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Chapter

Synthesis and Properties of Titanium Dioxide Nanoparticles

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Abstract

Natural titanium dioxide (TiO$_2$) occurs in three distinct polymorphs (rutile, anatase, and brookite). Currently, TiO$_2$ gained the attention of several researchers around the world. TiO$_2$ is used in several applications because of its excellent properties (structural, optical, electrical, chemical, non-toxic, etc.). Thus, the applications are influenced by its surface, size, morphology, and crystal phase. TiO$_2$ as photocatalyst is widely used in energy and eco-friendly applications involving water purification, hydrogen production, phenol degradation, etc. The novelty of the present chapter lies in explaining the recently reported methods that are used to synthesize TiO$_2$ nanoparticles, such as sol-gel, hydrothermal, precipitation, etc. The different properties of TiO$_2$ are also provided in this chapter.

Keywords: titanium dioxide nanoparticles, properties, synthesis, structure, natural titanium dioxide (TiO$_2$)

1. Introduction

Titanium dioxide, with the chemical formula TiO$_2$, is one of the most valuable raw material and has been used in several applications including photocatalysis, medicine, sensors, paints, environment, solar energy, and others. TiO$_2$ has excellent corrosion resistance, good thermal and chemical stability, and low cost [1].

With the development of nanotechnology, TiO$_2$ nanoparticles (NPs), with attractive properties, have been widely fabricated and developed. In the past decades, the demand of titanium dioxide NPs observed remarkable growth because of its specific properties. Moreover, titania is accepted as a pharmaceutical and food additive [2]. It is also used in destruction of viruses and bacteria, inactivation of cancerous cells, as well as clean-up of oil spills [3]. TiO$_2$ NPs are employed for elimination of emerging contaminants [4]. Moreover, TiO$_2$ NPs are one of the excellent semi-conducting materials applied in solar cells because of their good chemical stability, low toxicity, low cost, and high photocatalytic activity for the degradation of organic impurity [5, 6]. Furthermore, TiO$_2$ NPs are widely used as photo-anode materials because of their powerful absorption of light particularly in UV range, good chemical solubility, excellent photo-corrosion resistance and low cost [7, 8]. TiO$_2$ is widely used as photocatalyst material due to its suitable energy band gap, which is less than 3.5 eV [9].

The recent advances in TiO$_2$ nanostructures and their applications have been summarized by Reghunath et al. [10]. Chen and Mao [11] have reported a review on the
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Synthesis, properties, modifications, and applications of TiO$_2$ NPs. Environmental and energy applications of titanium dioxide have been discussed by Ge et al. [12]. Mao et al. [13] have completed a review on the recent progress in TiO$_2$ based catalysis for energy systems. In their work, Nur et al. [14] have investigated the development of TiO$_2$ for improved dye degradation under UV-vis irradiation. In addition, the correlation between the improved in photocatalytic activity and various surface modifications have been reported [15]. Fujishima and Honda [16] prepared TiO$_2$ used as photoelectrode for splitting water via photoelectrochemical water splitting.

This chapter provides recent advances in the synthesis of titanium dioxide NPs and their performance in different applications.

2. Synthesis methods of titanium dioxide nanoparticles

A number of methods have been used for the synthesis of TiO$_2$ NPs, which are detailed below.

2.1 Polyol method

Recently, the polyol method has been found to be a very powerful route for the fabrication of nano-oxide and chalcogenide materials [17, 18]. In addition, polyol method is a simple and low cost route for fabricating metal oxide NPs. Thus, a number of studies have been reported on the synthesis of TiO$_2$ NPs by polyol method. For example, Shah and Rather [19] prepared TiO$_2$ NPs by polyol method using titanium (IV) butoxide, ethylene glycol, and acetone. They concluded that the mean crystallite size increased from 9.3 to 66.9 nm when calcination temperature rises from 300 to 1000°C. In addition, the obtained products showed greater stability (zeta potential of $-30.8$ to $-37.5$ mV) in aqueous solutions. Also, Sasikala et al. [20] prepared a dispersed SnO$_2$ on TiO$_2$ NPs via polyol method at calcination temperature of 500°C. They concluded that the TiO$_2$ containing SnO$_2$ showed improved photocatalytic activity compared to pure TiO$_2$ because of improved charge separation. Ultrafine anatase TiO$_2$ nanocrystals, with size of 2–5 nm, have been prepared through polyol process [21]. Figure 1 shows the TEM images of TiO$_2$ nanocrystals. The samples exhibited excellent photocatalytic activities.

Furthermore, polyol method was used to synthesize TiO$_2$ NPs by using different mole ratios of titanium tetrachloride and polyvinylpyrrolidone [22].

Figure 1.
TEM images of TiO$_2$ NPs prepared by polyol method [21].
photocatalytic performance of the prepared TiO₂ NPs attained 97.83% with a power conversion efficiency of 4.6%. Kang and co-workers [23] synthesized TiO₂ NPs, with average size of 25 nm, via polyol from titanium isopropoxide by refluxing at 270°C during 12 h. After that, the sample was heated at 600°C for 3 h. The final product showed an excellent electrochemical performance.

2.2 Hydrothermal method

Hydrothermal method is one of the most used route for nanomaterials synthesis. BiOI nanoflowers/TiO₂ nanotubes were developed for the detection of atrazine [24]. The sensing platform showed good analytical performance for detecting atrazine.

Alev et al. [25] prepared TiO₂ nanorods, with diameter of 100 nm, by hydrothermal using titanium butoxide, hydrochloric acid and deionised water. They concluded that the sensor response was 200% for 1000 ppm H₂. Additionally, TiO₂ NPs with size of 20 nm were prepared by hydrothermal method [26]. Figure 2 shows the TEM image of TiO₂ NPs. The result obtained by UV-VIS analysis revealed that the decrease in size of TiO₂ NPs is beneficial to the blue shift of their absorption peak.

Le et al. [27] synthesized TiO₂/graphene by hydrothermal method using TiCl₄ as a precursor. High performance was attained for the catalysts including well dispersed TiO₂ NPs on the graphene surface with loadings ranging from 16.5% to 26%. Similarly, Yang et al. [28] prepared TiO₂ NPs by hydrothermal. The results revealed that the peptization of the precipitate favored formation of the rutile phase and highly crystalline anatase. Europium (Er) doped TiO₂ NPs were prepared by hydrothermal method for photonic application [29]. TEM analysis showed that the average particle size was about 50 nm. Indeed, the Er doping leads to a change in morphology of NPs from rodlike to triangular for Er ions increased from 1 to 3 mol%, respectively (as presented in Figure 3).

Ag doped TiO₂ NPs, with crystallite size of 10/13 nm, were prepared via hydrothermal at temperature of 180°C for 120 min [30]. It was revealed that the maximum photodegradation of indigo blue attained 75% after irradiation time of 150 min. Dadkhah et al. [31] prepared anatase TiO₂ NPs by hydrothermal. They achieved conversion efficiency higher than 2.61% with the influence of amine ligands as a shape controller.
2.3 Sol-gel method

Sol-gel process is a powerful pathway for the synthesis of multi-component materials because of its mild synthesis conditions and low temperature. Thus, several researches have been reported on the fabrication of TiO$_2$ NPs by sol-gel method. For example, Sabry et al. [32] synthesized TiO$_2$ NPs by sol-gel process. The prepared material showed efficient photocatalytic activity of up to 68% after 180 min. Hsiung et al. [33] investigated the structure of photocatalytic active sites of TiO$_2$ NPs prepared by sol-gel. They concluded that the material exhibited an excellent photocatalytic activity. Additionally, TiO$_2$ NPs used as catalyst was prepared by sol-gel in acid at pH 3 [34]. The result showed that the material exhibited excellent reactivity for the photocatalytic reduction of nitric oxide.

Venkatachalam et al. [35] prepared alkaline earth metal (Mg$^{2+}$ and Ba$^{2+}$) doped TiO$_2$ NPs by sol-gel method using titanium isopropoxide as precursor. Figure 4 illustrates the SEM image of the metal-doped TiO$_2$ NPs, which are spherical in shape. Furthermore, the final product exhibited higher photocatalytic activity for the bisphenol.

Saravanan and Duby [36] investigated the optical and morphological properties of TiO$_2$ NPs synthesized via sol-gel method using titanium butoxide as a precursor. UV-Visible analyses revealed the absorbance peak in the UV region (about 380 nm) and FTIR spectrum confirmed the existence of anatase TiO$_2$ in the range of 400–1000 cm$^{-1}$. The average particle size of the TiO$_2$ NPs determined by dynamic light scattering (DLS) was found 131 nm. Govindaraj et al. [37] synthesized TiO$_2$ NPs to be used as a photo-anode by the sol-gel method. UV-Visible spectrum revealed the light absorption in the UV region with optical bandgap of 3.2 eV (see Figure 5).

Sinha et al. [38] studied the structural, optical, and antibacterial performance of the Mg doped TiO$_2$ NPs prepared by the sol-gel method. They reported that optical transmittance increases from 3 to 3.07 eV. In addition, the photoluminescence emission shows inner UV to blue resign from pure and doped TiO$_2$ NPs. Furthermore, Mugundan et al. [39] synthesized barium doped TiO$_2$ NPs by the sol-gel method. They concluded that the pure TiO$_2$ NPs revealed higher second harmonic generation efficiency compared to barium doped TiO$_2$ NPs. Nachit et al. [40] investigated the photocatalytic activity of TiO$_2$ NPs prepared by sol-gel process at low temperature. The mean crystallite size of TiO$_2$ NPs reached 30 nm at 500°C using an acid. In addition, the photocatalytic activity of TiO$_2$ NPs revealed that the degradation of Rhodamine B under UV light have a removal efficiency of 95% during 60 min.
2.4 Chemical vapor deposition method

Chemical vapor deposition (CVD) is a powerful method for the synthesis of nanomaterials with enhanced performances.

Several works have been reported on the fabrication of TiO₂ NPs by CVD. For example, Liu et al. [41] prepared TiO₂ NPs by CVD method. They revealed that the gas phase hydrolysis reaction may be decomposed into two processes: (i) hydrolysis of TiCl₄ into TiO(OH)₂ and (ii) decomposition of TiO(OH)₂ to TiO₂. The influence of...
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of various concentrations of TiO$_2$ NPs on CVD grown graphene was investigated by electrical charge transport measurements and Raman spectroscopy [42]. The schematic diagram of TiO$_2$ doped CVD grown single layer graphene devices is presented in Figure 6. The obtained results showed that TiO$_2$ change the electronic properties besides the structure of the CVD grown graphene.

Similarly, Li et al. [43] synthesized TiO$_2$ NPs, with mean particle size of 22 nm, by CVD method. The TEM image of TiO$_2$ NPs is presented in Figure 7. They concluded that the TiO$_2$ NPs with the metal ion dopants possess elevated photocatalytic activities compared to un-doped TiO$_2$ NPs.

Ding et al. [44] synthesized TiO$_2$ NPs via CVD process. The results obtained by XPS and nitrogen ads/desorption revealed that most of TiO$_2$ NPs were distributed on the external surface of the support and the coating was stable. V$_2$O$_5$-TiO$_2$ NPs were prepared from two precursors by CVD [45]. They revealed that the CVD process was a suitable method for the single step synthesis of nanocomposite coatings. Lee et al. [46] prepared TiO$_2$ NPs by CVD method. The results revealed that a 60 min sample coating time gave the most highly photocatalytic activity.

![TiO$_2$ NPs](image)

**Figure 6.** Schematic diagram of TiO$_2$ doped CVD grown single layer graphene devices [42].

![TEM image of TiO$_2$ NPs prepared by CVD](image)

**Figure 7.** TEM image of TiO$_2$ NPs prepared by CVD [43].
2.5 3D printing method

In the last few years, several works have been developed to fabricate 3D porous materials; principally 3D porous TiO$_2$ based materials.

Arango et al. [47] prepared a porous TiO$_2$ by 3D printing. They suggested that a large surface area could be realized for the TiO$_2$ via 3D printing technology.

Liu et al. [48] used 3D printing to prepare the porous Pb/TiO$_2$ composites applied to remove the organic contamination in the wastewater. The obtained materials exhibited high catalytic activity, good stability, and reusability against the treatment of high concentration 4-NP wastewater. The optical images of the Pb/TiO$_2$ scaffolds with 4, 8, 12, and 16 layers are presented in Figure 8.

Additionally, Aleni et al. [49] used 3D printing to fabricate a 3D dense and porous TiO$_2$ structure. The final products exhibited similar mechanical properties to those of porous ceramics prepared via conventional methods.

Xu et al. [50] developed 3D printing to assemble TiO$_2$ powders into hierarchical porous structures at macro and microscale. The schematic illustration of 3D printing process is presented in Figure 9. The obtained results showed that the TiO$_2$ structures with abundant light absorption sites and high surface area could enhance the conversion efficiency of N$_2$ and NH$_3$.

Furthermore, Wang et al. [51] synthesized TiO$_2$ NPs containing macrostructures by 3D printing for Arsenic (III) removal in water. They showed that 3D printing could fabricate and design macrostructures with special functions.

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Figure 8.
Optical images of the Pb/TiO$_2$ scaffolds with (a): 4, (b): 8, (c): 12, and (d): 16 layers.

Figure 9.
Schematic illustration of 3D printing of a hierarchical porous TiO$_2$ [50].
2.6 Mechanical alloying

Mechanical alloying (MA) is a low cost and simple route for preparing nanostructured materials among them TiO$_2$ NPs. The schematic illustration of the MA is presented in Figure 10.

Yao et al. [52] prepared nanostructured TiO$_2$ coating by mechanical alloying process. The results showed that the obtained material exhibited an excellent photocatalytic activity. Vilchez et al. [53] synthesized TiO$_2$ NPs by MA during 5 min. The TEM images of TiO$_2$ NPs are presented in Figure 11. The obtained material, with size in the range of 2–4 nm and specific surface area of 298 m$^2$ g$^{-1}$, exhibiting a good photocatalytic activity.

Kim et al. [54] prepared TiO$_2$ NPs by MA and heat treatment. The mean crystallite size was less than 6 nm. The UV-Visible spectrum showed that the obtained TiO$_2$ NPs had an elevated wavelength rage (in the range of 650 and 700 nm) compared to Ni doped TiO$_2$ (480–500 nm) and rutile (380–400 nm). In addition, PL spectrum exhibited a new emission peak confirming the decrease in the band gap. Furthermore, Fe (III) doped TiO$_2$ NPs have been synthesized via MA [55]. The final product showed excellent selectivity, stability, sensitivity, and fast response. Additionally, Eadi et al. [56] developed new Fe doped TiO$_2$ NPs by MA from FeCl$_3$ and TiO$_2$ powder. The results showed that the mean particle size was about 28 nm and the prepared material could be applied for gas sensing and photocatalytic degradation. Carniero et al. [57] investigated the effect of process parameters on the structural, optical, magnetic,

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**Figure 10.** Schematic illustration of the MA process.

**Figure 11.** TEM images of TiO$_2$ NPs prepared by MA [55].
and photocatalytic properties of iron doped TiO\textsubscript{2} NPs prepared by MA. The results showed that the incorporation of iron in the TiO\textsubscript{2} NPs has improved their photocatalytic activity.

2.7 Green synthesis

Green synthesis is a simple and ecofriendly method used for the preparation of nanomaterials. Abisharani et al. [58] synthesized TiO\textsubscript{2} NPs from titanium trichloride using Cucurbita pepo seeds extract. FTIR results showed that the existence of different functional biomolecules acted as a reducing factor for conversion of TiO\textsubscript{4} into TiO\textsubscript{2} NPs.

Isnaeni et al. [59] prepared TiO\textsubscript{2} NPs by green method including TiCl\textsubscript{3} hydrolysis with mango-peel extract. They revealed that the used method could be employed as an alternative to prepare phase pure anatase and rutile. Helmy et al. [60] synthesized S doped TiO\textsubscript{2} NPs by a novel green synthesis using Malva parviflora plant extract. They also studied their photocatalytic, antimicrobial, and antioxidant activities. The results showed that the samples exhibited good antibacterial and photocatalytic activities.

In addition, Samhitha et al. [61] studied the TiO\textsubscript{2} NPs prepared by various green synthesis methods for anticancer applications. Shen et al. [62] prepared Ce doped TiO\textsubscript{2} NPs supported on porous glass. Figure 12 shows TEM image of TiO\textsubscript{2} NPs. The mean diameter was about 5 nm. This study concludes that the green method makes Ce doped TiO\textsubscript{2} NPs immobilized on porous glass.

Additionally, TiO\textsubscript{2} NPs were synthesized through green method from Demostachaya bipinnata extract [63]. It has been shown that the prepared TiO\textsubscript{2} NPs are a good candidate for controlling mosquito vectors and agricultural pest management. Nabi et al. [64] prepared TiO\textsubscript{2} NPs, with mean crystallite size in the range of 80–100 nm, by green method using citrus limetta extract (as presented in Figure 13). The results showed that the degradation activity was more than 90% within 80 min. This excellent photocatalytic activity confirms that TiO\textsubscript{2} NPs are ecofriendly and have powerful applications in purification of water.

![Figure 12](image_url)

*Figure 12.* TEM image of TiO\textsubscript{2} NPs prepared by green method [62].
3. Properties of titanium dioxide nanoparticles

Figure 14 shows the different crystal structures of TiO$_2$ [65]. As it can be seen in this figure, there are three forms (polymorphs) namely anatase, rutile, and brookite, which are classified according to their crystalline arrangements. Thus, rutile is the most stable at higher temperature, whereas anatase is the most stable at lower temperature. Furthermore, at high temperature, anatase and brookite could be transformed into rutile. Brookite in the powder or thin film forms reveals excellent stability and superior photocatalytic activity to that of anatase [66]. In addition, anatase is favored in photocatalysis because of its high photocatalytic activity between all the three polymorphs [19].

Figure 14. Different crystal structures of TiO$_2$ [65].
Table 1 illustrates the different properties of titanium dioxide NPs. As it can be concluded from these values, TiO₂ NPs possess interesting physicochemical properties, which are influenced by different factors such as exposed crystal faces, morphology, and size of particles. Chen and Mao have published a review on the synthesis, properties, and applications of TiO₂ NPs [11].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</tr>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Appearance</td>
<td>White solid</td>
</tr>
<tr>
<td>Melting point (°C)</td>
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</tr>
<tr>
<td>Boiling point (°C)</td>
<td>2500–3000</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
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</tr>
<tr>
<td>Chemical formula</td>
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</tr>
<tr>
<td>Young’s modulus (GPa)</td>
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</tr>
<tr>
<td>Thermal conductivity at 800°C (W m⁻¹ K⁻¹)</td>
<td>8</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (10⁻⁶/Κ)</td>
<td>9</td>
</tr>
<tr>
<td>Refractive index</td>
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<td>Specific gravity</td>
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</tr>
<tr>
<td>Size range (nm)</td>
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</tbody>
</table>

Table 1. Various properties of titanium dioxide NPs [67].

Figure 15 shows the different hierarchical nanostructures of TiO₂. Four morphologies, involving 0D (quantum dots), 1D (nanotubes, nanorods, nanofibers,…), 2D (nanoflakes nanosheets,…), and 3D (nanospheres, nanoflowers,…), can be obtained.
4. Conclusions

In this chapter, we summarized some advances in the synthesis and properties of titanium dioxide nanoparticles. TiO$_2$ is basically found in three crystalline forms: brookite, anatase, and rutile. Its important potential application including its use as a food additive, in cosmetics, as a pigment, semiconductor, as well as in catalysis and photocatalysis, for UV adsorption and hydrogen storage has contributed to its massive elaboration by different methods and processes. On the other hand, materials with a nanometric structure display structural, mechanical, physical, chemical, optical, and electrical properties that are distinctly improved in comparison to the materials with a micrometric structure. However, each synthesis method allows favoring one or more of the above mentioned properties, allowing to promote the application of the obtained material in a specific field.

Several researches have been made on the preparation and characterization of TiO$_2$ NPs for various applications. Different synthesis methods have been presented to prepare titanium dioxide nanoparticles. For instance polyol process, which combines simplicity and low cost, allows to obtain TiO$_2$ NPs with different shapes and sizes depending on the starting reagents and operating conditions for photocatalytic activities applications. Hydrothermal is the most used method for nanomaterials synthesis and titanium dioxide can be successfully synthesized with different nanoscale shapes as sensors including dispersed TiO$_2$ NPs on the graphene surface. Nevertheless, the sol-gel method remains a powerful alternative for the synthesis of multi-component materials at mild and low temperature conditions leading to efficient photocatalytic activity of TiO$_2$. However, the Chemical vapor deposition process is suitable for the single step synthesis of nanocomposite coatings with enhanced properties. In this context, single layer graphene devices doped with TiO$_2$ have been obtained by CVD. This doping has shown that TiO$_2$ modifies the electronic properties as well as the structure of the CVD grown graphene. On the other hand, 3D porous TiO$_2$ based materials with high catalytic activity and good stability can be obtained through 3D printing technology. Among the simplest and most cost-effective processes for nanostructured materials synthesis, mechanical alloying is a very powerful technique for rapid elaboration of TiO$_2$ NPs with excellent photocatalytic activity. Nevertheless, compared to conventional methods, green method has been proven to be far more efficient; low cost, and eco-friendly route to the synthesis of TiO$_2$ NPs.

The results obtained in this work enable a better understanding of the synthesis methods as well as the different related properties of titanium dioxide nanoparticles. However, the selection of the synthesis method is conditioned by the required properties of the titanium dioxide NPs and the cost of the final material to be obtained. This is all the more sought after for a value-added and large-scale TiO$_2$ elaboration, which promotes the development of more innovative applications.

XRD, SEM, and TEM are the most used techniques for the nanostructured titanium dioxide characterization. The structural, morphological, and intrinsic properties of TiO$_2$ NPs were also discussed and related to its performance in various applications. Titanium dioxide was a prime candidate material because of its low-cost, high-abundance, and ease of synthesis.

Acknowledgements

The authors would like to thank Ms. Maja Bozicevic, Author Service Manager, for her remarkable efforts. This work was supported by Scientific Research Projects Coordination Unit of Zonguldak Bülent Ecevit University, project n° 2022-73338635-01.
Conflict of interest

The authors declare no conflict of interest.

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