates. A precursor solution (150 ml) was prepared by dissolving of acetylacetone (0.9 ml) and titanium tetraisopropoxide (0.9 ml) in water and methanol. In order to study the effect of water to methanol ratio on the structural, optical and photocatalytic properties of TiO_2 films, the volume ratio of water to methanol was set as 0 %, 1 %, 5 %, 10 % and 20 % for comparison. During the process of chemical vapor deposition from the precursor solution, mist droplets are formed by ultrasonic atomization at 2.4 MHz and transferred to the reaction chamber using N_2 gas as carrier. Thick TiO_2 films (300 nm) were deposited on glass substrates, which were placed in a reaction chamber and heated to a temperature of 400 °C during the deposition process.

In a similar study [42], thin films of TiO_2 (anatase phase) with a thickness of 300 nm were deposited on a quartz glass substrate by CVD-method. The precursor solution was prepared by dissolving titanium tetraisopropoxide in ethanol. The concentration of titanium tetraisopropoxide was 0.10 mol/L. The solution was atomized by ultrasound using ultrasonic transducers (2.4 MHz) and the precursor droplets were transferred to the reaction chamber using compressed air as a carrier and dilute gas. The substrate was placed in a reaction chamber, which was heated and kept at a temperature of 400 ºC. To study the thermal stability, the precipitated TiO_2 films were calcined in the temperature range of 600 - 1100 ºC in pure oxygen medium (1 bar) for 1 hour in an oven for rapid thermal annealing. The leaf-like grains were observed in the obtained TiO_2 thin film. The transformation of anatase to rutile took place at an annealing temperature of 1100 ºC. It was found that the leaf-like grains, the small size of the crystallites and the absence of faces (112) contribute to the high-temperature stability of TiO_2 films.

In a study [43], carbon-based TiO_x-DLC coatings were prepared on silicon substrates using a capacitively coupled radiofrequency (RF, 13.56 MHz) of plasma discharge in a vacuum system. The substrates were sonicated in an acetone bath and placed on a water-cooled radiofrequency electrode. The vacuum chamber was pumped to a base pressure of 2 Pa. Before the deposition process, samples purified and activated by Ar-ion sputtering in a high-frequency plasma discharge for 10 minutes with a negative self-deflection of 1100 V and a residual pressure of 4 Pa. The deposition was performed at a negative self-deflection of 400 V, a pressure of 20 Pa, and three combinations of CH_4 and $Ti[OCH(CH_3)_2]_4$ atmospheres. The bubble with liquid titanium precursor was heated to a temperature of 80 ºC. Titanium(IV) isopropoxide vapors were transferred to the deposition chamber using a shower (copper tube with a diameter of 6 mm), bent in a circle with a diameter of 100 mm, and placed at a height of 50 mm above the top of the electrode. The flow of methane was controlled by a mass flow meter, while the flow of titanium(IV) isopropoxide was controlled by a needle valve. All processes were performed at once for 2 minutes. The proposed technology allows us to obtain a coating of TiO-DLC with a concentration of Ti up to 10 at %.

In work [45], a study of the electrophoretic transfer of TiO_2 nanoparticles (which are internally charged through thermal emission) under uniform electric fields is presented. The nanoparticles are released by means of support supported by flame burners of pre-mixed low pressure at the geometric point of stagnation from the corresponding organometallic vapor of the precursor (Fig. 10).

The precursor of titanium tetraisopropoxide evaporates and enters the carrier gas through a heated and temperature-controlled bubble device, then combines with flammable premixed gases (e.g. hydrogen/oxygen) and is delivered to the burner. The mass flow regulators determine the flow measurement system, the flow lines are heated and the temperature is controlled to prevent condensation of the precursor (Fig. 10). A bipolar high voltage source (0 ± 10 kV, 3 - 10 mA) establishes a uniform electric field. Chemical precursors are pyrolyzed and oxidized in the flame and condensed into nanoparticles as cooled gases, when they reached and deposited onto substrate. Material processing is investigated in-situ using laser-induced fluorescence to determine the OH radicals concentration and the gas temperature. Experimental results of particle growth at different applied electric fields are compared with calculations using monodisperse and sectional models. The results show that the application of such an electric field can reduce the total particle size (e.g., from 40 to 18 nm), maintain metastable phases and particle crystallinity, and unmonotonically affect the initial particle size (e.g., from 6 to 5 nm) and powder surface area. The specific surface area for anatase nanopowder is 310 m^2/g in the synthesis under an applied electric field of 125 V/cm.

In work [46], the flame aerosol synthesis was used to obtain a TiO_2 photocatalyst by oxidation of titanium tetrachloride ($TiCl_4$) (Fig. 11). Fuel gas (methane) and oxidant (oxygen) were mixed with nitrogen until the flame rose above the burner. Titanium tetrachloride vapors are formed by passing dry argon gas (pre-mixed with other gas components at room temperature) through a bubble containing a liquid precursor. Each gas mixture was then introduced into the burner. The flame temperature during the synthesis was about 900 °C. The formed particles were collected on a fiberglass filter placed in a stainless steel holder, which was connected to a vacuum pump and fixed approximately 50 cm above the flame. The exhaust stream from the particulate collection unit was then passed through a flask containing 0.1 M of sodium hydroxide solution. The overall synthesis reaction was as follows:

$$TiCl_4\,(g) + 4O_2\,(g) + 2CH_4\,(g) \rightarrow$$
$$\rightarrow TiO_2\,(s) + 4HCl\,(g) + 2CO_2\,(g) + 2H_2O\,(g)$$

The effect of precursor loading on particle growth and rutile phase formation was studied using a laminar premixed flame with the $(Ar + TiCl_4)/CH_4/O_2/N_2$ configuration. Increasing the flow rate of the precursor from 2.5 to 29.5 mmol/h, as the main parameter of the synthesis, led to an increase in the average particle diameter from 11 to 22 nm and a decrease in the specific surface area from 145 to 71 m^2/g, respectively.

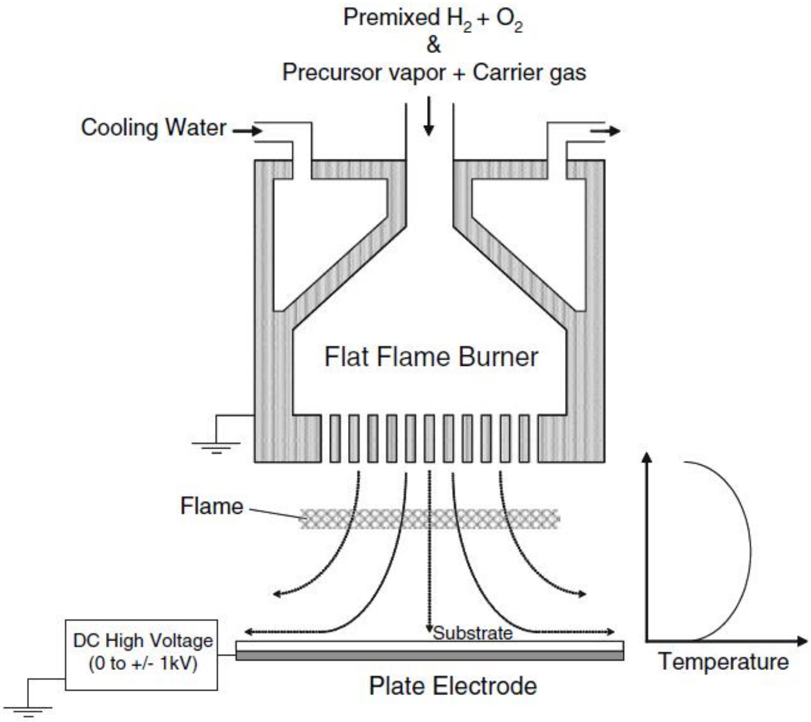


Fig. 10. Installation for electric flame amplification [45].

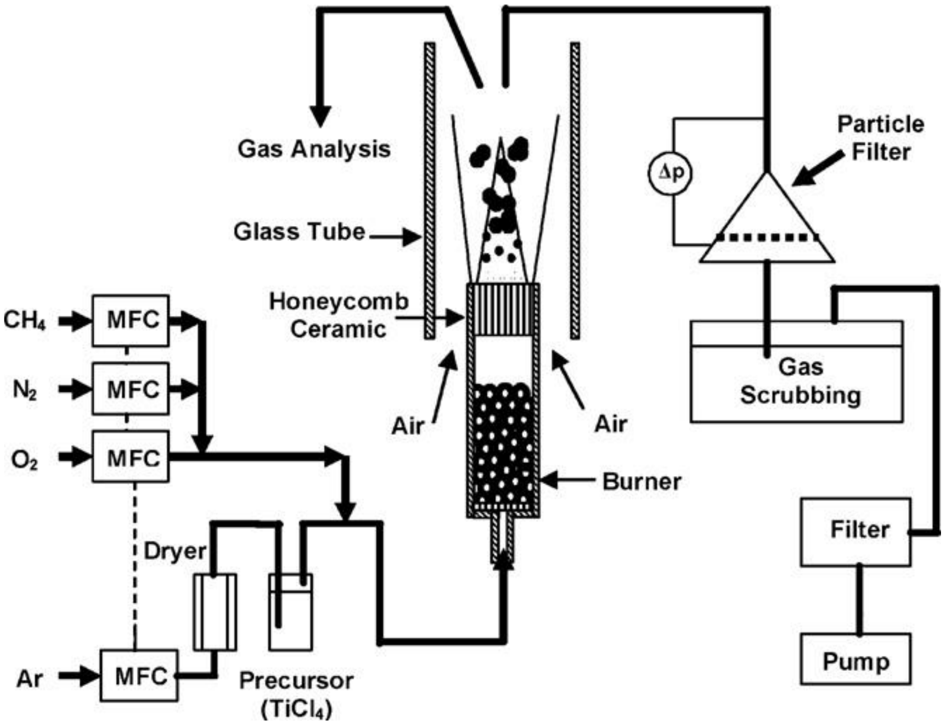


Fig. 11. The scheme of the experimental setup for flame aerosol synthesis of TiO_2 [46].

The precursor of titanium tetraisopropoxide evaporates and enters the carrier gas through a heated and temperature-controlled bubble device, then combines with flammable premixed gases (e.g. hydrogen/oxygen) and is delivered to the burner. The mass flow regulators determine the flow measurement system, the flow lines are heated and the temperature is controlled to prevent condensation of the precursor (Fig. 10). A bipolar high voltage source (0 ± 10 kV, 3 – 10 mA) establishes a uniform electric field. Chemical precursors are pyrolyzed and oxidized in the flame and condensed into nanoparticles as cooled gases, when they reached and deposited onto substrate. Material processing is investigated in-situ using laser-induced fluorescence to determine the OH radicals concentration and the gas temperature. Experimental results of particle growth at different applied electric fields are compared with calculations using monodisperse and sectional models. The results show that the application of such an electric field can reduce the total particle size (e.g., from 40 to 18 nm), maintain metastable phases and particle crystallinity, and unmonotonically affect the initial particle size (e.g., from 6 to 5 nm) and powder surface area. The specific surface area for anatase nanopowder is 310 m^2/g in the synthesis under an applied electric field of 125 V/cm.

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A series of TiO_2 nanopowders were synthesized by a similar technology in work [47] using a flame aerosol method. The particles with an average particle size of from 7.1 to 21 nm with a high rutile content were obtained. It was found that the particle growth regime promotes the formation of defect-rich anatase nanoparticles, which determine the total number of reactive polydisperse nanostructured powders. In the study [48], TiO_2 nanopowder, synthesized by this method, had an average particle size of 13 nm, anatase content of 97% (wt.), and a specific surface area of 102 m_2/g.

VII. «Green» method

"Green" synthesis of TiO_2 nanoparticles is an environmentally friendly alternative to the chemical approach for the nanomaterials synthesis. The biological method provides a wide range of resources for the synthesis of nanoparticles using biological agents such as bacteria, fungi, actinomycetes, yeast, and plants [49-52]. The rate of reduction of metal ions with the help of biological agents is much faster, as well as due to ambient temperature and pressure. The obtaining of TiO_2 nanoparticles using plant extracts has led to significant progress in "green" synthesis methods for the synthesis of many nanoparticles [53].

In work [54], the authors have synthesized mesoporous TiO_2 nanoparticles by the sol-gel method using green tea extract. A mixture of 9 ml of titanium isopropoxide and 60 ml of isopropanol was stirred continuously with a magnetic stirrer at room temperature for 1 hour. Then green tea extract was added in various ratios (0.5, 1, and 1.5 g in 30 ml of distilled water) and stirred slowly for 3 hours in order to obtain a colloidal solution. It was found that the pH of the solution was 6.0 during the TiO_2 nanoparticles synthesis. The resulting sol was kept at rest for 10 hours to obtain a gel. Then the gel was filtered, dried at 110°C for 3 hours and calcined at 500°C for 10 hours. The calcined samples were designated as NTG0.5, NTG1, and NTG1.5, which corresponded to mass ratios in samples 1:0.06, 1:0.12, and 1:0.18 TiO_2:GTE (extract), respectively. TiO_2 nanoparticles prepared without extract were monitored and were designated as NT. The mild, non-toxic, and inexpensive green tea extract, which hass active organic components, limited agglomeration, and promoted the growth of TiO_2 nanoparticles.

In work [55], the authors have synthesized titanium dioxide nanoparticles by an improved hydrothermal method using Morinda citrifolia leaf extract. 50 ml of M. citrifolia leaf extract was added to 0.1 M $TiCl_4$ solution. The solution was transferred to a 100 ml stainless steel autoclave at 120 °C for 8 hours and then cooled to room temperature. A white suspension was obtained, which was centrifuged at 5,000 rpm/min for 10 minutes to remove unreacted chemicals. The resulting suspension was filtered and washed several times with deionized water and ethanol. The filtered suspension was dried in an oven at 100°C for 5 hours. Titanium hydroxide was calcined at 400°C for 4 hours in a muffle furnace, resulting in quasi-microspheres of TiO_2 nanoparticles. The SEM images of TiO_2 NPs are shown in Fig. 12. X-ray diffraction patterns showed the presence of rutile phase TiO_2 and confirmed an average crystallites size of 10 nm.

The authors [56] synthesized TiO_2 nanoparticles by the hydrothermal method using *Aloe Vera* gel for use as a photocatalyst in the degradation of picric acid. *Aloe Vera* was peeled and the gel was washed seven times under running water. 10 ml of the gel was added to 100 ml of deionized water and stirred for 1 hour. To this aqueous solution was added dropwise 0.1 M titanium(IV) isopropoxide. The reaction mixture was stirred continuously for one hour at 20 °C. The solution was kept in an autoclave at a temperature of 180 °C for 4 hours. Then the solution was heated on a hot plate at a temperature of 80 °C. The resulting product was ground and calcined in a muffle furnace at a temperature of 500 °C for 5 hours. The size of the synthesized TiO_2 nanoparticles ranged from 6 to 13 nm.

In a study [57], titanium dioxide nanoparticles were efficiently synthesized using aqueous extracts of

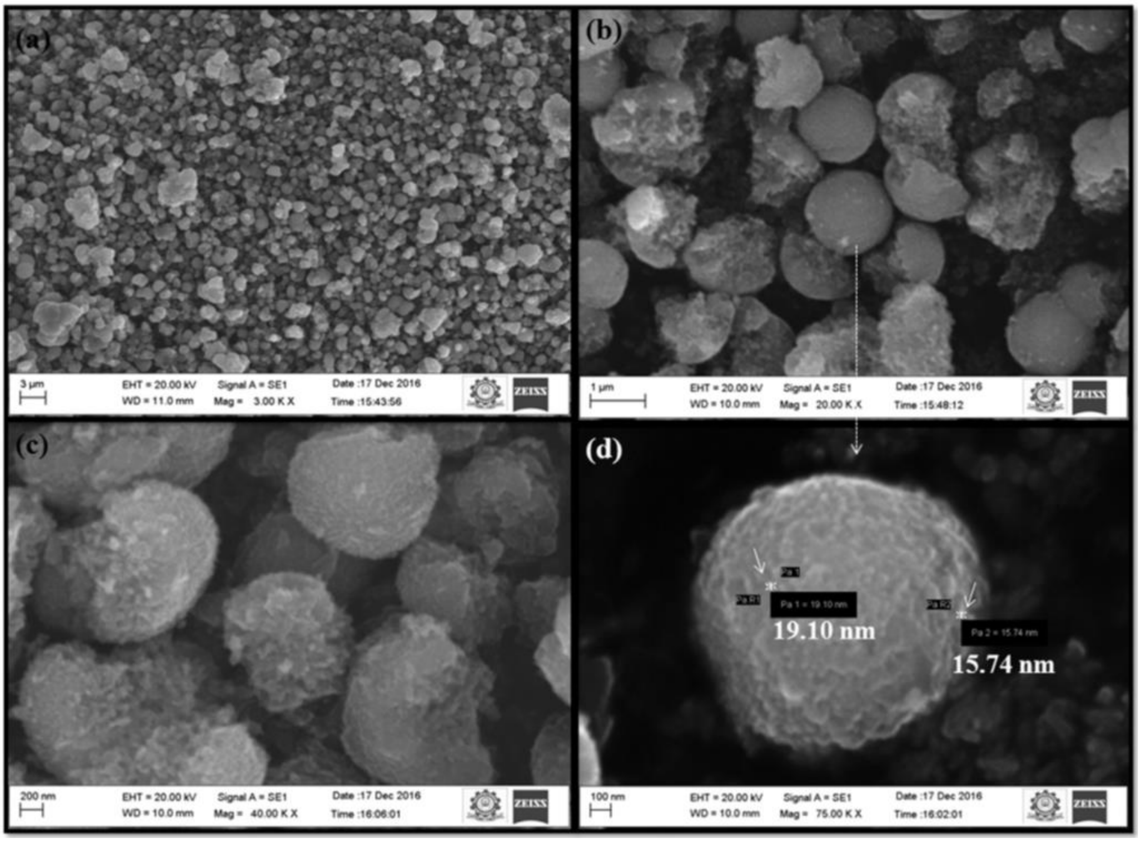

Fig. 12. SEM image of TiO_2 nanoparticles synthesized using *Morinda citrifolia* leaf extract [51].

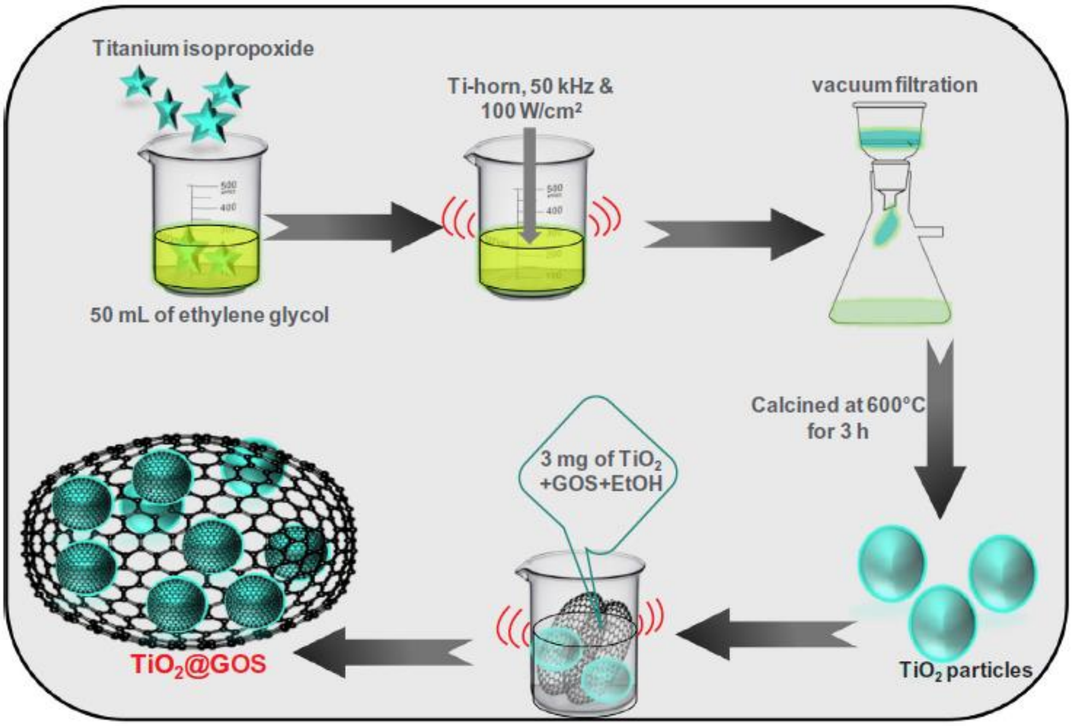

Fig. 13. Scheme of sonochemical synthesis of TiO_2 electrocatalyst based on graphene oxide composite [60].

Parthenium hysterophorus leaves by microwave irradiation. The collected leaves were washed with distilled water to remove dust particles and contaminants. About 20 g of leaves were weighed and crushed into small pieces with a mortar and pestle. The samples were added to 100 ml of distilled water and boiled for 10 minutes at 60 °C in a microwave oven. After boiling, the extract left to cool at room temperature. It was then filtered with Whatman №1 filter paper. About 100 ml of boiled aqueous extract of *P. hysterophorus* leaves were mixed with 900 ml of an aqueous solution of TiO_4 (5 mm) in an Erlenmeyer flask. This reaction solution was stirred by hand and incubated under light for 48 hours. TiO_2 nanoparticles were spherical in shape with an average size of 20 - 50 nm.

In work [58] the "green" synthesis of TiO_2 nanoparticles using an aqueous extract of *Eucalyptus globulus* leaves is presented. Titanium tetraisopropoxide (3 ml) was dissolved in ethanol (50 ml). The 50 ml of a *Eucalyptus globulus* extract solution (ratio of 1:1 (v/v)) was added dropwise to the precursor solution using a peristaltic pump and kept with vigorous stirring for 2 - 3 hours until a brown-yellow precipitate is formed. Subsequently, the solution was centrifuged at 10,000 rpm/min for 15 minutes and washed with ethanol to remove any other impurities. The brownish-yellow precipitate was dried at 80 °C for 2 hours in a hot air oven, finely ground using an agate mortar with a pestle, and annealed at 500 °C for 3 hours.

VIII. Other methods

TiO_2 nanomaterials can be obtained by direct oxidation of titanium metal using oxidants or by anodization. Crystalline TiO_2 nanotubes are obtained by direct anodic oxidation of a titanium metal plate with hydrogen peroxide. Titanium dioxide nanotubes are oriented perpendicular to the metal substrate surface. Their diameter varies within several tens of nanometers. The crystalline phase of nanotubes can be controlled by adding inorganic salts of NaF, NaCl, and Na_2SO_4. The addition of F^- and SO_4^{2-} promotes the formation of pure anatase, while the addition of Cl^- promotes the formation of rutile [5].

In the synthesis of nanostructured titanium oxide materials, the sonochemical method [59-61] has been used, which is associated with the acoustic cavitation of air bubbles and their explosive collapse in a liquid medium. Cavitation collapse of bubbles leads to a local increase in temperature (~ 5000 K) and pressure (~ 1000 atm). The rate of local heating and cooling of the medium can be $> 10^9$ $K \cdot s^{-1}$ [4, 5]. In [60], rutile TiO_2 microspheres decorated with graphene oxide composite were synthesized by the sonochemical method (Fig. 13).

The method of electrodeposition is usually used to obtain a metal coating on the surface during a reduction at the cathode. The substrate, which should be coated, used as a cathode and immersed in a solution, containing a precipitated metal salt. The metal ions, which are presented in the solution, are attracted to the cathode and reduced to the metal form [5, 62-65].

Conclusions

TiO_2 nanoparticles can be synthesized using a variety of methods, which include: sol-gel technology, hydrothermal and solvothermal methods, the use of high-frequency electromagnetic waves (microwave method), template method, anodic oxidation, electrodeposition sonochemical method, chemical and physical vapor deposition, etc. These methods allow to obtain titanium dioxide in the form of spheres, rods, fibers, tubes with the anatase, rutile, or brookite structure. The sol-gel method makes it possible to influence the structure and morphology of TiO_2 nanoparticles, optimize energy costs, as well as use of simple and affordable technological equipment, but it is a long process. The use of hydrothermal and solvothermal methods is complicated by the need to use autoclaves at high pressures. The originality of the liquid-phase low-temperature method lies in the use of the aqua complex precursor $[Ti(H_2O)_6]^{3+}\cdot 3Cl^-$, which allows the obtaining of TiO_2 nanoparticles with unique physicochemical properties. The sonochemical method, electrodeposition method, and microwave method generally do not give samples with nanometer-sized particles. Depending on the oxidation parameters, the anodic oxidation method allows to obtain titanium dioxide nanotubes with a diameter within several tens of nanometers. The advantages of this method are its simplicity, lower energy costs, minimal impact on the environment, and the ability to adjust the dispersion of the obtained TiO_2 nanotubes depending on the anodization time and annealing temperature. Methods of chemical and physical vapor deposition are carried out at high pressures and temperatures in vacuum chambers.

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Методи синтезу титан (IV) оксиду (огляд)

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Наноматеріали на основі TiO_2 привертають велику увагу в багатьох сферах застосування, таких як фотокаталіз, фотоелектрика, зондування, електрохромність, фотохромність тощо. Вони широко використовуються у лакофарбових та полімерних матеріалах, сонцезахисній косметиці та зубних пастах. Існують різноманітні шляхи синтезу, що впливають на розмір, форму та кристалічність наночастинок TiO_2. До основних методів отримання діоксиду титану у вигляді сфер, голок, волокон та трубок (зі структурою анатазу, рутилу або брукіту) можна віднести золь-гель технології, гідротермальні та сольвотермальні способи, мікрохвильовий метод за участю високочастотних електромагнітних хвиль, темплатний метод, способи прямого окиснення, електроосадження, сонохімічний метод з використанням дії ультразвуку, хімічне та фізичне осадження з парової фази, «зелені» методи тощо. У даному літературному огляді приведені сучасні наукові результати з питань отримання наночастинок TiO_2 різноманітними методами.

Ключові слова: титан(IV) оксид, золь-гель метод, гідротермальний метод, аквакомплексний прекурсор, «зелений» синтез, анатаз, рутил, брукіт, темплат.