crystals

Review

Synthesis, Characterisation, and Applications of TiO and Other Black Titania Nanostructures Species (Review)

Simonas Ramanavicius * and Arunas Jagminas *

Department of Electrochemical Material Science, State Research Institute Center for Physical Sciences and Technology, Sauletekio av. 3, LT-10257 Vilnius, Lithuania
* Correspondence: simonas.ramanavicius@ftmc.lt (S.R.); arunas.jagminas@ftmc.lt (A.J.)

Abstract: Black titania, a conductive ceramic material class, has garnered significant interest due to its unique optical and electrochemical properties. However, synthesising and properly characterising these structures pose a considerable challenge. This diverse material family comprises various titanium oxide phases, many of them non-stoichiometric. The term "black TiO_2" was first introduced in 2011 by Xiaobo Chen, but Arne Magneli's groundbreaking discovery and in-depth investigation of black titania in 1957 laid the foundation for our understanding of this material. The non-stoichiometric black titanium oxides were then called the Magneli phases. Since then, the science of black titania has advanced, leading to numerous applications in photocatalysis, electrocatalysis, supercapacitor electrodes, batteries, gas sensors, fuel cells, and microwave absorption. Yet, the literature is rife with conflicting reports, primarily due to the inadequate analysis of black titania materials. This review aims to provide an overview of black titania nanostructures synthesis and the proper characterisation of the most common and applicable black titania phases.

Keywords: Black TiO_2; black titania; reduced TiO_2; reduced titania; Magneli phases; titanium suboxide; TiO; Ti_2O_3; Ti_4O_7; Ti_3O_5

Citation: Ramanavicius, S.; Jagminas, A. Synthesis, Characterisation, and Applications of TiO and Other Black Titania Nanostructures Species (Review). *Crystals* **2024**, *14*, 647. https://doi.org/10.3390/cryst14070647

Academic Editor: Zhonghua Yao

Received: 31 May 2024
Revised: 10 July 2024
Accepted: 12 July 2024
Published: 14 July 2024

1. Introduction

Titania (TiO_2) is a well-known white ceramic material with broad applications [1]. It is obtainable in three main crystal phases: anatase, rutile, and brookite [2]. However, these are not all the possible structures that belong to titania; some of the structures addressed are called black TiO_2 or black titania. The term "Black TiO_2" was coined after its discovery by Chen et al. in 2011 due to its black appearance, which was in stark contrast to the usual white colour of TiO_2 [3]. This discovery of a new, black variant of TiO_2, known as black titania, has sparked significant interest in the scientific community. This materials group consists of non-stoichiometric titanium oxides, so-called Magneli phases discovered by Arne Magneli in 1957 [4], which possess attractive optical and electrical properties [5]; however, the analysis of these structures is highly challenging [6]. Up to now, there have been many contradicting reports about black titania synthesis and characterisation methods [7].

The primary method for the formation of Magneli phase black titania is heat treatment methods [8–11]; however, for practical applications, in most cases, nanostructured materials are required, which are challenging to obtain [12–15]. Many synthesis methods are applied to overcome these challenges, such as hydrothermal synthesis [16–18], plasma treatment [19–21], reduction [11,22,23], molten salts [12,24], etc. [25]. Despite this fact, the application areas are highly dependent on the chosen synthesis method, as every method has its advantages and disadvantages and gives control over specific parameters [26]. Up to now, the most advanced application is related to the optical properties of Magneli phase black titania. It is focused on solar cells, renewable energetics, and visible light photocatalysis for air and wastewater remediation [13]. Besides these thoroughly investigated applications, several other directions show promising results. One such is self-heating gas sensors [27,28], where Magneli phases-based heterostructures enable this unconventional design; others are substrates for efficient HER catalysts [29] and electrodes for the design of supercapacitors and batteries [17]. Not least important is the characterisation of synthesised structures. While SEM and TEM can easily characterise morphology, internal structural analysis is more challenging. XRD, Raman spectroscopy, EDX, XPS, and EPR are applied to do so [14,16,30]. However, the proper analysis of Magneli phase black titania requires a focus on synthesis methods with the prediction of the final product and the application of several independent analysis methods.

Several reports on various aspects of Magneli phase black titania synthesis, characterisation, and application have been published; however, the results are contradictory in many cases. This review aims to focus on the synthesis methods and proper characterisation of obtained structures.

2. The Family of Black Titania Materials

The rise of Magneli phase black titania started with Arne Magneli, who discovered that titanium oxide can be obtainable in Ti_2O, TiO, Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15}, Ti_9O_{17}, and $Ti_{10}O_{19}$ non-stoichiometric oxides, shown in Figure 1. After their discovery, these oxides were called Magneli phases [4]. Up to now, more non-stoichiometric titanium oxides, such as Ti_2O_3 [31,32] and Ti_3O_5 [33,34], have been synthesised. The first synthesis procedure for Magneli phase formation was the thermal annealing of pure metallic titanium in an argon atmosphere.

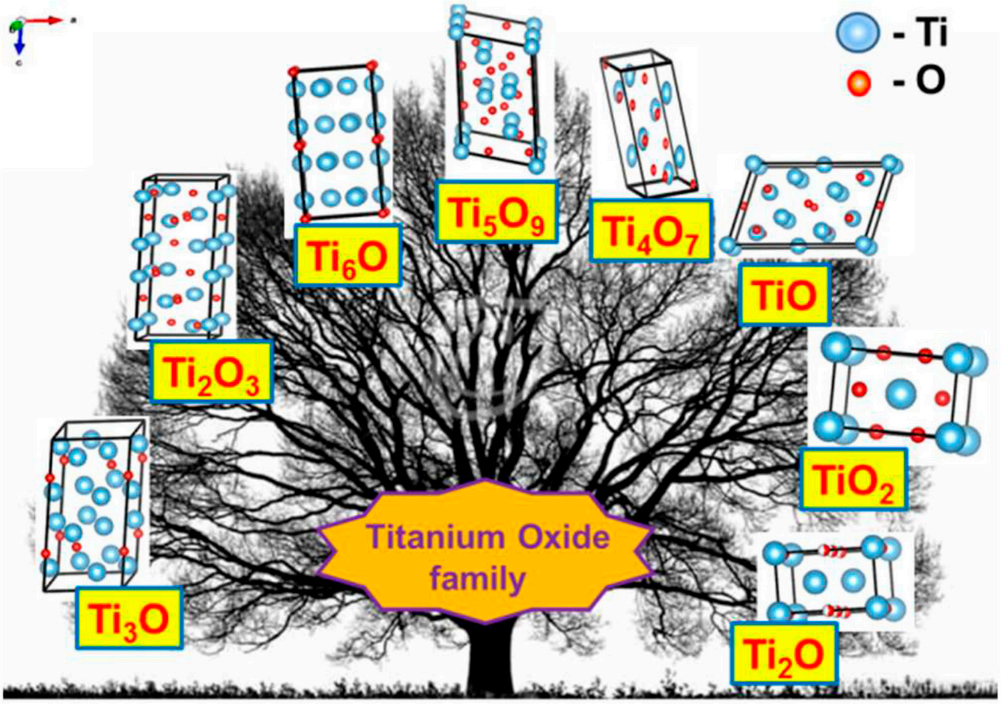

Figure 1. Family of Magneli phase black titania. Reprinted from [35].

While not all of these titania structures are well studied, there are contradicting reports that TiO might possess a metallic conductivity, while some studies show that it is a low bandgap semiconductor [16,36,37]. The narrow band gap is one of the main characteristics common for most Magneli phase black titania species [38]. There are currently many advanced synthesis methods for Magneli phases, many of which can provide nano-size products with huge potential for practical applications [26]. Proper selection and an understanding of the synthesis method are crucial for controlling the materials' properties.

3. Synthesis Routes for the Formation of Black Titania

The production of Magneli phase black titania, especially on a large scale, is a challenging but hot research topic [38,39]. While the studies on this field were started by Magneli in 1957, up to now, only several methods for various Magneli phase black TiO_2 structures have been reported [1,26]. The main challenge, which is hard to cope with, is the formation of non-stoichiometric structures and their stabilisation [40–42]. Moreover, the formation of nanostructures or nanostructured surfaces and the scalability of the processes are also among the main challenges. In most formation methods, the annealing step is necessary to form crystalline Magneli phase black titania fully; however, in the case of particle formation, it leads to the sintering and aggregation of the structures [26,39]. Below, the main synthesis methods for the formation of Magneli phase black titania are overviewed.

3.1. Annealing under Various Atmospheres

The first studies performed by Arne Magneli used slow heat treatment methods in an argon atmosphere for the production of the first reported non-stoichiometric titanium oxides [4,43,44]. Various modifications of heat treatment methods have been reported [45]. While all these methods have the same advantage of a simple procedure, the control of synthesis products is challenging. One of the main challenges is to have pure phase materials, as it is with this method; usually, a heterostructure of various phases is reached. Another critical challenge is the formation of nanomaterials (Figure 2), which is a must for many novel applications nowadays. While these methods are primarily applicable to powder samples, they are an excellent strategy for Magneli phase black titania-based thin film formation, as reported by Arunas Jagminas et al. [16].

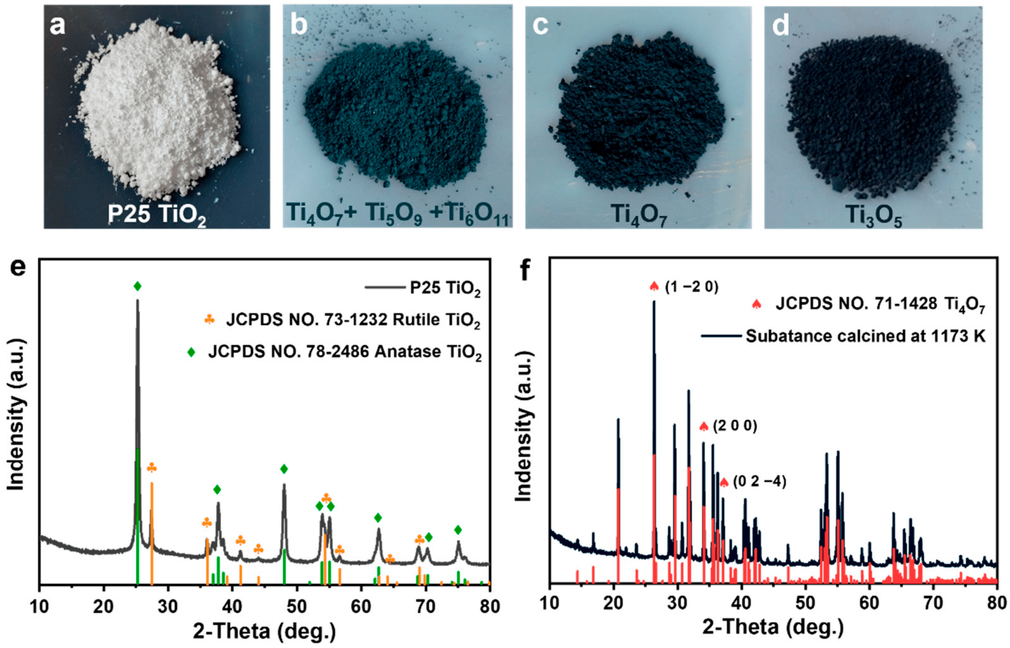

Figure 2. Images of (**a**) P25 TiO_2 powder calcined at (**b**) 1123 K, (**c**) 1173 K, and (**d**) 1223 K. XRD patterns of (**e**) P25 TiO_2 (**f**) powder calcined at 1173 K. Reprinted from [46].

One of the most popular heat treatment methods is TiO_2 reduction under a pure H_2 or H_2/N_2 Ag and H_2/Ar gas mixture atmosphere at a temperature higher than 1000 °C [3,10,46]. This method is applied widely to prepare some of the most common Magneli phases (Figure 3). However, the main disadvantage is that the sintering process happens simultaneously with reduction, leading to large-size structure formation [47]. Moreover, the reduction in the H_2 atmosphere is a precarious method, requiring not only specific equipment but also rigorous safety precautions.

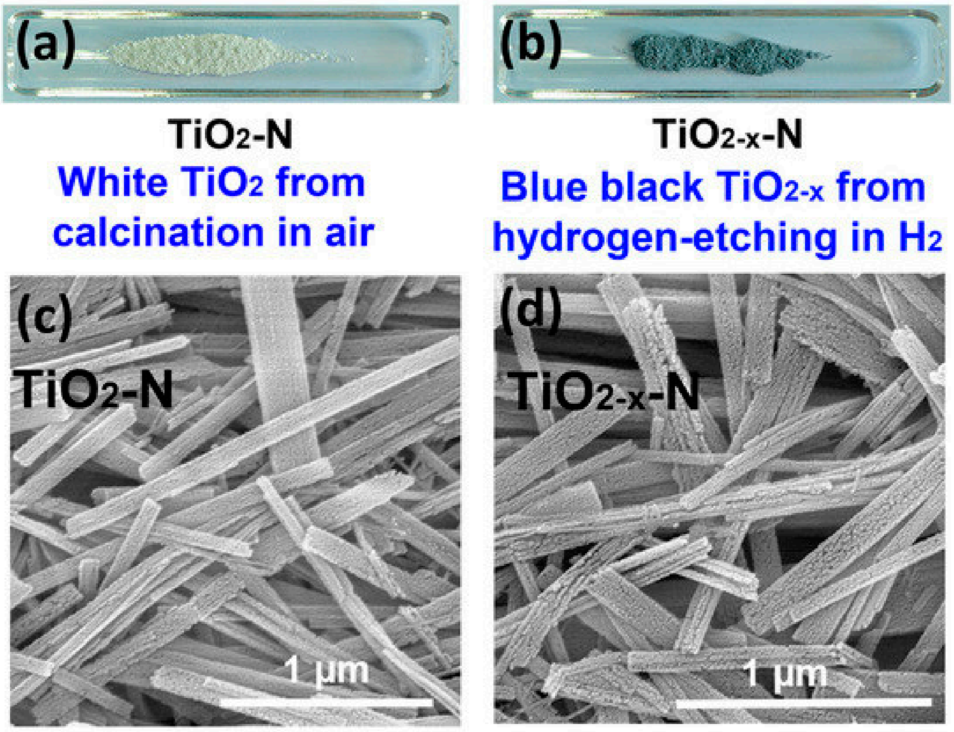

Figure 3. (**a**,**b**) Images of TiO_2 powder calcined in air and Magneli phase black TiO_{2-x} calcined under H_2 atmosphere; (**c**,**d**) scanning electron microscopy images of TiO_2 and TiO_{2-x} powders. Reprinted from [48].

Vacuum annealing is another heat treatment method applicable for the formation of Magneli phase black TiO_2. Several independent research groups have reported on the successful employment of this method [48–50]. In most cases, the temperature range is as it is for the regular titania annealing, not exceeding 800 °C. Moreover, Magneli phase black titania is reported to be attainable by mixing P-25 powder with metallic Mg or Al [51,52], which can extract oxygen during annealing in a vacuum or argon [53,54]. Reducing TiO_2 with $NaBH_4$ employed a similar technique [55]. The temperature and number of additives mainly control the formation of Magneli phases.

3.2. Wet Chemical Methods

Several reports of solvothermal synthesis being employed for the formation of Magneli phase black titania exist. One such method was reported by Shangjun Ding et al. [56], which consisted of titanium n-butoxide and organic carboxylic acids in addition to alcohol followed by 20 h of synthesis under 200 °C. Under these conditions, the crystalline anatase spherical structures were obtained without needing an additional annealing step.

Jagminas et al. reported the hydrothermal Magneli phase black titania phase formation by oxidising metallic titanium foil or particles in an alkaline solution with a selenite anion additive [16,17,29]. This method leads to the formation of porous nanoplatelet thin films and particles with a high surface area and a low bandgap (Figure 4). Its morphology and phase composition are controlled by varying the synthesis temperature, pH, and selenite anion concentration. However, the synthesis products are amorphous, and annealing under a vacuum is needed for the final formation of crystal phases.

Another hydrothermal method for the formation of Magneli phase black titania is based on microwave synthesis. In this case, a small amount of metallic titanium powder is dissolved in the mixture of the HCl and HF acids, and the formation under hydrothermal conditions begins. This method reported the formation of Magneli phase black TiO_2 nanoparticles [18].

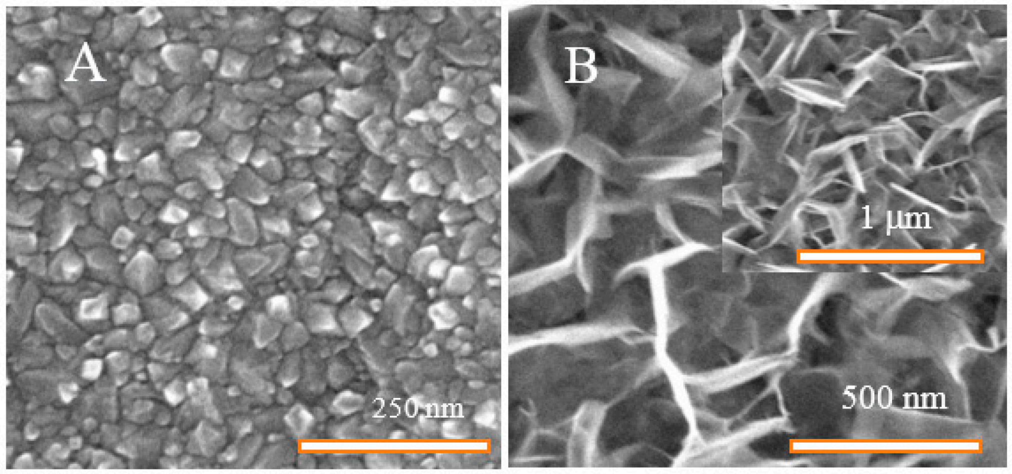

Figure 4. SEM images of hydrothermally formed titania thin film in the alkaline solution at 150 °C for 15 h (**A**); Magneli phase black titania thin film under the same reaction conditions but with H_2SeO_3 additive (**B**). Reprinted from [17].

Sol-gel is a standard method for large-scale Magneli phase black titania formation [57,58]. The most common precursors used in this type of synthesis are $TiCl_4$ [59] and titanium isopropoxide [60]. Figure 5 shows the principal scheme of how the carbon and carbon-nitrogen-doped Magneli phase black TiO_2 can be obtained.

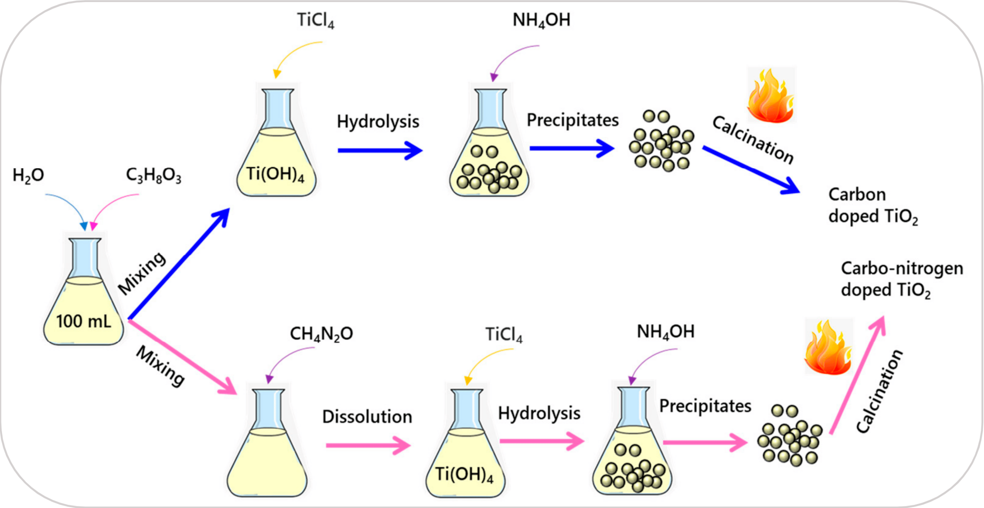

Figure 5. Schematic illustration of Magneli phase black titania formation by sol-gel method. Reprinted from [61].

One-pot gel combustion is one of the variations of the method, where titanium (IV) butoxide is mixed with diethylene glycol, and a small amount of water is added [61]. This method leads to the formation of hydroxylated particles. While the sol-gel process is easily scalable, the main disadvantage is the need for the calcination step, which leads to the sintering and aggregation of the structures [62]. There have been several reports of similar methods applied for the Magneli phase black titania thin film formation [57,58]. However, in all cases, further annealing is required after the substrate preparation step.

3.3. Laser Ablation

One of the most novel materials formation methods is laser ablation, a rapidly developing technology finding many application areas [63,64]. Danwen Yao et al. [65] reported the ablation of P-25 titania nanopowder and turned it into Magneli phase black TiO_2 by tuning the parameters of generated linearly polarised femtosecond laser pulses with a centre wavelength of 800 nm and a repetition rate of 500 Hz. The principal scheme of this process is depicted in Figure 6.

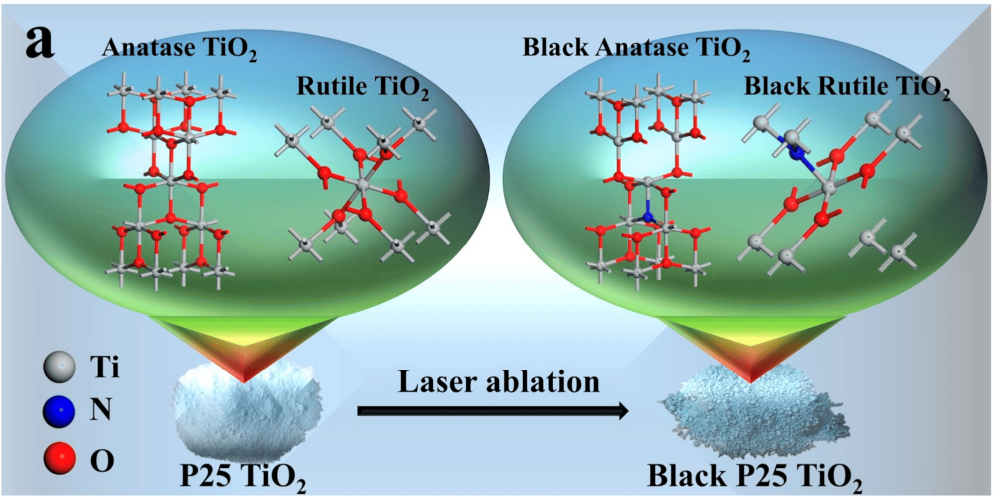

Figure 6. Schematic illustration of P25 titania and Magneli phase black TiO_2 fabricated by laser ablation. Reprinted from [65].

Several studies investigate laser ablation processes on titania, aiming to form Magneli phase black TiO_2 [65,66]. Xing Chen et al. reported that the laser ablation-prepared samples had a tunable illumination time, leading to different Magneli phases, which possess a narrow bandgap compared to regular titania [67]. The advantage of this method is that it can be performed in liquid media or solid-state if needed.

3.4. Molten Salt Method

The Molten salt method is the least discovered of all the Magneli phase black titania formation methods. However, it shows promising results for a simple, safe, large-scale nanocrystal synthesis. Several reports show the formation of various Magneli phase black TiO_2 species from different salts. Jijian Xu et al. reported the facile synthesis of hexagonal nanosheets through oxidising TiH_2 in eutectic $ZnCl_2/KCl$ salt melt [24]. Guilian Zhu et al. prepared Magneli phase black titania via a similar procedure but using a TiO_2 and $AlCl_3{-}NaCl$ salts mixture, where the molten salts-assisted aluminium reduction is the crucial parameter [12]. This method's main advantage is that it leads to the formation of nano-sized structures with a highly controllable morphology, which is a vast improvement over many other methods.

3.5. Plasma Treatment

One of the titania reduction to Magneli phase black TiO2 strategies is plasma treatment, and reductive H_2 plasma is the most widely reported and investigated method. This strategy can be applied to powders [20,68,69] and thin films [70], resulting in a controllable phase formation. The principal scheme of the methods is explained in the Figure 7. The reduction by plasma is usually performed under vacuum conditions, and it has principal similarities to annealing methods. However, the phase control of this method is more precise.

Besides the H_2 plasma treatment, there are other similar methods, such as mixed Ar and H_2 plasma [68], water plasma-assisted [21], and atmospheric-pressure plasma [19] treatment methods. All these Magneli phase black titania formation methods are similar, as the primary formation mechanism is based on titania reduction.

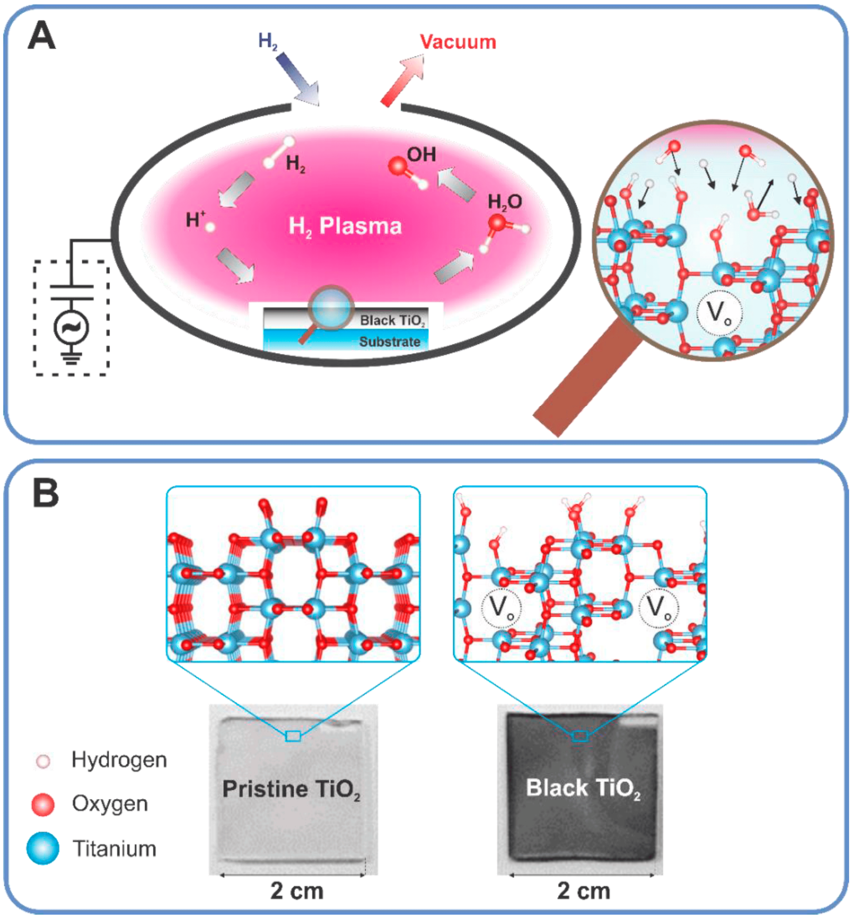

Figure 7. Schematic diagram of hydrogen plasma interaction with samples (**A**); images of pristine TiO_2 thin films before treatment with hydrogen plasma and after (**B**). Reprinted from [71].

4. Identification of Magneli Phase Black Titania

Properly identifying the Magneli phases is essential to understanding how different synthesis methods affect the internal structure and morphology as well as what is significantly influencing materials' properties [12,15]. While the pure phase materials' characterisation is simple, the Magneli phases are usually obtainable in heterostructures, which makes characterisation more complex [47]. Due to this issue, characterisation with several methods is always a must; as in most cases, the data from the different analysis methods provide the information required to understand materials fully. Below, the leading Magneli phase black titania characterisation methods are summarised, with emphasis on the most meaningful analysis points.

4.1. Identification through X-ray Diffraction (XRD)

The XRD is a gold standard for evaluating most ceramic materials' internal structure and crystal phases. However, it is not as helpful in analysing the Magneli phases' crystal structure due to the frequently occurring formation of complex heterostructured samples of many phases, which can be challenging to identify [72,73]. Another limitation of this analysis method is the inability to analyse amorphous materials. Regardless, many studies have successfully employed this analysis technique to analyse Magneli phase black titania for many purposes. Tingting Hu et al. employed XRD for the investigation of thermal stability and phase composition [47], as depicted in Figure 8.

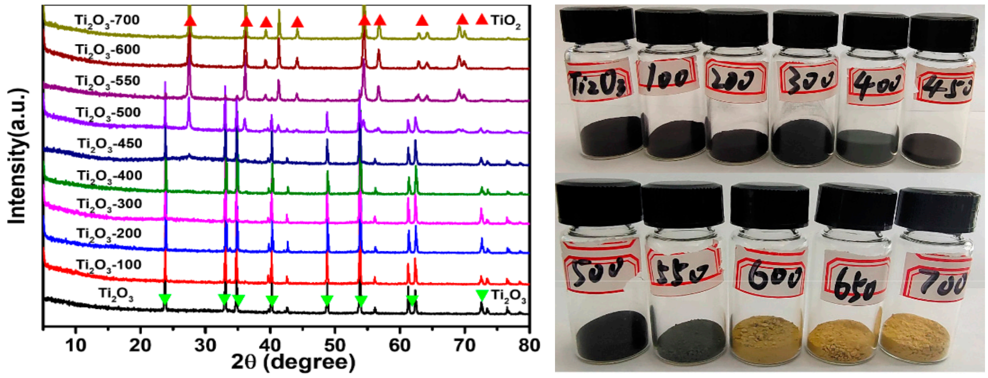

Figure 8. XRD patterns of Ti_2O_3 annealed under different temperatures. Reprinted from [47].

Chao Tang et al. reported a diligent investigation of TiO_2 reduction under the NH_3 gases atmosphere, where the XRD was employed as the main method to evaluate the crystal structure [71]. In this study, the Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}, Ti_9O_{17}, and Ti_3O_5 crystal phases were successfully registered. Although there are several reports on the characterisation of black titania Magneli phases by XRD, which can be used as a reference for other studies [27,74], the additional characterisation by XPS, EPR, and Raman spectroscopy is crucial to confirm the crystal phases.

4.2. Identification through Raman Spectroscopy

Raman spectroscopy is a powerful tool for analysing materials, and black titania Magneli phases are no exception. One of the main advantages is that there are a variety of laser excitations to choose from, and all of them provide slightly different spectrums with different information. Moreover, Raman spectroscopy is a susceptible analysis method that detects even slight changes in the samples, making it valuable for analysing Magneli phases' heterostructures [75]. As shown in Figure 9, the appearance of a new crystal phase in the spectra is usually detected by the shift of peaks in the case of a low concentration of detectable phases and by the appearance/disappearance of some peaks.

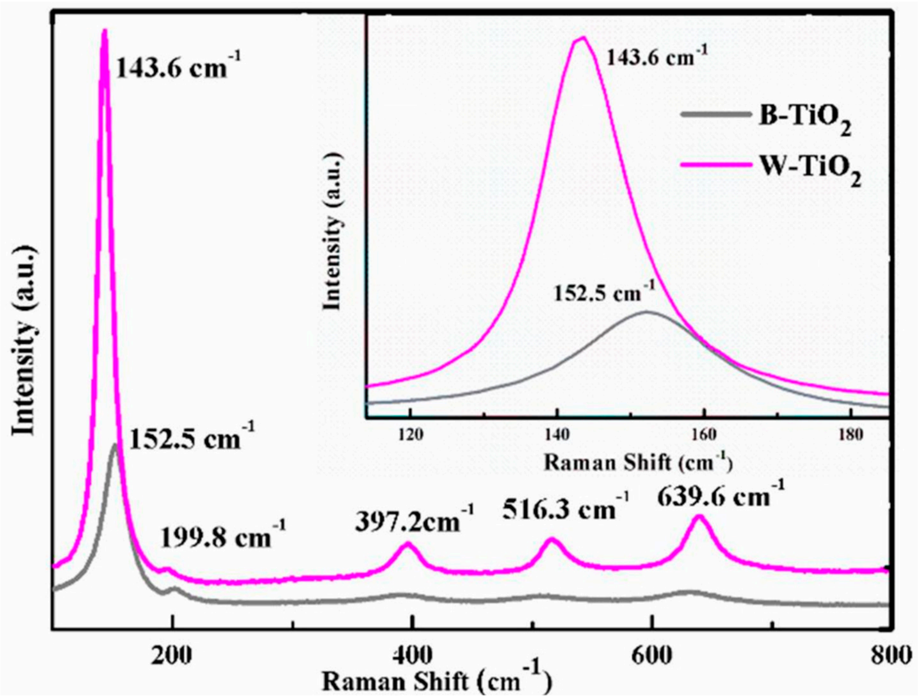

Figure 9. Characteristic Raman spectra of white TiO_2 (W-TiO_2) and black TiO_2 (B-TiO_2). Reprinted from [76].

The Raman spectroscopy spectra of black titania Magneli phases highly depend on the excitation wavelength, and while the most common excitation is 785 nm, in some cases, different lasers might be used during the analysis. The band at ~143 cm^{-1} blueshift is an indisputable indication of Magneli phase black TiO_2 formation reported by several deep analyses of Magneli phases where Raman spectroscopy was employed [19,72,73]. It is important to mention that in all these studies, the XRD patterns were not informative and gave the same information; the Raman spectroscopy was the primary method for identifying the internal structural changes of black titania Magneli phases.

4.3. Identification through Electron Paramagnetic Resonance (EPR)

Another essential identification method for black titania Magneli phases is the EPR analysis, as showed in the Figure 10, which can give information about the electronic structure of elements in the structure [77]. Specifically, for Magneli phases, EPR is focused on two effects: (1) the existence of Ti^{3+} and (2) the oxygen vacancies in the samples, which is secondary evidence of the presence of Ti^{3+} [16]. The detection of Ti^{3+} is crucial evidence of non-stoichiometric titania formation, and this analysis is essential in supporting XRD or Raman spectroscopy analysis data.

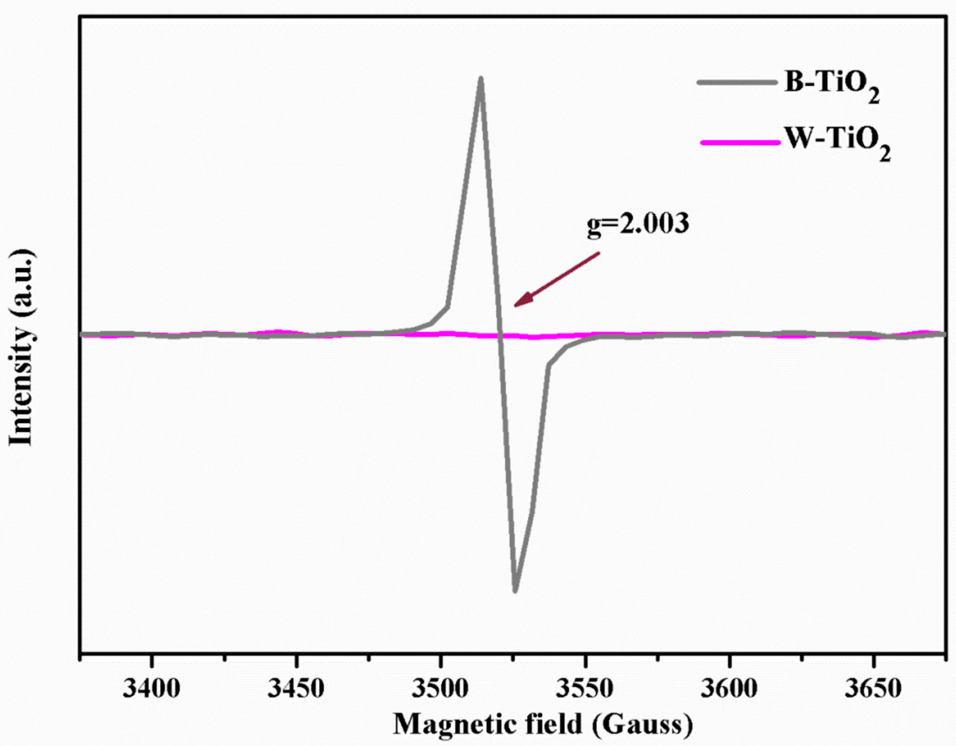

Figure 10. Typical EPR spectra of white TiO_2 (W-TiO_2) and Ti^{3+} rich Magneli phase black titania (B-TiO_2). Reprinted from [76].

The Ti^{3+} presence is determined by EPR spectra, where at g = 2.003, the characteristic peak is seen. However, depending on the crystal phase and preparation method, the second peak associated with oxygen vacancy formation might appear at g = 1.961 [16]. The Ti^{3+} presence in the structures is linked to the unique optical properties of Magneli phases. The narrow bandgap, up to lower than 1 eV, has been reported, and the diffuse reflectance measurements are crucial for characterising this property [78].

4.4. Identification through X-ray Photoelectron Spectroscopy (XPS)

XPS can obtain precise information about black titania Magneli phases, which is a suitable method for surface evaluation [70]. However, modern types of this equipment can also etch the sample and analyse its internal structure. If performed carefully, the XPS analysis can provide essential insights into the samples, as shown in Figures 11 and 12. As shown in the XPS spectra depicted in Figure 11, the analysis of the peak in the 453 to 463 eV range is essential to detect and separate the Ti^{4+}, Ti^{3+}, and Ti^{2+} species [71].

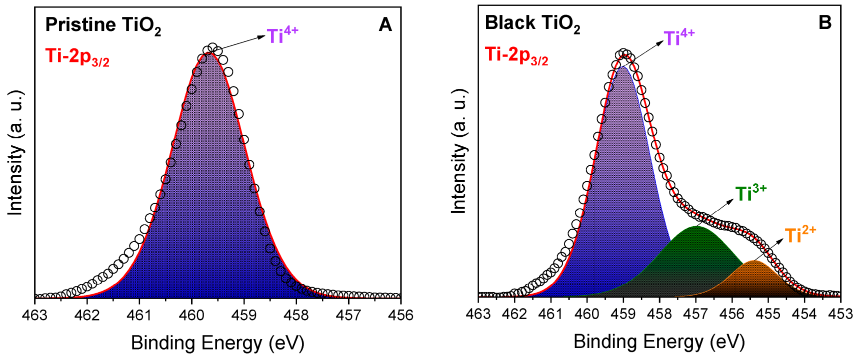

Figure 11. XPS Ti-$2p_{3/2}$ peaks of pristine (**A**) and black (**B**) TiO_2 sample. Reprinted from [71].

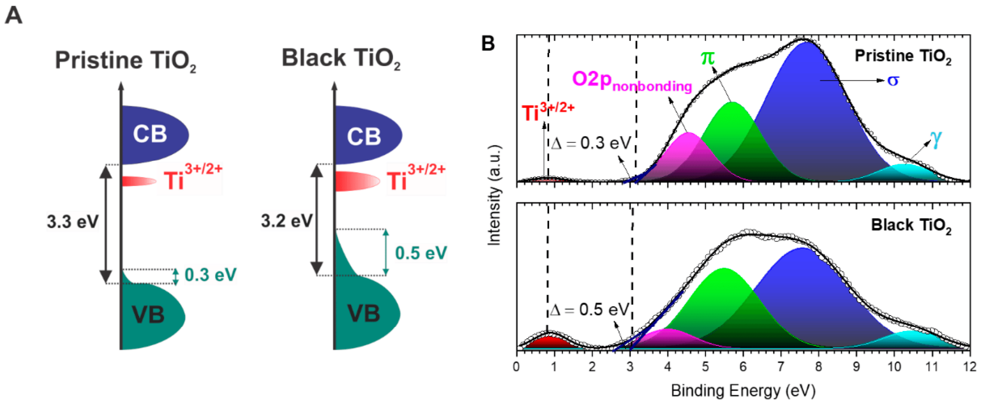

Figure 12. Pristine and black TiO_2 sample electronic structure (**A**) and XPS Ti-$2p_{3/2}$ peaks (**B**). Reprinted from [71].

Moreover, the XPS data of low energies in the range of 0 to 12 eV is also essential, as these spectra give information about the occupied density of the state. This spectra range gives information about oxygen vacancies and explains the sample's electronic structure [55]. Marcin Janczarek et al. employed the XPS for deep sample analysis in their study [53].

Despite XPS being a suitable method for analysing Magneli phase black titania's internal structure, it has some limitations, mainly because it is employed for thin films. Moreover, XPS alone is not sufficient to prove the formation of Magneli phase black titania, as it is a technique for analysis of the surfaces and can not provide enough data to prove the formation of Magneli phases. The supporting information from XRD, EPR, and Raman spectroscopy is necessary for the correct analysis of XPS data.

5. Applications

The Magneli phases of titania possess two main advantages compared to regular titania: (1) a narrow bandgap and (2) some phases with close to metallic conductivity [26]. Most Magneli phase black titania applications are based on these properties and focus on photocatalysis [79–81], supercapacitor electrodes [17,82], gas sensors [27,83], fuel cells [84–86], and surface-enhanced Raman spectroscopy substrates [87,88]. In recent years, Magneli phase black Titania has contributed significantly to these application areas and extended practical application possibilities. Below are several application fields where Magneli phase black titania significantly improved.

5.1. Supercapacitors

Electrochemical energy storage has become a substantial practical problem nowadays, as renewable power sources have greatly improved and are integrated widely into the electrical grids. However, the storage of electrochemical energy does not improve as fast as production, and there is a massive gap in this field, which is one of the main limiting factors for the further development of renewable power sources [89]. The technologies for efficient supercapacitors are developing fast; however, new materials are required for performance improvements, and Magneli phase black titania perfectly fits this application [90,91].

Tomas Sabirovas et al. demonstrated that, specifically, titanium monoxide (TiO) in the composition with polyaniline (PANI) can form an electrode possessing enhanced conductivity together with electron-transfer kinetics and near-ideal supercapacitive properties, which is shown in [17]. It was also reported that the hydrogen-reduced TiO_2 nanotube arrays, in combination with graphene, formed a high-performance supercapacitor electrode [82]. The impressive performance of these electrodes is associated with a high specific surface area and outstanding conductivity due to the formation of Magneli phase black titania. Recently, an investigation of Magneli phase black TiO_2 nanotubes decorated biomass-derived spongy carbon as an electrode material was published, with promising capacitance results [92].

The application of Magneli phase black titania in supercapacitors has not been fully studied, and many fundamental questions remain open, such as what Magneli phase black titania phase would be the most favourable for such applications. Moreover, little information exists on how the Magneli phase black titania-based heterostructures perform as electrodes. As Magneli phase black titania-based electrodes show promising results for application in the field of supercapacitors, these fundamental issues are expected to be answered.

5.2. Self-Heating Gas Sensors

Self-heating gas sensors are a novel fast developing research direction. The main advantage of such a design of sensors is an extremely low energy consumption, which extends the potential application cases and makes it possible to use with low-energy power sources. In most cases, these sensors are designed by many steps, and the self-heating effect is triggered by a metal/metal oxide/metal structure [93]. At the same time, there are several reports about Magneli phase black titania's application in gas sensing [28,94]. However, in most cases, these sensors have a relatively low working temperature while still showing good sensitivity [83]. Despite this fact, there are reports about self-heating Magneli phase-based gas sensors; however, this type of sensor can be highly applicable in various alcohol sensing applications, as depicted in Figure 13.

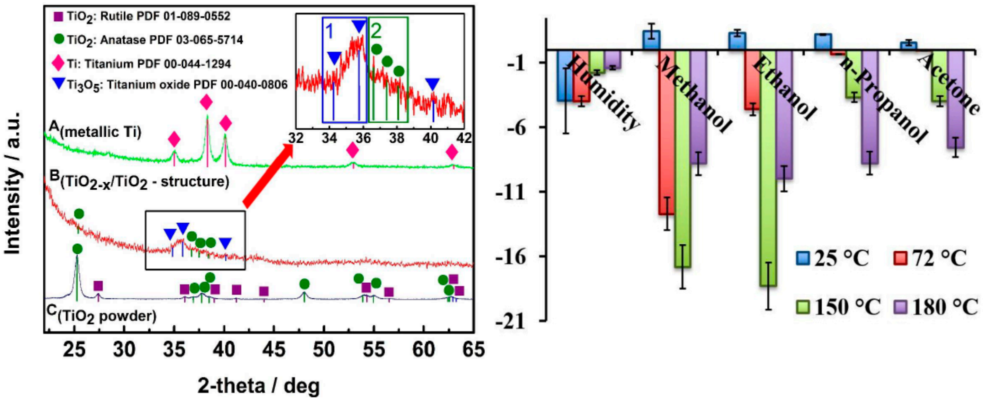

Figure 13. XRD pattern of self-heating gas sensor TiO_{2-x}/TiO_2 heterostructure and the sensitivity to various volatile organic compounds. Reprinted from [27].

The explanation of the self-heating Magneli phase black titania-based gas sensors phenomenon is not very clear; however, it is expected that the heterostructure of TiO_{2-x}/TiO_2

is responsible for the heating. Moreover, it was discovered that such sensors are applicable for the detection of various alcohols with good sensitivity and high selectivity. The sensitivity to particular alcohol vapours depends on the operating temperature, and while, at room temperature, the surface was blocked by adsorbed humidity, at the elevated temperatures starting from 72 °C, the sensitivity increased. The sensors were operating in the temperature range from 72 to 180 °C, and it was discovered that the highest sensitivity was reached for methanol and ethanol. Moreover, the operating temperatures controlled these sensors' selectivity [27,28].

5.3. Fuel Cells

Magneli phase black titania shows advancements in the design of various types of fuel cells, and there have been several applications in this field. The Magneli phase black TiO_2 is usually decorated in noble metals to enhance performance. Keerti M. Naik et al. demonstrated palladium decorated defect-rich Magneli phase black titania application in the design of fuel cells for oxygen reduction and glycerol oxidation [84]. Aikaterini Touni et al. reported the application of platinum-coated Magneli phase black titanium nanotubes for methanol oxidation. In this study, the high mass specific activity towards MOR (ca 700 mA $mgPt^{-1}$ at the voltammetric peak of 5 mVs^{-1} in 0.5 M MeOH) makes the material ideal as a MOR catalyst in DMFCs and electrolysers [85]. These studies show promising results for Magneli phase black titania application in developing direct alcohol fuel cells.

Luiz Felipe Placa et al. demonstrated a novel Magneli phase black titania-based photocatalytic fuel cells (PFCs) design, which can harvest solar energy through relatively low-cost semiconductor material to convert the chemical energy of renewable fuels and oxidants directly into electricity. [86]. The noble metal free fuel cell employing chemically reduced Magneli phase black titania performance for methanol oxidation and oxygen reduction was ∼2000% higher in comparison to the regular titania. This investigation shows promising results for constructing a PFC without noble metals for the methanol conversion under sunlight.

5.4. Surface-Enhanced Raman Spectroscopy

Surface-enhanced Raman spectroscopy (SERS) is a novel sensing technique with a sensitivity up to a single molecule. One of the main challenges preventing this technique's practical application is the requirement of noble metal substrates for the analysis. Many studies have been done to change the substrates to be cheaper and more suitable for mass application; however, up to now, there has been no breakthrough. The Magneli phase black titania has several favourable properties applicable to the substrates for SERS, such as a sensitivity that is similar to noble metals [87,88,95] and a photocatalytic self-cleaning ability [88,96,97], making the substrates highly reusable.

Lili Yang et al. reported a study comparing the regular and Magneli phase black titania nanowires SERS enhancement factors for Rhodamine 6G dyes. It was discovered that Magneli phase black TiO_2 has an enhancement factor of up to 1.2×10^6, comparable to the results of silver substrate. Moreover, the Magneli phase black titania substrate photocatalytically decomposes organic dyes, making substrates reusable. The high enhancement factor also shows that Magneli phase black titania-based substrates overcome one of the main challenges using semiconductors for SER; as in most cases, the enhancement factor mechanisms are based on chemical enhancement mechanisms, leading to an enhancement factor in the power of 10^2. However, the Magneli phase black titania experiments show that these substrates possess electromagnetic enhancement mechanisms [87].

Similarly, Y. Shan et al. introduced substrates constituted of Magneli phase black titania nanowires decorated with silver nanoparticles for the enhanced SERS technique. The substrates showed an improved enhancement factor comparable to that of a pure, noble metal substrate for Rhodamine 6G dyes while maintaining self-cleaning properties [88]. Magneli phase black titania's self-cleaning properties and high reusability distinguishes it from other substrates while showing its promising sensitivity for broader application in SERS.

5.5. Visible Light Photocatalytic Applications

Visible light-induced photocatalysis is a novel application area under the experimental development phase; however, it shows great potential to solve many problems that humankind is facing nowadays [98]. This technology is primarily applicable to the photocatalytic decomposition of wastewater pollutants. For several decades, similar applications have been investigated with TiO_2 under UV light [99]; however, the use of Magneli phase black titania and visible light extends the applications and shows great potential for broad practical application [38].

The main Magneli phase black titania application is the visible-light-induced photocatalytic decomposition of various organic pollutants [73]. This application is highly novel, and there are many reports about Magneli phase black titania with tunable bandgap decomposition results [100]. There are reports of Magneli phase black titania being used to decompose organic molecules such as organic dyes [21] and antibiotics [79], and other drugs such as paracetamol [80] and aspirin [81]. The most advanced applications of Magneli phase black titania-based photocatalysts are for the decomposition of antibiotics [79], which highly affect human health and are relatively stable under natural conditions [47].

5.6. Medicine

Several Magneli phase black titania cytotoxicity studies reveal that these structures are not hazardous and are compatible with humans [101,102]. These studies open the avenue for Magneli phase black titania application for implant coatings [103,104], photothermal therapy [18,105], and antimicrobial coatings [106,107]. Medical devices and implants coated with Magneli phase black titania exhibit antibacterial solid properties due to photocatalytic activity. Under light exposure, the material generates reactive oxygen species, which destroys bacterial cell walls [106,107]. This capability is crucial in reducing the risk of infections associated with surgical implants and other medical devices [107,108]. Another notable application of Magneli phase black titania is photothermal therapy [109,110]. This method employed the Magneli phase black titania-generated reactive oxygen species to treat cancerous tumours. Despite its promising applications, Magneli phase black titania's safety and its long-term effects in medical applications need thorough investigation. While initial studies indicate that Magneli phase black titania is biocompatible and less toxic than other nanoparticles, comprehensive in vivo studies and clinical trials are essential to confirm its safety profile.

5.7. Microwave Absorption

The rapid evolution of telecommunications, radar systems, and electronic devices has increased the demand for materials capable of absorbing microwaves to mitigate electromagnetic interference (EMI) and enhance stealth technology. Several reports show the application of Magneli phase black titania for efficient microwave absorption [111–116]. For instance, Ti_4O_7 [112,113], Ti_2O_3 [114], TiO [117], and Ti_3O_5 [115,116] have shown remarkable performance as microwave absorbers due to their ability to maintain high conductivity and stability under electromagnetic fields. The efficiency of these materials is explained by the defects introduced, which create localised states within the bandgap, facilitating the dissipation of electromagnetic energy as heat, thus reducing the reflection and transmission of microwaves [111,114,117]. This effect is particularly applicable in stealth technology, where reducing radar cross-sections is crucial for making objects less detectable by radar systems. As the demand for high-performance microwave-absorbing materials continues to rise, Magneli phase black titania is a promising candidate to meet these technological challenges.

5.8. Commercial Applications

A titanium Magneli phase materials brand, Ebonex®, is marketed mainly by Atraverda [35], Atranova, and Vector Corrosion Technologies [43]. Ebonex® has several applications, such as electrodes for electrochemical processes, fuel cell components, and corrosion-resistant coatings [43,118]. The high conductivity and chemical stability of Magneli phases improve the efficiency of electrochemical processes such as electrochlorination [119]. Moreover, Ebonex® is utilised in the gas diffusion layers and electrodes of fuel cells, contributing to better performance and longevity due to its excellent electrical conductivity and resistance to corrosion. These layers facilitate the distribution of gases to the catalyst sites and improve the fuel cell's overall efficiency [43]. The significant stability of Ebonex® under harsh conditions is one of the main advantages of challenging precious metal electrodes [119,120].

6. Conclusions and Future Outlook

Although the first Magneli phase black titania was reported in 1957, interest in this material started to rise after Xiaobo Chen's work was reported in 2011 and the term "Black TiO_2" was introduced. Since then, the formation methods improved significantly, encouraging the broader application of these unique materials. A few unique Magneli phase black titania applications were reported, such as self-heating gas sensors, supercapacitors, fuel cells, medicine, photocatalysis, microwave absorption, and SERS substrates. Moreover, several commercial Mangeli-phase black titania products under the product brand Ebonex® are widely applicable in various electrochemical applications.

The synthesis of Magneli phase black titania with a precisely controllable crystal phase composition and tunable properties on a large scale is challenging. However, the rising need for these materials for broader applications is pushing the development of new synthesis methods. The synthesis methods and characterisation discussed in the article will guide researchers in identifying Magneli phase black titania more precisely.

Author Contributions: Conceptualisation, S.R.; data curation, S.R.; writing—original draft preparation, S.R; writing—review and editing, A.J.; visualisation, S.R.; supervision, A.J.; All authors have read and agreed to the published version of the manuscript.

Funding: This project received funding from the Research Council of Lithuania (LMTLT), agreement No S-PD-22-155.

Data Availability Statement: No new data were created or analysed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Chen, X.; Mao, S.S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. *Chem. Rev.* **2007**, *107*, 2891–2959. [CrossRef] [PubMed]
2. Reinhardt, A. Phase Behavior of Empirical Potentials of Titanium Dioxide. *J. Chem. Phys.* **2019**, *151*, 064505. [CrossRef]
3. Chen, X.; Liu, L.; Yu, P.Y.; Mao, S.S. Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* **2011**, *331*, 746–750. [CrossRef]
4. Andersson, S.; Collén, B.; Kuylenstierna, U.; Magnéli, A. Phase Analysis Studies on the Titanium-Oxygen System. *Acta Chem. Scand.* **1957**, *11*, 1641–1652. [CrossRef]
5. Liu, Y.; Tian, L.; Tan, X.; Li, X.; Chen, X. Synthesis, Properties, and Applications of Black Titanium Dioxide Nanomaterials. *Sci. Bull. (Beijing)* **2017**, *62*, 431–441. [CrossRef]
6. Tian, M.; Liu, C.; Ge, J.; Geohegan, D.; Duscher, G.; Eres, G. Recent Progress in Characterization of the Core–Shell Structure of Black Titania. *J. Mater. Res.* **2019**, *34*, 1138–1153. [CrossRef]
7. Rajaraman, T.S.; Parikh, S.P.; Gandhi, V.G. Black TiO_2: A Review of Its Properties and Conflicting Trends. *Chem. Eng. J.* **2020**, *389*, 123918. [CrossRef]
8. Mao, C.-C.; Weng, H.-S. Effect of Heat Treatment on Photocatalytic Activity of Titania Incorporated with Carbon Black for Degradation of Methyl Orange. *Environ. Prog. Sustain. Energy* **2012**, *31*, 306–317. [CrossRef]
9. Ivanovskaya, M.; Chernyakova, K.; Ovodok, E.; Poznyak, S.; Kotsikau, D.; Micusik, M. Synthesis and Structural Features of Black TiO_2 Nanotubes after Annealing in Hydrogen. *Mater. Chem. Phys.* **2023**, *297*, 127416. [CrossRef]

10. Khanam, R.; Taparia, D.; Mondal, B.; Mohanta, D. Black Titania: Effect of Hydrogenation on Structural and Thermal Stability of Nanotitania. *Appl. Phys. A* **2016**, *122*, 92. [CrossRef]
11. Naldoni, A.; Altomare, M.; Zoppellaro, G.; Liu, N.; Kment, Š.; Zbořil, R.; Schmuki, P. Photocatalysis with Reduced TiO_2: From Black TiO_2 to Cocatalyst-Free Hydrogen Production. *ACS Catal.* **2019**, *9*, 345–364. [CrossRef] [PubMed]
12. Zhu, G.; Xu, J.; Zhao, W.; Huang, F. Constructing Black Titania with Unique Nanocage Structure for Solar Desalination. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31716–31721. [CrossRef] [PubMed]
13. Ullattil, S.G.; Narendranath, S.B.; Pillai, S.C.; Periyat, P. Black TiO_2 Nanomaterials: A Review of Recent Advances. *Chem. Eng. J.* **2018**, *343*, 708–736. [CrossRef]
14. Yang, C.; Wang, Z.; Lin, T.; Yin, H.; Lü, X.; Wan, D.; Xu, T.; Zheng, C.; Lin, J.; Huang, F.; et al. Core-Shell Nanostructured "Black" Rutile Titania as Excellent Catalyst for Hydrogen Production Enhanced by Sulfur Doping. *J. Am. Chem. Soc.* **2013**, *135*, 17831–17838. [CrossRef] [PubMed]
15. Nguyen, T.-D.; Li, J.; Lizundia, E.; Niederberger, M.; Hamad, W.Y.; MacLachlan, M.J. Black Titania with Nanoscale Helicity. *Adv. Funct. Mater.* **2019**, *29*, 1904639. [CrossRef]
16. Jagminas, A.; Ramanavičius, S.; Jasulaitiene, V.; Šimėnas, M. Hydrothermal Synthesis and Characterization of Nanostructured Titanium Monoxide Films. *RSC Adv.* **2019**, *9*, 40727–40735. [CrossRef]
17. Sabirovas, T.; Ramanavicius, S.; Naujokaitis, A.; Niaura, G.; Jagminas, A. Design and Characterization of Nanostructured Titanium Monoxide Films Decorated with Polyaniline Species. *Coatings* **2022**, *12*, 1615. [CrossRef]
18. Shu, G.; Wang, H.; Zhao, H.-X.; Zhang, X. Microwave-Assisted Synthesis of Black Titanium Monoxide for Synergistic Tumor Phototherapy. *ACS Appl. Mater. Interfaces* **2019**, *11*, 3323–3333. [CrossRef] [PubMed]
19. Sener, M.E.; Quesada-Cabrera, R.; Parkin, I.P.; Caruana, D.J. Facile Formation of Black Titania Films Using an Atmospheric-Pressure Plasma Jet. *Green. Chem.* **2022**, *24*, 2499–2505. [CrossRef]
20. Teng, F.; Li, M.; Gao, C.; Zhang, G.; Zhang, P.; Wang, Y.; Chen, L.; Xie, E. Preparation of Black TiO_2 by Hydrogen Plasma Assisted Chemical Vapor Deposition and Its Photocatalytic Activity. *Appl. Catal. B* **2014**, *148–149*, 339–343. [CrossRef]
21. Panomsuwan, G.; Watthanaphanit, A.; Ishizaki, T.; Saito, N. Water-Plasma-Assisted Synthesis of Black Titania Spheres with Efficient Visible-Light Photocatalytic Activity. *Phys. Chem. Chem. Phys.* **2015**, *17*, 13794–13799. [CrossRef] [PubMed]
22. Andronic, L.; Enesca, A. Black TiO_2 Synthesis by Chemical Reduction Methods for Photocatalysis Applications. *Front. Chem.* **2020**, *8*, 565489. [CrossRef] [PubMed]
23. Xu, J.; Tian, Z.; Yin, G.; Lin, T.; Huang, F. Controllable Reduced Black Titania with Enhanced Photoelectrochemical Water Splitting Performance. *Dalton Trans.* **2017**, *46*, 1047–1051. [CrossRef] [PubMed]
24. Xu, J.; Zhu, G.; Lin, T.; Hong, Z.; Wang, J.; Huang, F. Molten Salt Assisted Synthesis of Black Titania Hexagonal Nanosheets with Tuneable Phase Composition and Morphology. *RSC Adv.* **2015**, *5*, 85928–85932. [CrossRef]
25. Sahoo, S.S.; Mansingh, S.; Babu, P.; Parida, K. Black Titania an Emerging Photocatalyst: Review Highlighting the Synthesis Techniques and Photocatalytic Activity for Hydrogen Generation. *Nanoscale Adv.* **2021**, *3*, 5487–5524. [CrossRef] [PubMed]
26. Soleimani, M.; Ghasemi, J.B.; Badiei, A. Black Titania; Novel Researches in Synthesis and Applications. *Inorg. Chem. Commun.* **2022**, *135*, 109092. [CrossRef]
27. Ramanavicius, S.; Tereshchenko, A.; Karpicz, R.; Ratautaite, V.; Bubniene, U.; Maneikis, A.; Jagminas, A.; Ramanavicius, A. TiO_2-x/TiO_2-Structure Based 'Self-Heated' Sensor for the Determination of Some Reducing Gases. *Sensors* **2020**, *20*, 74. [CrossRef] [PubMed]
28. Ramanavicius, S.; Ramanavicius, A. Insights in the Application of Stoichiometric and Non-Stoichiometric Titanium Oxides for the Design of Sensors for the Determination of Gases and VOCs (TiO_2-x and $TinO_2n-1$ vs. TiO_2). *Sensors* **2020**, *20*, 6833. [CrossRef] [PubMed]
29. Jagminas, A.; Naujokaitis, A.; Gaigalas, P.; Ramanavičius, S.; Kurtinaitienė, M.; Trusovas, R. Substrate Impact on the Structure and Electrocatalyst Properties of Molybdenum Disulfide for HER from Water. *Metals* **2020**, *10*, 1251. [CrossRef]
30. Varnagiris, S.; Medvids, A.; Lelis, M.; Milcius, D.; Antuzevics, A. Black Carbon-Doped TiO_2 Films: Synthesis, Characterization and Photocatalysis. *J. Photochem. Photobiol. A Chem.* **2019**, *382*, 111941. [CrossRef]
31. Veremchuk, I.; Antonyshyn, I.; Candolfi, C.; Feng, X.; Burkhardt, U.; Baitinger, M.; Zhao, J.-T.; Grin, Y. Diffusion-Controlled Formation of Ti_2O_3 during Spark-Plasma Synthesis. *Inorg. Chem.* **2013**, *52*, 4458–4463. [CrossRef] [PubMed]
32. Ohwada, M.; Kimoto, K.; Suenaga, K.; Sato, Y.; Ebina, Y.; Sasaki, T. Synthesis and Atomic Characterization of a Ti_2O_3 Nanosheet. *J. Phys. Chem. Lett.* **2011**, *2*, 1820–1823. [CrossRef]
33. Zhao, P.F.; Li, G.S.; Li, W.; Cheng, P.; Pang, Z.; Xiong, L.; Zou, X.L.; Xu, Q.; Lu, X.G. Progress in Ti_3O_5: Synthesis, Properties and Applications. *Trans. Nonferrous Met. Soc. China* **2021**, *31*, 3310–3327. [CrossRef]
34. Li, X.; Liu, Y.; Ma, S.; Ye, J.; Zhang, X.; Wang, G.; Qiu, Y. The Synthesis and Gas Sensitivity of the β-Ti_3O_5 Powder: Experimental and DFT Study. *J. Alloys Compd.* **2015**, *649*, 939–948. [CrossRef]
35. Jayashree, S.; Ashokkumar, M. Switchable Intrinsic Defect Chemistry of Titania for Catalytic Applications. *Catalysts* **2018**, *8*, 601. [CrossRef]
36. Xu, J.; Wang, D.; Yao, H.; Bu, K.; Pan, J.; He, J.; Xu, F.; Hong, Z.; Chen, X.; Huang, F. Nano Titanium Monoxide Crystals and Unusual Superconductivity at 11 K. *Adv. Mater.* **2018**, *30*, 1706240. [CrossRef] [PubMed]
37. Kostenko, M.G.; Lukoyanov, A.V.; Zhukov, V.P.; Rempel, A.A. Vacancies in Ordered and Disordered Titanium Monoxide: Mechanism of B1 Structure Stabilization. *J. Solid State Chem.* **2013**, *204*, 146–152. [CrossRef]

38. Liu, X.; Zhu, G.; Wang, X.; Yuan, X.; Lin, T.; Huang, F. Progress in Black Titania: A New Material for Advanced Photocatalysis. *Adv. Energy Mater.* **2016**, *6*, 1600452. [CrossRef]
39. Zimbone, M.; Cacciato, G.; Boutinguiza, M.; Gulino, A.; Cantarella, M.; Privitera, V.; Grimaldi, M.G. Hydrogenated Black-TiO_x: A Facile and Scalable Synthesis for Environmental Water Purification. *Catal. Today* **2019**, *321–322*, 146–157. [CrossRef]
40. Peng, X.; Chen, A. Large-Scale Synthesis and Characterization of TiO_2-Based Nanostructures on Ti Substrates. *Adv. Funct. Mater.* **2006**, *16*, 1355–1362. [CrossRef]
41. Lee, Y.-J.; Lee, T.; Soon, A. Phase Stability Diagrams of Group 6 Magnéli Oxides and Their Implications for Photon-Assisted Applications. *Chem. Mater.* **2019**, *31*, 4282–4290. [CrossRef]
42. Serratos, M.; Bronson, A. The Effect of Oxygen Partial Pressure on the Stability of Magneli Phases in High Temperature Corrosive Wear. *Wear* **1996**, *198*, 267–270. [CrossRef]
43. Walsh, F.C.; Wills, R.G.A. The Continuing Development of Magnéli Phase Titanium Sub-Oxides and Ebonex® Electrodes. *Electrochim. Acta* **2010**, *55*, 6342–6351. [CrossRef]
44. Andersson, S.; Collén, B.; Kruuse, G.; Kuylenstierna, U.; Magnéli, A.; Pestmalis, H.; Åsbrink, S. Identification of Titanium Oxides by X-Ray Powder Patterns. *Acta Chem. Scand. (Den.) Divid. Into Acta Chem. Scand. Ser. A Ser. B* **1957**, *1*, 1653–1657. [CrossRef]
45. Åsbrink, S.; Magnéli, A. Crystal Structure Studies on Trititanium Pentoxide, Ti_3O_5. *Acta Crystallogr.* **1959**, *12*, 575–581. [CrossRef]
46. Sun, X.; Wang, Z.; Yan, W.; Zhou, C. Study of the Relationship between Metal–Support Interactions and the Electrocatalytic Performance of Pt/Ti_4O_7 with Different Loadings. *Catalysts* **2022**, *12*, 480. [CrossRef]
47. Hu, T.; Feng, P.; Guo, L.; Chu, H.; Liu, F. Construction of Built-In Electric Field in TiO_2@Ti_2O_3 Core-Shell Heterojunctions toward Optimized Photocatalytic Performance. *Nanomaterials* **2023**, *13*, 2125. [CrossRef] [PubMed]
48. Song, L.; Lu, Z.; Zhang, Y.; Su, Q.; Li, L. Hydrogen-Etched TiO_2-x as Efficient Support of Gold Catalysts for Water–Gas Shift Reaction. *Catalysts* **2018**, *8*, 26. [CrossRef]
49. Agarwal, R.; Himanshu; Patel, S.L.; Verma, M.; Chander, S.; Ameta, C.; Dhaka, M.S. Tailoring the Physical Properties of Titania Thin Films with Post Deposition Air and Vacuum Annealing. *Opt. Mater. (Amst.)* **2021**, *116*, 111033. [CrossRef]
50. Katal, R.; Salehi, M.; Davood Abadi Farahani, M.H.; Masudy-Panah, S.; Ong, S.L.; Hu, J. Preparation of a New Type of Black TiO_2 under a Vacuum Atmosphere for Sunlight Photocatalysis. *ACS Appl. Mater. Interfaces* **2018**, *10*, 35316–35326. [CrossRef]
51. Zhang, X.; Cai, M.; Cui, N.; Chen, G.; Zou, G.; Zhou, L. Defective Black TiO_2: Effects of Annealing Atmospheres and Urea Addition on the Properties and Photocatalytic Activities. *Nanomaterials* **2021**, *11*, 2648. [CrossRef] [PubMed]
52. Wang, Z.; Yang, C.; Lin, T.; Yin, H.; Chen, P.; Wan, D.; Xu, F.; Huang, F.; Lin, J.; Xie, X.; et al. Visible-Light Photocatalytic, Solar Thermal and Photoelectrochemical Properties of Aluminium-Reduced Black Titania. *Energy Environ. Sci.* **2013**, *6*, 3007–3014. [CrossRef]
53. Ye, M.; Jia, J.; Wu, Z.; Qian, C.; Chen, R.; O'Brien, P.G.; Sun, W.; Dong, Y.; Ozin, G.A. Synthesis of Black TiO_x Nanoparticles by Mg Reduction of TiO_2 Nanocrystals and Their Application for Solar Water Evaporation. *Adv. Energy Mater.* **2017**, *7*, 1601811. [CrossRef]
54. Gao, J.; Shen, Q.; Guan, R.; Xue, J.; Liu, X.; Jia, H.; Li, Q.; Wu, Y. Oxygen Vacancy Self-Doped Black TiO_2 Nanotube Arrays by Aluminothermic Reduction for Photocatalytic CO2 Reduction under Visible Light Illumination. *J. CO2 Util.* **2020**, *35*, 205–215. [CrossRef]
55. Janczarek, M.; Endo-Kimura, M.; Wang, K.; Wei, Z.; Akanda, M.M.A.; Markowska-Szczupak, A.; Ohtani, B.; Kowalska, E. Is Black Titania a Promising Photocatalyst? *Catalysts* **2022**, *12*, 1320. [CrossRef]
56. Kang, Q.; Cao, J.; Zhang, Y.; Liu, L.; Xu, H.; Ye, J. Reduced TiO_2 Nanotube Arrays for Photoelectrochemical Water Splitting. *J. Mater. Chem. A* **2013**, *1*, 5766–5774. [CrossRef]
57. Ding, S.; Lin, T.; Wang, Y.; Lü, X.; Huang, F. New Facile Synthesis of TiO_2 Hollow Sphere with an Opening Hole and Its Enhanced Rate Performance in Lithium-Ion Batteries. *New J. Chem.* **2013**, *37*, 784–789. [CrossRef]
58. Bottein, T.; Wood, T.; David, T.; Claude, J.B.; Favre, L.; Berbézier, I.; Ronda, A.; Abbarchi, M.; Grosso, D. "Black" Titania Coatings Composed of Sol–Gel Imprinted Mie Resonators Arrays. *Adv. Funct. Mater.* **2017**, *27*, 1604924. [CrossRef]
59. Wu, M.C.; Chang, I.C.; Hsiao, K.C.; Huang, W.K. Highly Visible-Light Absorbing Black TiO_2 Nanocrystals Synthesized by Sol–Gel Method and Subsequent Heat Treatment in Low Partial Pressure H_2. *J. Taiwan Inst. Chem. Eng.* **2016**, *63*, 430–435. [CrossRef]
60. Nawaz, R.; Sahrin, N.T.; Haider, S.; Ullah, H.; Junaid, M.; Akhtar, M.S.; Khan, S. Photocatalytic Performance of Black Titanium Dioxide for Phenolic Compounds Removal from Oil Refinery Wastewater: Nanoparticles vs Nanowires. *Appl. Nanosci.* **2022**, *12*, 3499–3515. [CrossRef]
61. Rahman, S.; Nawaz, R.; Khan, J.A.; Ullah, H.; Irfan, M.; Glowacz, A.; Lyp-Wronska, K.; Wzorek, L.; Asif Khan, M.K.; Jalalah, M.; et al. Synthesis and Characterization of Carbon and Carbon-Nitrogen Doped Black TiO_2 Nanomaterials and Their Application in Sonophotocatalytic Remediation of Treated Agro-Industrial Wastewater. *Materials* **2021**, *14*, 6175. [CrossRef] [PubMed]
62. Mills, A.; Elliott, N.; Hill, G.; Fallis, D.; Durrant, J.R.; Willis, R.L. Preparation and Characterisation of Novel Thick Sol-Gel Titania Film Photocatalysts. *Photochem. Photobiol. Sci.* **2003**, *2*, 591–596. [CrossRef] [PubMed]
63. Ullattil, S.G.; Periyat, P. A 'One Pot' Gel Combustion Strategy towards Ti_{3+} Self-Doped 'Black' Anatase TiO_2-x Solar Photocatalyst. *J. Mater. Chem. A* **2016**, *4*, 5854–5858. [CrossRef]
64. Siuzdak, K.; Haryński, Ł.; Wawrzyniak, J.; Grochowska, K. Review on Robust Laser Light Interaction with Titania—Patterning, Crystallisation and Ablation Processes. *Prog. Solid. State Chem.* **2021**, *62*, 100297. [CrossRef]

65. Yao, D.; Hu, Z.; Zheng, R.; Li, J.; Wang, L.; Yang, X.; Lü, W.; Xu, H. Black TiO_2-Based Dual Photoanodes Boost the Efficiency of Quantum Dot-Sensitized Solar Cells to 11.7%. *Nanomaterials* **2022**, *12*, 4294. [CrossRef] [PubMed]
66. Raveendran Nair, P.; Rosa Santiago Ramirez, C.; Angel Gracia Pinilla, M.; Krishnan, B.; Avellaneda Avellaneda, D.; Fabian Cienfuegos Pelaes, R.; Shaji, S. Black Titanium Dioxide Nanocolloids by Laser Irradiation in Liquids for Visible Light Photo-Catalytic/Electrochemical Applications. *Appl. Surf. Sci.* **2023**, *623*, 157096. [CrossRef]
67. Zimbone, M.; Cacciato, G.; Boutinguiza, M.; Privitera, V.; Grimaldi, M.G. Laser Irradiation in Water for the Novel, Scalable Synthesis of Black TiO_x Photocatalyst for Environmental Remediation. *Beilstein J. Nanotechnol.* **2017**, *8*, 196–202. [CrossRef] [PubMed]
68. Chen, X.; Zhao, D.; Liu, K.; Wang, C.; Liu, L.; Li, B.; Zhang, Z.; Shen, D. Laser-Modified Black Titanium Oxide Nanospheres and Their Photocatalytic Activities under Visible Light. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16070–16077. [CrossRef] [PubMed]
69. Lepcha, A.; Maccato, C.; Mettenbörger, A.; Andreu, T.; Mayrhofer, L.; Walter, M.; Olthof, S.; Ruoko, T.-P.; Klein, A.; Moseler, M.; et al. Electrospun Black Titania Nanofibers: Influence of Hydrogen Plasma-Induced Disorder on the Electronic Structure and Photoelectrochemical Performance. *J. Phys. Chem. C* **2015**, *119*, 18835–18842. [CrossRef]
70. Tian, Z.; Cui, H.; Zhu, G.; Zhao, W.; Xu, J.J.; Shao, F.; He, J.; Huang, F. Hydrogen Plasma Reduced Black TiO_2B Nanowires for Enhanced Photoelectrochemical Water-Splitting. *J. Power Sources* **2016**, *325*, 697–705. [CrossRef]
71. Godoy Junior, A.; Pereira, A.; Gomes, M.; Fraga, M.; Pessoa, R.; Leite, D.; Petraconi, G.; Nogueira, A.; Wender, H.; Miyakawa, W.; et al. Black TiO_2 Thin Films Production Using Hollow Cathode Hydrogen Plasma Treatment: Synthesis, Material Characteristics and Photocatalytic Activity. *Catalysts* **2020**, *10*, 282. [CrossRef]
72. Zhu, G.; Yin, H.; Yang, C.; Cui, H.; Wang, Z.; Xu, J.; Lin, T.; Huang, F. Black Titania for Superior Photocatalytic Hydrogen Production and Photoelectrochemical Water Splitting. *ChemCatChem* **2015**, *7*, 2614–2619. [CrossRef]
73. El-Gendy, D.M.; Abdel Ghany, N.A.; Allam, N.K. Black Titania Nanotubes/Spongy Graphene Nanocomposites for High-Performance Supercapacitors. *RSC Adv.* **2019**, *9*, 12555–12566. [CrossRef]
74. Tang, C.; Zhou, D.; Zhang, Q. Synthesis and Characterization of Magneli Phases: Reduction of TiO_2 in a Decomposed NH_3 Atmosphere. *Mater. Lett.* **2012**, *79*, 42–44. [CrossRef]
75. Arif, A.F.; Balgis, R.; Ogi, T.; Iskandar, F.; Kinoshita, A.; Nakamura, K.; Okuyama, K. Highly Conductive Nano-Sized Magnéli Phases Titanium Oxide (TiO_x). *Sci. Rep.* **2017**, *7*, 3646. [CrossRef]
76. Chen, S.; Xiao, Y.; Wang, Y.; Hu, Z.; Zhao, H.; Xie, W. A Facile Approach to Prepare Black TiO_2 with Oxygen Vacancy for Enhancing Photocatalytic Activity. *Nanomaterials* **2018**, *8*, 245. [CrossRef]
77. Surmacki, J.; Wroński, P.; Szadkowska-Nicze, M.; Abramczyk, H. Raman Spectroscopy of Visible-Light Photocatalyst—Nitrogen-Doped Titanium Dioxide Generated by Irradiation with Electron Beam. *Chem. Phys. Lett.* **2013**, *566*, 54–59. [CrossRef]
78. Roessler, M.M.; Salvadori, E. Principles and Applications of EPR Spectroscopy in the Chemical Sciences. *Chem. Soc. Rev.* **2018**, *47*, 2534–2553. [CrossRef] [PubMed]
79. Wu, S.; Li, X.; Tian, Y.; Lin, Y.; Hu, Y.H. Excellent Photocatalytic Degradation of Tetracycline over Black Anatase-TiO_2 under Visible Light. *Chem. Eng. J.* **2021**, *406*, 126747. [CrossRef]
80. Feng, X.; Wang, P.; Hou, J.; Qian, J.; Wang, C.; Ao, Y. Oxygen Vacancies and Phosphorus Codoped Black Titania Coated Carbon Nanotube Composite Photocatalyst with Efficient Photocatalytic Performance for the Degradation of Acetaminophen under Visible Light Irradiation. *Chem. Eng. J.* **2018**, *352*, 947–956. [CrossRef]
81. Plodinec, M.; Grčić, I.; Willinger, M.G.; Hammud, A.; Huang, X.; Panžić, I.; Gajović, A. Black TiO_2 Nanotube Arrays Decorated with Ag Nanoparticles for Enhanced Visible-Light Photocatalytic Oxidation of Salicylic Acid. *J. Alloys Compd.* **2019**, *776*, 883–896. [CrossRef]
82. Guan, S.; Cheng, Y.; Hao, L.; Yoshida, H.; Tarashima, C.; Zhan, T.; Itoi, T.; Qiu, T.; Lu, Y. Oxygen Vacancies Induced Band Gap Narrowing for Efficient Visible-Light Response in Carbon-Doped TiO_2. *Sci. Rep.* **2023**, *13*, 14105. [CrossRef] [PubMed]
83. Yang, W.; Shen, H.; Min, H.; Ge, J. Enhanced Acetone Sensing Performance in Black TiO_2 by Ag Modification. *J. Mater. Sci.* **2020**, *55*, 10399–10411. [CrossRef]
84. Naik, K.M.; Hamada, T.; Higuchi, E.; Inoue, H. Defect-Rich Black Titanium Dioxide Nanosheet-Supported Palladium Nanoparticle Electrocatalyst for Oxygen Reduction and Glycerol Oxidation Reactions in Alkaline Medium. *ACS Appl. Energy Mater.* **2021**, *4*, 12391–12402. [CrossRef]
85. Touni, A.; Liu, X.; Kang, X.; Papoulia, C.; Pavlidou, E.; Lambropoulou, D.; Tsampas, M.N.; Chatzitakis, A.; Sotiropoulos, S. Methanol Oxidation at Platinum Coated Black Titania Nanotubes and Titanium Felt Electrodes. *Molecules* **2022**, *27*, 6382. [CrossRef] [PubMed]
86. Plaça, L.F.; Vital, P.-L.S.; Gomes, L.E.; Roveda, A.C., Jr.; Cardoso, D.R.; Martins, C.A.; Wender, H. Black TiO_2 Photoanodes for Direct Methanol Photo Fuel Cells. *ACS Appl. Mater. Interfaces* **2023**, *15*, 43259–43271. [CrossRef] [PubMed]
87. Yang, L.; Peng, Y.; Yang, Y.; Liu, J.; Li, Z.; Ma, Y.; Zhang, Z.; Wei, Y.; Li, S.; Huang, Z.; et al. Green and Sensitive Flexible Semiconductor SERS Substrates: Hydrogenated Black TiO_2 Nanowires. *ACS Appl. Nano Mater.* **2018**, *1*, 4516–4527. [CrossRef]
88. Shan, Y.; Yang, Y.; Cao, Y.; Yin, H.; Long, N.V.; Huang, Z. Hydrogenated Black TiO_2 Nanowires Decorated with Ag Nanoparticles as Sensitive and Reusable Surface-Enhanced Raman Scattering Substrates. *RSC Adv.* **2015**, *5*, 34737–34743. [CrossRef]
89. Gür, T.M. Review of Electrical Energy Storage Technologies, Materials and Systems: Challenges and Prospects for Large-Scale Grid Storage. *Energy Environ. Sci.* **2018**, *11*, 2696–2767. [CrossRef]

90. Chen, X.; Li, C.; Grätzel, M.; Kostecki, R.; Mao, S.S. Nanomaterials for Renewable Energy Production and Storage. *Chem. Soc. Rev.* **2012**, *41*, 7909–7937. [CrossRef]
91. Zhi, J.; Cui, H.; Wang, Z.; Huang, F. Surface Confined Titania Redox Couple for Ultrafast Energy Storage. *Mater. Horiz.* **2018**, *5*, 691–698. [CrossRef]
92. El-Gendy, D.M.; Maafa, I.M.; Zouli, N.; Abutaleb, A.; Yousef, A. Synthesis of Black TiO_2 Nanotubes Decorated Biomass-Derived Spongy Carbon as an Electrode Material for Producing Deionized Water through Capacitive Deionization Technology. *Ceram. Int.* **2024**, *50*, 7775–7788. [CrossRef]
93. Jo, M.-S.; Kim, S.-H.; Park, S.-Y.; Choi, K.-W.; Kim, S.-H.; Yoo, J.-Y.; Kim, B.-J.; Yoon, J.-B. Fast-Response and Low-Power Self-Heating Gas Sensor Using Metal/Metal Oxide/Metal (MMOM) Structured Nanowires. *ACS Sens.* **2024**, *9*, 1896–1905. [CrossRef] [PubMed]
94. Ramanavicius, S.; Jagminas, A.; Ramanavicius, A. Gas Sensors Based on Titanium Oxides (Review). *Coatings* **2022**, *12*, 699. [CrossRef]
95. Bontempi, N.; Cavaliere, E.; Cappello, V.; Pingue, P.; Gavioli, L. Ag@TiO_2 Nanogranular Films by Gas Phase Synthesis as Hybrid SERS Platforms. *Phys. Chem. Chem. Phys.* **2019**, *21*, 25090–25097. [CrossRef]
96. Wang, Z.; Yang, C.; Lin, T.; Yin, H.; Chen, P.; Wan, D.; Xu, F.; Huang, F.; Lin, J.; Xie, X.; et al. H-Doped Black Titania with Very High Solar Absorption and Excellent Photocatalysis Enhanced by Localized Surface Plasmon Resonance. *Adv. Funct. Mater.* **2013**, *23*, 5444–5450. [CrossRef]
97. Ma, X.; Dai, Y.; Yu, L.; Huang, B. Noble-Metal-Free Plasmonic Photocatalyst: Hydrogen Doped Semiconductors. *Sci. Rep.* **2014**, *4*, 3986. [CrossRef] [PubMed]
98. Djurišić, A.B.; He, Y.; Ng, A.M.C. Visible-Light Photocatalysts: Prospects and Challenges. *APL Mater.* **2020**, *8*, 030903. [CrossRef]
99. Chen, D.; Cheng, Y.; Zhou, N.; Chen, P.; Wang, Y.; Li, K.; Huo, S.; Cheng, P.; Peng, P.; Zhang, R.; et al. Photocatalytic Degradation of Organic Pollutants Using TiO_2-Based Photocatalysts: A Review. *J. Clean. Prod.* **2020**, *268*, 121725. [CrossRef]
100. Bi, Q.; Huang, X.; Dong, Y.; Huang, F. Conductive Black Titania Nanomaterials for Efficient Photocatalytic Degradation of Organic Pollutants. *Catal. Lett.* **2020**, *150*, 1346–1354. [CrossRef]
101. Kononenko, V.; Drobne, D. In Vitro Cytotoxicity Evaluation of the Magnéli Phase Titanium Suboxides (Ti_xO_{2x-1}) on A549 Human Lung Cells. *Int. J. Mol. Sci.* **2019**, *20*, 196. [CrossRef] [PubMed]
102. Jemec Kokalj, A.; Novak, S.; Talaber, I.; Kononenko, V.; Bizjak Mali, L.; Vodovnik, M.; Žegura, B.; Eleršek, T.; Kalčikova, G.; Žgajnar Gotvajn, A.; et al. The First Comprehensive Safety Study of Magnéli Phase Titanium Suboxides Reveals No Acute Environmental Hazard. *Environ. Sci. Nano* **2019**, *6*, 1131–1139. [CrossRef]
103. Cao, H.; Liu, X. Activating Titanium Oxide Coatings for Orthopedic Implants. *Surf. Coat. Technol.* **2013**, *233*, 57–64. [CrossRef]
104. Hasan, J.; Jain, S.; Chatterjee, K. Nanoscale Topography on Black Titanium Imparts Multi-Biofunctional Properties for Orthopedic Applications. *Sci. Rep.* **2017**, *7*, 41118. [CrossRef] [PubMed]
105. Dai, T.; Ren, W.; Wu, A. Cancer Theranostics of Black TiO2 Nanoparticles. In TiO2 Nanoparticles; Wiley (United States) 2020; pp. 185–215. ISBN 9783527825431. [CrossRef]
106. Zhang, M.; Wu, N.; Yang, J.; Zhang, Z. Photoelectrochemical Antibacterial Platform Based on Rationally Designed Black TiO_{2-x} Nanowires for Efficient Inactivation against Bacteria. *ACS Appl. Bio Mater.* **2022**, *5*, 1341–1347. [CrossRef] [PubMed]
107. Yang, F.; Zhang, Z.; Li, Y.; Xiao, C.; Zhang, H.; Li, W.; Zhan, L.; Liang, G.; Chang, Y.; Ning, C.; et al. In Situ Construction of Black Titanium Oxide with a Multilevel Structure on a Titanium Alloy for Photothermal Antibacterial Therapy. *ACS Biomater. Sci. Eng.* **2022**, *8*, 2419–2427. [CrossRef]
108. Abir, M.M.M.; Otsuka, Y.; Ohnuma, K.; Miyashita, Y. Effects of Composition of Hydroxyapatite/Gray Titania Coating Fabricated by Suspension Plasma Spraying on Mechanical and Antibacterial Properties. *J. Mech. Behav. Biomed. Mater.* **2022**, *125*, 104888. [CrossRef] [PubMed]
109. Shen, J.; Karges, J.; Xiong, K.; Chen, Y.; Ji, L.; Chao, H. Cancer Cell Membrane Camouflaged Iridium Complexes Functionalized Black-Titanium Nanoparticles for Hierarchical-Targeted Synergistic NIR-II Photothermal and Sonodynamic Therapy. *Biomaterials* **2021**, *275*, 120979. [CrossRef] [PubMed]
110. Du, W.; Chen, W.; Wang, J.; Cheng, L.; Wang, J.; Zhang, H.; Song, L.; Hu, Y.; Ma, X. Oxygen-Deficient Titanium Dioxide-Loaded Black Phosphorus Nanosheets for Synergistic Photothermal and Sonodynamic Cancer Therapy. *Biomater. Adv.* **2022**, *136*, 212794. [CrossRef]
111. Green, M.; Van Tran, A.T.; Smedley, R.; Roach, A.; Murowchick, J.; Chen, X. Microwave Absorption of Magnesium/Hydrogen-Treated Titanium Dioxide Nanoparticles. *Nano Mater. Sci.* **2019**, *1*, 48–59. [CrossRef]
112. Li, Y.; Qing, Y.; Zhao, B.; Bai, P.; Zhang, R.; Yao, H.; Luo, F. Tunable Magnetic Coupling and Dipole Polarization of Core-Shell Magnéli Ti_4O_7 Ceramic/Magnetic Metal Possessing Broadband Microwave Absorption Properties. *Ceram. Int.* **2021**, *47*, 33373–33381. [CrossRef]
113. Li, Y.; Qing, Y.; Yao, H.; Xu, H.; Wu, H. A Novel Plasma-Sprayed Ti_4O_7/Carbon Nanotubes/Al_2O_3 Coating with Bifunctional Microwave Application. *J. Colloid. Interface Sci.* **2023**, *645*, 165–175. [CrossRef] [PubMed]
114. Fu, X.; Yang, B.; Chen, W.; Li, Z.; Yan, H.; Zhao, X.; Zuo, L. Electromagnetic Wave Absorption Performance of Ti_2O_3 and Vacancy Enhancement Effective Bandwidth. *J. Mater. Sci. Technol.* **2021**, *76*, 166–173. [CrossRef]
115. Fu, X.; Liu, H. High Purity λ-Ti_3O_5 Prepared by Sc Doping for Enhanced Microwave Absorption. *J. Mater. Chem. C.* [CrossRef]

116. Fu, X.; Chen, W.; Hao, X.; Zhang, Z.; Tang, R.; Yang, B.; Zhao, X.; Zuo, L. Preparing High Purity λ-Ti_3O_5 and Li/λ-Ti_3O_5 as High-Performance Electromagnetic Wave Absorbers. *J. Mater. Chem. C* **2021**, *9*, 7976–7981. [CrossRef]
117. Wei, Y.; Shi, Y.; Zhang, X.; Li, D.; Zhang, L.; Gong, C.; Zhang, J. Preparation of Black Titanium Monoxide Nanoparticles and Their Potential in Electromagnetic Wave Absorption. *Adv. Powder Technol.* **2020**, *31*, 3458–3464. [CrossRef]
118. Bejan, D.; Malcolm, J.D.; Morrison, L.; Bunce, N.J. Mechanistic Investigation of the Conductive Ceramic Ebonex® as an Anode Material. *Electrochim. Acta* **2009**, *54*, 5548–5556. [CrossRef]
119. Smith, J.R.; Walsh, F.C.; Clarke, R.L. Electrodes Based on Magnéli Phase Titanium Oxides: The Properties and Applications of Ebonex® Materials. *J. Appl. Electrochem.* **1998**, *28*, 1021–1033. [CrossRef]
120. Lačnjevac, U.Č.; Jović, B.M.; Jović, V.D.; Radmilović, V.R.; Krstajić, N.V. Kinetics of the Hydrogen Evolution Reaction on Ni-(Ebonex-Supported Ru) Composite Coatings in Alkaline Solution. *Int. J. Hydrog. Energy* **2013**, *38*, 10178–10190. [CrossRef]