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Review

TiO_2 for Photocatalysis and Energy Conversion: A Detailed Overview of the Synthesis, Applications, Challenges, Advances and Prospects for Sustainable Development

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Abstract: The term 'photocatalysis' has recently gained high popularity, and various products using photocatalytic functions have been commercialized. Of all the materials that may be used as photocatalysts, TiO_2 is virtually the only one that is now and most likely will remain appropriate for industrial application. Water and air purification systems, sterilization, hydrogen evolution, self-cleaning surfaces, and photoelectrochemical conversion are just a few of the products and applications in the environmental and energy domains that make extensive use of TiO_2 photocatalysis. This is due to the fact that TiO_2 has the lowest cost, most stability, and most effective photoactivity. Furthermore, history attests to its safety for both people and the environment because it has been used as a white pigment since antiquity. This review discusses some important aspects and issues concerning different synthesis methods and their influence on the structure and properties of TiO_2, as well as the concept of photocatalysis based on it as a promising biocompatible functional material that has been widely used in recent years. The advantages of TiO_2 applications in various fields of science and technology are discussed, including environmental protection, photocatalysis including self-cleaning surfaces, water and air purification systems, hydrogen liberation, photovoltaic energy, cancer diagnosis and therapy, coatings and dental products, etc. Information on the structure and properties of TiO_2 phases, as well as modern methods of synthesis of functional materials based on them are presented. This is followed by a detailed review of the basic principles of TiO_2 photocatalysis with a brief introduction to the modern concept of TiO_2 photocatalysis. Finally, the challenges and prospects of TiO_2 photocatalysis for various applications are briefly discussed. Recent advances in the fundamental understanding of TiO_2 photocatalysis at the atomic-molecular level are highlighted, and important recent advances in TiO_2 photocatalysis are summarized in terms of the design and engineering of new materials.

Keywords: titanium dioxide; thin films; catalytic reactions; photocatalysis; photocatalyst; surface interaction; nanomaterials; water purification; sustainable development

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1. Introduction

Fossil fuel usage is rising quickly due to the expansion of human society and unchecked industrial progress. The development of clean, safe, and sustainable energy technologies is therefore one of the most pressing issues facing humanity today, especially for researchers in related physical and chemical sciences. As a result, the world's population may face environmental pollution (e.g., toxic emissions and industrial wastes) and a lack of resources for renewable energy sources]. Solar energy is easily turned into chemical and electrical energy, making it one of the most significant clean and renewable energy sources on Earth [5]. One way to make pure hydrogen (H_2) is to split solar

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water (H_2O) [6,7]. To address the global energy and environmental issues, solar-powered clean energy solutions have to be extensively researched and implemented. Of all the energy technologies, one of the most significant developments in this regard is photocatalysis, which uses solar energy to regulate energy and chemical reactions [8–11].

Back in 1901, the Italian chemist Giacomo Chamizian conducted experiments on the systematic study of the effect of light on chemical reactions [12,13]. However, photocatalyst was not used in these experiments. Only in 1911, the key word "photocatalysis" appeared in scientific literature for the first time [14,15]. Then it was reported that ZnO was a photocatalyst for the bleaching of Prussian blue and other reactions, including the reduction of Ag^+ to Ag [16]. In 1932, TiO_2 and Nb_2O_5 were found to be active in the photocatalytic reduction of $AuCl_3$ and $AgNO_3$ to Au and Ag, respectively [17]. Later, in 1938, titanium dioxide was first used as a photosensitizer for the bleaching of O_2 dyes [18], but at that time, researchers did not pay much attention to photocatalysis due to the lack of practical applications. In the early 1970s, the "oil crisis" and the environmental impact of industrial plants led scientists to search for alternative and renewable energy sources [19–22]. Just since that time, several pioneering works in this direction have been reported. In 1968, it was discovered that O_2 is formed on TiO_2 in an electrolytic cell under ultraviolet (UV) light [22,23]. In 1972, Fujishima and Honda [22] experimentally showed that photoelectrochemical cleavage of H_2O to produce O_2 on TiO_2 and H_2 on platinum black dye electrode and can be achieved by irradiating TiO_2 electrode with UV light. The photocatalytic splitting of H_2O on TiO_2 powder to form H_2 and O_2 with a molar ratio of 2:1 in an argon atmosphere was also reported in 1977 [24,25]. A little later, it became known that methanol (CH_3OH), as a sacrificial reagent, can significantly enhance the photocatalytic production of H_2 from CH_3OH-H_2O mixture [26]. In addition, photocatalytic reduction of CO_2 using different types of semiconductors as photocatalysts has been reported [27–30]. These pioneering works have shown that photocatalysis will be used in many fields in the future, and tremendous research attention has been paid to similar reactions using titanium dioxide as a photocatalyst in recent years. Besides TiO_2, various other materials such as Ta_2O_5, Ta_3N_5, $SrTiO_3$, Ag_3PO_4, $BiVO_4$, MoS_2, WSe_2, $LaTiO_3$, $SrTaO_2N$, CdS, TaON, RuO_2, Nb_2O_5 and their nanoparticles, have been applied directly to enable the utilization of solar energy for various photocatalytic reactions [31–58]. Due to the rapid increase in the use of heterogeneous photocatalysis, the literature describing this field has been summarized in numerous publications that not only review the development of photocatalysts and the characterization of photocatalytic processes, but also point out the challenges and opportunities encountered in heterogeneous photocatalysis [59–68].

Among various photocatalysts, titanium dioxide, as the most widely used "promising" photocatalyst, has been widely used in heterogeneous photocatalysis because of its chemical stability, non-toxicity and low cost [68–79]. In the past two decades, heterogeneous photocatalysis of titanium dioxide has spread very rapidly, undergoing various energy and environmental challenges such as direct solar splitting of H_2O into H_2 and decomposition of pollutants [80]. Although much progress has been made in heterogeneous TiO_2 photocatalysis, much remains unknown, which poses an interesting challenge not only to engineers but also to basic research scientists. Generally, a typical TiO_2 photocatalytic reaction contains many fundamental processes, including charge carrier formation, separation, relaxation, trapping, transport, recombination and transport, and bond breaking/forming, which need to be thoroughly investigated. Only when all these fundamental processes are clearly identified can a better understanding of TiO_2 photocatalysis be achieved [81–83], which is vital for the development of new photocatalysts and the characterization of new photocatalytic processes.

Ideally, investigating the fundamental processes of TiO_2 photocatalysis under real environmental conditions (e.g., in solution) is the best way to gain a deep understanding of TiO_2 photocatalysis. At present, the processes of charge carrier formation, separation, relaxation, capture, recombination and transport, as well as the stages of single charge transfer in TiO_2 photocatalysis have been systematically investigated by various methods using appropriate electron acceptors or electron donors under real environmental conditions [84–87]. However, in TiO_2 photocatalysis, the whole reaction is usually completed by several charge transfer and bond breaking/ bond formation

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steps. In addition, most of the reactants are neither good electron acceptors nor good electron donors. This makes it very difficult to identify mechanistic studies of TiO_2 photocatalysis under real environmental conditions. To achieve this goal, a number of surface science methods (including desorption-oriented methods, spectroscopy and electron spectroscopy) have been used to investigate the photocatalytic reactions on single crystal TiO_2 surfaces to provide important information for TiO_2 photocatalysis and gain an in-depth understanding of TiO_2 photocatalysis [88–91]. Therefore, fundamental studies of photocatalytic reactions on various TiO_2 single crystal surfaces (rutile and anatase) have been mainly carried out in recent years. Due to the chemical stability and ease of preparation of rutile TiO_2 (110), this surface has become one of the most widely studied surfaces to gain a fundamental understanding of adsorption, thermal and photochemical reactions of adsorbates on TiO_2 surfaces [92–98]. Using scanning tunneling microscopy (STM) and other ensemble averaging techniques (electron/photon/desorption spectroscopy), the adsorption, diffusion and reaction of various adsorbates in TiO_2 photocatalysis can be clearly identified at the molecular level on TiO_2 model surfaces [99–106], which can provide important information for understanding the photocatalysis of TiO_2 under real environmental conditions. As a result, a considerable amount of research has focused on the fundamental processes of TiO_2 photocatalysis, and many studies in this area have been summarized in a large number of reviews [32–56,107–116]. It is generally believed that the bond breaking/forming stages in TiO_2 photocatalysis are induced by photogenerated electrons/holes [117–121].

However, a complete understanding of how photogenerated charge carriers contribute to bond formation/breaking in TiO_2 photocatalysis is still lacking, which is crucial to unravel the nature of TiO_2 photocatalysis. Fundamental studies of these processes using surface science techniques are needed to achieve a thorough understanding of these processes. In this review, we aim to provide a comprehensive overview of TiO_2 photocatalysis and its applications.

2. Titanium Dioxide, Synthesis, Characterization and Properties

2.1. Brief Introduction and Applications of TiO2

Titanium dioxide, also known as titanium (IV) oxide, is the inorganic compound derived from titanium with the chemical formula TiO_2. TiO_2 as a white inorganic powder, has been industrially produced and used in a wide variety of industries for more than a century [122–127]. Due to its non-toxic properties, light scattering ability, UV resistance and ultra-white color, titanium dioxide is used in a thousand different products and products, because it enhances the whiteness, brightness and attractiveness of products. In nature, titanium dioxide is found in the form of the minerals rutile, anatase and brukite. TiO_2 production is steadily increasing worldwide, as the demand for it is constantly growing. Titanium dioxide is extracted in several countries from titanium-containing raw materials, mainly for this purpose ilmenite ore is used, TiO_2 content in which reaches 60% [128]. It should be noted that only 5% of raw materials are used to produce pure titanium, and the rest is used to produce its oxides [129].

In terms of properties, TiO_2 is a versatile semiconductor material that has attracted considerable attention in recent years due to its potential in photocatalytic applications and environmental sensing. Due to its large surface area, chemical stability, unique electronic and optical properties, TiO_2 has been investigated for the determination of various volatile organic compounds (VOCs) in air and water [131,132]. TiO_2-based sensors have been developed for the detection of various VOCs, including benzene, toluene, xylene, and formaldehyde, with high sensitivity and selectivity. TiO_2-based sensors are also used to detect gases such as nitrogen dioxide and ozone, which are major air pollutants. In addition, the application of TiO_2 photocatalysis to decompose organic pollutants in water and air makes it a promising material for environmental remediation [133–135].

Having a specific gravity of 3.9-4.2, a melting point of 1854 °C, and a hardness of 5.5-6.5, titanium oxide (TiO_2) is soluble in hot sulfuric and hydrofluoric acids, but insoluble in water, organic acids, and dilute alkaline solutions [136,137]. Large band gap in TiO_2 semiconductor. Its anatas structure, located in the ultraviolet region of the spectrum (100-400 nm), has an optical gap of 3.2 eV and an

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absorption edge of 388 nm [138]. In the visible region of the spectrum (400-700 nm), rutile has a lower optical slit of 3.02 eV with an absorption edge of 410 nm, while the go-kita phase absorbs light in the near visible region with an energy slit of 2.96 eV [139]. Titanium dioxide thin films absorb ultraviolet light well but show good transparency in the visible wavelength range [139]. At λ = 550 nm, the rutile phase of titanium oxide thin films has an index of refraction of 2.8 and the anatase phase has an index of refraction of 2.49. TiO_2 used in industry is shown in Figure 1 [140–142]. With a high dielectric coefficient of 80-110 for the rutile phase and 50-60 for the anatase phase, titanium oxide (TiO_2) is electrically insulating. Its electrical resistance to breakdown voltage is 4 kVmm-1. Compared to semiconductors such as SnO_2, which has a resistivity of 30 Ohm-cm, the surface electrical resistivity of thin films for anatase and rutile structures is 1012 Ohm-cm, which is a high resistivity [143].

Figure 1. Current applications and potential future use of TiO_2 [144].

Due to its high dielectric coefficient, this material has several applications including anti-reflection surfaces and metal-oxide-semiconductor field-effect transistors as a dielectric gate material [145]. An electron is excited from the valence band to the conduction band of a semiconductor when a photon with energy equal to or greater than the gate energy (greater than 3 eV for titanium oxide (TiO2)) hits the semiconductor [146]. As a result, an electron-hole pair is formed. These charge carriers can react with an electron donor or acceptor, becoming trapped, or recombine with radiation and dissipate energy as heat when indirect gap semiconductors (or direct gap semiconductors) are used [147]. Due to its excellent advantages, titanium dioxide-based materials are attracting more and more attention every day, and hundreds of studies are devoted to their properties and applications every year. However, despite numerous works in this field, many aspects and problems still remain insufficiently studied and relevant. This statement highlights the need for an in-depth study of TiO_2 and emphasizes the significance of our review article.

2.2. *Crystal Structures of TiO_2*

TiO_2 belongs to the class of transition metal oxides and has several modifications: anatase, rutile, brookite, TiO_2 (B), TiO_2 (II), and TiO_2 (H) [148–152]. It is worth noting that the first three are widely distributed in nature. TiO_2 (B), with monoclinic structure is also found in nature, but rarely. TiO_2 (II) with the structure of PbO_2 and TiO_2 (H) with the structure of hollandite were obtained artificially from rutile under high-pressure conditions. In this review, only the main three crystal structures, anatase, rutile, and brukite, are discussed and their characteristics are summarized in Table 1 [150–153].

Table 1. Characteristics of the crystalline structure of TiO_2.

Parameter	Anatase	Rutile	Brookite
Crystal structure	Tetragonal	Tetragonal	Rhombic

Lattice parameters, nm	a= 0.3784 c= 0.9515	a= 0.45936 c= 0.29587	a= 0.9184 b = 0.5447 c = 0.5154
Density, g/cm³	3.79	4.13	3.99
Space group	L4/amd	P4/mnm	Pbca
Number of units in cell	2	2	4
O-Ti-O bond angle	77.7º, 92.6º	81.2º, 90.0º	77.0º -105º
Ti-O bond length, nm	0.1937(4) 0.1965(2)	0.1949(4) 0.1980(2)	0.187-0.204

Each of these crystal structures has a unique arrangement of atoms and lattice parameters, but the basis of the crystal structure of these polymorphic modifications are TiO_6 octahedrons (see Figure 2). The octahedrons are arranged in such a way that they may share common vertices or edges. In anatase there are 4 common edges per octahedron, in rutile there are 2 [148]. Anatase has a tetragonal lattice with space group L4/amd and rutile P4/mnm, while the space group number of anatase and rutile is 141 and 136, respectively. This is the reason for the difference of their characteristics. Titanium dioxide with the structure of brukite belongs to the rhombic crystal system, with space group Pbca (space group number 29). In brukite, each octahedron shares common edges with two neighboring octahedrons, and they have a shorter length than the others. The unit cell consists of 8 TiO_2 units and is formed from TiO_6 octahedra (see Figure 2 (b)). Brukite has a more complex unit cell structure, larger volume, and is also the least dense of the 3 considered forms and is not often used for experimental studies [148].

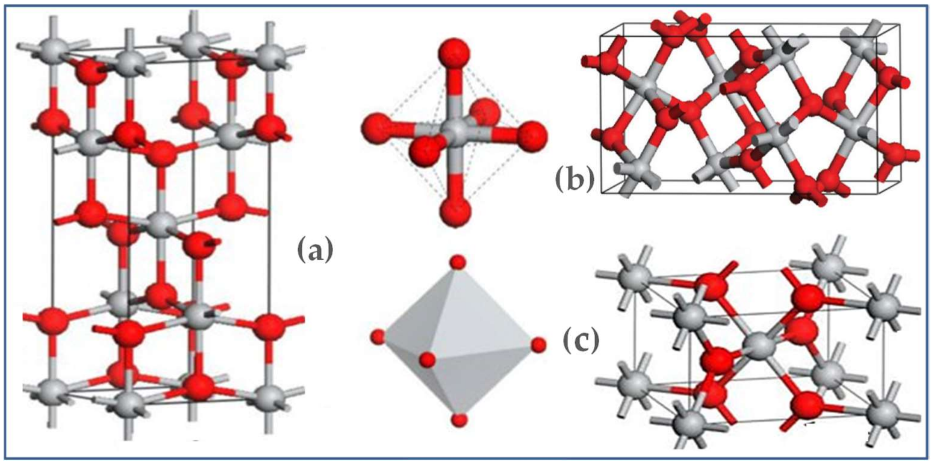

Figure 2. Crystal structure of TiO_2: anatase (a), brukite (b), rutile (c) during thermal treatment, anatase and brukite change to rutile at temperatures of 400-1000 °C and ~750 °C, respectively [154].

2.3. *Electronic Properties and Band Structure*

The electronic structure of titanium dioxide has been well studied using various approaches [155–157]. The TiO_2 phases described above often have O 2p and Ti 3d states near their band edges, respectively, in their valence bands (VB) and conduction bands (CB). A large bandgap makes stoichiometric TiO_2 an excellent electrical insulator [158]. However, all of the TiO_2 crystalline materials contain point defects, such as Ovs, interstitial titanium ions (Ti^{3+}), and substituted ions. Within crystalline materials, interstitial ions and vacancies are intrinsic imperfections that can have a substantial impact on the materials' electrical conduction, mass transport, and catalytic properties. New electronic states, referred to as defect states, are introduced by point defects into the TiO_2 bandgap (Figure 3). The phases and surface features of TiO_2 influence the locations of defect states in the bandgap. R-TiO_2 (110) defect states, for instance, are situated roughly 0.8–1.0 eV below the CB edge [159]. On the other hand, A-TiO_2 (101) defect states are situated approximately 0.4-1.1 eV below the CB edge [160].

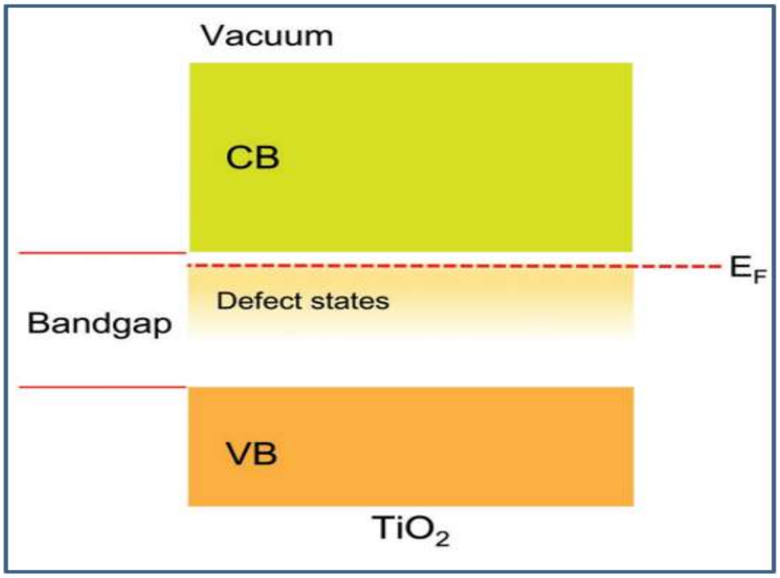

Figure 3. Schematic diagram of the electronic structure of TiO_2 [161].

Photoemission experiments [162] report no band bending on the stoichiometric defect-free TiO_2 surfaces (e.g., R-TiO_2(110) and R-TiO_2(100)). TiO_2 is actually an n-type semiconductor due to point defects that can occur in the bulk or on the surface. When surface lattice oxygen atoms are removed during the preparation process, unpaired electrons (in the Ti 3d orbitals) remain on the surfaces, which is how defects on TiO_2 surfaces often appear as Ovs [163]. This is one of the bandgap's defect states' sources. As seen in Figure 4, the extra electrons given up by Ovs (which function as donor states) will collect in the near-surface region and cause a downward bending of the band [164]. In practical scenarios, charge transfer between the surface and adsorbates will occur when electron-rich TiO_2 surfaces adsorb different adsorbates. This could potentially change the direction of the band bend and further influence the chemistry of the TiO_2 surface. The valence band of TiO_2 is formed by external p - electrons of oxygen, and the bottom of the conduction band is predominantly formed by excited titanium ions [156]. Of particular importance for the electronic properties of titanium dioxide is the presence of partially reduced titanium (Ti^{3+}), the level of which is located ~ 0.2 - 0.8 eV below the conduction band [157] and acts as donors. The presence of Ti^{3+} determines in many cases the conductivity of TiO_2. The resistivity of unalloyed anatase and rutile are in the range of 10^4 - 10^7 Ω-cm, but when Ti^{3+} is formed, it decreases to 10^{-1} Ω·cm for anatase and 10^2 Ω·cm for rutile [165]. With the nanotube structure of TiO_2, its conductivity is important because it determines the efficiency with which electrons can be transferred along the length of the nanotubes. Thus, the electronic properties of TiO_2 are mainly determined by the crystal structure and the presence of Ti^{3+}. Titanium dioxide has an inherent bend in the space charge region at the semiconductor/electrolyte interface, which is characteristic of a group of semiconductors. This bend is formed spontaneously on the surface and has a steeper bend in anatase than in rutile [166].

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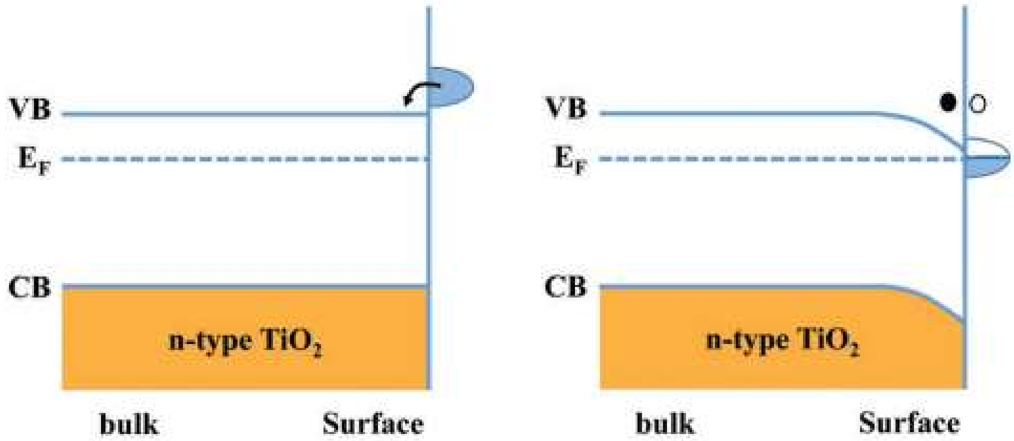

Figure 4. Scheme of surface band bending on a clean TiO_2 surface under vacuum conditions, induced by the donor-like surface defect states (●, electron; ○, hole).

In TiO_2 with anatase structure, the process of hole capture by the surface dominates, since the spatial charge separation is achieved due to the transfer of photogenerated holes to the particle surface through a steep upward bend of the zones. In this case, in the rutile phase there is a bulk recombination of electrons and holes, and only holes generated very close to the surface are transferred to the surface. It is known that the concentration of charge carriers determines the depth of the bulk charge region [167]. The presence of impurities in the TiO_2 structure can contribute to an increase or decrease in the concentration of electrons and holes. Therefore, the presence of impurity compounds has a significant effect on the depth of the volume charge region bending and the photocatalytic activity of TiO_2.

2.4. *Optical Properties of TiO_2*

TiO_2 belongs to semiconductors with a wide bandgap width. According to literature data, the forbidden band width for anatase structure is 3.2 eV, brukite is 3.3 eV, and rutile is 3.0 eV [156]. Figure 5 shows the absorption spectrum of TiO_2 with anatase structure [168].

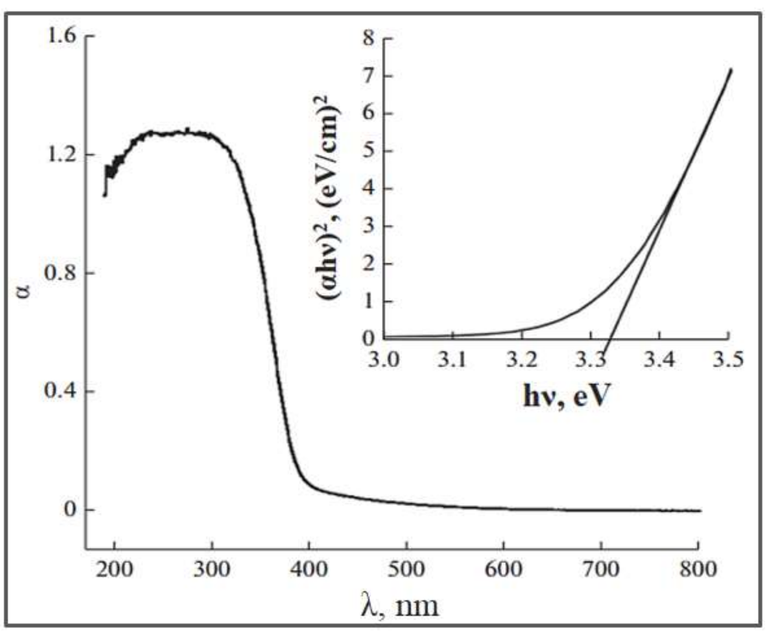

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Figure 5. Absorption spectrum of TiO_2 with anatase structure [168].

As can be seen from Figure 5, the absorption spectrum of titanium dioxide is limited to the ultraviolet region of solar radiation. Consequently, pure TiO_2 exhibits photocatalytic activity only when irradiated with ultraviolet light whose wavelength is less than 400nm. In the solar spectrum, the share of ultraviolet light does not exceed 7% [169]. To utilize the energy of visible radiation, it is necessary to expand the absorption spectrum of TiO_2. This would allow the utilization of solar radiation for photocatalytic processes. In the last 5 years, there have been many studies based on the idea of extending the wavelength range of photoactivation of TiO_2 in the visible light region and improving the efficiency of solar energy utilization. Activation and optimization of TiO_2 by visible light can be done by implanting metal ions, doping non-metallic atoms or sensitizing TiO_2 with dyes. Therefore, many efforts have been directed to overcome the drawbacks and optimize the absorptivity and photocatalytic properties of TiO_2, especially in the visible light range. Among them, ionic and cationic doping with the formation of structure defects is an effective approach [170,171]. The possibility of using these approaches is precisely due to the fact that the energy levels of such defects can be located in the forbidden zone, so that the absorption of light by defects (impurity absorption) is also possible in the longer wavelength region [171]. In many works, it has been shown that modified TiO_2 has a higher efficiency compared to pure TiO_2, but the conversion efficiency depends on many other parameters, such as the concentration of the doping additive, the energy levels of the additive in the titanium dioxide lattice, the distribution of doping atoms in the unit cell, etc. [169–174]. According to the literature [173], the presence of metal ion in the titanium oxide matrix significantly affects the absorption spectrum, the recombination rate of charge carriers and their dynamics, on the surface. At doping with metal ions often observed bathochromic effect, due to the emergence of additional levels in the forbidden zone. Doping of ions with stable configuration, such as Fe^{3+}, Gd^{3+}, Ru^{3+} and Os^{3+} leads to the narrowing of the forbidden zone or the appearance of additional energy levels [174], which improve charge transfer to the semiconductor surface and contribute to the absorption of visible light, improving their optoelectronic properties.

In most cases, titanium dioxide doped with nonmetallic elements in the anionic site shows an increase in absorption in the ultraviolet-visible part of the spectrum. For example, N-doped TiO_2 has recently been shown to be more active than pure TiO_2 (Figure 6) [175].

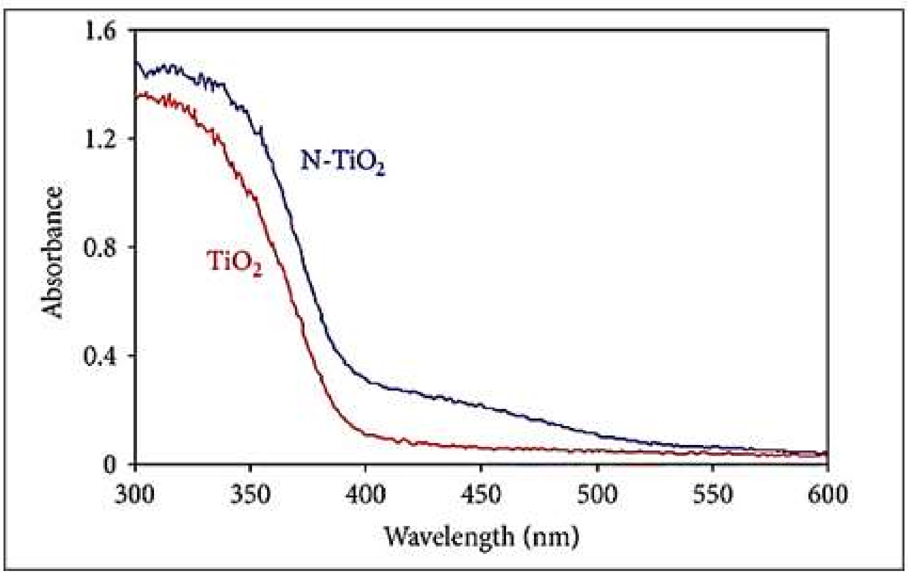

Figure 6. UV-vis absorption spectra of TiO_2 and N-TiO_2 [175].

The study shows that doping nitrogen at the titanium position shifts the absorption edge to lower energies and increases the absorption capacity of the material in the visible region by reducing

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the forbidden band width [176,177]. Moreover, it is shown that doping nitrogen in the oxygen position is highly optimal due to comparable atom size, small ionization energy, and stability as well as shallow donor and acceptor levels in the conduction band and valence band due to oxygen vacancy [177]. It has also been reported that TiO_2 (anatase and rutile) containing nitrogen in the interstitials of the crystal lattice has isolated impurity levels in the forbidden zone [178].

3. Efficient Methods of TiO_2 Synthesis

3.1. Hydrothermal Method of TiO_2 Preparation

TiO_2 can be obtained by high-temperature hydrolysis of various precursors directly in the autoclave or by hydrothermal treatment [179]. For example, nanosized TiO_2 powders are obtained by adding a 0.5M solution of titanium butylate in isopropanol to deionized water ($[H_2O]/[Ti]=50$). Then peptization is carried out at 70°C for 1 hour in the presence of hydroxycitetraalkylammonium [180]. This method is also widely used for the synthesis of monodisperse TiO_2 nanoparticles. In [181], TiO_2 nanorods were obtained by hydrothermal treatment of a dilute $TiCl_4$ solution in the temperature range of 333–423 °K with a synthesis duration of 12 h. In [181], TiO_2 nanotubes were synthesized by hydrothermal treatment of commercial photocatalyst P25 in a 10 M aqueous NaOH solution at 130°C and 24 h of synthesis.

The glycolate-oxo-peroxo-titanium (IV) complex was subjected to hydrothermal treatment in [182] to obtain titanium dioxide. In an ice bath at room conditions, 20 mmol of titanium metal powder was dissolved in a combination of 40 ml of hydrogen peroxide solution and 10 ml of ammonia solution. After two hours, all of the titanium powder dissolved and a yellow solution containing the peroxo-titanium complex was formed. Then 30 mmol of glycolic acid was immediately added and the mixture was heated to 353 K to promote complexation and remove excess hydrogen peroxide and ammonia until it formed an orange gel. To obtain an aqueous solution of the ammonium salt of the glycolate-oxo-peroxo-titanium (IV) complex, it was dissolved in distilled water. Using 2, 4, 8, 12 and 16 cm^3 of stock solution and the required amount of distilled water, 40 cm3 of titanium solutions with Ti = 12.5, 25.0, 50.0, 50.0, 75.0 and 100 mM concentration were created in the next step. After the solution was placed in a 50 cm3 jar, it was sealed with a stainless steel shroud and heated in an oven for 1 to 168 hours at 473 K. The autoclaves were then allowed to cool to ambient temperature Centrifugation was used to separate the precipitate formed, which was then washed thoroughly three times with deionised water. After drying overnight at 353 K in an oven, the sample was extracted. The particle sizes of TiO_2 polymorphs in the samples that were extracted from the Ti complex solution with a concentration of 50.0 mM as a function of the procedure duration are shown in Table 2.

Table 2. Particle sizes of TiO_2 [182].

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

The authors of the study [183] used the hydrothermal method to efficiently grow TiO_2 nanorods. To reduce hydrolysis and condensation, an equal volume of acetylacetone was combined with tetrabutyl orthotitanate. The mixture was then gradually stirred for five minutes at room temperature by adding 40 milliliters of water. Thirty milliliters of 28-30% aqueous ammonia solution was gradually added to the mixture dropwise with continuous stirring. The solution was then transferred

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to a 250 mL stainless steel autoclave and immersed in a silicone oil bath. The precursor solution was then heated to 170 °C and stirred continuously at this temperature for twenty-four hours. The autoclave was then spontaneously cooled down to ambient temperature. The final product was repeatedly thoroughly purified with aqueous HCl, 2-propanol and water. It was then dried for 12 h at 120 °C. Finally, the collected samples were incinerated for one hour in a high temperature furnace at 450 °C. X-ray examination of the samples showed that they contained a large number of anatase nanorods with an average pore width of 3.1 nm and a specific surface area of about 34.82 m2/g. To enhance the charge transfer ability, the authors of another work [184] obtained TiO_2 nanorods/nanoparticles using hydrothermal method. The obtained nanoparticles have a specific surface area of 84.83 m2/g and a pore diameter of 5.7 nm.

Using surfactant-assisted hydrothermal technology, TiO_2 with different morphologies including nanosheets, nanorods, nanotubes and nanoflowers were produced by adjusting the pH during the preparation process. The experimental results showed that the pH value is critical for controlling the shape of the generated TiO_2, as it can change the adsorption potential of surfactant on the surface of TiO_2 and its charge state in solution. The experimental protocols are summarised below: A solution resistant to hydrolysis at room temperature was created by mixing titanium isopropoxide and TEOA in the following ratio: TTIP: TEOA = 1:2. DI water was added to create solution A. Dodecanediamine was mixed with DI water to create solution B, which acts as a shape adjuster. Next, solution A and solution B were mixed. The pH of the mixed solution was adjusted by adding $HClO_4$ or NaOH. It was then placed in a 100 mL Teflon autoclave and incubated at 100°C for 24 h, after which the temperature was raised to 140°C for 72 h for nucleation and growth of TiO_2 particles. TiO2 nanospheres with particle sizes ranging from 30 to 60 nm were formed under acidic conditions at pH = 5.6. When the pH was increased, most of the prepared TiO_2 particles transformed from ellipsoids to nanorods. When the pH of the solution was changed to a value greater than 11, TiO_2 nanoflowers were formed. In the process of creating these structures, TiO2 nanosheets were initially formed and then folded to form the final structures at different pH values [185].

Hollow TiO_2 nanospheres can be obtained by hydrothermal method with the addition of aggressive chemicals, and they usually have large surface area and low density [185–187]. For example, the hydrothermal method was used to obtain porous hollow TiO_2 aggregates with a BET surface area of 168 m2/g and an average pore size of 12 nm. $Ti(SO_4)_2$ and NH_4F were dissolved in DI water for Liu preparation, then the resulting mixture was stirred and placed in a Teflon-lined autoclave. The hydrothermal synthesis was carried out in an electric furnace for six hours at 160°C. The appearance of the products is shown in Figure 7 (a-d). Despite having a greater estimated bandgap of 3.36 eV than P25 (~ 3.18 eV), the porous TiO_2 products exhibited double the activity of P25 when it came to the photodegradation of Rhodamine B [187]. The HF produced by NH_4F during the hydrothermal process is responsible for the production of porous, hollow TiO_2 aggregates. HF, a chemical etchant that is corrosive, will erode the inside of TiO_2 to create TiF4, which will ultimately result in hollow nanospheres. Using a similar hydrothermal technique, their subsequent investigation employed the metallic Ti powder as reactants together with a specific quantity of NH_4F and H_2O_2 (30 wt.%). With a diameter of about 1 μm, a shell thickness of 150 nm and a cavity size of about 600 nm, the obtained anatase TiO_2 resembled hollow spheres. The critical factors for the creation of TiO_2 hollow spheres from metallic Ti powders were reaction time, NH_4F concentration and H_2O_2 concentration. The H_2O_2 served as both an oxidant and a bubble generator, creating O2 bubbles that served as the aggregation centre when combined with Ti particles. After that, as shown in Figure 7(e, f) [186], TiO_2 nanoparticles gradually aggregated at the gas-liquid interface to form hollow TiO_2 spheres.

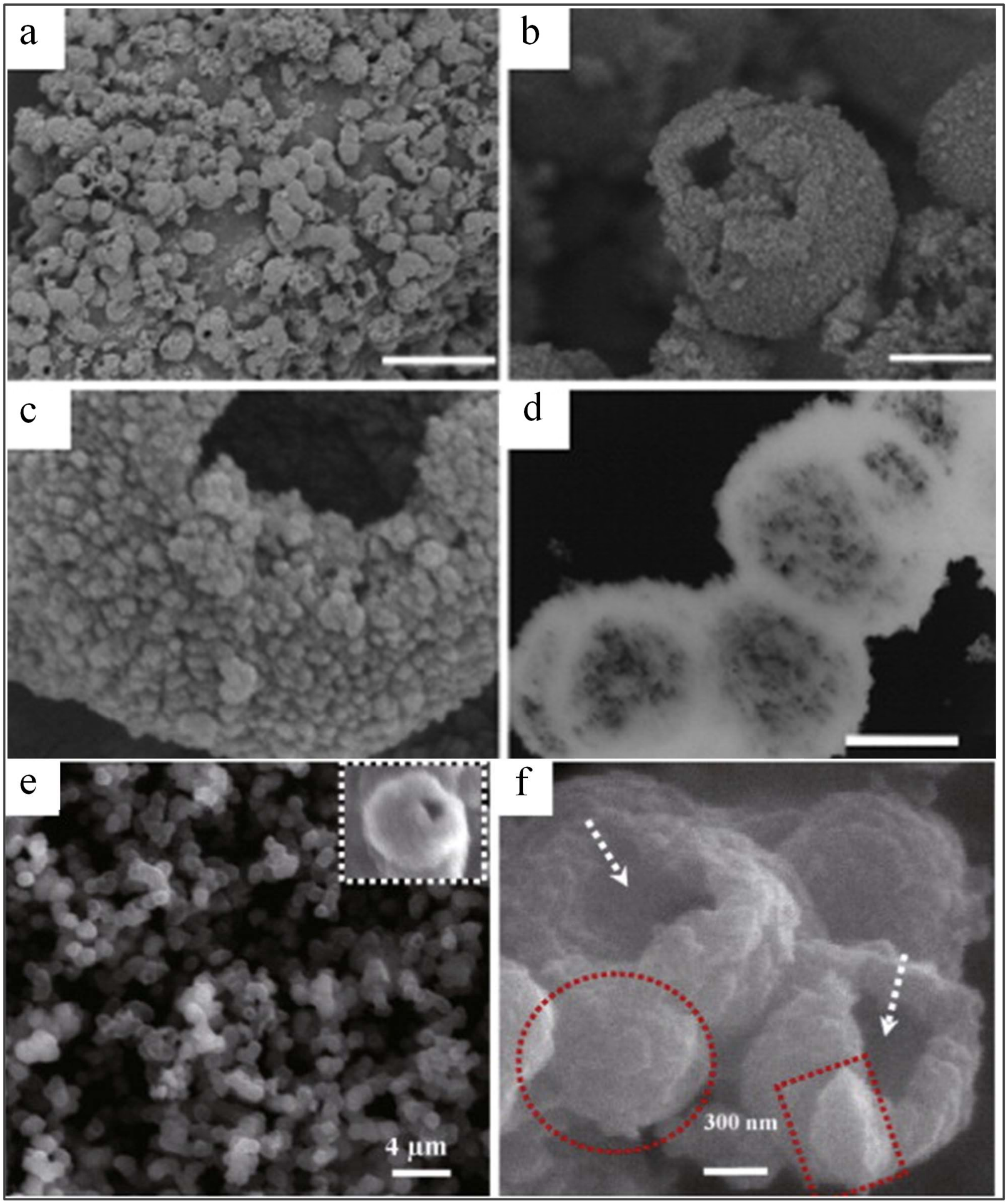

Figure 7. (a-c) FESEM and (d) TEM images of the porous, hollow TiO_2 aggregates prepared by the hydrothermal treatment at 160°C for 6 hr [187]; (e, f) SEM overviews of the TiO_2 hollow spheres synthesized by the hydrothermal method at 423 K for 10 hr [186]. The scale bars for (a-d) are 5 mm, 500 nm, 100 nm, and 500 nm, respectively.

The hydrothermal method can be used to create rutile-brucite TiO_2 nanocomposite by replacing NaOH with HCl. The obtained TiO_2 was used for photooxidation of methyl blue as well as for photocatalytic conversion of CO_2. In [186], titanium chloride was combined with 2 mol/L HCl to obtain a clear solution. The solution was then combined with 1.0 mL of 5 V/V% Triton X-100 in

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ethanol. After transfer to a flask, the prepared solution was refluxed for 22 h at 100°C. The final rutile-brucite nanocomposite structures were obtained by centrifuging the obtained products, washing them in water, drying them at room temperature and then calcination at 500°C [187].

3.2. Solvothermal Synthesis of TiO_2

The solvothermal and hydrothermal methods are practically identical except that the solvothermal method uses a non-aqueous solvent. The temperature of the solvothermal process can be much higher because some organic solvents have higher boiling points [188]. Usually, the size, shape and crystal structure of the obtained TiO_2 nanoparticles can be well controlled using the solvothermal method. The method is a versatile way to synthesize various nanoparticles with narrow size and dispersity distributions. Using the solvothermal method, TiO_2 nanoparticles with a characteristic size of less than 5 nm can be obtained [189].

The alcohol solvothermal method was first applied to obtain TiO_2 by Kang et al. [190]. In Kang's study, 1,4-butanediol was used as a solvent and titanium isopropoxide was used as a source of TiO_2. The 1,4-butanediol was mixed with titanium isopropoxide at 300°C for 50 min to facilitate the synthesis. The obtained TiO_2 powder was cleaned repeatedly with acetone and then left to dry for five hours at 100°C without calcination. The obtained anatase TiO_2 nanoparticles of size 20-50 nm were highly hydrophilic and were much more efficient in photocatalytic decomposition of chloroform than TiO_2 nanoparticles obtained by sol-gel method [190]. Subsequently, Nam and Han used the obtained TiO_2 for photodegradation of methyl orange and investigated the effect of several alcoholic solvents under the same conditions [191]. They got ready in the following ways: Titanium isopropoxide (0.1 mol) was added to glycerol, 1-butanol, and 1,4-butanediol, in that order. The combinations were heated to 300°C and kept there for an hour under auto-generated pressure. The findings demonstrated that the kinds of solvents employed during the reaction had a significant impact on the physical characteristics of the produced TiO_2, including crystal size, shape, and structure. Figure 8 (a-c) displays the SEM pictures of the TiO_2 that they produced [191].

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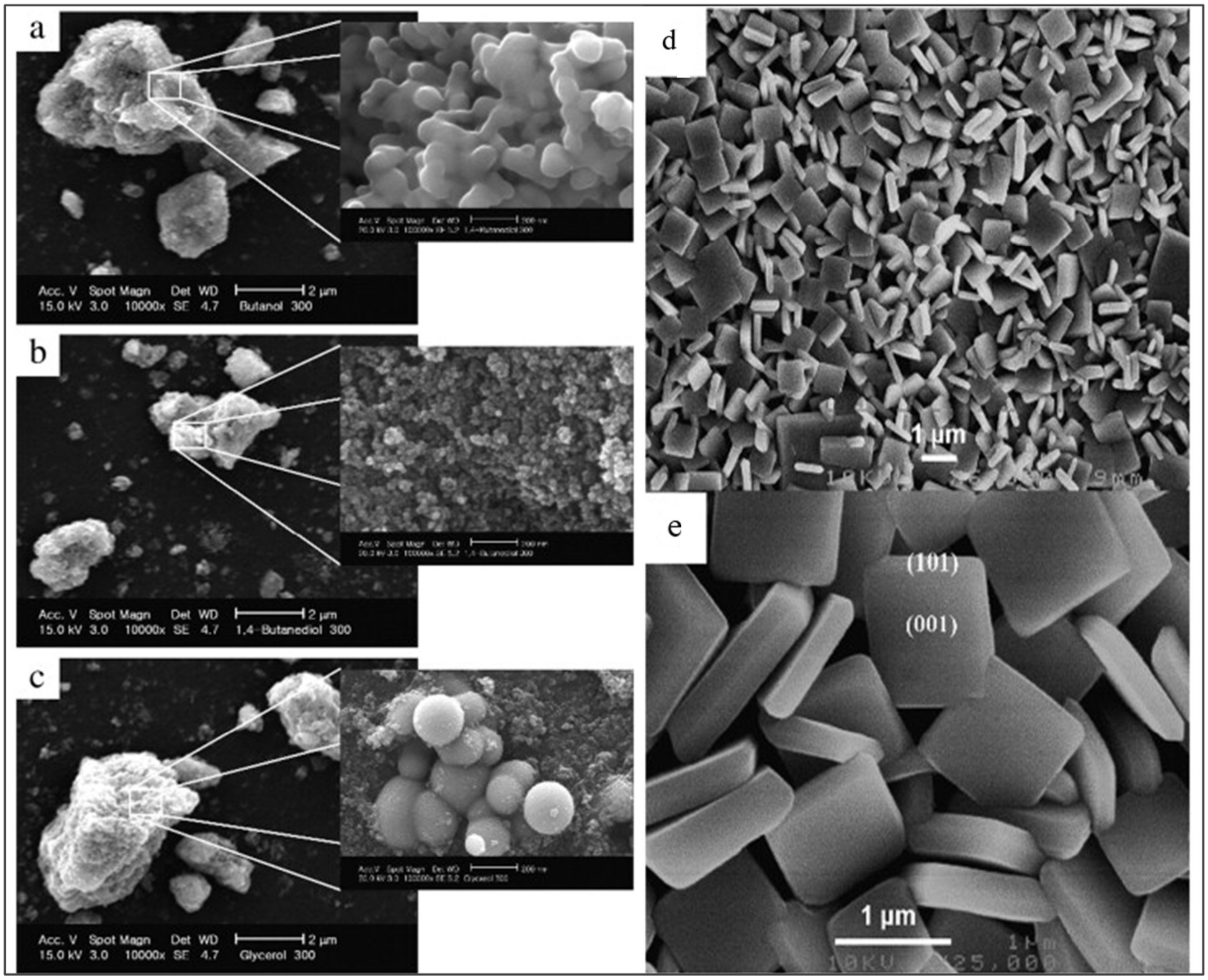

Figure 8. (a-c) SEM images for the TiO_2 prepared by the solvothermal method in various alcohol solutions [191]: (a) 300°C, butanol, (b) 300°C, 1,4-butanediol, and (c) 300°C, glycerol; (d, e) SEM images of the anatase TiO2 nanosheets synthesized with a reaction time of 11 hr [192].

The authors of [192] synthesized anatase TiO_2 nanosheets with pronounced {001} facets using an alcohol solvothermal technique. This procedure is a common method for fabricating nanosheets and can provide insight into subsequent methods. In a typical experiment, the pH was set to 1.8 and sufficient TiF_4 was added to a combination of hydrochloric acid and DI water to create a TiF_4 solution. Then 14.5 mL of the above aqueous solution of TiF_4, 13.38 mL of 2-propanol, and 0.5 mL of HF were placed in a Teflon-coated stainless steel autoclave. The autoclave was kept at 180°C for 5.5-44 h in an electric oven. Monocrystalline anatase TiO_2 nanosheets were obtained by centrifugation after the reaction, then washed three times with DI water and dried under vacuum overnight. Heat treatment at 600°C for 90 min was used to remove fluorine from the surface of anatase TiO_2. They showed that 2-propanol and HF promoted the isotropic development of single-crystalline TiO_2 nanosheets and that 2-propanol could enhance the stabilizing effect associated with fluorine adsorption on the (001) surface using first-order theoretical calculations. Figure 8 (d, e) shows the SEM images of the anatase TiO_2 nanosheets. TiO_2 nanosheets have the potential to remove organic pollutants by photocatalysis because they can produce five times more oxidative hydroxyl radicals (•OH) than P25 upon irradiation [193].

Huang et al. [193] prepared highly crystalline TiO_2 hollow spheres by alcohol solvothermal method without corrosion additives and shape controllers at 350°C, as shown in Figure 9. Although the surface area of the TiO_2 hollow spheres was only 28.2 m2/g by BET, they possessed good ability

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for photocatalytic degradation of methyl orange. Titanium n-butoxide (TNB) and ethanol (EtOH) were used for their synthesis. A mixed solution of TNB and EtOH was prepared by slowly adding TNB to EtOH with a certain volume ratio.

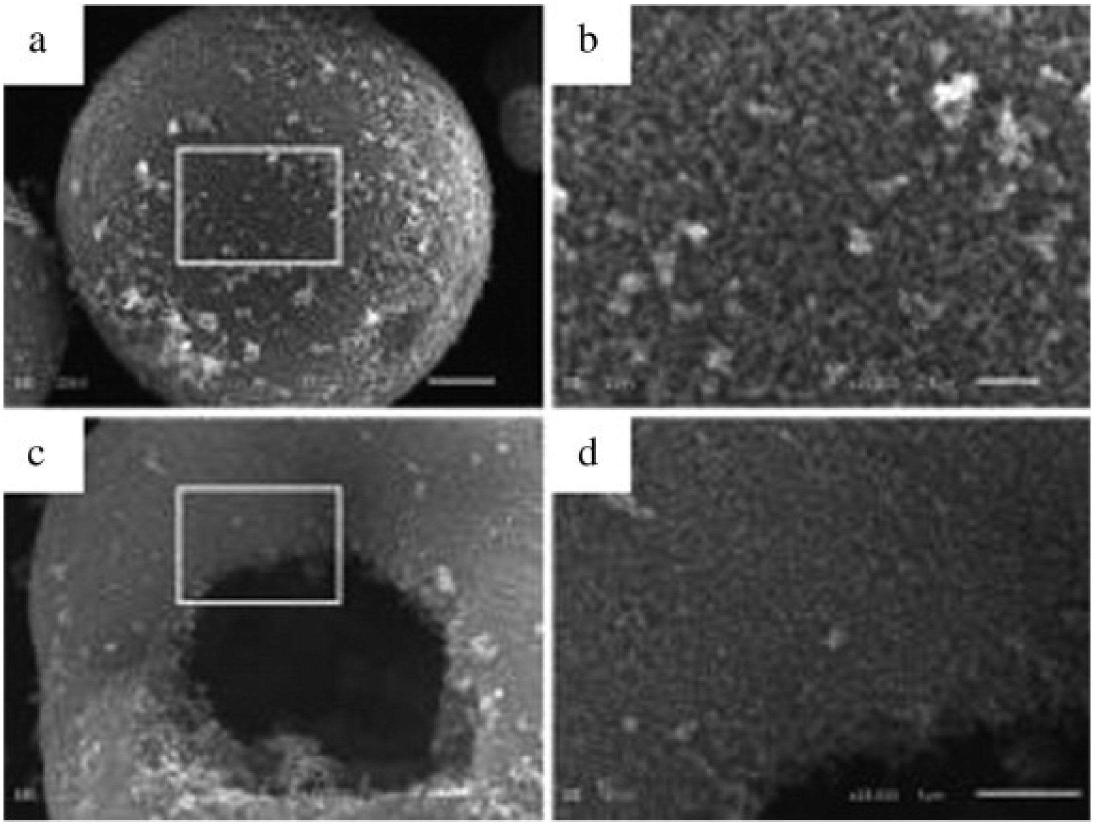

Figure 9. SEM images of the TiO_2 samples made by the solvothermal method [195]: (a) a whole sphere, (b) magnified image of the selected part in (a), (c) a broken hollow sphere, (d) magnified image of the selected part in (c).

After stirring for 30 min, the mixture was transferred to a stainless steel autoclave for the solvothermal reaction at 350 °C for 4 h. The precipitate was then washed three times with anhydrous ethanol and dried overnight. The precipitate was then washed three times with anhydrous ethanol and dried overnight. The prepared anatase TiO_2 spheres consisted of nanoparticles with an average diameter of 30.2 nm. According to their observations, pure TNB can decompose into TiO_2 nanoparticles at temperatures above 350°C to form 1-butene as in the reaction $Ti(OBu)_4 \rightarrow TiO_2 + CH_3CH_2CHCHCHCH$, which can serve as bubble templates for growing hollow TiO_2 microspheres from nanoparticles [195].

With LA serving as a suitable coordination surfactant to promote the anisotropic crystal growth of TiO_2, nanorods would be formed. If controlling NH_4HCO_3 and LA in a desired mole ratio, TiO_2 with different morphologies could be acquired. Figure 10 are the TEM images of the TiO_2 nanoparticles and nanorods prepared. Adding a small amount of metal chloride or nitrate into the mixed solution of NH_4HCO_3, LA, triethylamine, cyclohexane and $Ti(OBu)_4$, metal-doped (Fe^{3+}, Co^{2+}, Sn^{4+}, Ni^{2+}) TiO_2 nanocrystallines can be obtained [196].

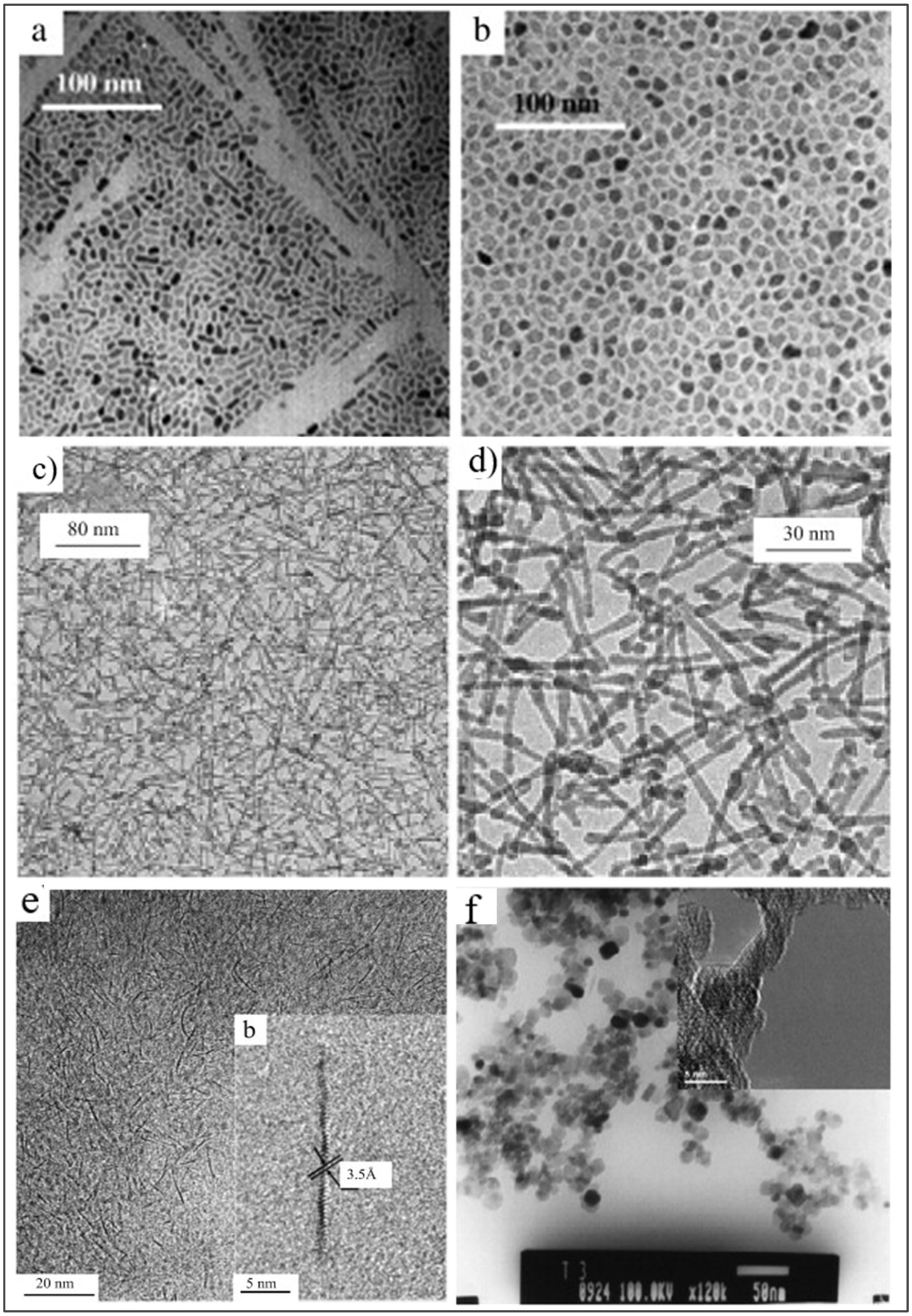

Figure 10. TEM images of TiO_2 nanoparticles (a, b) and TiO_2 nanorods (c, d) [196]; (e) TEM image of atomically thin N-TiO_2 wires grown at 180°C for 1 hr [197]; (f) TEM image of as-prepared [199].

Atomically thin anatase TiO_2 wires with a diameter of 4.5 Å were prepared by the carboxylic acid solvothermal process. These diameter-tunable, ultrathin TiO_2 nanowires were obtained as a

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result of optimized reaction temperature and reaction time. In Yang's synthesis [196], a certain amount of oleic acid and cyclohexane were mixed, and then $Ti(OBu)_4$ was added dropwise to the mixed solution. The resulting solution was heated to 150°C for 25 hr in a Teflon-lined stainless steel autoclave. The precipitation was extracted with an excess of ethanol. The titanium complex precursor was then redispersed in a mixture of octadecene, oleic acid, and oleylamine. The solution was heated to 180°C under stirring and maintained at that temperature for 1 hr to acquire N-doped TiO_2. Their research results suggested that a uniform mixture of oleic acid and oleylamine solution favors self-assembly of the wires. In addition, an increase in reaction temperature mainly increased the wire diameter, whereas prolongation of the precursor treatment time mainly caused an increase in the wire length. Their characterization data indicated that N-doping originated from the oxidative coupling of oleylamine on the surfaces of the atomically thin wires, forming the N–O–Ti surface structures. UV–vis absorption spectra indicated that the light absorption edge was 257 nm for the atomically thin TiO_2 wires, whereas it shifted to 600 nm with N doping. Figure 10 (e) is a TEM image of the N-TiO_2 obtained [197]. To further investigate the capping roles of oleic acid and oleylamine in the solvothermal system, Dinh found out that oleic acid and oleylamine had different binding strengths in controlling the growth of TiO_2 nanoparticles. By varying the ratio of them, TiO_2 with different shapes such as spherical, dog-bone, truncated and elongated rhombic was prepared. The thus-obtained TiO_2 was ascertained to be an excellent support for the synthesis of metal/TiO_2 photocatalyst in which metal clusters could be uniformly deposited on the surface of TiO_2 [198].

Thermal decomposition of titanium alkoxides by the solvothermal reaction in inert organic solvents, such as toluene and acetone, can produce crystallized TiO_2 nanoparticles [199,200]. In Praserthdam's research, nanocrystalline TiO_2 was prepared by toluene using the solvothermal method. In their synthesis, titanium n-butoxide was used as the starting material and was suspended in toluene in a test tube, which was then placed in a 300 mL autoclave. The autoclave was purged by nitrogen, after which it was heated up to 300°C and was held at 300°C for 2 hr before cooling down to room temperature. The obtained TiO_2 was washed by methanol several times and quenched in air at 77 K. The as-prepared anatase powders were of spherical shape with a size of 8–15 nm. The quenching in their research contributed to the formation of Ti^{3+} surface defects due to the thermal shock effect and promoted the photocatalytic ethylene decomposition ability of TiO_2. Figure 10 (f) displays a TEM image of the TiO_2 as prepared [199].

The preparation of TiO_2 microspheres is usually promoted by the addition of surfactants, while [201–204] prepared TiO_2 microspheres (Figure 11) with the solvothermal method in acetone without surfactants. Acetone itself might serve as a shape controller, but it hasn't been confirmed yet. In their preparation, a certain volume of $TiCl_4$ was added dropwise to acetone under vigorous stirring at 0°C. The concentration of $TiCl_4$ was adjusted to 0.3 mol/L. This mixed solution was transferred into an autoclave afterwards and was maintained at 120°C for 12 hr in an oven for solvothermal treatment. After reaction, the mixture was cooled to room temperature naturally. The resulting precipitates were filtered and thoroughly washed with excessive acetone and then dried at 120°C for 12 hr under vacuum. The precipitate was calcined under 500°C for 5 hr in air. The diameter of the layered microspheric anatase TiO_2 was about 3 μm with each layer around 300 [204]. On the contrary, the solvothermal preparation of TiO_2 in Chen's work also used acetone as a solvent, but TiO_2 nanoparticles were formed instead of microspheres.

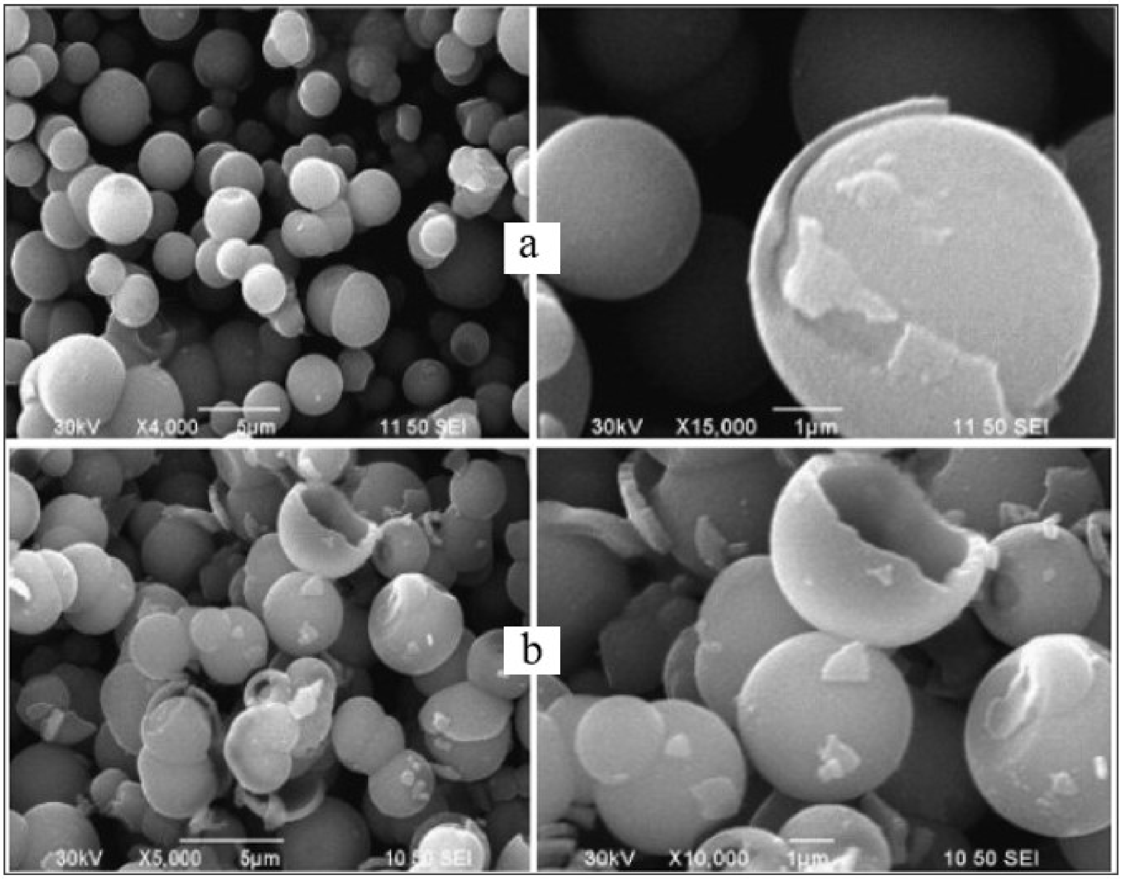

Figure 11. TEM images of the anatase samples treated at 120°C (a), and calcined at 500°C for 5 hr (b) with different magnifications [201–204].

3.3. Sol-Gel Method of TiO_2 Production

Nanoscale TiO_2 particles are synthesized by sol-gel method using hydrolysis of titanium precursors [205]. Titanium alkoxide or titanium tetrachloride are used as precursor. At the first stage of sol-gel process hydrolysis of titanium (IV) precursor is carried out with subsequent polycondensation, which leads to the formation of colloidal solution -sol of hydroxide particles, the size of which does not exceed several tens of nanometers. Low water content (low level of hydrolysis) and excess of titanium alkoxide in the reaction mixture contribute to the development of Ti-O-Ti bond chains. Chain formation leads to the formation of a three-dimensional polymer skeleton with a near-ordered degree. The high rate of hydrolysis promotes the formation of $Ti(OH)_4$, which interrupts the development of the Ti-O-Ti skeleton. The presence of a large number of Ti-OH groups and insufficient development of the three-dimensional polymer skeleton leads to loose packing of particles [205–207].

The use of low processing temperatures (<100°C) and molecular level composition uniformity makes the sol-gel technique very promising for the synthesis and manufacture of inorganic and organic-inorganic hybrid nanomaterials, as compared to the previously stated approaches [207]. The sol-gel process makes it simple to adjust the size and form of the particles. The sol-gel technique, which is commonly used to create TiO2 materials, generates fine, spherical powders of uniform size and typically starts with an acid-catalyzed stage involving titanium (IV) alkoxides [208,209]. The ability to mold the resultant material into desired shapes, such as fiber, film, and monodispersed powder, is one of the most appealing aspects of the sol-gel process. Figure 12 illustrates how a sol-gel technique, as proposed by Mehrotra and Singh [208], applies a number of variables and phases to regulate the final morphology.

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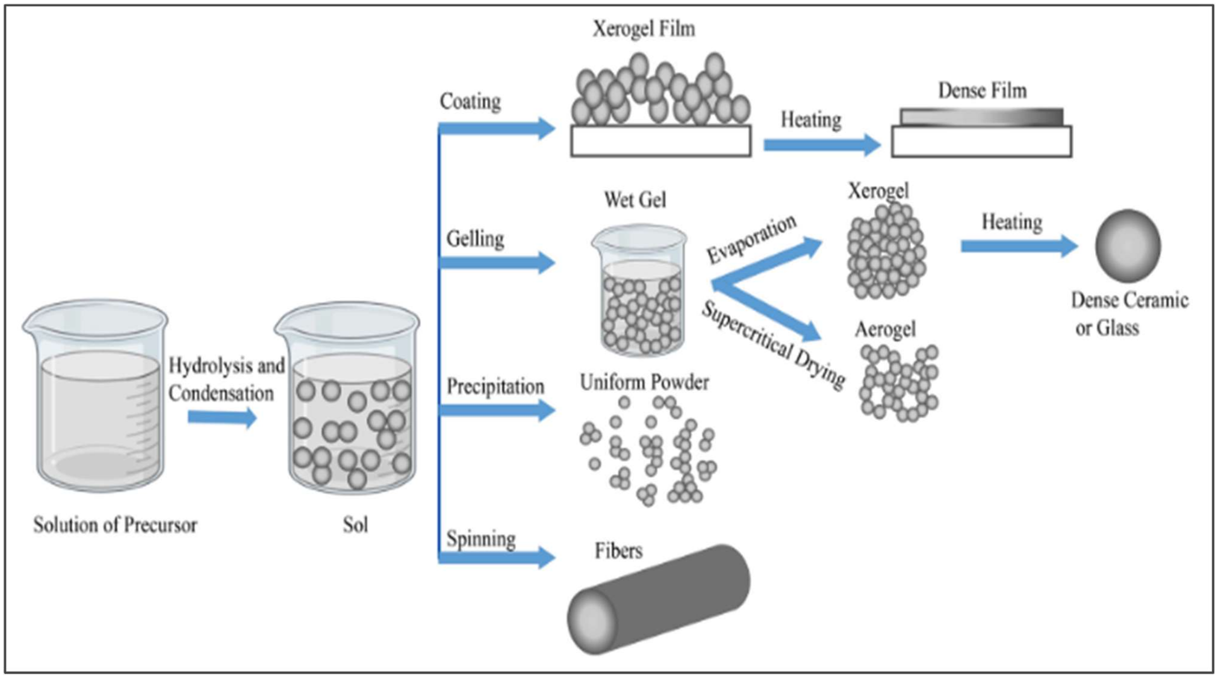

Figure 12. Different sol-gel process steps to control the final morphology of the product [209].

Metal oxides and metal chlorides are common precursors. The compound M─O─R, where M is metal, O is oxygen, and R is an alkyl group, is a metal alkoxide. The M─O bond is polarised, making it vulnerable to nucleophilic attack. Hydrolysis is a process in which an alkoxide in the presence of water undergoes a nucleophilic substitution reaction in which hydroxyl groups from water replace alkoxy groups (OR). Condensation is a process in which metal hydroxide groups combine with each other to form a hydrated metal-oxide network in which tiny nuclei are eventually formed.

The reactivity of metal alkoxides used in the sol-gel process needs to be controlled to obtain sols and gels with desired properties. This can be done by adding chelating ligands such as β-diketones, carboxylic acids or other complex ligands, or by using modifiers. To improve the control of the hydrolysis-condensation process in sol-gel fabrication, modifiers react with alkoxides to form new molecular precursors. These new precursors reduce functionality and reactivity, inhibit condensation and induce smaller species. The potential of acetylacetone to improve sol-gel processing of metal alkoxides was studied by Livage et al. in 1988 [209]. Susceptibility to hydrolysis is reduced when modifiers change the number of M-OR bonds available for hydrolysis. Since β-diketones are surface capping reagents and polymerisation fixatives, their use reduces nuclearity and results in the formation of fine particles. Acetic acid and other carboxylate ligands mainly act as bridging chelating ligands.

The sol-gel method has several advantages, which include [210]: (I) low-temperature preparation; (II) easy and efficient control of particle size, shape and properties; (III) improve the homogeneity of the raw materials; (IV) increase the purity of the starting material; and (IV) create the structure and properties of the material by appropriate choice of precursor.

3.4. Sonochemical and Microwave-Assisted Methods of TiO_2 Synthesis

The sonochemical strategy has been applied to deliver exceptionally photoactive TiO_2 nanoparticles by the hydrolysis of titanium tetraisopropoxide (TTIP) in unadulterated water or in an ethanol/water blend under ultrasonic radiation [211]. Acoustic cavitation, or the formation, growth, and collapse of bubbles within a liquid medium, is the basis for sonochemistry. Heat (~5000 K) and high tensions (~1000 atm) are delivered by cavitational breakdown [212]. Microwaves, which are electromagnetic waves with wavelengths ranging from 1 mm to 1 m and frequencies ranging from

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0.3 to 300 GHz, are utilized in microwave-assisted techniques. As indicated by Zhu and Chen [213], microwave warming includes two principal systems to be specific dipolar polarization and ionic conduction. Any materials that contain versatile electric charges, for example, polar particles or leading particles are by and large intensity by microwaves. When polar molecules attempt to align themselves with the rapidly shifting alternating electric field in the microwave, they generate heat through rotation, friction, and collision. Assuming particles are available in arrangement, they will travel through the arrangement and continually taking an alternate route in view of the direction of the electric field bringing about nearby temperature climb because of erosion and impact [214].

Microwave warming is as an elective intensity hotspot for quick warming with more limited response time and higher response rate, selectivity and yield when contrasted with the regular warming techniques [213]. Pulsed microwave heating and continuous microwave heating are the two types of microwave heating. In 1995, Jacob et al. came up with two models for how microwaves increase reaction rates. The main instrument expects to be that, albeit the response time is vigorously abbreviated for a microwave-instigated response, the energy or component of the compound response isn't modified suggesting that the upgrade of the response rate is because of the warm warming impact [215]. The second proposed system makes a supposition that there are "nonthermal microwave impacts" notwithstanding the warm impacts thus the impacts of microwave light in substance responses are because of both warm impacts and nonthermal impacts [216]. The nonthermal impacts are because of direct communication of microwaves with specific particles in the response medium.

Microwave radiations can likewise be applied to deliver different TiO_2 nanomaterials [217]. This method has the advantage of rapid heat transfer and selective heating for industrial processing. This procedure gives uniform conveyance of energy inside the example, better reproducibility and amazing control of exploratory boundaries. When compared to the several hours required for the conventional methods of forced hydrolysis at high temperatures (195°C), the colloidal TiO_2 nanoparticles can be prepared in a short amount of time (within 5–60 minutes) [218]. TiO_2 nanotubes which are unassuming and multi-walled with breadths of 8-12 nm and lengths somewhere in the range of 200 and 1000 nm were additionally pre-arranged utilizing this technique [219]. TiO_2 nanoparticles in the anatase stage were ready by Baldassari et al. [220] utilizing microwave-helped hydrolysis of titanium tetrachloride ($TiCl_4$) in a weaken acidic watery medium. Under microwave-hydrothermal conditions, they discovered that the product nearly crystallized within 30 minutes. Because the sulfate prevented brookite from crystallizing, they used H_2SO_4 as the acid to produce a pure anatase phase. In another review, they likewise pre-arranged TiO_2 nanoparticles in the rutile stage from $TiCl_4$ by a microwave-aqueous cycle at various temperatures somewhere in the range of 100 and 160°C for 5-120 min [220]. The morphology and size of the subsequent nanoparticles can be fluctuated by changing the hour of response, microwave power and reactant fixation.

In [221], titanium slags were converted into rutile TiO_2 powder by microwave activation (Figure 13). Then, the effects of the Na_2CO_3 additive on the calcined product's surface functional groups, crystallinity, phase transformation, and surface microstructure were examined. The following is the makeup of titanium slag: 9.72% Fe, 5.87% Al_2O_3, 5.23% SiO_2, 1.23% MgO, 1.81% CaO, 75.34% TiO_2, and other trace elements, such S and P.Using a planetary ball mill (model: QM-3SP4), the material was first processed into a powder for 180 minutes in order to improve the specific surface area of the slag. The obtained titanium slag sample, weighing 100 g, was then equally divided into five pieces, each of which was mixed with Na_2CO_3 in an agate mortar for ten minutes.

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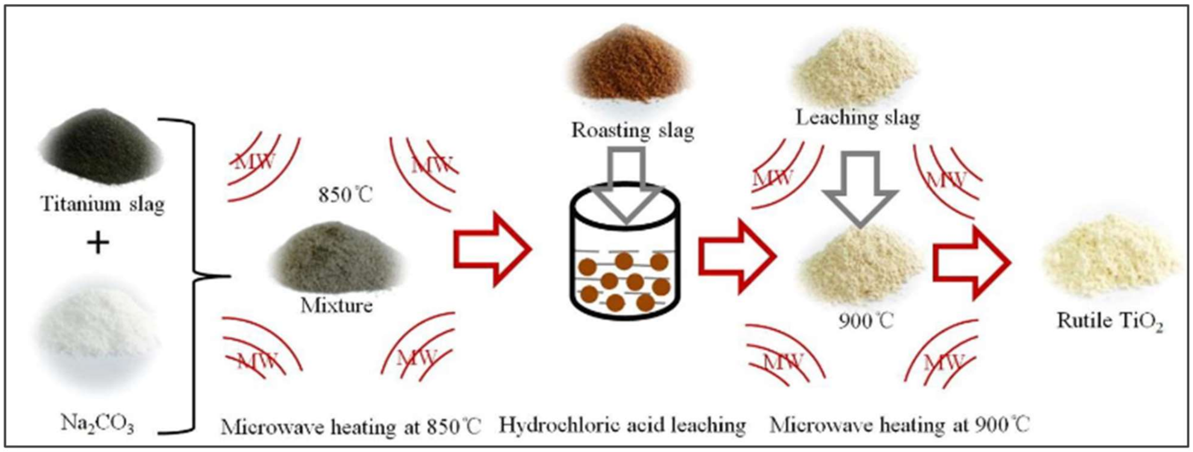

Figure 13. Scheme of the microwave synthesis of rutile TiO_2 [221].

For the mixes, the mass ratios of Na_2CO_3 to titanium slag were 0.2, 0.3, 0.4, 0.5, and 0.6, respectively. After that, the mixture was put in a corundum crucible and heated to 850°C for 30 minutes using a 1 kW microwave heating power in a microwave box reactor. With the use of a magnetic stirrer, 10 g of calcined slag was leached for 4 hours at 92–95°C using 20% HCl (mass ratio of liquid/solid: 4:1). Following three rounds of water washing, the residue from the leaching process was collected and put in a corundum crucible for high-temperature annealing in a microwave box reactor set at 900°C for 60 minutes with a 1 kW microwave heating power. The calcined product was then cooled and put to use in an analysis. The findings demonstrated that the ideal mass ratio of Na_2CO_3 was 0.4, at which point the average size of the crystallites was 43.5 nm and the rutile TiO_2 crystallinity attained its maximum value of 99.21 percent.

3.5. Synthesis of TiO_2 by Oxidation Method

These methods involve the oxidation of titanium metal using oxidants or anodization. Anodization of titanium sheet under a voltage between 10 and 20 V in 0.5% hydrogen fluoride leads to the formation of aligned TiO_2 nanotubes whose diameter is controlled by varying the applied voltage [212]. In another study, crystallized TiO_2 nanotubes were obtained when anodized titanium plate was heat treated at 500°C for 6 h in an oxygen environment [211]. Direct oxidation of the titanium metal with hydrogen peroxide has also been found to lead to the formation of TiO_2 nanorods. The TiO_2 can be obtained by placing a cleaned Ti metal plate in a 50 mL solution of 30 wt% H_2O_2 at 353 K for 72 h [222]. Formation of crystalline TiO_2 occurs via mechanism of dissolution precipitation and this phase can be controlled by addition of NaX (X = F^-, Cl^-, SO_4^{2-}) inorganic salts. Addition of Na_2SO_4 and NaF results in the formation of anatase phase and when rutile phase is needed, NaCl can be added during dissolution precipitation [223].

Acetone, pure oxygen and a mixture of oxygen and argon can be used as sources of oxygen for oxidation of titanium metal. Acetone is a good source of oxygen and when used at high temperatures, it results in nanorods which are well aligned and highly dense. Use of pure oxygen or a mixture of oxygen and argon results in crystal grain films and morphology of the nanoparticles can be controlled by the diffusion competition of oxygen and titanium [223,224].

3.6. Synthesis of TiO_2 by Chemical Vapor Deposition (CVD)

In these methods, materials in the vapor state are condensed to form a solid phase material. The process is normally carried out in a vacuum chamber and if a chemical reaction takes place, it is called chemical vapor deposition (CVD) and physical vapor deposition (PVD) if no reaction occurs. Examples of CVD include electrostatic spray hydrolysis, diffusion flame pyrolysis, thermal plasma pyrolysis, ultrasonic spray pyrolysis, laser-induced pyrolysis and ultrasonic-assisted hydrolysis. TiO_2

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films with grain size less than 30 nm and TiO_2 nanoparticles with sizes less than 10 nm were synthesized by pyrolysis of titanium tetraisopropoxide (TTIP) in a helium/oxygen atmosphere [225]. Thermal plasma synthesis [226] and spray pyrolysis [227] have been used in some studies but they are complex, capital and energy-intensive and the properties of the powder are not easy to control.

Chemical vapor deposition (CVD) is a method of producing thin films or powders by means of high-temperature decomposition reactions and/or gas-vapor interactions. is a method of producing thin films or powders by high-temperature decomposition reactions and/or interactions of gaseous precursors on a substrate (producing films) or in a reactor volume (producing powders) [228]. To date, it has been established that the nature of the substrate affects the size and distribution of crystals in TiO_2 films [229]. This method is used to obtain TiO_2 at 300-750°C, using titanium tetraisopropoxide as a precursor [230].

3.7. Green Synthesis of TiO_2

An ecologically benign substitute for the chemical method of creating nanomaterials is the "green" synthesis of TiO_2 functional materials. Using biological agents including bacteria, fungus, actinomycetes, yeast, and plants, the biological technique offers a multitude of resources for the production of nanoparticles [231,232]. The pace at which metal ions are reduced with the aid of biological agents is substantially quicker than it is because of the surrounding pressure and temperature. Significant advancements in "green" synthesis techniques for the creation of many nanoparticles have resulted from the extraction of TiO_2 from plant extracts [233]. Green tea extract was used by the authors in study [234] to create mesoporous TiO_2 nanoparticles using the sol-gel technique. 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 [235], 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. X-ray diffraction patterns showed the presence of rutile phase TiO_2 and confirmed an average crystallites size of 10 nm. The authors [236] synthesized TiO_2 nanoparticles by the hydrothermal method using Aloe Veragel for use as a photocatalyst in the degradation of picric acid. Aloe Verawas 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 0.1M 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 TiO2 nanoparticles ranged from 6 to 13 nm. In a study [237], titanium dioxide nanoparticles were efficiently synthesized using aqueous extracts of 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

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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.

3.8. Electrodeposition and Ionic Liquid-Assisted Methods

Electrodeposition is a plating process in which ions in a solution migrate under the influence of an electric field (electrophoresis) and are deposited onto an electrode. In a normal process, components containing one or more dissolved metal salts are immersed in electrolytes, and the metallic ions are attracted to the cathode to be deposited. Electrodeposition is easily controlled, can produce tight coating with uniform thickness and is able to coat complex fabricated objects [238,239]. Electrodeposition of TiO_2 nanoparticles onto multiwalled carbon nanotube arrays was conducted in an electrolyte consisting of 3 mol/L KCl solution, 10 mmol/L H_2O_2, and 10 mmol/L $Ti(SO_4)_2$. Multiwalled carbon nanotube arrays were used as the working electrode, an Ag/AgCl electrode as the reference electrode, and Pt as the counter electrode. The working potential was − 0.10 V and the deposition time was 30 min [240].

Ionic liquids refer to salts in the liquid state. Actually, when heated to a high temperature, almost all salts can become ionic liquids. The ionic liquid referred to here is a kind of salt that is in liquid states at low temperatures (< 100°C) or even room temperature. The ion size of these liquids is usually large and poorly coordinated, resulting in a low bounding force and a loose structure, thus forming a liquid rather than a solid at a relatively low temperature. Ionic liquids have many merits, they exhibit excellent thermal stability, powerful solubility, good electrical conducting ability, low viscosity, and have almost no vapor pressure. Usually, the low temperature ionic liquids have at least an organic cation (such as methylimidazolium and pyridinium ions) and an inorganic canion (such as halide, tetrafluoro-borate, and hexafluoro-phosphoric ions). Despite the fact that the ionic liquid is usually poisonous, it has found its way into the research of pharmaceuticals, gas treatment, cellulose processing, solar thermal energy, etc., and is recently used to modify the preparation process of TiO_2 [241–243].

Different binary ionic liquids were applied to synthesize TiO_2 hollow spheres. It was found out that the shape, size and crystallinity were different by varying the binary ionic liquid composition, which is a result of different interface interactions. In a typical process, 3.6 mL of binary ionic liquids were mixed with 0.4 mL of anhydrous toluene solution containing 0.2 mol/L titanium isopropoxide. 6 mL methanol was then added and centrifuged. The final mesoporous TiO_2 was obtained after filtration and calcination at 500°C. They tested all the binary mixtures of six different ionic liquids, which were 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([Hmim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF_6]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4]), and 1-octyl-3-methylimidazolium tetrafluoroborate ([Omim][BF_4]) and discovered that [Bmim][BF_4] + [Omim][PF_6] mixtures were the most effective group and would make anatase TiO_2 with a surface area of about 100 m^2/g after calcination [244]. Ionic liquid-assisted hydrothermal synthesis was reported by using 3-carboxymethyl-1-methylimidazoliurn bisulfate ([CMIM][HSO_4]), titanium isopropoxide, concentrated HCl and H_2O to fabricate rutile TiO_2 nanorod films. In a typical process, 0.5 mL titanium isopropoxide was added to a mixed solution of DI water, concentrated HCl and 0.5 mL [CMIM][HSO_4]. The resulting transparent mixture was then transferred to a hydrothermal autoclave with a piece of glass immersed in the solution. The autoclave was heated to 180°C for 3 hr. When ionic liquids weren't used in the process, the diameter of TiO_2 was about 250 nm, but when [CMIM][HSO_4] was used, the diameter of TiO_2 nanorods decreased to 62 nm. This was not only due to the effective prevention of the gathering of the nanoparticles by the surfactant-acted ionic liquids, but also because of the extended hydrogen bonding and ionic strength which favored the formation of small crystals. Figure 14 (a) is an FESEM image of TiO_2 nanorods in Mali's work [245].

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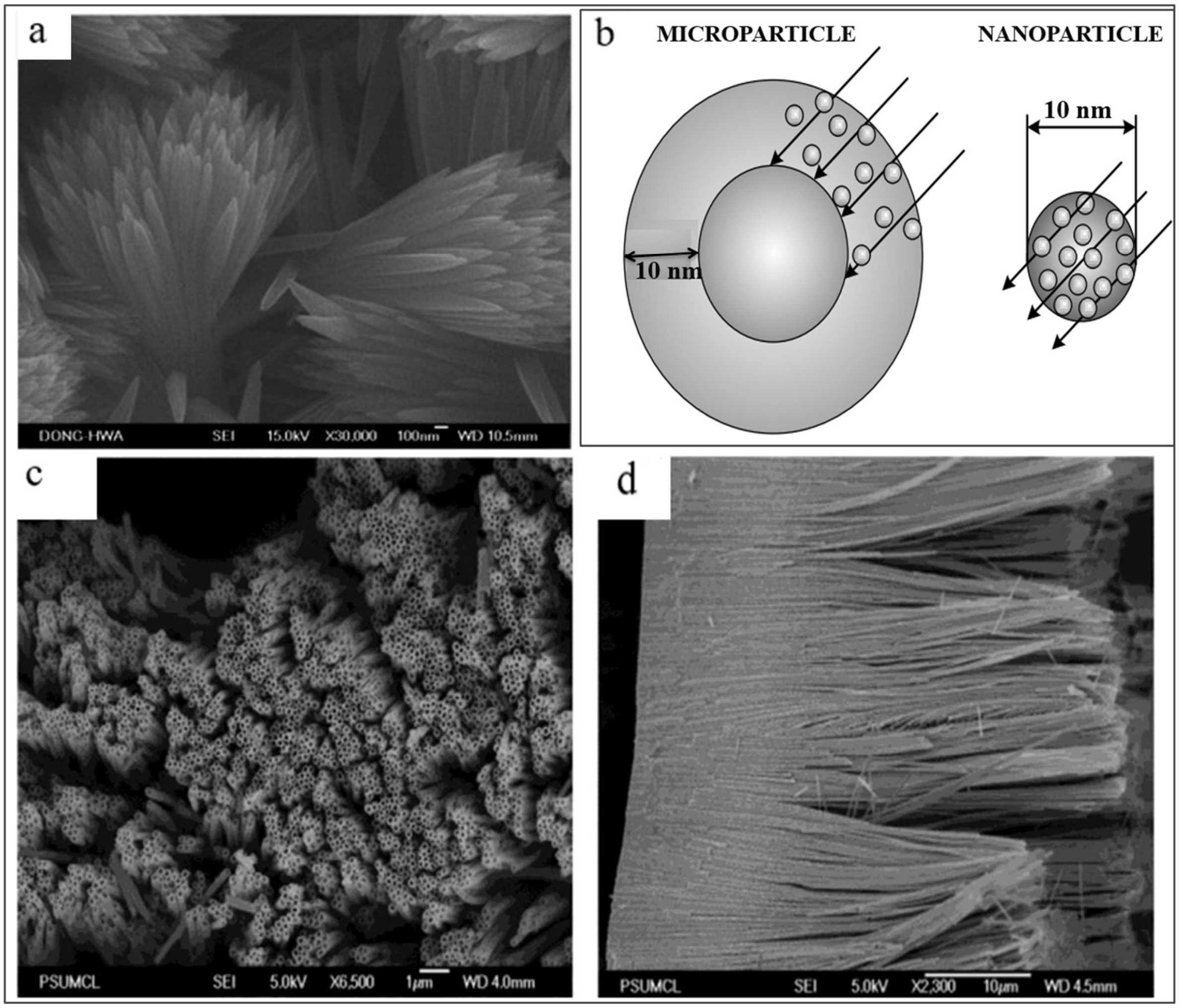

Figure 14. (a) An FESEM image of TiO_2 nanorods in Mali's work [245]; (b) absorption of light quanta in TiO_2 micro- and nanoparticles [190]; Microphotographs of the TiO_2 coating obtained by anodizing titanium in a fluoride-containing electrolyte: (c)-surface, (d)-slip [256].

3.9. Synthesis of Nanoscale and Thin Film Structures of TiO_2

It is obvious that the use of nanosized TiO_2 particles leads to a significant increase in its photocatalytic activity. An undoubted advantage of nanoparticles compared to microparticles is the greater probability of charge release on the catalyst surface. Due to the fact that the penetration depth of UV light of TiO_2 particles is limited (~100 nm), only the outer surface is active [246]. Figure 14 (b) shows a diagram of light absorption by TiO_2 nano- and microparticles.

As can be seen from Figure 14 (b), reducing the size of the photocatalyst particles to nanoscale values promotes light absorption by the entire volume of particles. In this regard, the use of TiO_2 in heterogeneous photocatalysis processes is associated with the need to obtain nanosized particles. To date, TiO_2 nanoparticles are obtained with various morphologies, mainly nanotubes, nanowires, nanorods and mesoporous structures [247].

Thus, the properties and applications of titanium oxide (TiO_2) nanostructures largely depend on the particle size, structure, effective surface area, and surface properties. Since these properties are in turn influenced with synthesis methods, in this section we will have an overview of different methods of synthesis of nanoparticles Titanium oxide (TiO_2) thin films [248–250]. Chemical reactions for the synthesis of substances can take place in gaseous, liquid or solid forms. The rate of penetration of reactants in the gas or liquid phase is several times faster than in the solid phase. Therefore, the synthesis methods for titanium dioxide-based nanostructures are mainly divided into liquid-phase

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synthesis and vapour-phase synthesis [251–253]. Moreover, nanostructured TiO_2 particles can be obtained by oxidation of metallic titanium using various chemical oxidants [254]. TiO_2 nanorods were obtained by this method (by oxidation of a titanium metal plate with hydrogen peroxide). In [255], the authors showed that anodic oxidation of titanium in a fluoride-containing electrolyte allows obtaining nanostructured coatings consisting of TiO_2 tubes, the properties of which can be controlled by varying the oxidation conditions. However, the authors showed that such coatings with a nanotube length of more than 1 μm have low adhesion, and their application is still very limited. Then the authors in [256] proved that poor adhesion is due to the low packing density of the nanotubes (Figure 14 (c, d)).

According to modern concepts, the growth model of TiO_2 nanotubes during potentiostatic anodizing consists of several stages, and the reactions responsible for the formation of porous aluminum oxide and TiO_2 nanotubes [254–257] are identical. Despite the similarity of the processes occurring during the anodization of titanium and aluminum, the morphology of the resulting oxides differs greatly. For example, during the anodization of aluminum, a mesoporous structure is formed, whereas during the anodization of titanium, both mesoporous and nanotubular structures can be obtained [257]. At the same time, the use of porous carriers active only under the influence of UV light, inside the pores of which there are particles activated by light with a wavelength of 400–700 nm, seems very promising. Such an approach will make it possible to use both visible and UV radiation in photocatalytic processes.

4. Concept of Photocatalysis Using TiO_2

In 1967, while Professor Fujishima and his colleague Honda [22,237,258] were experimenting, they encountered a strange phenomenon. They observed that when TiO_2 and Pt electrodes were placed in water, the formed circuit is capable of decomposing water into oxygen and hydrogen without an external electricity input, only when exposed to light [259,260]. Following this phenomenon, Honda discovered that Titanium oxide (TiO_2) has strong oxidizing properties, and focused his subsequent studies on the effect of this valuable substance on environmental phenomena such as sterilization, disinfection and pollution removal [261–267]. This important discovery, known as the photocatalytic or Honda-Fujishima effect, resulted in antibacterial products, being one of the most advanced tools for disinfection of spaces and one of the main branches studied in the materials industry [264–267].

TiO_2 photocatalysis is a photon-driven reaction process [214], starting with a photoadsorption event on the surface or bulk of TiO_2 (Figure 15). When TiO_2 adsorbs photons with energies greater than or equal to its band gap (Eg), electrons in the filled VB are excited to the vacant CBs, leaving holes in the VB.

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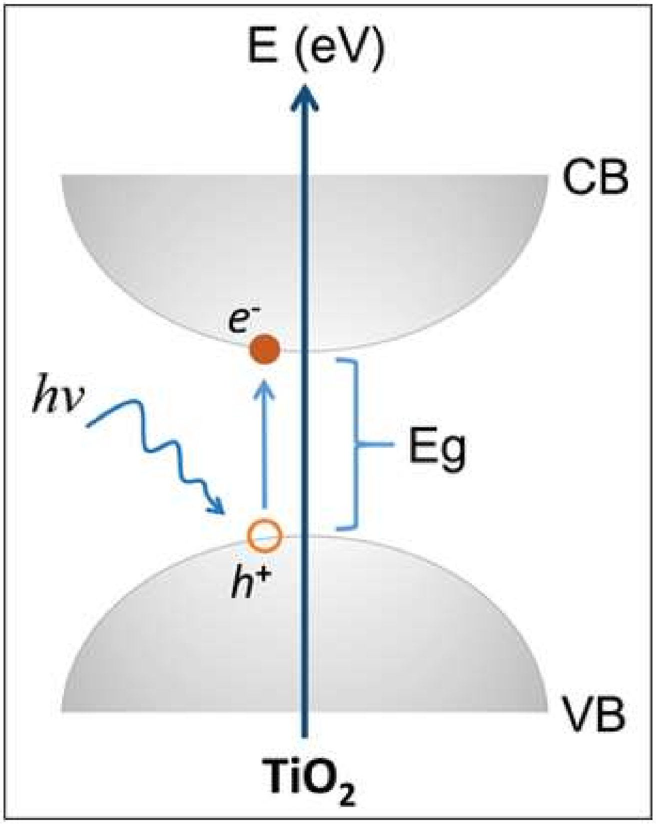

Figure 15. Schematic diagram of a typical excitation of electrons from the filled TiO_2 valence band to the unoccupied conduction band via band-to-band excitation.

The photocatalysts TiO_2 exhibits light absorption property and redox ability based on the position of the VB and CB band edges and the value of Eg. Essentially, the photocatalytic properties of TiO_2 are based on the generation of electron-hole pairs within the semiconductor particle by electromagnetic radiation. These pairs then interact with adsorbed molecules through redox reactions once they reach the surface of the TiO_2 particle. In this case, a part of the electrons and holes can be subjected to recombination in the volume or on the surface of TiO_2 (Figure 16). For effective photocatalytic processes, it is necessary that redox reactions involving electron-hole pairs be more efficient than recombination processes. It is known that for most reactions, titanium dioxide in the anatase phase state exhibits higher activity than other polymorphic modifications [269]. It has been suggested that the high photoreactivity of anatase is due to the higher location of the Fermi level, which reduces the ability to absorb oxygen and increases the degree of hydroxylation (i.e., the number of hydroxyl groups on the surface) [270]. In general, semiconductor photocatalysis is considered, from this point of view, as a multi-step process, which is illustrated in Figure 15. Such a process is initiated by the photoexcitation with electromagnetic radiation equal to or exceeding Eg (1), the separation of the charge carrier pairs (2), the diffusion of e^-/h^+ species within the material towards the surface, and the surface charge transfer for the reduction of adsorbed electron acceptors (3), and the oxidation of adsorbed electron donors (4), respectively [268]. Accordingly, the photo-induced electrons and holes should migrate to reach the surface of the material and react with adsorbed chemical species via surface charge transfer. Therefore, the Eg of a semiconductor is the minimum thermodynamic requirement for photocatalysis [270].

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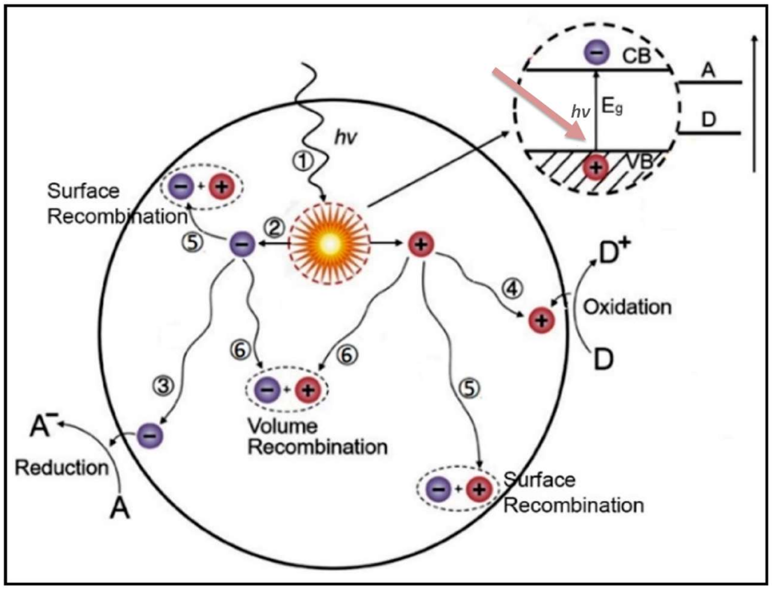

Figure 16. Pathways of the photogenerated charge carriers in a semiconductor photocatalyst [270].

One of the main limitations of semiconductor photocatalysis is the recombination of the photogenerated charge carriers, dissipating the absorbed energy as heat and affecting negatively the lifetime of the electrons and holes [268]. This undesired recombination occurred either indirectly, i.e., via surface defects (5), or directly, i.e., by band-to-band recombination (6). Such phenomena are highly reliant on the crystal structure of the semiconductor. To enhance effectively the redox reactions while minimizing recombination, the photogenerated charge carriers must migrate to the liquid junction through the solid and should react with adsorbed species directly at the semiconductor surface [270]. In the literature, there are data on reactions in which both crystalline phases show the same activity [271], and there are also data on the higher activity of rutile [272]. In addition, there are works in which the authors claim that a mixture of anatase (70–75%) and rutile (30–25%) is a more active photocatalyst than pure anatase [273]. The discrepancy in results may be due to various factors such as specific surface area, pore size, crystallite size, method of preparation, or the form in which the activity is expressed. A commercial titanium dioxide photocatalyst P25 (Evonik Industrials, Germany), consisting of an amorphous phase and an 80/20 mixture of anatase and rutile, shows higher activity in some reactions than pure crystalline phases [274]. The enhanced activity of the catalyst results from the efficient separation of charge carriers due to the multiphase nature of the particles [275]. Another commercial TiO_2 photocatalyst is Hombikat UV 100 (“Sachtlebem”, Germany), which consists only of anatase and has high activity due to the high rate of interfacial electron transfer. For example, it is known that the deposition of platinum on the surface of TiO_2 can lead to both an increase and a decrease in activity [275]. In most cases, this is explained by different ways of depositing Pt particles.

5. Growing Interest in the Application of TiO_2 Photocatalysis

In recent years, photocatalytic processes have found increasing applications in a variety of fields. Heterogeneous photocatalysis has already established itself as an inexpensive and sustainable technology for purifying water and air from a variety of hazardous pollutants, including organic substances and heavy metals [276]. The most active development of this technology is in Japan, USA, India and China. Figure 17 shows the number of scientific publications devoted to this field from 1967 to 2024, where it can be seen that in the last decade the interest in this field is steadily increasing [277]. According to the statistics on publications in the National Library of Medicine (PubMed) from

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1967 to 2000, from 3 to 7 publications were published annually, but from 2001 to 2013 and 2014 to 2024 there is a high growth of interest in research in the field of photocatalysis.

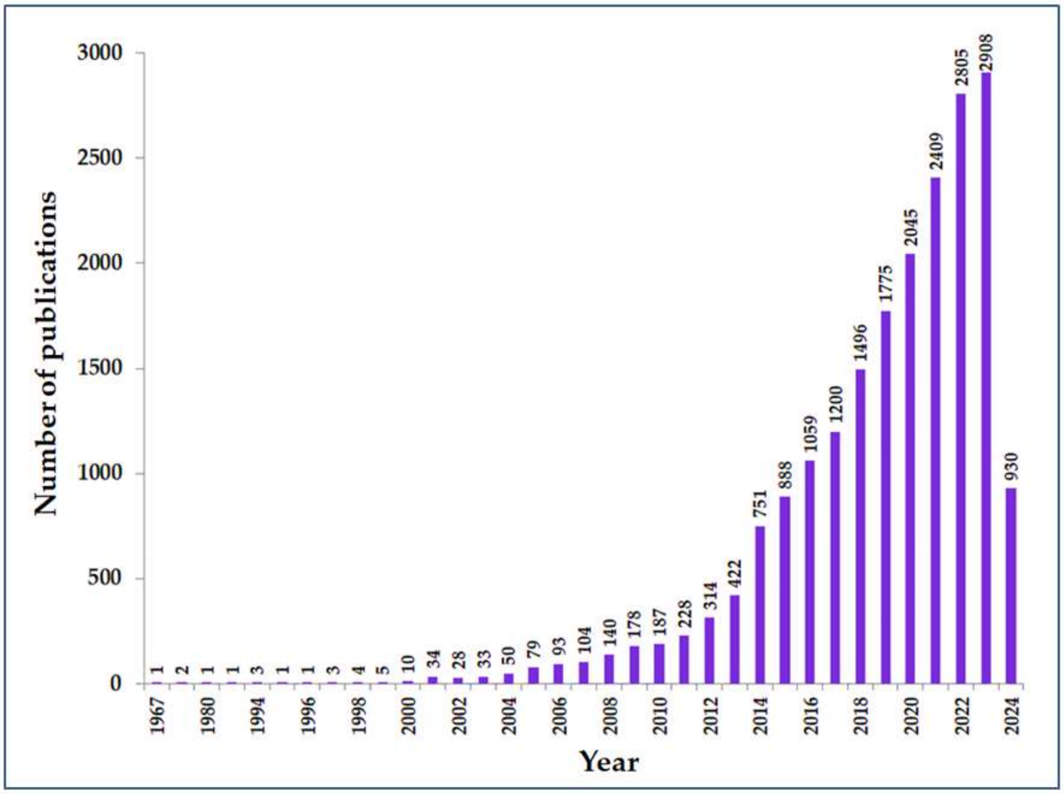

Figure 17. Annual statistics of scientific publications on photocatalysis.

The growing interest in this field is due to the fact that, unlike other processes such as reverse osmosis, nanofiltration, and ultrafiltration, photocatalysis is a cheap and potentially “stand-alone” water purification technology. At the same time, titanium dioxide, as a low-cost photocatalytic material, is prominent among other solid materials. In fact, according to Figure 18, the number of scientific publications dealing with titanium dioxide-based photocatalysis accounts for the bulk of publications in the field of photocatalysis. A total of 127 out of the total number (930) articles on photocatalysis have been published on the topic of titanium dioxide photocatalysis in the first trimester of 2024, of which titanium dioxide can be noted as the most sought-after material in this field of photocatalysis.

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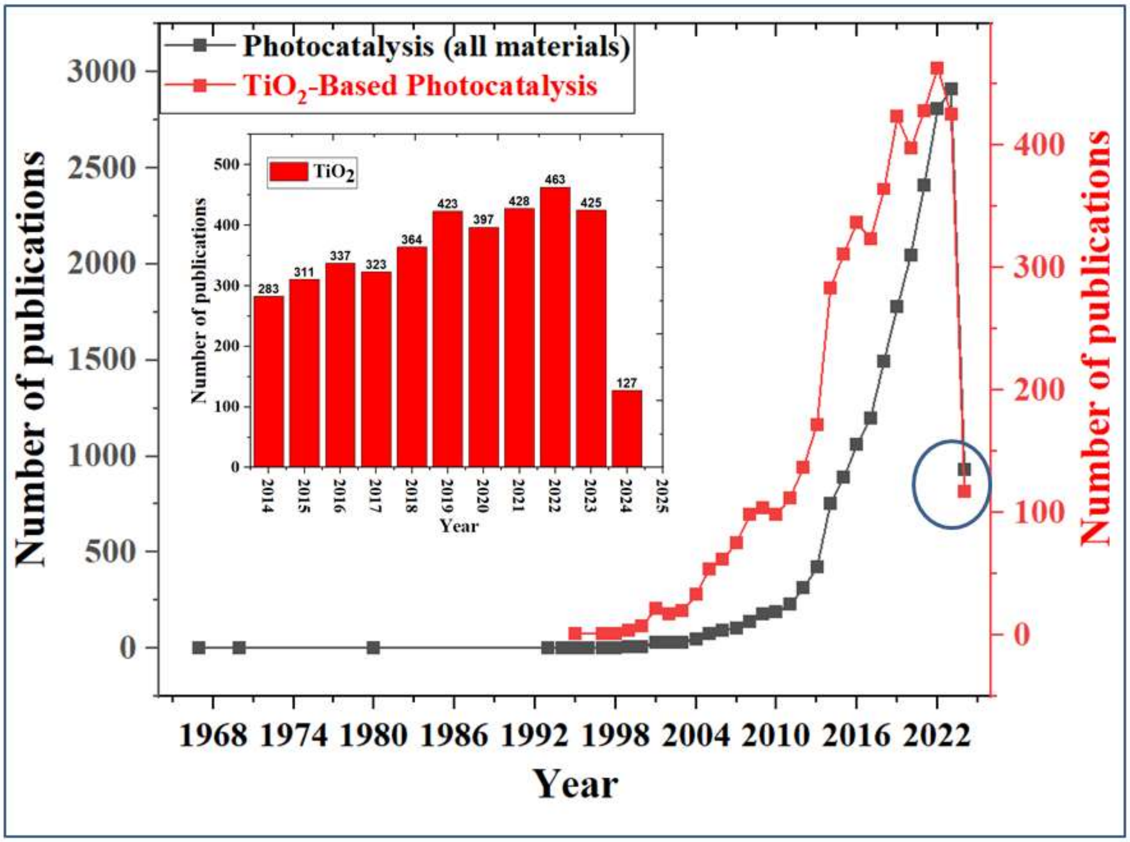

Figure 18. Comparison of the total number of scientific publications on photocatalysis with those on titanium dioxide-based photocatalysis.

The use of sunlight or ultraviolet radiation makes photocatalytic purification technology inexpensive, environmentally friendly, and possible to use worldwide. The use of photocatalysis processes requires minimal equipment and is suitable for developing countries as well as remote sites without access to electricity. TiO_2 photocatalysis has been successfully used in many developing countries for fresh water disinfection and decolorization [278]. Future environmental purification technologies also involve the use of TiO_2 as a photocatalyst capable of utilizing organic pollutants from water, air, and other media due to the formation of free OH radicals during the transformation reaction [278]. It is known that titanium oxide dust particles can act bactericidally [279] and even inhibit cancer cells [280] under the influence of UV light. Those or other properties of titanium oxide depend on its structural and morphological features and chemical varieties. This in turn depends on the technological conditions of synthesis and surface modifications. Specific examples of photocatalysis applications are given below.

5.1. Purification of Water and Air from Organic Pollutants

Recently, considerable attention has been paid to the use of photocatalysis for the oxidation of organic pollutants in wastewater, in particular because of its ability to oxidize almost any toxic organic substance to CO_2 and H_2O [281]. The essence of the photocatalytic process of oxidation of organic compounds is as follows: under the action of light energy, electron-hole pairs are formed in TiO_2 particles. Holes, when coming to the surface of the particle, interact with the electron donor in solution or with hydroxyl ions to form strong oxidizing agents such as hydroxyl or superoxide radicals. In turn, the conduction electrons reaching the surface of TiO_2 interact with oxygen [282], which leads to the formation of superoxide anion radical, electron can interact with organic substances that can act as electron acceptors. The formation of such particles makes the TiO_2 surface

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a very strong oxidizer, which allows the mineralization of harmful substances by their photocatalytic oxidation to H_2O and CO_2. Figure 19 shows the scheme of formation of such oxidants on the surface of TiO_2 under the action of light energy.

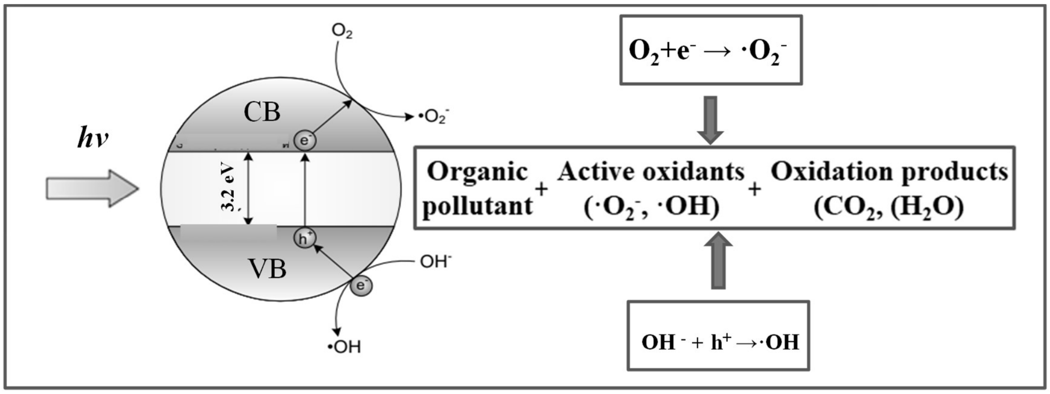

Figure 19. Scheme of formation of $OH^{\bullet}$, and O^{2-} particles on the surface of TiO_2 under the action of light.

Redox potentials (relative to the standard hydrogen electrode) for a number of the strongest oxidizing agents are presented in Table 3.

Table 3. Oxidizing potentials of various chemical agents.

Oxidizing agent	Oxidizing potential, V
Hydroxyl radical, $HO^{\bullet}$	+2.80
Electron hole in valence band, h^+	+2.70
Ozone, O_3	+2.07
Hydrogen peroxide, H_2O_2	+1.78
Permanganate ion, $(MnO4)^{2-}$	+1.70
Chlorine dioxide, ClO_2	+ 1.15
Chlorine, Cl_2	+1.40
Oxygen, O_2	+1.20
Superoxide radical, O^{2-}	-0.33
Electron in the conduction band, e^-	-0.50

As can be seen from Table 3, the $HO^{\bullet}$- particle is a very strong oxidizing agent (standard redox potential of 2.8 V), which allows the oxidation of most organic substances to CO_2 and H_2O. The processes occurring on the TiO_2 surface as a result of the oxidation of organic pollutants can be expressed by the following reactions:

$$TiO_2 + hv \rightarrow TiO_2(e_{CB}^- + h_{VB}^+)$$
$$TiO_2(h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^{\bullet}$$
$$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^{\bullet}$$
$$TiO_2(e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^-$$
$$O_2^- + OH^{\cdot} \rightarrow HO_2^-$$
$$\text{Organics} + OH^{\bullet} \rightarrow Oxidation\ products$$
$$\text{Organics} + h_{VB}^+ \rightarrow Oxidation\ products$$
$$\text{Organics} + e_{CB}^- \rightarrow Oxidation\ products$$

Photocatalytic water and air purification systems with artificial UV radiation have been on the market for several years, while solar photocatalytic purification plants are at the stage of

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demonstration and pilot projects. In addition, the combination of photocatalysis and membrane treatment can reduce the fouling of the filter membrane and thus significantly increase the efficiency of water treatment. Nitrogen oxides in tunnels are a serious problem during the summer months, especially in dense and large cities with high traffic levels. Japan and a number of European countries are actively using cement with TiO_2 additives for tunnel construction. The installation of ultraviolet lamps in such tunnels allows controlling exhaust gas emissions, mainly NO and NO_2 [283].

5.2. TiO_2 and Water Photolysis

Hydrogen is an environmentally friendly source of energy. Currently, hydrogen is produced from various primary sources such as natural gas, fuel oil, methanol, biomass, and coal [284–289]. Among these sources, photolysis of water, using solar energy, has attracted the most attention because of its potential. Direct photocatalytic using sunlight is the most efficient way to produce hydrogen because it avoids energy losses in the process of electricity transmission. Interest in this process intensified after the work of Japanese scientists Haunda and Fujishima in 1972 [286], who were able to obtain hydrogen by irradiating aqueous suspension of TiO_2 with UV light. From the thermodynamic point of view, the reaction of water photolysis proceeds with a significant positive change in the Gibbs free energy (ΔG^o = 237.2 kJ/mol, 1.23 eV per electron) [287]. For water splitting, the absorbed photon energy must overcome this energy. From the electrochemical point of view, the process of water decomposition into hydrogen and oxygen is stepwise and two electrons take part in it. To overcome the Gibbs free energy, a semiconductor photocatalyst must have a forbidden zone width with an energy greater than 1.23 eV. In addition, the conduction band must be located higher than the water reduction potential, and the valence band ceiling must be located lower than the water oxidation potential.

5.3. Treatment of Water from Inorganic Compounds

In addition to organic compounds, wastewater contains a wide range of inorganic compounds that are sensitive to photochemical transformations on the catalyst surface. Bromate, chlorate, azide, halide ions, and oxidazote can be photodegraded on the TiO_2 surface. Metal salts such as $AgNO_3$, HgCl, and organometallic compounds (e.g., CH_3HgCl) can be removed from water [289–291].The content of metals in water, such as mercury (Hg), chromium (Cr), and lead (Pb), is very hazardous to human health. Removal of these toxic metals is a fundamental task in obtaining quality water. With the help of heterogeneous photocatalysis, it is possible to remove heavy metals from wastewater through their reduction by TiO_2. The authors of [292,293] demonstrated the possibility of photoreduction of metals from industrial wastewater, such as gold (Au), platinum (Pt), and silver (Ag).

5.4. Medical Applications of TiO_2

Hospitals and medical equipment are the only places where climate-controlled treatment and disinfection are required. However, in other environments where plants and animals grow and reproduce, making them susceptible to contamination, microbes and pests must be removed from surfaces, water and air [294]. A basic method of eradicating these microbes must be developed because microbial, viral and fungal structures are becoming increasingly resistant to the use of chemical disinfectants, and these chemicals themselves are dangerous and lethal to human life [295]. DNA damage can affect any biological structure. Therefore, one effective method of getting rid of them is to create proteins that disrupt DNA cell division cycles [296]. On the other hand, the increase in oxygen gas pressure is harmful and deadly for all types of life [297]. Thus, titanium surfaces, along with their photocatalytic properties, produce oxygen free radicals and create an oxygen poisoning for microorganisms [298]. Japanese scientists have found that adding TiO_2 to fabrics helps create an antibactericidal material. Thus, gowns sewn from this fabric can be treated with UV for disinfection after working hours [299]. In their works [299,300], the authors managed to find an application of the photocatalysis effect of TiO_2 nanoparticles in photodynamic therapy to destroy cancer cells. The

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researchers managed to remove cancerous tumors from the colon in mice using photo-catalytic oxidation [300]. TiO_2 nanoparticles were injected at the site of the cancerous tumor, and illumination was performed using a fiber optic cable. As a result, the light produced reactive oxygen species that oxidized the tumor cells.

Cancer is considered one of the greatest challenges for modern medicine. Despite the continuous development of modern cancer therapies, the first line of therapy is surgical removal of the tumour and/or radiation therapy. Chemotherapy is usually an adjunctive therapy, but its use is limited by many factors [301,302]. First of all, chemotherapeutic drugs are extremely toxic to rapidly proliferating, both cancerous and healthy, tissues of the human body. Therefore, new delivery systems are still being sought to increase the tissue specificity of therapy and reduce systemic effects. Many chemotherapeutic drugs are also ineffective due to the multidrug resistance (MDR) mechanism exhibited by cancer cells, which is related to the overexpression of some members of the ABC efflux transporter superfamily, which perceive the drug as a poison and eliminate it from the matrix. Currently, one of the most frequently studied chemotherapeutic drugs is doxorubicin (DOX). Although it offers many advantages in the therapy of various cancers, the use of doxorubicin is associated with side effects, among which cardiotoxicity is the most severe and dangerous [302,303]. The use of nanoparticles and the combination of chemotherapy with photodynamic or photothermal therapy could be a potential solution to both problems (Figure 20). Titanium nanoparticles have significant advantages in this field, providing efficient delivery of drug molecules, hence better pharmacokinetics, and targeted delivery.

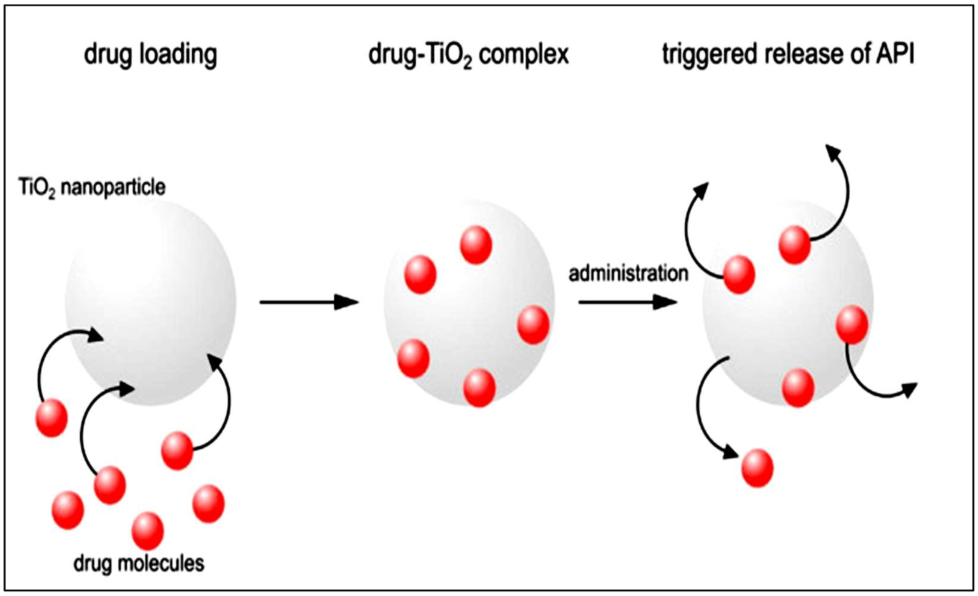

Figure 20. Simplified mechanism of titanium (IV) oxide as drug delivery vehicle [302].

The potential application of one-dimensional TiO_2 whiskers for drug delivery in cancer therapy and their synergistic effect on the internalization and accumulation of daunorubicin in SMMC-7721 cells were first investigated by Li et al. [304]. In addition, conjugation of doxorubicin (DOX) to TiO_2 nanoparticles was reported to induce a synergistic response in breast cancer cell lines [305]. For blood-contacting medical materials, it is important to minimize the tendency of their surface to adsorb blood proteins and enhance blood coagulability to reduce the risk of thrombosis. Titanium oxides are known to be highly compatible with blood, so they are often proposed as coatings for blood-contacting implants. The conducted study of the interaction of blood plasma proteins with titanium oxides will allow a better understanding of the nature of the interaction of foreign surfaces with blood, as well as their integration into tissues, starting from the first meeting with blood during surgery and then in the subsequent process of wound healing. Research in this area is being carried out at an accelerating pace and in recent years, optimization of the properties of titanium oxide

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nanoparticles for photodynamic therapy with excitation by UV or visible light after doping with organic photosensitizers has been developing.

Applications of titanium dioxide in medicine are going further than the design of drug delivery systems or applications as vehicles for chemotherapeutics. Titanium Oxide Nanoparticles have been applied in pharmacy, especially in pharmaceutical chemistry and technology, as well as medicine, including growing areas related to dentistry and surgery [306].

5.5. Photocatalytic Reduction of CO_2

The process of direct conversion of CO_2 and water vapour into hydrocarbon fuel using sunlight is aimed at solving two main global problems: ecological - reduction of CO_2 content in the atmosphere and energetic - obtaining high-energy fuel using the energy of sunlight. In [307], the process of CO_2 reduction by H_2O vapor on the surface of various semiconductor compounds (in the form of TiO_2, ZnO, CdS, SiC, and WO_3 powders) under xenon lamp illumination was studied. American scientists have developed a composite photocatalyst that acts selectively with respect to the process of reducing CO_2 to CO under the influence of visible light. The main components of this photocatalyst are an enzyme (catalyst), sensitizer, and nanoparticles of titanium dioxide [308]. The enzyme included in the composite photocatalyst catalyzes exclusively the two-electron reduction of CO_2 to CO, bypassing the undesirable one-electron radical pathway. In contrast to other TiO_2-based systems, the investigated system is characterized by selectivity and allows obtaining the target product without impurities.

The greatest success in this direction was achieved by American scientists, who, as a photocatalyst, used TiO_2 nanotubes obtained by anodic oxidation of titanium modified with Cu or Pt nanoparticles [309]. The total productivity for all hydrocarbons obtained in the laboratory was 160 μL/hour per gram of nanotubes. These results are 20 times higher than all previously described methods, but they are still too low for direct practical application. At present, there is an extensive search for new photocatalysts for CO_2 reduction, but despite the abundance of different photocatalysts, the main preference is still given to TiO_2, the surface of which is doped with metal nanoparticles [310]. Thus, water photolysis and carbon dioxide reduction are among the promising areas that have both scientific and applied significance for mankind.

6. Current Challenges

Despite intensive research over the past decades, the desired photocatalytic efficiency of TiO_2 has not yet been achieved at a level suitable for large-scale practical applications. For example, a survey of more than 80 major global water treatment companies showed that only about 4% have utilized photocatalysis on a pilot scale [311]. This is a clear sign of lack of patronage of the technology. If TiO_2 is chosen for the application of such technology, the effect of anions on the lifetime of TiO_2 reactor layers cannot be adequately addressed until the electronic, structural and optical properties of TiO_2 nanoparticles and their interactions in aqueous media are addressed in detail ciently, both theoretically and experimentally. The approach will focus on modifying the model of research methods and presentation and discussion of results. The style of research methods and discussion in reported cases of TiO_2 deactivation in aqueous suspensions does not reflect differences in the lattices or phase stability of TiO_2, while these differences (in lattices) play an important role in computational and experimental analysis. Early thermodynamic analyses of the phase stability of nanocrystalline anatase and rutile were performed by Zhang and Banfield [312]. They concluded that when the particle size is reduced to 14 nm, the structure of anatase becomes more stable than that of rutile. Penn and Banfield [313] indicated that anatase clusters dominate on 101 surfaces while rutile clusters usually dominate on 110 surfaces according to the results of Ramamurthy, Vanderbilt and King-Smith calculations [314]. The reason for the change in phase stability is the higher free energy of rutile arising from the energetics of the dominant surface facet types in such small particles [315]. These minute details should be taken into account in future modeling and experiments.

The behavior in volume also deserves consideration. In the case of bulk quantities, rutile is the most stable crystalline structure of TiO_2. For nanoparticles, however, the anatase structure becomes more favorable for medical applications [315]. This has been observed experimentally, for example, in the case of thin layers of TiO_2 [316]. The driving force behind this phase transformation is the surface energetics of the different surfaces of TiO_2. A nanoparticle is a closed object bounded by surface boundaries and the surface-to-volume ratio increases dramatically compared to larger particles, and the various surface energies begin to play an increasingly important role in particle energetics.

In addition, reports on the deactivation of TiO_2 in aqueous media often do not specify the reaction conditions (except pH and opacity), despite the fact that photoreactions are sensitive to reaction conditions. The phenomenon of photo-induced hydrophilic effect and its conditions are often ignored, and it is a well-known phenomenon in surface science research, describing a process in which UV irradiation in air causes water droplets to wet the surface of a TiO_2 film, resulting in a decrease in contact angle over time. Although temperature is also a factor when molecules or atoms come into contact with a surface, numerous analyses of temperature dependence, especially in gas-TiO_2 photocatalysis, have been published in Temperature Programmed Desorption (TPD) [317] as it provides information on how reaction temperature affects the binding energy of the adsorbate and surface, but its influence is often ignored when discussing aqueous photodegradation. Among the various materials that have been studied for photocatalytic CO_2 reduction, titanium dioxide is of great interest because of its high photocatalytic activity, high physical and chemical stability, non-toxicity and low cost [318,319]. But also in this area, there are two major problems faced by TiO_2-based photocatalysts for conventional applications. Thus, the large forbidden band width (3.3 eV), which limits its photoabsorption to ultraviolet (UV) light only, and the rapid recombination of electron-hole pairs that limits the photocatalytic efficiency negatively affect the yield fraction in CO_2 photoreduction. Regarding the problem of medical applications, studies have shown that exposure to TiO_2 can reduce cell viability and increase caspase-3 levels, indicating the possibility of inducing cell cytotoxicity and apoptosis. One study found that only particles smaller than 100 nm at doses of 50 and 100 g/mL could induce apoptosis of Caco-2 cells [320], which prompts a comprehensive investigation into the cause and solution of this problem. The toxicity of TiO_2 depends on factors such as particle size, shape, exposure scenario, dose, crystal structure and surface charge. It is crucial to thoroughly investigate the combined cytotoxic effect of doped TiO_2. TiO_2 is a common pigment in the plastic industry that may pose a threat to aquatic life due to the potential leaching of TiO_2 and other toxic plastic additives during environmental weathering of large pigmented plastic wastes [321]. In the former case, the surface functions of pigmented TiO_2 or TiO_2 nanoparticles differ between the two particle types and within each size class. In the latter case, the exposure pathway for human or environmental exposure differs between studies, with results showing that particle efficacy and biological model sensitivity differ between published reports. Although the knowledge base on industrially significant titanium dioxide and its environmental health effects is large, the fine details of the physicochemical properties of the particles combined with the design of the toxicology study add notable differences in the types and extent of adverse health effects observed [321]. However, despite the existing barriers, the development and understanding of a highly efficient TiO_2-based photocatalyst will continue, so the challenges of large-scale application of TiO_2 for water disinfection, cancer eradication, and carbon dioxide reduction are only a matter of time. Further work in this area should focus on optimizing the properties of this material by tuning and engineering its structure.

6. Opportunities

To date, most of the fundamental processes in TiO_2 photocatalysis can be studied on model TiO_2 surfaces by ensemble-averaged experimental methods, including STM, TPD, PSD, IRAS, etc. However, detailed dynamical information on the transient structure of adsorbates, reaction intermediates, bond breaking/formation, and changes in the electronic structures of adsorbates cannot yet be obtained using these methods. Fortunately, the development of ultrafast time-resolved methods gives us the ability to follow these dynamic processes in the photocatalysis of TiO_2. For example, the dynamic processes of bond breaking and bond formation during CO desorption and CO oxidation on Ru (0001) have been successfully tracked by Nilsson and co-workers [322] using

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time-resolved femtosecond emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS) techniques. In addition, time-resolved UPS and 2PPE techniques have been successfully utilized to monitor electron transfer dynamics and valence band changes associated with electron-mediated surface reactions [314–322]. In addition, time-resolved SFG (TD-SFG) can monitor the transition structures of adsorbates in photocatalysis by tracking molecular vibrations. With the advent of new methodology and high-knockdown technology, it may provide opportunities to further deepen the understanding of TiO_2 photocatalysis and shed light on the fundamental photochemical mechanisms and basic principles of TiO_2 photocatalysis.

6. Summary and Future Perspectives

Photocatalysis is an environmentally friendly technological process in which solar energy is converted into useful chemical reactions. In claiming the most efficient photocatalytic activity of TiO_2, challenges and limitations arise, which are mainly related to the synthesis methods of functionalized titanium dioxide-based materials. Therefore, researchers aim to propose and/or modify various methods to overcome the existing barriers in TiO_2 photocatalysis applications and thereby enhance the further development of photocatalytic applications using titanium dioxide. In this review, the known methods for the synthesis of titanium dioxide are reviewed and summarized, and the advantages and challenges related to the properties and morphology of titanium dioxide-based functional materials obtained by these methods are discussed. Great importance in this context is given to the use of nanoparticles, which improve the expected results by modifying the size, shape and physicochemical properties of the particles. It is revealed that poor recombination of charge carriers is one of the main limitations in the photocatalytic process involving titanium dioxide, which can be solved by doping, metals and non-metallic modifiers that have the ability to suppress the recombination of photogenerated electrons and holes, providing charge carrier separation. At the same time, it can improve the photoenergy capture by narrowing the forbidden band of TiO_2. The applications of TiO_2 photocatalysis are based on environmental decontamination, biomedical, pharmaceutical and energy applications. Thus, TiO_2 photocatalysis plays a crucial role in achieving higher technological development while maintaining a balance with environmental sustainability, which is in line with some of the main goals of the UN sustainable development strategy.

Consideration of future perspectives is important to fill the gaps in the development process of TiO_2-based photocatalysis, which requires gradual development towards practical applications in different scenarios. Future research should focus on theoretical (DFT, machine learning predictions) and experimental studies based on the electron capture mechanism, to study in detail and precisely modify the process to achieve higher photocatalytic efficiency and extend the lifetime of photoexcited electrons and holes in TiO_2.

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Abbreviation List

TiO_2, titanium dioxide
BG, bandgap
CB, conduction band
VB, valence band

References

1. Wang J, Azam W. Natural resource scarcity, fossil fuel energy consumption, and total greenhouse gas emissions in top emitting countries. Geoscience Frontiers. 2024; 15(2):101757. doi:10.1016/j.gsf.2023.101757
2. Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiuchi Y, Anpo M, et al. Understanding TiO_2 Photocatalysis: Mechanisms and Materials. Chem Rev. 2014; 114(19):9919–86. doi:10.1021/cr5001892
3. Xuan VN, Hoa PX, Thu NTP, Huong LM. Factors affecting environmental pollution for green economy: The case of ASEAN countries. Environmental Challenges. 2024; 14:100827. doi:10.1016/j.envc.2023.100827

4. Kabir M, Habiba UE, Khan W, Shah A, Rahim S, Rios-Escalante PRDL, et al. Climate change due to increasing concentration of carbon dioxide and its impacts on environment in 21st century; a mini review. Journal of King Saud University - Science. 2023; 35(5):102693. doi:10.1016/j.jksus.2023.102693
5. Bordet A, Leitner W. Adaptive Catalytic Systems for Chemical Energy Conversion. Angew Chem Int Ed. 2023; 62(33):e202301956. doi:10.1002/anie.202301956
6. 6. Hassan, Q., Tabar, V. S., Sameen, A. Z., Salman, H. M., & Jaszczur, M. (2024). A review of green hydrogen production based on solar energy; techniques and methods. *Energy Harvesting and Systems*, *11*(1), 20220134.
7. Dang V-H, Nguyen T-A, Le M-V, Nguyen DQ, Wang YH, Wu JC-S. Photocatalytic hydrogen production from seawater splitting: Current status, challenges, strategies and prospective applications. Chemical Engineering Journal. 2024; 484:149213. doi:10.1016/j.cej.2024.149213
8. Zhang C, Li N, An G. Review of Concentrated Solar Power Technology Applications in Photocatalytic Water Purification and Energy Conversion: Overview, Challenges and Future Directions. Energies. 2024 ; 17(2):463. doi:10.3390/en17020463
9. Mohtaram, S., Mohtaram, M. S., Sabbaghi, S., You, X., Wu, W., & Golsanami, N. (2024). Enhancement strategies in CO2 conversion and management of biochar supported photocatalyst for effective generation of renewable and sustainable solar energy. *Energy Conversion and Management*, 117987.
10. Worku AK, Ayele DW, Deepak DB, Gebreyohannes AY, Agegnehu SD, Kolhe ML. Recent Advances and Challenges of Hydrogen Production Technologies via Renewable Energy Sources. Adv Energy and Sustain Res. 2024; 5(5):2300273. doi:10.1002/aesr.202300273
11. Kumar A, Rana S, Dhiman P, Sharma G, Stadler FJ. Current progress in heterojunctions based on Nb2O5 for photocatalytic water treatment and energy applications. Journal of Molecular Liquids. 2024; 399:124360. doi:10.1016/j.molliq.2024.124360
12. Albini A, Fagnoni M. 1908: Giacomo Ciamician and the Concept of Green Chemistry. ChemSusChem. 2008; 1(1–2):63–6. doi:10.1002/cssc.200700015
13. Zhu S, Wang D. Photocatalysis: Basic Principles, Diverse Forms of Implementations and Emerging Scientific Opportunities. Advanced Energy Materials. 2017; 7(23):1700841. doi:10.1002/aenm.201700841
14. Bruner L, Kozak J. Zur Kenntnis der Photokatalyse. I. Die Lichtreaktion in Gemischen: Uransalz + Oxalsäure. Zeitschrift für Elektrochemie und angewandte physikalische Chemie. 1911; 17(9):354–60. doi:10.1002/bbpc.19110170905
15. Eibner, A. (1911). Action of light on pigments I. *Chem.-Ztg*, *35*, 753-755.
16. Baur E, Perret A. Über die Einwirkung von Licht auf gelöste Silbersalze in Gegenwart von Zinkoxyd. Helvetica Chimica Acta. 1924; 7(1):910–5. doi:10.1002/hlca.192400701109
17. Renz C. Über die Einwirkung von Oxyden auf Silbernitrat und Goldchlorid im Licht. Helvetica Chimica Acta. 1932; 15(1):1077–84. doi:10.1002/hlca.193201501118
18. Goodeve CF, Kitchener JA. The mechanism of photosensitisation by solids. Trans Faraday Soc. 1938; 34:902. doi:10.1039/tf9383400902
19. Ravelli D, Dondi D, Fagnoni M, Albini A. Photocatalysis. A multi-faceted concept for green chemistry. Chem Soc Rev. 2009; 38(7):1999. doi:10.1039/b714786b
20. Lotfabadi P. Analyzing passive solar strategies in the case of high-rise building. Renewable and Sustainable Energy Reviews. 2015; 52:1340–53. doi:10.1016/j.rser.2015.07.189
21. Boddy PJ. Oxygen Evolution on Semiconducting TiO[sub 2]. J Electrochem Soc. 1968; 115(2):199. doi:10.1149/1.2411080
22. Fujishima, A., & Honda, K. (1972). Electrochemical photolysisof water at a semiconductor electrode. *nature*, *238*(5358), 37-38.
23. Tuntithavornwat S, Saisawang C, Ratvijitvech T, Watthanaphanit A, Hunsom M, Kannan AM. Recent development of black TiO2 nanoparticles for photocatalytic H2 production: An extensive review. International Journal of Hydrogen Energy. 2024; 55:1559–93. doi:10.1016/j.ijhydene.2023.12.102
24. Schrauzer, G. N., & Guth, T. D. (2002). Photolysis of water and photoreduction of nitrogen on titanium dioxide. *Journal of the American Chemical Society*, *99*(22), 7189-7193.
25. Aldosari OF, Hussain I. Unlocking the potential of TiO2-based photocatalysts for green hydrogen energy through water-splitting: Recent advances, future perspectives and techno feasibility assessment. International Journal of Hydrogen Energy. 2024; 59:958–81. doi:10.1016/j.ijhydene.2024.01.306
26. Dai W, Wang H, Xiao M, Wang Z, Chen X, Fu X. Visible Photocatalytic Hydrogen Production from Ch3oh Over Cuo/Wo3: The Effect of Electron Transfer Behavior of the Adsorbed Ch3oh. SSRN Journal. 2022; doi:10.2139/ssrn.4147104
27. Arora I, Garg S, Sapi A, Ingole PP, Chandra A. Insights into photocatalytic CO2 reduction reaction pathway: Catalytic modification for enhanced solar fuel production. Journal of Industrial and Engineering Chemistry. 2024; 137:1–28. doi:10.1016/j.jiec.2024.03.011
28. Alli YA, Oladoye PO, Onawole AT, Anuar H, Adewuyi S, Ogunbiyi OD, et al. Photocatalysts for CO2 reduction and computational insights. Fuel. 2023; 344:128101. doi:10.1016/j.fuel.2023.128101

29. Chen Z, Zhang G, Cao S, Chen G, Li C, Izquierdo R, et al. Advanced semiconductor catalyst designs for the photocatalytic reduction of CO2. Materials Reports: Energy. 2023; 3(2):100193. doi:10.1016/j.matre.2023.100193
30. Fang, S., Rahaman, M., Bharti, J., Reisner, E., Robert, M., Ozin, G. A., & Hu, Y. H. (2023). Photocatalytic CO2 reduction. *Nature Reviews Methods Primers*, *3*(1), 61.
31. Wang Z, Seo J, Hisatomi T, Nakabayashi M, Xiao J, Chen S, et al. Efficient visible-light-driven water oxidation by single-crystal Ta3N5 nanoparticles. Nano Res. 2023; 16(4):4562–7. doi:10.1007/s12274-022-4732-5
32. Zhan X, Lei T, Wang L, Zhang H, Ou D, Yang M, et al. Enhanced photocatalytic removal of tetracycline and methyl orange using Ta3N5@ZnIn2S4 nanocomposites. Journal of Photochemistry and Photobiology A: Chemistry. 2024; 451:115538. doi:10.1016/j.jphotochem.2024.115538
33. Zhao T, Ye Z, Zeng M, Li W, Luo W, Xiao Q, et al. Molten Salt Synthesis of Mg-Doped Ta_3N_5 Nanoparticles with Optimized Surface Properties for Enhanced Photocatalytic Hydrogen Evolution. Energy Fuels. 2023; 37(23):18194–203. doi:10.1021/acs.energyfuels.3c02587
34. Liu Z, Fan S, Li X, Niu Z, Wang J, Bai C, et al. Synergistic effect of single-atom Cu and hierarchical polyhedron-like Ta3N5/CdIn2S4 S-scheme heterojunction for boosting photocatalytic NH3 synthesis. Applied Catalysis B: Environmental. 2023; 327:122416. doi:10.1016/j.apcatb.2023.122416
35. Dong Y, Ai F, Sun-Waterhouse D, Murai K, Moriga T, Waterhouse GIN. Optical and Photocatalytic Properties of Three-Dimensionally Ordered Macroporous Ta_2O_5 and Ta_3N_5 Inverse Opals. Chem Mater. 2023; 35(19):8281–300. doi:10.1021/acs.chemmater.3c01903
36. Li S, Cai M, Wang C, Liu Y. Ta3N5/CdS Core–Shell S-scheme Heterojunction Nanofibers for Efficient Photocatalytic Removal of Antibiotic Tetracycline and Cr(VI): Performance and Mechanism Insights. Adv Fiber Mater. 2023; 5(3):994–1007. doi:10.1007/s42765-022-00253-5
37. Zhao T, Ye Z, Zeng M, Li W, Luo W, Xiao Q, et al. Molten Salt Synthesis of Mg-Doped Ta_3N_5 Nanoparticles with Optimized Surface Properties for Enhanced Photocatalytic Hydrogen Evolution. Energy Fuels. 2023; 37(23):18194–203. doi:10.1021/acs.energyfuels.3c02587
38. Akter J, Hanif MdA, Islam MdA, Sapkota KP, Lee I, Hahn JR. Visible-light-active novel α-Fe2O3/Ta3N5 photocatalyst designed by band-edge tuning and interfacial charge transfer for effective treatment of hazardous pollutants. Journal of Environmental Chemical Engineering. 2021; 9(6):106831. doi:10.1016/j.jece.2021.106831
39. Jia X, Wang C, Li Y, Zhang R, Shi Z, Liu X, et al. All-Solid-State Z-scheme Ta3N5/Bi/CaTaO2N photocatalyst transformed from perovskite CaBi2Ta2O9 for efficient overall water splitting. Chemical Engineering Journal. 2022; 431:134041. doi:10.1016/j.cej.2021.134041
40. Hussain E, Ishaq A, Abid MZ, Waleed MZ, Rauf A, Jin R, et al. Sunlight-Driven Hydrogen Generation: Acceleration of Synergism between Cu–Ag Cocatalysts on a CdS System. ACS Appl Energy Mater. 2024; 7(5):1914–26. doi:10.1021/acsaem.3c03010
41. Li M, Zhang J, Wang L, Cheng X, Gao X, Wang Y, et al. Direct Z-Scheme Oxygen-vacancy-rich TiO2/Ta3N5 heterojunction for degradation of ciprofloxacin under visible light: Degradation pathways and mechanism insight. Applied Surface Science. 2022; 583:152516. doi:10.1016/j.apsusc.2022.152516
42. Lim K-L, Sin J-C, Lam S-M, Zeng H, Lin H, Li H, et al. Controlled solvothermal synthesis of self-assembled SrTiO3 microstructures for expeditious solar-driven photocatalysis dye effluents degradation. Environmental Research. 2024; 251:118647. doi:10.1016/j.envres.2024.118647
43. Sakthivel S, Paramasivam S, Velusamy P, Jerries Infanta JAD, Ragavendran V, Mayandi J, et al. Experimental investigation of structural, morphological, and optical characteristics of $SrTiO_3$ nanoparticles using a shock tube for photocatalytic applications. Zeitschrift für Physikalische Chemie. 2024; 0(0). doi:10.1515/zpch-2023-0486
44. Liu M, Xu X, Xiao W, Liu Y, Cui Y, Zhang H, et al. Au nanoparticles decorated SrTiO3−x hollow structure for plasmatic enhanced hydrogen production in UV–visible and near-infrared region. Journal of Alloys and Compounds. 2024; 983:173859. doi:10.1016/j.jallcom.2024.173859
45. Zhuang H, Chen X, Xia J, Lu K, Huang W, Liu X, et al. State-of-the-art progress in Ag3PO4-based photocatalysts: Rational design, regulation and perspective. Applied Materials Today. 2023; 31:101742. doi:10.1016/j.apmt.2023.101742
46. Hamrouni A, Azzouzi H, Rayes A, Palmisano L, Ceccato R, Parrino F. Enhanced Solar Light Photocatalytic Activity of Ag Doped TiO2–Ag3PO4 Composites. Nanomaterials. 2020; 10(4):795. doi:10.3390/nano10040795
47. Madanu TL, Mouchet SR, Deparis O, Liu J, Li Y, Su B-L. Tuning and transferring slow photons from TiO2 photonic crystals to BiVO4 nanoparticles for unprecedented visible light photocatalysis. Journal of Colloid and Interface Science. 2023; 634:290–9. doi:10.1016/j.jcis.2022.12.033
48. Heckel S, Wittmann M, Reid M, Villa K, Simmchen J. An Account on $BiVO_4$ as Photocatalytic Active Matter. Acc Mater Res. 2024; 5(4):400–12. doi:10.1021/accountsmr.3c00021

49. Zhang X, Puttaswamy M, Bai H, Hou B, Kumar Verma S. CdS/ZnS core–shell nanorod heterostructures co-deposited with ultrathin MoS2 cocatalyst for competent hydrogen evolution under visible-light irradiation. Journal of Colloid and Interface Science. 2024; 665:430–42. doi:10.1016/j.jcis.2024.03.066
50. Suresh M, Pravina R, Sivasamy A. Facile synthesis of MoS2 nanoparticles anchored graphene nanocomposite for enhanced photocatalytic activity under solar irradiation. Journal of Molecular Structure. 2024; 1305:137760. doi:10.1016/j.molstruc.2024.137760
51. Panchal D, Sharma A, Pal S. Engineered MoS2 nanostructures for improved photocatalytic applications in water treatment. Materials Today Sustainability. 2023; 21:100264. doi:10.1016/j.mtsust.2022.100264
52. Balan B, Xavier MM, Mathew S. MoS_2 -Based Nanocomposites for Photocatalytic Hydrogen Evolution and Carbon Dioxide Reduction. ACS Omega. 2023; 8(29):25649–73. doi:10.1021/acsomega.3c02084
53. Xu Y, Liu K, Zhang J, Zhang B, Zhang J, Shi K, et al. NH4Cl-assisted synthesis of TaON nanoparticle applied to photocatalytic hydrogen and oxygen evolution from water. Journal of Energy Chemistry. 2024; 94:541–50. doi:10.1016/j.jechem.2024.02.051
54. Jiang H, Shi Y, Zang S. Pd/PdO and hydrous RuO2 difunction-modified SiO2@TaON@Ta3N5 nano-photocatalyst for efficient solar overall water splitting. International Journal of Hydrogen Energy. 2023; 48(47):17827–37. doi:10.1016/j.ijhydene.2023.01.219
55. Maekawa T, Huang Y-S, Tateishi N, Nakanishi A, Onoe T, Dong Y, et al. Slow photon photocatalytic enhancement of H2 production in TaON inverse opal photonic crystals. Journal of Solid State Chemistry. 2024; 329:124404. doi:10.1016/j.jssc.2023.124404
56. Qu H, Yang S, Zhou X. Theoretical insights into the effect of surface structure and anion ordering on the properties of $SrTaO_2N$ for photocatalytic water splitting. Int J of Quantum Chemistry. 2024; 124(1):e27321. doi:10.1002/qua.27321
57. Tao, X., Tsugawa, T., Hatakeyama, K., & Ida, S. (2024). Synthesis and photocatalytic activity of LaTiO 2 N using titanium oxide nanosheet/La 3+ hybrids as a precursor. Sustainable Energy & Fuels.
58. Xia Z, Wang X, Liu K, Wang H, Wang Y, Lu W, et al. Preparation and photocatalytic properties of WSe2/BiVO4 p-n heterojunction photocatalytic materials. Catalysis Communications. 2024 ; 187:106857. doi:10.1016/j.catcom.2024.106857
59. Rengifo-Herrera, J. A., & Pulgarin, C. (2023). Why five decades of massive research on heterogeneous photocatalysis, especially on TiO2, has not yet driven to water disinfection and detoxification applications? Critical review of drawbacks and challenges. *Chemical Engineering Journal*, 146875.
60. Sohail M, Rauf S, Irfan M, Hayat A, Alghamdi MM, El-Zahhar AA, et al. Recent developments, advances and strategies in heterogeneous photocatalysts for water splitting. Nanoscale Adv. 2024; 6(5):1286–330. doi:10.1039/D3NA00442B
61. Qahtan TF, Owolabi TO, Olubi OE, Hezam A. State-of-the-art, challenges and prospects of heterogeneous tandem photocatalysis. Coordination Chemistry Reviews. 2023; 492:215276. doi:10.1016/j.ccr.2023.215276
62. Lotfi S, Ouardi ME, Ahsaine HA, Assani A. Recent progress on the synthesis, morphology and photocatalytic dye degradation of $BiVO_4$ photocatalysts: A review. Catalysis Reviews. 2024; 66(1):214–58. doi:10.1080/01614940.2022.2057044
63. Low J, Zhang C, Ma J, Murzin DYu, Xiong Y. Heterogeneous photocatalysis: what is being overlooked? Trends in Chemistry. 2023; 5(2):121–32. doi:10.1016/j.trechm.2022.11.007
64. Okab AA, Jabbar ZH, Graimed BH, Alwared AI, Ammar SH, Hussein MA. A comprehensive review highlights the photocatalytic heterojunctions and their superiority in the photo-destruction of organic pollutants in industrial wastewater. Inorganic Chemistry Communications. 2023; 158:111503. doi:10.1016/j.inoche.2023.111503
65. Sohail M, Rauf S, Irfan M, Hayat A, Alghamdi MM, El-Zahhar AA, et al. Recent developments, advances and strategies in heterogeneous photocatalysts for water splitting. Nanoscale Adv. 2024; 6(5):1286–330. doi:10.1039/D3NA00442B
66. Masri M, K. B Girisha, Hezam A, Alkanad K, Prashantha K, Manjunath SH, et al. Metal halide perovskite-based photocatalysts for organic pollutants degradation: Advances, challenges, and future directions. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2024; 687:133387. doi:10.1016/j.colsurfa.2024.133387
67. Baaloudj O, Vu N-N, Assadi AA, Le VQ, Nguyen-Tri P. Recent advances in designing and developing efficient sillenite-based materials for photocatalytic applications. Advances in Colloid and Interface Science. 2024; 327:103136. doi:10.1016/j.cis.2024.103136
68. Kumar A, Rana S, Dhiman P, Sharma G, Stadler FJ. Current progress in heterojunctions based on Nb2O5 for photocatalytic water treatment and energy applications. Journal of Molecular Liquids. 2024; 399:124360. doi:10.1016/j.molliq.2024.124360
69. Anucha CB, Altin I, Bacaksiz E, Stathopoulos VN. Titanium dioxide (TiO_2)-based photocatalyst materials activity enhancement for contaminants of emerging concern (CECs) degradation: In the light of modification strategies. Chemical Engineering Journal Advances. 2022; 10:100262. doi:10.1016/j.ceja.2022.100262

70. Dharma HNC, Jaafar J, Widiastuti N, Matsuyama H, Rajabsadeh S, Othman MHD, et al. A Review of Titanium Dioxide (TiO2)-Based Photocatalyst for Oilfield-Produced Water Treatment. Membranes. 2022; 12(3):345. doi:10.3390/membranes12030345
71. Gatou M-A, Syrrakou A, Lagopati N, Pavlatou EA. Photocatalytic TiO2-Based Nanostructures as a Promising Material for Diverse Environmental Applications: A Review. Reactions. 2024; 5(1):135–94. doi:10.3390/reactions5010007
72. Sangeeta, Onisha, Sandhu N, Kumar C, Mohajer F, Tomar R. Critical Review on Titania-Based Nanoparticles: Synthesis, Characterization, and Application as a Photocatalyst. Chemistry Africa. 2024; 7(4):1749–68. doi:10.1007/s42250-023-00875-1
73. Rashid Al-Mamun Md, Hossain KT, Mondal S, Afroza Khatun Most, Shahinoor Islam Md, Zaved Hossain Khan DrMd. Synthesis, characterization, and photocatalytic performance of methyl orange in aqueous TiO2 suspension under UV and solar light irradiation. South African Journal of Chemical Engineering. 2022; 40:113–25. doi:10.1016/j.sajce.2022.02.002
74. Ahmadpour N, Nowrouzi M, Madadi Avargani V, Sayadi MH, Zendehboudi S. Design and optimization of TiO2-based photocatalysts for efficient removal of pharmaceutical pollutants in water: Recent developments and challenges. Journal of Water Process Engineering. 2024; 57:104597. doi:10.1016/j.jwpe.2023.104597
75. Yao Y, Han Y, Qi S, Sun D, Lang J, Hu B, et al. Metal-free thiophene-based covalent organic frameworks achieve efficient photocatalytic hydrogen evolution by accelerating interfacial charge transfer. International Journal of Hydrogen Energy. 2024; 63:184–92. doi:10.1016/j.ijhydene.2024.03.176
76. Liu X, Jing X, Liu R, Guo P, Yin Z. Plasmon-Enhanced Perovskite Photocatalysts for CO_2 Reduction: A Mini Review. Energy Fuels. 2024; 38(6):4966–79. doi:10.1021/acs.energyfuels.3c05197
77. Rawat J, Sharma H, Dwivedi C. Microwave-assisted synthesis of carbon quantum dots and their integration with TiO2 nanotubes for enhanced photocatalytic degradation. Diamond and Related Materials. 2024; 144:111050. doi:10.1016/j.diamond.2024.111050
78. Puri N, Gupta A. Water remediation using titanium and zinc oxide nanomaterials through disinfection and photo catalysis process: A review. Environmental Research. 2023; 227:115786. doi:10.1016/j.envres.2023.115786
79. Chen X, Ren Y, Qu G, Wang Z, Yang Y, Ning P. A review of environmental functional materials for cyanide removal by adsorption and catalysis. Inorganic Chemistry Communications. 2023; 157:111298. doi:10.1016/j.inoche.2023.111298
80. Ibhadon A, Fitzpatrick P. Heterogeneous Photocatalysis: Recent Advances and Applications. Catalysts. 2013; 3(1):189–218. doi:10.3390/catal3010189
81. Hossain R, Uddin MA, Khan MA. Mechanistic Understanding in Manipulating Energetics of TiO_2 for Photocatalysis. J Phys Chem C. 2023; 127(23):10897–912. doi:10.1021/acs.jpcc.2c06981
82. Eder M, Tschurl M, Heiz U. Toward a Comprehensive Understanding of Photocatalysis: What Systematic Studies and Alcohol Surface Chemistry on TiO_2 (110) Have to Offer for Future Developments. J Phys Chem Lett. 2023; 14(26):6193–201. doi:10.1021/acs.jpclett.3c00504
83. Sumaria, V., Rawal, T. B., Li, Y. F., Sommer, D., Vikoren, J., Bondi, R. J., ... & Prasad, D. (2024). Machine Learning, Density Functional Theory, and Experiments to Understand the Photocatalytic Reduction of CO $ _2 $ by CuPt/TiO $ _2$. *arXiv preprint arXiv:2402.08884*.
84. M. A. Henderson, Surf. Sci. Rep. 2021, 66, 185
85. Ali S, Ismail PM, Khan M, Dang A, Ali S, Zada A, et al. Charge transfer in TiO_2 -based photocatalysis: fundamental mechanisms to material strategies. Nanoscale. 2024; 16(9):4352–77. doi:10.1039/D3NR04534J
86. Ali S, Ismail PM, Khan M, Dang A, Ali S, Zada A, et al. Charge transfer in TiO_2 -based photocatalysis: fundamental mechanisms to material strategies. Nanoscale. 2024; 16(9):4352–77. doi:10.1039/D3NR04534J
87. Aldosari OF, Hussain I. Unlocking the potential of TiO2-based photocatalysts for green hydrogen energy through water-splitting: Recent advances, future perspectives and techno feasibility assessment. International Journal of Hydrogen Energy. 2024; 59:958–81. doi:10.1016/j.ijhydene.2024.01.306
88. Yin S, Liu L, Li J, Wu H, Lv Z, He Y, et al. Mesoporous TiO_2 Single-Crystal Particles from Controlled Crystallization-Driven Mono-Micelle Assembly as an Efficient Photocatalyst. J Am Chem Soc. 2024; 146(2):1701–9. doi:10.1021/jacs.3c12727
89. Alamoudi M, Katsiev K, Idriss H. Monitoring the Lifetime of Photoexcited Electrons in a Fresh and Bulk Reduced Rutile TiO_2 Single Crystal. Possible Anisotropic Propagation. J Phys Chem Lett. 2023; 14(41):9238–44. doi:10.1021/acs.jpclett.3c02301
90. Li C, Shen S, Niu J, Reka AA, Feng P, Garcia H. Mesoporous single-crystal-based TiO2 microspheres decorated by carbon nitride for obviously improved photocatalytic performance and recyclability. Inorganic Chemistry Communications. 2023; 150:110524. doi:10.1016/j.inoche.2023.110524
91. He T, Wang D, Xu Y, Zhang J. The Facile Construction of Anatase Titanium Dioxide Single Crystal Sheet-Connected Film with Observable Strong White Photoluminescence. Coatings. 2024; 14(3):292. doi:10.3390/coatings14030292

92. Petrik NG, Baer MD, Mundy CJ, Kimmel GA. Mixed Molecular and Dissociative Water Adsorption on Hydroxylated TiO_2 (110): An Infrared Spectroscopy and Ab Initio Molecular Dynamics Study. J Phys Chem C. 2022; 126(51):21616–27. doi:10.1021/acs.jpcc.2c07063
93. Jiménez-Calvo P, Caps V, Keller V. Plasmonic Au-based junctions onto TiO2, gC3N4, and TiO2-gC3N4 systems for photocatalytic hydrogen production: Fundamentals and challenges. Renewable and Sustainable Energy Reviews. 2021; 149:111095. doi:10.1016/j.rser.2021.111095
94. Azizi ZL, Daneshjou S. Bacterial nano-factories as a tool for the biosynthesis of TiO2 nanoparticles: characterization and potential application in wastewater treatment. Appl Biochem Biotechnol. 2024; doi:10.1007/s12010-023-04839-6
95. Barakat NAM, Irfan OM, Mohamed OA. TiO2 NPs-immobilized silica granules: New insight for nano catalyst fixation for hydrogen generation and sustained wastewater treatment. Nguyen V-H, editor. PLoS ONE. 2023; 18(6):e0287424. doi:10.1371/journal.pone.0287424
96. Azizi ZL, Daneshjou S. Bacterial nano-factories as a tool for the biosynthesis of TiO2 nanoparticles: characterization and potential application in wastewater treatment. Appl Biochem Biotechnol. 2024; doi:10.1007/s12010-023-04839-6
97. Suhan MdBK, Al-Mamun MdR, Farzana N, Aishee SM, Islam MdS, Marwani HM, et al. Sustainable pollutant removal and wastewater remediation using TiO2-based nanocomposites: A critical review. Nano-Structures & Nano-Objects. 2023; 36:101050. doi:10.1016/j.nanoso.2023.101050
98. Ariaeinezhad F, Mohammadnezhad G, Zare M, Akintola O, Plass W. Controllable and facile one-pot synthesis of high surface area amorphous, crystalline, and triphasic TiO_2: catalytic and photocatalytic applications. J Mater Chem A. 2024; 12(11):6488–506. doi:10.1039/D3TA07610E
99. Chen Z, Chen H, Wang K, Chen J, Li M, Wang Y, et al. Enhanced TiO_2 Photocatalytic 2 e^- Oxygen Reduction Reaction via Interfacial Microenvironment Regulation and Mechanism Analysis. ACS Catal. 2023; 13(10):6497–508. doi:10.1021/acscatal.3c00994
100. Eder M, Tschurl M, Heiz U. Toward a Comprehensive Understanding of Photocatalysis: What Systematic Studies and Alcohol Surface Chemistry on TiO_2 (110) Have to Offer for Future Developments. J Phys Chem Lett. 2023; 14(26):6193–201. doi:10.1021/acs.jpclett.3c00504
101. Jabraoui H, Rouhani MD, Rossi C, Esteve A. Towards H2 production from water and ethanol interactions on hydrated TiO2(101): Insights from ReaxFF molecular dynamics. Applied Surface Science. 2024; 656:159692. doi:10.1016/j.apsusc.2024.159692
102. Patidar A, Dugyala VR, Chakma S, Galodiya MN, Giri AS. Reactive oxygen species aided photocatalytic degradation of tetracycline using non-metal activated carbon doped TiO2 nanocomposite under UV-light irradiation. Res Chem Intermed. 2024; 50(3):1035–63. doi:10.1007/s11164-023-05203-3
103. Zhang, R., Luo, T., Zeng, W. W., Zhou, C., Yang, X., & Ren, Z. (2023). Methanol Adsorption and Reaction on TiO2 (110) at Near Ambient Pressure. *The Journal of Physical Chemistry C*, *127*(2), 1049-1056.
104. Lin Y-P, Bocharov D, Isakoviča I, Pankratov V, Popov AA, Popov AI, et al. Chlorine Adsorption on TiO2(110)/Water Interface: Nonadiabatic Molecular Dynamics Simulations for Photocatalytic Water Splitting. Electronic Materials. 2023; 4(1):33–48. doi:10.3390/electronicmat4010004
105. Abbas, M. (2021). Factors influencing the adsorption and photocatalysis of direct red 80 in the presence of a TiO2: equilibrium and kinetics modeling. *Journal of Chemical Research*, *45*(7-8), 694-701.
106. Lang, X., Liang, Y., Zhang, J., Li, L., Cao, L., & Zhang, H. (2020). Structure and reactivity of a water-covered anatase TiO 2 (001) surface. *Physical Chemistry Chemical Physics*, *22*(3), 1371-1380.
107. Guo Q, Zhou C, Ma Z, Yang X. Fundamentals of TiO_2 Photocatalysis: Concepts, Mechanisms, and Challenges. Advanced Materials. 2019; 31(50):1901997. doi:10.1002/adma.201901997
108. Ali S, Ismail PM, Khan M, Dang A, Ali S, Zada A, et al. Charge transfer in TiO_2 -based photocatalysis: fundamental mechanisms to material strategies. Nanoscale. 2024; 16(9):4352–77. doi:10.1039/D3NR04534J
109. Lettieri S, Pavone M, Fioravanti A, Santamaria Amato L, Maddalena P. Charge Carrier Processes and Optical Properties in TiO2 and TiO2-Based Heterojunction Photocatalysts: A Review. Materials. 2021; 14(7):1645. doi:10.3390/ma14071645
110. Rosa D, Abbasova N, Di Palma L. Titanium Dioxide Nanoparticles Doped with Iron for Water Treatment via Photocatalysis: A Review. Nanomaterials. 2024; 14(3):293. doi:10.3390/nano14030293
111. Vorontsov AV, Valdés H, Smirniotis PG, Paz Y. Recent Advancements in the Understanding of the Surface Chemistry in TiO2 Photocatalysis. Surfaces. 2020; 3(1):72–92. doi:10.3390/surfaces3010008
112. Jeon, J. P., Kweon, D. H., Jang, B. J., Ju, M. J., & Baek, J. B. (2020). Enhancing the photocatalytic activity of TiO2 catalysts. *Advanced Sustainable Systems*, *4*(12), 2000197.
113. Mohsin M, Bhatti IA, Zeshan M, Yousaf M, Iqbal M. Prospects, challenges, and opportunities of the metals-modified TiO2 based photocatalysts for hydrogen generation under solar light irradiation: A review. FlatChem. 2023; 42:100547. doi:10.1016/j.flatc.2023.100547
114. Kirk CH, Wang P, Chong CYD, Zhao Q, Sun J, Wang J. TiO2 photocatalytic ceramic membranes for water and wastewater treatment: Technical readiness and pathway ahead. Journal of Materials Science & Technology. 2024; 183:152–64. doi:10.1016/j.jmst.2023.09.055

115. Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results. Chem Rev. 1995; 95(3):735–58. doi:10.1021/cr00035a013
116. Wang C, Liu H, Qu Y. TiO 2 -Based Photocatalytic Process for Purification of Polluted Water: Bridging Fundamentals to Applications. Yu J, editor. Journal of Nanomaterials. 2013; 2013(1):319637. doi:10.1155/2013/319637
117. Henderson MA, Lyubinetsky I. Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on TiO 2 (110). Chem Rev. 2013; 113(6):4428–55. doi:10.1021/cr300315m
118. Guo Q, Zhou C, Ma Z, Yang X. Fundamentals of TiO 2 Photocatalysis: Concepts, Mechanisms, and Challenges. Advanced Materials. 2019; 31(50):1901997. doi:10.1002/adma.201901997
119. Henderson MA, Lyubinetsky I. Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on TiO 2 (110). Chem Rev. 2013; 113(6):4428–55. doi:10.1021/cr300315m
120. Guo Q, Zhou C, Ma Z, Ren Z, Fan H, Yang X. Elementary Chemical Reactions in Surface Photocatalysis. Annu Rev Phys Chem. 2018; 69(1):451–72. doi:10.1146/annurev-physchem-052516-044933
121. Waghmode MS, Gunjal AB, Mulla JA, Patil NN, Nawani NN. Studies on the titanium dioxide nanoparticles: biosynthesis, applications and remediation. SN Appl Sci. 2019; 1(4):310. doi:10.1007/s42452-019-0337-3
122. Kang, X., Liu, S., Dai, Z., He, Y., Song, X., & Tan, Z. (2019). Titanium dioxide: from engineering to applications. *Catalysts*, *9*(2), 191.
123. Bai J, Zhou B. Titanium Dioxide Nanomaterials for Sensor Applications. Chem Rev. 2014; 114(19):10131–76. doi:10.1021/cr400625j
124. Ghosh S, Das AP. Modified titanium oxide (TiO 2) nanocomposites and its array of applications: a review. Toxicological & Environmental Chemistry. 2015; 97(5):491–514. doi:10.1080/02772248.2015.1052204
125. Hsu C-Y, Mahmoud ZH, Abdullaev S, Ali FK, Ali Naeem Y, Mzahim Mizher R, et al. Nano titanium oxide (nano-TiO2): A review of synthesis methods, properties, and applications. Case Studies in Chemical and Environmental Engineering. 2024; 9:100626. doi:10.1016/j.cscee.2024.100626
126. Qamar OA, Jamil F, Hussain M, Bae S, Inayat A, Shah NS, et al. Advances in synthesis of TiO2 nanoparticles and their application to biodiesel production: A review. Chemical Engineering Journal. 2023; 460:141734. doi:10.1016/j.cej.2023.141734
127. Анисонян, К. Г. (2015). Физико-химические основы магнетизирующего обжига лейкоксеновых руд и концентратов для разделения лейкоксена и кварца магнитной сепарацией (Doctoraldissertation, Ин-т металлургии и материаловедения им. АА Байкова РАН).
128. Zhang W, Zhu Z, Cheng CY. A literature review of titanium metallurgical processes. Hydrometallurgy. 2011; 108(3–4):177–88. doi:10.1016/j.hydromet.2011.04.005
129. Umar, M., & Aziz, H. A. (2013). Photocatalytic degradation of organic pollutants in water. *Organic pollutants-monitoring, risk and treatment*, *8*, 196-197.
130. Wu J, Zhong L. Predictive modeling for VOC adsorption on TiO2 filters: Implications for enhanced photocatalytic oxidation in indoor air quality management. Chemical Engineering Journal. 2024; 480:148222. doi:10.1016/j.cej.2023.148222
131. Zhou, W., Chen, F., Li, M., Cheng, Q., Deng, J., Wang, P., ... & Sun, S. (2024). Facet-Dependent Photocatalytic Behavior of Rutile TiO2 for the Degradation of Volatile Organic Compounds: In Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy and Density Functional Theory Investigations. *Langmuir*, *40*(4), 2120-2129.
132. Lin, Z., Jiang, X., Xu, W., Li, F., Chen, X., Wang, H., ... & Lu, X. (2024). The effects of water, substrate, and intermediate adsorption on the photocatalytic decomposition of air pollutants over nano-TiO 2 photocatalysts. *Physical Chemistry Chemical Physics*.
133. Kharouf M, Zyoud AH, Zyoud SH, Zyoud SH, Qamhieh N, Hajamohideen A, et al. Enhanced photocatalytic degradation of phenazopyridine using rutile TiO2/clay composite: catalyst recovery and environmental implications. Int J Environ Sci Technol. 2024; 21(11):7491–508. doi:10.1007/s13762-024-05492-0
134. Pavel M, Anastasescu C, State R-N, Vasile A, Papa F, Balint I. Photocatalytic Degradation of Organic and Inorganic Pollutants to Harmless End Products: Assessment of Practical Application Potential for Water and Air Cleaning. Catalysts. 2023; 13(2):380. doi:10.3390/catal13020380
135. Kanan S, Moyet MA, Arthur RB, Patterson HH. Recent advances on TiO 2 -based photocatalysts toward the degradation of pesticides and major organic pollutants from water bodies. Catalysis Reviews. 2020; 62(1):1–65. doi:10.1080/01614940.2019.1613323
136. Badr, P., Sajjadnejad, M., & Haghshenas, S. M. (2023). Influence of incorporating B4C nanoparticles and pulse electrodeposition parameters on the surface morphology and wear behavior of nickel based nanocomposite coatings. *Progress in Chemical and Biochemical Research*, *6*(4), 292-313.
137. Belhachem, A., Amara, N., Belmekki, H., Yahia, Y., Cherifi, Z., Amiar, A., ... & Toumi, H. (2023). Synthesis, characterization and anti-inflammatory activity of an alginate-zinc oxide nanocomposite. *Asian J. Nanosci. Mater*, *3*, 173-185.

138. Puri, Jaya, Umesh Pravin Dhuldhaj, and Abdulbasit Shaikh. "Nano-biochar production and its characteristics: overview." (2023): 206-220.
139. Eddy DR, Nur Sheha GA, Permana MD, Saito N, Takei T, Kumada N, et al. Study on triphase of polymorphs TiO2 (anatase/rutile/brookite) for boosting photocatalytic activity of metformin degradation. Chemosphere. 2024; 351:141206. doi:10.1016/j.chemosphere.2024.141206
140. Zahra Z, Habib Z, Chung S, Badshah MA. Exposure Route of TiO2 NPs from Industrial Applications to Wastewater Treatment and Their Impacts on the Agro-Environment. Nanomaterials. 2020; 10(8):1469. doi:10.3390/nano10081469
141. Berardinelli, A., & Parisi, F. (2021). TiO2 in the food industry and cosmetics. In *Titanium Dioxide (Tio_2) and Its Applications* (pp. 353-371). Elsevier.
142. Janczarek M, Klapiszewski Ł, Jędrzejczak P, Klapiszewska I, Ślosarczyk A, Jesionowski T. Progress of functionalized TiO2-based nanomaterials in the construction industry: A comprehensive review. Chemical Engineering Journal. 2022; 430:132062. doi:10.1016/j.cej.2021.132062
143. Samuel, Humphrey Sam, Maraizu Ugo Nweke, and Emmanuel Edet Etim. "Supercritical fluids: properties, formation and applications." (2023): 176-188.
144. Ziental D, Czarczynska-Goslinska B, Mlynarczyk DT, Glowacka-Sobotta A, Stanisz B, Goslinski T, et al. Titanium Dioxide Nanoparticles: Prospects and Applications in Medicine. Nanomaterials. 2020; 10(2):387. doi:10.3390/nano10020387
145. Taheri, A., & Rezayati-Zad, Z. (2023). Characterization of tribological and electrochemical corrosion behavior of GO coatings formed on 6061 Al alloy processed by plasma electrolytic oxidation. *Progress in Chemical and Biochemical Research*, *6*(4), 261-276.
146. Asaad Mahdi M, Farhan MA, Mahmoud ZH, Mahdi Rheima A, Sabri Abbas Z, Kadhim MM, et al. Direct sunlight photodegradation of congo red in aqueous solution by TiO2/rGO binary system: Experimental and DFT study. Arabian Journal of Chemistry. 2023; 16(8):104992. doi:10.1016/j.arabjc.2023.104992
147. Mahmoud ZH, Hamrouni A, Kareem AB, Mostafa MA, Jalil Alhakim Z, Majeed AH. Synthesis and characterization of chitosan sheet modified by varied weight ratio of anatase (TiO2) nano mixture with Cr(VI) adsorbing. Kuwait Journal of Science. 2023; 50(3):290–9. doi:10.1016/j.kjs.2023.05.006
148. Eddy DR, Nur Sheha GA, Permana MD, Saito N, Takei T, Kumada N, et al. Study on triphase of polymorphs TiO2 (anatase/rutile/brookite) for boosting photocatalytic activity of metformin degradation. Chemosphere. 2024; 351:141206. doi:10.1016/j.chemosphere.2024.141206
149. Simons PY, Dachille F. The structure of TiO_2 II, a high-pressure phase of TiO_2. Acta Cryst. 1967; 23(2):334–6. doi:10.1107/S0365110X67002713
150. Latroche M, Brohan L, Marchand R, Tournoux M. New hollandite oxides: TiO2(H) and K0.06TiO2. Journal of Solid State Chemistry. 1989; 81(1):78–82. doi:10.1016/0022-4596(89)90204-1
151. Cromer DT, Herrington K. The Structures of Anatase and Rutile. J Am Chem Soc. 1955; 77(18):4708–9. doi:10.1021/ja01623a004
152. Mo S-D, Ching WY. Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. Phys Rev B. 1995; 51(19):13023–32. doi:10.1103/PhysRevB.51.13023
153. Kandiel TA, Robben L, Alkaima A, Bahnemann D. Brookite versus anatase TiO2 photocatalysts: phase transformations and photocatalytic activities. Photochem Photobiol Sci. 2013; 12(4):602–9. doi:10.1039/c2pp25217a
154. Sanjines, R., Tang, H., Berger, H., Gozzo, F., Margaritondo, G., & Lévy, F. (1994). Electronic structure of anatase TiO2 oxide. Journal of Applied Physics, 75(6), 2945-2951.
155. Landmann M, Rauls E, Schmidt WG. The electronic structure and optical response of rutile, anatase and brookite TiO_2. J Phys: Condens Matter. 2012; 24(19):195503. doi:10.1088/0953-8984/24/19/195503
156. Thompson T. L., Yates J. T. Surface Science Studies of the Photoactivation of TiO2 –New Photochemical Processes // Chemical Reviews. 2023. V.106. №10. P. 4428-4453.
157. Tang, H., Prasad K., Sanjines R., Schmid P. E., Levy F. Electrical and optical properties of TiO2 anatase thin films // Journal of Applied Physics. 1994. V.75. №.4. P. 2042-2047.
158. Yang HG, Sun CH, Qiao SZ, Zou J, Liu G, Smith SC, et al. Anatase TiO2 single crystals with a large percentage of reactive facets. Nature. 2008; 453(7195):638–41. doi:10.1038/nature06964
159. Wang Z, Wen B, Hao Q, Liu L-M, Zhou C, Mao X, et al. Localized Excitation of Ti^{3+} Ions in the Photoabsorption and Photocatalytic Activity of Reduced Rutile TiO_2. J Am Chem Soc. 2015; 137(28):9146–52. doi:10.1021/jacs.5b04483
160. Yin W-J, Wen B, Zhou C, Selloni A, Liu L-M. Excess electrons in reduced rutile and anatase TiO2. Surface Science Reports. 2018; 73(2):58–82. doi:10.1016/j.surfrep.2018.02.003
161. Guo Q, Zhou C, Ma Z, Yang X. Fundamentals of TiO_2 Photocatalysis: Concepts, Mechanisms, and Challenges. Advanced Materials. 2019; 31(50):1901997. doi:10.1002/adma.201901997
162. Hardman, P. J., Raikar, G. N., Muryn, C. A., Van Der Laan, G., Wincott, P. L., Thornton, G., ... & Dale, P. A. D. M. A. (1994). Valence-band structure of TiO 2 along the Γ-Δ-X and Γ-Σ-M directions. *Physical Review B*, *49*(11), 7170.

163. Lindan PJD, Harrison NM, Gillan MJ, White JA. First-principles spin-polarized calculations on the reduced and reconstructed TiO 2 (110) surface. Phys Rev B. 1997; 55(23):15919–27. doi:10.1103/PhysRevB.55.15919
164. Diebold U. The surface science of titanium dioxide. Surface Science Reports. 2003; 48(5–8):53–229. doi:10.1016/S0167-5729(02)00100-0
165. Li G, Chen L, Graham ME, Gray KA. A comparison of mixed phase titania photocatalysts prepared by physical and chemical methods: The importance of the solid–solid interface. Journal of Molecular Catalysis A: Chemical. 2007; 275(1–2):30–5. doi:10.1016/j.molcata.2007.05.017
166. Morrison S. R. Electrochemistry at Semiconductor and Oxidized Metal Electrodes. New York and London. Plenum Press, 1980. 401 p.
167. Zhao Y, Li C., Liu X., Gu F., Jiang H., Shao W., Zhang L., He Y. Synthesis and optical properties of TiO2 nanoparticles // Materials Letters. 2007. V.61. №1. P. 79-83.
168. Amanizadehfini F, Salehi-Mobarakeh H, Mahdavian A, Jahanmardi R. Study on preparation, structure, and cooling properties of TiO_2 /acrylonitrile–styrene–acrylate terpolymer solar reflective nanocomposite. Polymer Composites. 2024; 45(5):4107–23. doi:10.1002/pc.28046
169. Shon, H., Phuntsho, S., Okour, Y., Cho, D. L., Kim, K. S., Li, H. J., ... & Kim, J. H. (2008). Visible light responsive titanium dioxide (TiO 2). Journal of the Korean Industrial and Engineering Chemistry.
170. Mathew RM, Jose J, Zachariah ES, Thomas V. Defect Induced Ultrafast Organic Dye Adsorption by Amorphous Titanium Dioxide/Phosphorus-Doped Carbon Nanodot Hybrid. J Clust Sci. 2024; 35(4):1045–62. doi:10.1007/s10876-023-02529-1
171. Ahad A, Podder J, Saha T, Das HN. Effect of chromium doping on the band gap tuning of titanium dioxide thin films for solar cell applications. Heliyon. 2024; 10(1):e23096. doi:10.1016/j.heliyon.2023.e23096
172. Kuranov D, Grebenkina A, Bogdanova A, Platonov V, Polomoshnov S, Krivetskiy V, et al. Effect of Donor Nb(V) Doping on the Surface Reactivity, Electrical, Optical and Photocatalytic Properties of Nanocrystalline TiO2. Materials. 2024; 17(2):375. doi:10.3390/ma17020375
173. Devi LG, Kumar SG. Influence of physicochemical–electronic properties of transition metal ion doped polycrystalline titania on the photocatalytic degradation of Indigo Carmine and 4-nitrophenol under UV/solar light. Applied Surface Science. 2011; 257(7):2779–90. doi:10.1016/j.apsusc.2010.10.062
174. Basavarajappa PS, Patil SB, Ganganagappa N, Reddy KR, Raghu AV, Reddy ChV. Recent progress in metal-doped TiO2, non-metal doped/codoped TiO2 and TiO2 nanostructured hybrids for enhanced photocatalysis. International Journal of Hydrogen Energy. 2020; 45(13):7764–78. doi:10.1016/j.ijhydene.2019.07.241
175. Kuriechen SK, Murugesan S, Paul Raj S. Mineralization of Azo Dye Using Combined Photo-Fenton and Photocatalytic Processes under Visible Light. Journal of Catalysts. 2013; 2013:1–6. doi:10.1155/2013/104019
176. Chakraborty AK, Ganguli S, Sabur MA. Nitrogen doped titanium dioxide (N-TiO2): Electronic band structure, visible light harvesting and photocatalytic applications. Journal of Water Process Engineering. 2023; 55:104183. doi:10.1016/j.jwpe.2023.104183
177. Ishikawa T, Sahara R, Ohno K, Ueda K, Narushima T. Electronic structure analysis of light-element-doped anatase TiO 2 using all-electron GW approach. Computational Materials Science. 2023; 220:112059. doi:10.1016/j.commatsci.2023.112059
178. Gao C, Guo M, Liu Y, Zhang D, Gao F, Sun L, et al. Surface modification methods and mechanisms in carbon nanotubes dispersion. Carbon. 2023; 212:118133. doi:10.1016/j.carbon.2023.118133
179. Yang J, Mei S, Ferreira JMF. Hydrothermal synthesis of TiO2 nanopowders from tetraalkylammonium hydroxide peptized sols. Materials Science and Engineering: C. 2001; 15(1–2):183–5. doi:10.1016/S0928-4931(01)00274-0
180. Wang D, Yu B, Zhou F, Wang C, Liu W. Synthesis and characterization of anatase TiO2 nanotubes and their use in dye-sensitized solar cells. Materials Chemistry and Physics. 2009; 113(2–3):602–6. doi:10.1016/j.matchemphys.2008.08.011
181. Wahi RK, Liu Y, Falkner JC, Colvin VL. Solvothermal synthesis and characterization of anatase TiO2 nanocrystals with ultrahigh surface area. Journal of Colloid and Interface Science. 2006; 302(2):530–6. doi:10.1016/j.jcis.2006.07.003
182. Kobayashi M, Kato H, Miyazaki T, Kakihana M. Hydrothermal Synthesis of Pseudocubic Rutile-Type Titania Particles. Ceramics. 2019; 2(1):56–63. doi:10.3390/ceramics2010005
183. Govindaraj R, Santhosh N, Senthil Pandian M, Ramasamy P. Synthesis of nanocrystalline TiO2 nanorods via hydrothermal method: An efficient photoanode material for dye sensitized solar cells. Journal of Crystal Growth. 2017; 468:125–8. doi:10.1016/j.jcrysgro.2016.11.004
184. Rajamanickam G, Narendhiran S, Muthu SP, Mukhopadhyay S, Perumalsamy R. Hydrothermally derived nanoporous titanium dioxide nanorods/nanoparticles and their influence in dye-sensitized solar cell as a photoanode. Chemical Physics Letters. 2017; 689:19–25. doi:10.1016/j.cplett.2017.09.044
185. Wang F, Shi Z, Gong F, Jiu J, Adachi M. Morphology Control of Anatase TiO2 by Surfactant-assisted Hydrothermal Method. Chinese Journal of Chemical Engineering. 2007; 15(5):754–9. doi:10.1016/S1004-9541(07)60158-X

186. Lei L, Yuming C, Bo L, Xingfu Z, Weiping D. Study on the surface erosion route to the fabrication of TiO2 hollow spheres. Applied Surface Science. 2010; 256(8):2596–601. doi:10.1016/j.apsusc.2009.11.001
187. Liu Z, Sun DD, Guo P, Leckie JO. One-Step Fabrication and High Photocatalytic Activity of Porous TiO_2 Hollow Aggregates by Using a Low-Temperature Hydrothermal Method Without Templates. Chemistry A European J. 2007; 13(6):1851–5. doi:10.1002/chem.200601092
188. Xue B, Sun T, Mao F, Sun L-C, Yang W, Xu Z-D, et al. Facile synthesis of mesoporous core-shell TiO2 nanostructures from TiCl3. Materials Research Bulletin. 2011; 46(9):1524–9. doi:10.1016/j.materresbull.2011.05.019
189. Yan X-M, Kang J, Gao L, Xiong L, Mei P. Solvothermal synthesis of carbon coated N-doped TiO2 nanostructures with enhanced visible light catalytic activity. Applied Surface Science. 2013; 265:778–83. doi:10.1016/j.apsusc.2012.11.111
190. Kang M, Lee S-Y, Chung C-H, Cho SM, Han GY, Kim B-W, et al. Characterization of a TiO2 photocatalyst synthesized by the solvothermal method and its catalytic performance for CHCl3 decomposition. Journal of Photochemistry and Photobiology A: Chemistry. 2001; 144(2–3):185–91. doi:10.1016/S1010-6030(01)00501-9
191. Nam WS, Han GY. Characterization and photocatalytic performance of nanosize TiO2 powders prepared by the solvothermal method. Korean J Chem Eng. 2003; 20(6):1149–53. doi:10.1007/BF02706953
192. Yang HG, Liu G, Qiao SZ, Sun CH, Jin YG, Smith SC, et al. Solvothermal Synthesis and Photoreactivity of Anatase TiO_2 Nanosheets with Dominant {001} Facets. J Am Chem Soc. 2009; 131(11):4078–83. doi:10.1021/ja808790p
193. Yang HG, Liu G, Qiao SZ, Sun CH, Jin YG, Smith SC, et al. Solvothermal Synthesis and Photoreactivity of Anatase TiO_2 Nanosheets with Dominant {001} Facets. J Am Chem Soc. 2009; 131(11):4078–83. doi:10.1021/ja808790p
194. Lü X, Ding S, Xie Y, Huang F. Non-Aqueous Preparation of High-Crystallinity Hierarchical TiO_2 Hollow Spheres with Excellent Photocatalytic Efficiency. Eur J Inorg Chem. 2011; 2011(18):2879–83. doi:10.1002/ejic.201100151
195. Li X, Peng Q, Yi J, Wang X, Li Y. Near Monodisperse TiO_2 Nanoparticles and Nanorods. Chemistry A European J. 2006; 12(8):2383–91. doi:10.1002/chem.200500893
196. Liu Z, Sun DD, Guo P, Leckie JO. One-Step Fabrication and High Photocatalytic Activity of Porous TiO_2 Hollow Aggregates by Using a Low-Temperature Hydrothermal Method Without Templates. Chemistry A European J. 2007; 13(6):1851–5. doi:10.1002/chem.200601092
197. Liu C, Sun H, Yang S. From Nanorods to Atomically Thin Wires of Anatase TiO_2 : Nonhydrolytic Synthesis and Characterization. Chemistry A European J. 2010; 16(14):4381–93. doi:10.1002/chem.200902524
198. Dinh C, Nguyen T, Kleitz F, Do T. A solvothermal single-step route towards shape-controlled titanium dioxide nanocrystals. Can J Chem Eng. 2012; 90(1):8–17. doi:10.1002/cjce.20574
199. Supphasrirongjaroen P, Praserthdam P, Panpranot J, Na-Ranong D, Mekasuwandumrong O. Effect of quenching medium on photocatalytic activity of nano-TiO2 prepared by solvothermal method. Chemical Engineering Journal. 2008; 138(1–3):622–7. doi:10.1016/j.cej.2007.09.035
200. Kim C-S, Moon BK, Park J-H, Choi B-C, Seo H-J. Solvothermal synthesis of nanocrystalline TiO2 in toluene with surfactant. Journal of Crystal Growth. 2003; 257(3–4):309–15. doi:10.1016/S0022-0248(03)01468-4
201. Gong D, Grimes CA, Varghese OK, Hu W, Singh RS, Chen Z, et al. Titanium oxide nanotube arrays prepared by anodic oxidation. J Mater Res. 2001; 16(12):3331–4. doi:10.1557/JMR.2001.0457
202. Zhang P, Yin S, Sato T. Synthesis of high-activity TiO2 photocatalyst via environmentally friendly and novel microwave assisted hydrothermal process. Applied Catalysis B: Environmental. 2009; 89(1–2):118–22. doi:10.1016/j.apcatb.2008.12.002
203. Zhang Q-H, Han W-D, Hong Y-J, Yu J-G. Photocatalytic reduction of CO2 with H2O on Pt-loaded TiO2 catalyst. Catalysis Today. 2009; 148(3–4):335–40. doi:10.1016/j.cattod.2009.07.081
204. Zhang Y, Zheng H, Liu G, Battaglia V. Synthesis and electrochemical studies of a layered spheric TiO2 through low temperature solvothermal method. Electrochimica Acta. 2009; 54(16):4079–83. doi:10.1016/j.electacta.2009.02.044
205. Fattakhova-Rohlfing D, Zaleska A, Bein T. Three-Dimensional Titanium Dioxide Nanomaterials. Chem Rev. 2014; 114(19):9487–558. doi:10.1021/cr500201c
206. Attar AS, Ghamsari MS, Hajiesmaeilbaigi F, Mirdamadi S, Katagiri K, Baetzold RC. Journal of the American Chemical Society. 1981; 103:6116.
207. Oskam G, Nellore A, Penn RL, Searson PC. The Growth Kinetics of TiO_2 Nanoparticles from Titanium(IV) Alkoxide at High Water/Titanium Ratio. J Phys Chem B. 2003; 107(8):1734–8. doi:10.1021/jp021237f
208. Mehrotra RC, Singh A. ChemInform Abstract: Recent Trends in Metal Alkoxide Chemistry. ChemInform. 1997; 28(49):chin.199749321. doi:10.1002/chin.199749321
209. Livage J, Henry M, Sanchez C. Sol-gel chemistry of transition metal oxides. Progress in Solid State Chemistry. 1988; 18(4):259–341. doi:10.1016/0079-6786(88)90005-2

210. Tseng TK, Lin YS, Chen YJ, Chu H. A Review of Photocatalysts Prepared by Sol-Gel Method for VOCs Removal. IJMS. 2010; 11(6):2336–61. doi:10.3390/ijms11062336
211. Yu JC, Yu J, Ho W, Zhang L. Preparation of highly photocatalytic active nano-sized TiO2 particles via ultrasonic irradiation. Chem Commun. 2001; (19):1942–3. doi:10.1039/b105471f
212. Chen X. Titanium Dioxide Nanomaterials and Their Energy Applications. Chinese Journal of Catalysis. 2009; 30(8):839–51. doi:10.1016/S1872-2067(08)60126-6
213. Zhu Y-J, Chen F. Microwave-Assisted Preparation of Inorganic Nanostructures in Liquid Phase. Chem Rev. 2014; 114(12):6462–555. doi:10.1021/cr400366s
214. Collins MJ. Future Trends in Microwave Synthesis. Future Med Chem. 2010; 2(2):151–5. doi:10.4155/fmc.09.133
215. Jacob J, Chia LHL, Boey FYC. Thermal and non-thermal interaction of microwave radiation with materials. JOURNAL OF MATERIALS SCIENCE. 1995; 30(21):5321–7. doi:10.1007/BF00351541
216. De La Hoz A, Díaz-Ortiz Á, Moreno A. Microwaves in organic synthesis. Thermal and non-thermal microwave effects. Chem Soc Rev. 2005; 34(2):164–78. doi:10.1039/B411438H
217. Gressel-Michel E, Chaumont D, Stuerga D. From a microwave flash-synthesized TiO2 colloidal suspension to TiO2 thin films. Journal of Colloid and Interface Science. 2005; 285(2):674–9. doi:10.1016/j.jcis.2004.12.055
218. Corradi AB, Bondioli F, Focher B, Ferrari AM, Grippo C, Mariani E, et al. Conventional and Microwave-Hydrothermal Synthesis of TiO_2 Nanopowders. Journal of the American Ceramic Society. 2005; 88(9):2639–41. doi:10.1111/j.1551-2916.2005.00474.x
219. Kim H, Noh K, Choi C, Khamwannah J, Villwock D, Jin S. Extreme Superomniphobicity of Multiwalled 8 nm TiO_2 Nanotubes. Langmuir. 2011; 27(16):10191–6. doi:10.1021/la2014978
220. Baldassari S, Komarneni S, Mariani E, Villa C. Rapid Microwave–Hydrothermal Synthesis of Anatase Form of Titanium Dioxide. Journal of the American Ceramic Society. 2005; 88(11):3238–40. doi:10.1111/j.1551-2916.2005.00562.x
221. Kang J, Gao L, Zhang M, Pu J, He L, Ruan R, et al. Synthesis of rutile TiO2 powder by microwave-enhanced roasting followed by hydrochloric acid leaching. Advanced Powder Technology. 2020; 31(3):1140–7. doi:10.1016/j.apt.2019.12.042
222. Kim H, Noh K, Choi C, Khamwannah J, Villwock D, Jin S. Extreme Superomniphobicity of Multiwalled 8 nm TiO_2 Nanotubes. Langmuir. 2011; 27(16):10191–6. doi:10.1021/la2014978
223. Malekshahi Byranvand M, Nemati Kharat A, Fatholahi L, Malekshahi Beiranvand Z. A review on synthesis of nano-TiO_2 via different methods. Journal of Nanostructures. 2013; 3(1):1-9
224. Chen X, Mao SS. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. Chem Rev. 2007; 107(7):2891–959. doi:10.1021/cr0500535
225. Seifried S, Winterer M, Hahn H. Nanocrystalline Titania Films and Particles by Chemical Vapor Synthesis. Chem Vap Deposition. 2000; 6(5):239–44. doi:10.1002/1521-3862(200010)6:5<239::AID-CVDE239>3.0.CO; 2-Q
226. Oh S-M, Ishigaki T. Preparation of pure rutile and anatase TiO2 nanopowders using RF thermal plasma. Thin Solid Films. 2004; 457(1):186–91. doi:10.1016/j.tsf.2003.12.043
227. Gablenz, S., Voltzke, D., Abicht, H. P., & Neumann-Zdralek, J. (1998). Preparation of fine TiO2 powders via spray hydrolysis of titanium tetraisopropoxide. *Journal of materials science letters*, *17*(7), 537-539.
228. Yu J, Zhao X. Effect of substrates on the photocatalytic activity of nanometer TiO2 thin films. Materials Research Bulletin. 2000; 35(8):1293–301. doi:10.1016/S0025-5408(00)00327-5
229. Zhang Q, Li C. High Temperature Stable Anatase Phase Titanium Dioxide Films Synthesized by Mist Chemical Vapor Deposition. Nanomaterials. 2020; 10(5):911. doi:10.3390/nano10050911
230. Sedky NK, Mahdy NK, Abdel-kader NM, Abdelhady MMM, Maged M, Allam AL, et al. Facile sonochemically-assisted bioengineering of titanium dioxide nanoparticles and deciphering their potential in treating breast and lung cancers: biological, molecular, and computational-based investigations. RSC Adv. 2024; 14(12):8583–601. doi:10.1039/D3RA08908H
231. Aswini R, Murugesan S, Kannan K. Bio-engineered TiO_2 nanoparticles using *Ledebouria revoluta* extract: Larvicidal, histopathological, antibacterial and anticancer activity. International Journal of Environmental Analytical Chemistry. 2021; 101(15):2926–36. doi:10.1080/03067319.2020.1718668
232. Danyliuk NV, Tatarchuk TR, Shyichuk AV. Batch microreactor for photocatalytic reactions monitoring. PCSS. 2020; 21(2):338–46. doi:10.15330/pcss.21.2.338-346
233. Mbonyiryivuze, A., Zongo, S., Diallo, A., Bertrand, S., Minani, E., Yadav, L. L., ... & Maaza, M. (2015). Titanium dioxide nanoparticles biosynthesis for dye sensitized solar cells application.
234. Saikumari N, Preethi T, Abarna B, Rajarajeswari GR. Ecofriendly, green tea extract directed sol–gel synthesis of nano titania for photocatalytic application. J Mater Sci: Mater Electron. 2019; 30(7):6820–31. doi:10.1007/s10854-019-00994-x
235. M. S, K. B, M. B, S. J, S. A, A. S, et al. Obtaining titanium dioxide nanoparticles with spherical shape and antimicrobial properties using M. citrifolia leaves extract by hydrothermal method. Journal of Photochemistry and Photobiology B: Biology. 2017; 171:117–24. doi:10.1016/j.jphotobiol.2017.05.003

236. Hariharan D, Jegatha Christy A, Mayandi J, Nehru LC. Visible light active photocatalyst: Hydrothermal green synthesized TiO 2 NPs for degradation of picric acid. Materials Letters. 2018; 222:45–9. doi:10.1016/j.matlet.2018.03.109
237. Thandapani K, Kathiravan M, Namasivayam E, Padiksan IA, Natesan G, Tiwari M, et al. Enhanced larvicidal, antibacterial, and photocatalytic efficacy of TiO2 nanohybrids green synthesized using the aqueous leaf extract of Parthenium hysterophorus. Environ Sci Pollut Res. 2018; 25(11):10328–39. doi:10.1007/s11356-017-9177-0
238. Gurrappa I, Binder L. Electrodeposition of nanostructured coatings and their characterization—A review. Science and Technology of Advanced Materials. 2008; 9(4):043001. doi:10.1088/1468-6996/9/4/043001
239. Hanaor D, Michelazzi M, Leonelli C, Sorrell CC. The effects of carboxylic acids on the aqueous dispersion and electrophoretic deposition of ZrO2. Journal of the European Ceramic Society. 2012; 32(1):235–44. doi:10.1016/j.jeurceramsoc.2011.08.015
240. Jiang, L. C., & Zhang, W. D. (2019). Electrodeposition of TiO2 nanoparticles on multiwalled carbon nanotube arrays for hydrogen peroxide sensing. *Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis*, *21*(8), 988-993.
241. Wasserscheid P, Keim W. Ionic Liquids—New "Solutions" for Transition Metal Catalysis. Angew Chem Int Ed. 2000; 39(21):3772–89. doi:10.1002/1521-3773(20001103)39:21<3772::AID-ANIE3772>3.0.CO; 2-5
242. Wasserscheid P., Welton T. (ed.). Ionic liquids in synthesis. – Weinheim : Wiley-Vch, 2008. – T. 1. – p. 145.
243. Ma Z, Yu J, Dai S. Preparation of Inorganic Materials Using Ionic Liquids. Advanced Materials. 2010; 22(2):261–85. doi:10.1002/adma.200900603
244. Hong K, Yoo KS. Synthesis of TiO2 hollow spheres using binary ionic liquids as an electrocatalyst. Res Chem Intermed. 2011; 37(9):1325–31. doi:10.1007/s11164-011-0400-1
245. Mali SS, Betty CA, Bhosale PN, Devan RS, Ma Y-R, Kolekar SS, et al. Hydrothermal synthesis of rutile TiO2 nanoflowers using Brønsted Acidic Ionic Liquid [BAIL]: Synthesis, characterization and growth mechanism. CrystEngComm. 2012; 14(6):1920. doi:10.1039/c2ce06476f
246. He Z, Yue G, Gao Y, Dong C, Tan F. Efficient flexible dye-sensitized solar cells from rear illumination based on different morphologies of titanium dioxide photoanode. J Semicond. 2024; 45(2):022801. doi:10.1088/1674-4926/45/2/022801
247. Kakihana M, Kobayashi M, Tomita K, Petrykin V. Application of Water-Soluble Titanium Complexes as Precursors for Synthesis of Titanium-Containing Oxides via Aqueous Solution Processes. Bulletin of the Chemical Society of Japan. 2010; 83(11):1285–308. doi:10.1246/bcsj.20100103
248. Younus LA, Mahmoud ZH, Hamza AA, Alaziz KMA, Ali ML, Yasin Y, et al. Photodynamic therapy in cancer treatment: properties and applications in nanoparticles. Braz J Biol. 2024; 84:e268892. doi:10.1590/1519-6984.268892
249. Abdul-Reda Hussein U, Mahmoud ZH, Alaziz KMA, Alid ML, Yasin Y, Ali FK, et al. Antimicrobial finishing of textiles using nanomaterials. Braz J Biol. 2024; 84:e264947. doi:10.1590/1519-6984.264947
250. Mohammadkhani A, Mohammadkhani F, Farhadyar N, Sadjadi MS, Kianfar E. Novel nanocomposite zinc phosphate/ polyvinyl alcohol / carboxymethyl cellulose: Synthesis, characterization and investigation of antibacterial and anticorrosive properties. Case Studies in Chemical and Environmental Engineering. 2024; 9:100591. doi:10.1016/j.cscee.2023.100591
251. Kianfar E. A review of recent advances in carbon dioxide absorption–stripping by employing a gas–liquid hollow fiber polymeric membrane contactor. Polym Bull. 2023; 80(11):11469–505. doi:10.1007/s00289-022-04626-z
252. Yi Hsu C, Mahmoud ZH, Abdullaev S, Abdulrazzaq Mohammed B, Altimari US, Laftah Shaghnab M, et al. Nanocomposites based on Resole/graphene/carbon fibers: A review study. Case Studies in Chemical and Environmental Engineering. 2023; 8:100535. doi:10.1016/j.cscee.2023.100535
253. AL-Salman HNK, Hsu C-Y, Nizar Jawad Z, Mahmoud ZH, Mohammed F, Saud A, et al. Graphene oxide-based biosensors for detection of lung cancer: A review. Results in Chemistry. 2024; 7:101300. doi:10.1016/j.rechem.2023.101300
254. Gong D, Grimes CA, Varghese OK, Hu W, Singh RS, Chen Z, et al. Titanium oxide nanotube arrays prepared by anodic oxidation. J Mater Res. 2001; 16(12):3331–4. doi:10.1557/JMR.2001.0457
255. Paulose M., Shankar K., Yoriya S., Prakasam H. E., Varghese O. K., Mor G. K., Latempa T. A., Fitzgerald A., Grimes C. A. Anodic Growth of Highly Ordered TiO2 Nanotube Arrays to 134 µm in Length // The Journal of Physical Chemistry B. V.110. №33. 2006. P. 16179-16184.
256. Ali G, Chen C, Yoo SH, Kum JM, Cho SO. Fabrication of complete titania nanoporous structures via electrochemical anodization of Ti. Nanoscale Res Lett. 2011; 6(1):332. doi:10.1186/1556-276X-6-332
257. Parmon V. N. Development of physico-chemical foundations of transformation solar energy by decomposing water into molecular photocatalytic systems. Diss... doc. chem. Sci. Novosibirsk, 1984, 680 pp.

258. Shijubo N, Honda Y, Fujishima T, Takahashi H, Kodama T, Kuroki Y, et al. Lung surfactant protein-A and carcinoembryonic antigen in pleural effusions due to lung adenocarcinoma and malignant mesothelioma. Eur Respir J. 1995; 8(3):403–6. doi:10.1183/09031936.95.08030403
259. Jasim SA, Ali MH, Mahmood ZH, Rudiansyah M, Alsultany FH, Mustafa YF, et al. Role of Alloying Composition on Mechanical Properties of CuZr Metallic Glasses During the Nanoindentation Process. Met Mater Int. 2022; 28(9):2075–82. doi:10.1007/s12540-021-01164-7
260. Bokov DO, Mustafa YF, Mahmoud ZH, Suksatan W, Jawad MA, Xu T. Cr-SiNT, Mn-SiNT, Ti-C70 and Sc-CNT as Effective Catalysts for CO2 Reduction to CH3OH. Silicon. 2022; 14(14):8493–503. doi:10.1007/s12633-022-01653-3
261. Krakowiak R, Musial J, Bakun P, Spychała M, Czarczynska-Goslinska B, Mlynarczyk DT, et al. Titanium Dioxide-Based Photocatalysts for Degradation of Emerging Contaminants including Pharmaceutical Pollutants. Applied Sciences. 2021; 11(18):8674. doi:10.3390/app11188674
262. Magaña-López R, Zaragoza-Sánchez PI, Jiménez-Cisneros BE, Chávez-Mejía AC. The Use of TiO2 as a Disinfectant in Water Sanitation Applications. Water. 2021; 13(12):1641. doi:10.3390/w13121641
263. Yang X, Zhao R, Zhan H, Zhao H, Duan Y, Shen Z. Modified Titanium dioxide-based photocatalysts for water treatment: Mini review. Environmental Functional Materials. 2024; S2773058124000322. doi:10.1016/j.efmat.2024.07.002
264. Khan, Mohammad Mansoob. "Principles and mechanisms of photocatalysis." *Photocatalytic systems by design*. Elsevier, 2021. 1-22.
265. Yadav HM, Kim J-S, Pawar SH. Developments in photocatalytic antibacterial activity of nano TiO2: A review. Korean J Chem Eng. 2016; 33(7):1989–98. doi:10.1007/s11814-016-0118-2
266. Hassan, Sona Ayadi, and Parinaz Ghadam. "Photocatalytic Properties of Metal-Based Nanoparticles." *Handbook of Green and Sustainable Nanotechnology: Fundamentals, Developments and Applications*. Cham: Springer International Publishing, 2022. 1-25.
267. Sedita, Silvia Rita, Yasunori Baba, and Naohiro Shichijo. "Pasteur scientists meet the market: An empirical illustration of the innovative performance of university–industry relationships." *Innovation, Alliances, and Networks in High-Tech Environments*. Routledge, 2015. 263-281.
268. Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results. Chem Rev. 1995 ; 95(3):735–58. doi:10.1021/cr00035a013
269. Munuera G., Gonzalez-Elipe A.R., Rives-Arnau V., Navio A., Malet P., Sokia J., Conesa J.C., Sanz J. Photo-adsorption of oxygen on acid and basic TiO2 surfaces // Adsorption and Catalysis on Oxide Surfaces. 1985. V.21. P. 113-126.
270. Mills A, Le Hunte S. An overview of semiconductor photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry. 1997; 108(1):1–35. doi:10.1016/S1010-6030(97)00118-4
271. Watson SS, Beydoun D, Scott JA, Amal R. The effect of preparation method on the photoactivity of crystalline titanium dioxide particles. Chemical Engineering Journal. 2003; 95(1–3):213–20. doi:10.1016/S1385-8947(03)00107-4
272. Ohno T, Sarukawa K, Tokieda K, Matsumura M. Morphology of a TiO2 Photocatalyst (Degussa, P-25) Consisting of Anatase and Rutile Crystalline Phases. Journal of Catalysis. 2001; 203(1):82–6. doi:10.1006/jcat.2001.3316
273. Gerischer H, Heller A. Photocatalytic Oxidation of Organic Molecules at TiO2 Particles by Sunlight in Aerated Water. J Electrochem Soc. 1992; 139(1):113–8. doi:10.1149/1.2069154
274. Gao L, Zhang Q. Effects of amorphous contents and particle size on the photocatalytic properties of TiO 2 nanoparticles. Scripta Materialia. 2001; 44(8–9):1195–8. doi:10.1016/S1359-6462(01)00681-9
275. Mohd Raub AA, Bahru R, Mohamed MA, Latif R, Mohammad Haniff MAS, Simarani K, et al. Photocatalytic activity enhancement of nanostructured metal-oxides photocatalyst: a review. Nanotechnology. 2024; 35(24):242004. doi:10.1088/1361-6528/ad33e8
276. https://pubmed.ncbi.nlm.nih.gov/?term=photocatalysis
277. Tanos F, Razzouk A, Lesage G, Cretin M, Bechelany M. A Comprehensive Review on Modification of Titanium Dioxide-Based Catalysts in Advanced Oxidation Processes for Water Treatment. ChemSusChem. 2024; 17(6):e202301139. doi:10.1002/cssc.202301139
278. Hamad TG, Salman TA. Green synthesis of titanium oxide nanoparticles using pomegranate leaf extract: Characterization and antibacterial activity evaluation. In Baghdad, Iraq; 2024. p. 030008. doi:10.1063/5.0209359
279. Kubota Y, Shuin T, Kawasaki C, Hosaka M, Kitamura H, Cai R, et al. Photokilling of T-24 human bladder cancer cells with titanium dioxide. Br J Cancer. 1994; 70(6):1107–11. doi:10.1038/bjc.1994.456
280. Sun S, Vikrant K, Kim K-H, Boukhvalov DW. Titanium dioxide–supported mercury photocatalysts for oxidative removal of hydrogen sulfide from the air using a portable air purification unit. Journal of Hazardous Materials. 2024; 470:134089. doi:10.1016/j.jhazmat.2024.134089

281. Shang H, Jia H, Zhang W, Li S, Wang Q, Yang Q, et al. Surface Hydrogen Bond-Induced Oxygen Vacancies of TiO_2 for Two-Electron Molecular Oxygen Activation and Efficient NO Oxidation. Environ Sci Technol. 2023; 57(48):20400–9. doi:10.1021/acs.est.3c06593
282. Serpone N. Heterogeneous Photocatalysis and Prospects of TiO2-Based Photocatalytic DeNOxing the Atmospheric Environment. Catalysts. 2018; 8(11):553. doi:10.3390/catal8110553
283. Safni S-, Patricia EO, Ollinovela T, Yusuf Y. Degradation of Phenol Using Sonolysis and Photolysis by TiO2/RHAC Catalyst and Analysis with Spectrophotometer UV-VIS and HPLC. AK. 2023; 10(1):50–6. doi:10.15575/ak.v10i1.24775
284. Yamaguti K, Sato S. Photolysis of water over metallized powdered titanium dioxide. J Chem Soc, Faraday Trans 1. 1985; 81(5):1237. doi:10.1039/f19858101237
285. Stevens CG, Wessman NJ, Bowman JE, Ramsey WJ. Photolysis of water vapor on titanium/TiO2 surfaces. Chemical Physics Letters. 1982; 91(5):335–8. doi:10.1016/0009-2614(82)83295-8
286. Fujishima A, Honda K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature. 1972; 238(5358):37–8. doi:10.1038/238037a0
287. Nosaka Y. Water Photo-Oxidation over TiO2—History and Reaction Mechanism. Catalysts. 2022; 12(12):1557. doi:10.3390/catal12121557
288. Eidsvåg H, Bentouba S, Vajeeston P, Yohi S, Velauthapillai D. TiO2 as a Photocatalyst for Water Splitting—An Experimental and Theoretical Review. Molecules. 2021; 26(6):1687. doi:10.3390/molecules26061687
289. Ni M, Leung MKH, Leung DYC, Sumathy K. A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. Renewable and Sustainable Energy Reviews. 2007; 11(3):401–25. doi:10.1016/j.rser.2005.01.009
290. Water Treatment by Heterogeneous Photocatalysis: An Review / Saline Water Desalination Research Institute; Al-Rasheed R.A. Jeddah, Saudi Arabia, 2005. 14 p.
291. Jafari, S., Mahyad, B., Hashemzadeh, H., Janfaza, S., Gholikhani, T., & Tayebi, L. (2020). Biomedical applications of TiO2 nanostructures: recent advances. International journal of nanomedicine, 3447-3470.
292. Lee S-Y, Park S-J. TiO2 photocatalyst for water treatment applications. Journal of Industrial and Engineering Chemistry. 2013; 19(6):1761–9. doi:10.1016/j.jiec.2013.07.012
293. Dharma HNC, Jaafar J, Widiastuti N, Matsuyama H, Rajabsadeh S, Othman MHD, et al. A Review of Titanium Dioxide (TiO2)-Based Photocatalyst for Oilfield-Produced Water Treatment. Membranes. 2022 [cited 2024 Aug 14]; 12(3):345. doi:10.3390/membranes12030345
294. Raya, I., Mansoor Al Sarraf, A. A., Widjaja, G., Ghazi Al-Shawi, S., F Ramadan, M., Mahmood, Z. H., ... & Ghaleb Maabreh, H. (2022). ZnMoO4 nanoparticles: novel and facile synthesis, characterization, and photocatalytic performance. *Journal of Nanostructures*, *12*(2), 446-454.
295. Mahmood ZH, Jarosova M, Kzar HH, Machek P, Zaidi M, Dehno Khalaji A, et al. Synthesis and characterization of Co_3O_4 nanoparticles: Application as performing anode in Li-ion batteries. J Chinese Chemical Soc. 2022; 69(4):657–62. doi:10.1002/jccs.202100525
296. Bahadoran, A., Jabarabadi, M. K., Mahmood, Z. H., Bokov, D., Janani, B. J., & Fakhri, A. (2022). Quick and sensitive colorimetric detection of amino acid with functionalized-silver/copper nanoparticles in the presence of cross linker, and bacteria detection by using DNA-template nanoparticles as peroxidase activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *268*, 120636.
297. Mahmoud ZH, AL-Bayati RA, Khadom AA. Electron transport in dye-sanitized solar cell with tin-doped titanium dioxide as photoanode materials. J Mater Sci: Mater Electron. 2022 [cited 2024 Aug 14]; 33(8):5009–23. doi:10.1007/s10854-021-07690-9
298. Raya, I., Widjaja, G., Mahmood, Z. H., Kadhim, A. J., Vladimirovich, K. O., Mustafa, Y. F., ... & Kafi-Ahmadi, L. (2022). Kinetic, isotherm, and thermodynamic studies on Cr (VI) adsorption using cellulose acetate/graphene oxide composite nanofibers. *Applied Physics A*, *128*(2), 167.
299. Çeşmeli S, Biray Avci C. Application of titanium dioxide (TiO_2) nanoparticles in cancer therapies. Journal of Drug Targeting . 2019; 27(7):762–6. doi:10.1080/1061186X.2018.1527338
300. Li Q, Wang X, Lu X, et al. The incorporation of daunorubicin in cancer cells through the use of titanium dioxide whiskers. Biomaterials. 2009; 30(27):4708–4715.
301. Rivankar S. An overview of doxorubicin formulations in cancer therapy. J Can Res Ther. 2014; 10(4):853. doi:10.4103/0973-1482.139267
302. Wang, Q., Huang, J. Y., Li, H. Q., Chen, Z., Zhao, A. Z. J., Wang, Y., ... & Lai, Y. K. (2016). TiO2 nanotube platforms for smart drug delivery: a review. *International journal of nanomedicine*, 4819-4834.
303. Raja G, Cao S, Kim D-H, Kim T-J. Mechanoregulation of titanium dioxide nanoparticles in cancer therapy. Materials Science and Engineering: C. 2020; 107:110303. doi:10.1016/j.msec.2019.110303
304. Akram MW, Raziq F, Fakhar-e-Alam M, Aziz MH, Alimgeer KS, Atif M, et al. Tailoring of Au-TiO2 nanoparticles conjugated with doxorubicin for their synergistic response and photodynamic therapy applications. Journal of Photochemistry and Photobiology A: Chemistry. 2019; 384:112040. doi:10.1016/j.jphotochem.2019.112040

 doi:10.20944/preprints202408.1733.v1

305. Inoue T, Fujishima A, Konishi S, Honda K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. Nature. 1979; 277(5698):637–8. doi:10.1038/277637a0
306. Kurzmann C, Verheyen J, Coto M, Kumar RV, Divitini G, Shokoohi-Tabrizi HA, et al. In vitro evaluation of experimental light activated gels for tooth bleaching. Photochem Photobiol Sci. 2019; 18(5):1009–19. doi:10.1039/c8pp00223a
307. Woolerton TW, Sheard S, Reisner E, Pierce E, Ragsdale SW, Armstrong FA. Efficient and Clean Photoreduction of CO_2 to CO by Enzyme-Modified TiO_2 Nanoparticles Using Visible Light. J Am Chem Soc. 2010; 132(7):2132–3. doi:10.1021/ja910091z
308. Roy SC, Varghese OK, Paulose M, Grimes CA. Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. ACS Nano. 2010; 4(3):1259–78. doi:10.1021/nn9015423
309. Thampi KR, Kiwi J, Grätzel M. Methanation and photo-methanation of carbon dioxide at room temperature and atmospheric pressure. Nature. 1987; 327(6122):506–8. doi:10.1038/327506a0
310. M. Dell'Angela, T. Anniyev, M. Beye, R. Coffee, A. Föhlisch, J. Gladh, T. Katayama, S. Kaya, O. Krupin, J. LaRue, A. Møgelhøj, D. Nordlund, J. K. Nørskov, H. Öberg, H. Ogasawara, H. Öström, L. G. M. Pettersson, W. F. Schlotter, J. A. Sellberg, F. Sorgenfrei, J. J. Turner, M. Wolf, W. Wurth, A. Nilsson, Science 2013, 339, 1302.
311. Farouk HU, Raman AAA, Daud WMAW. TiO2 catalyst deactivation in textile wastewater treatment: Current challenges and future advances. Journal of Industrial and Engineering Chemistry. 2016; 33:11–21. doi:10.1016/j.jiec.2015.10.022
312. Zhang H, Banfield JF. Structural Characteristics and Mechanical and Thermodynamic Properties of Nanocrystalline TiO_2. Chem Rev. 2014; 114(19):9613–44. doi:10.1021/cr500072j
313. Penn RL, Banfield JF. Morphology development and crystal growth in nanocrystalline aggregates under hydrothermal conditions: insights from titania. Geochimica et Cosmochimica Acta. 1999; 63(10):1549–57. doi:10.1016/S0016-7037(99)00037-X
314. Rahimi N, Pax RA, Gray EMacA. Review of functional titanium oxides. I: TiO2 and its modifications. Progress in Solid State Chemistry. 2016; 44(3):86–105. doi:10.1016/j.progsolidstchem.2016.07.002
315. Farouk HU, Raman AAA, Daud WMAW. TiO2 catalyst deactivation in textile wastewater treatment: Current challenges and future advances. Journal of Industrial and Engineering Chemistry. 2016; 33:11–21. doi:10.1016/j.jiec.2015.10.022
316. Kääriäinen M-L, Kääriäinen TO, Cameron DC. Titanium dioxide thin films, their structure and its effect on their photoactivity and photocatalytic properties. Thin Solid Films. 2009; 517(24):6666–70. doi:10.1016/j.tsf.2009.05.001
317. Ta N, Liu (Jimmy) J, Shen W. Tuning the shape of ceria nanomaterials for catalytic applications. Chinese Journal of Catalysis. 2013; 34(5):838–50. doi:10.1016/S1872-2067(12)60573-7
318. Lee K, Yoon H, Ahn C, Park J, Jeon S. Strategies to improve the photocatalytic activity of TiO_2: 3D nanostructuring and heterostructuring with graphitic carbon nanomaterials. Nanoscale. 2019; 11(15):7025–40. doi:10.1039/C9NR01260E
319. Nakata, K.; Fujishima, A. TiO_2 photocatalysis: Design and applications. *J. Photochem. Photobiol. C Photochem. Rev.* 2012, *13*, 169–189.
320. Yang S, Xiong F, Chen K, Chang Y, Bai X, Yin W, et al. Impact of Titanium Dioxide and Fullerenol Nanoparticles on Caco-2 Gut Epithelial Cells. j nanosci nanotechnol. 2018; 18(4):2387–93. doi:10.1166/jnn.2018.14540
321. Ayorinde T, Sayes CM. An updated review of industrially relevant titanium dioxide and its environmental health effects. Journal of Hazardous Materials Letters. 2023; 4:100085. doi:10.1016/j.hazl.2023.100085
322. Bauer M, Lei C, Read K, Tobey R, Gland J, Murnane MM, et al. Direct Observation of Surface Chemistry Using Ultrafast Soft-X-Ray Pulses. Phys Rev Lett. 2001; 87(2):025501. doi:10.1103/PhysRevLett.87.025501