

Optimizing the Structural and Photocatalytic Properties of TiO₂ Composites Synthesized via Sol-Gel Method

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Abstract: Titanium dioxide (TiO₂) is widely studied for its photocatalytic and optical properties, but its performance can be enhanced by forming composites with other materials. This research focuses on synthesizing TiO₂ composites using the sol-gel technique by incorporating Al₂O₃, WO₃, ZnO, CNT, and SiNT. Additionally, optimizing the calcination process by modifying time and temperature is crucial to improving structural and functional characteristics. TiO₂ composites were synthesized via the sol-gel method, followed by controlled calcination under varying temperature and time conditions. X-ray diffraction (XRD) was employed to analyze the crystalline phases, while surface area and porosity were examined to assess material properties. UV-Visible spectroscopy was used to study the absorption spectra and band structure alterations in the composites. XRD analysis confirmed that the TiO₂-Al₂O₃ composite contained both anatase and rutile phases, along with Al₂O₃, exhibiting a specific surface area of 32.1 m²/g and an average crystallite size of 18.09 nm. The TiO₂-WO₃ composite demonstrated the formation of a mixed oxide system at the interface, altering its electronic properties. Optical absorption spectra revealed significant modifications in band structures, affecting light absorption and photocatalytic efficiency. The structural and optical characteristics of TiO₂ composites were significantly influenced by the choice of secondary material and calcination conditions. The findings suggest that optimizing these parameters can enhance photocatalytic performance, making TiO₂ composites promising for applications in environmental remediation and materials science.

Keywords: TiO₂ composites, sol-gel synthesis, photocatalysis, X-ray diffraction, calcination, optical properties, band structure, nanomaterials.

1. Introduction

TiO₂ has a long history of application. However, it was not economically viable until the early twentieth century [1]. Kronos, a German chemical firm, developed large-scale TiO₂ production in the 1920s [2]. TiO₂ may be generated using synthetic rutile, a chemical derivative of ilmenite, or naturally occurring ilmenite [3-7].

TiO₂ exists in three forms: rutile, anatase, and leucosene. Rutile is a common kind recognized for its high refractive index and remarkable stability. While anatase and leucosene are uncommon, they offer unique properties that may be useful in specific circumstances [8]. TiO₂ is a common pigment for paints, coatings, polymers, and paper owing to its good scattering properties and refractive index. It also improves the brightness, hardness, and acid resistance of porcelain enamels when employed as an opacifier and whitening agent [9, 10]. TiO₂'s strong heat resistance makes it widely employed in industrial applications. These uses include missiles, power plants, airplanes, armor plate, and naval vessels [11-14].

Recent research suggests that TiO₂ has strong photocatalytic activity. Research shows that TiO₂ is a very efficient photocatalyst for removing organic pollutants. This is owing to its cheap cost, high chemical stability, and ecologically friendly properties [15-18]. TiO₂ has unique qualities that have led scientists to create solutions for air and water filtration, as well as self-cleaning surfaces. TiO₂ is becoming more popular for renewable energy applications. Recent research has explored the possible advantages of TiO₂ in energy conversion technologies, such as improving solar cell efficiency [19-21].

Researchers encounter several problems while creating TiO₂ composites. These challenges include regulating particle shape and size, ensuring stability, and attaining uniform dispersion. Researchers are now studying creative techniques to overcome these restrictions. Researchers are looking at novel synthesis procedures, adjusting current ones, and using additives to increase stability and dispersion. Furthermore, researchers apply modern characterisation tools to get a deeper understanding of the composite material's properties [22].

There are many ways for generating TiO₂ compounds, including solid-state reaction, coprecipitation, chemical vapor deposition, hydrothermal approach, sol-gel method, and electrochemical deposition [3, 18]. Various variables influence the experimental method for synthesizing TiO₂ compounds. These criteria include the components used, the compound's desirable qualities, and the intended use. The sol-gel process may create TiO₂ composites with unique properties for many applications [23-26].

This study aims to employ the sol-gel process to make TiO₂ composites with Al₂O₃, WO₃, ZnO, CNT, and SiNT. The purpose is to optimize the calcination parameters by adjusting the temperature and time. A comprehensive investigation will be conducted to evaluate the structural and optical properties of the composites that have been manufactured, as well as to determine their surface area and porosity. By improving TiO₂ composites durability and effectiveness, the researchers want to make them more useful for a range of applications.

2. Methodology

2.1 Synthesis of TiO₂ using the sol-gel

Isopropyl alcohol (IPA) and titanium tetra isopropoxide (TTIP) swirled together to form a continuous sol-gel solution (SGS). Nitric acid (HNO₃) and distilled water was combined drop by drop to create a homogenous solution. At 80⁰ C, the liquid was then agitated until it took on the consistency of gel and solidified into a little lump. The TiO₂ gel was heated to 550⁰ C and calcined for six hours in a furnace. The sample underwent a particular calcination process before cooling to room temperature for further examination to examine its structural and optical properties. This dependable experimental method uses the sol-gel procedure to produce TiO₂.

2.2 Synthesis of TiO₂ Composites.

The sol-gel method yielded nano crystalline TiO₂ molecules. The updated method comprises dispersing 0.3 g of the nano crystalline material in 40 ml of isopropyl alcohol and gradually adding titanium isopropoxide (TTIP) to the mixture. TTIP is a predecessor of TiO₂. Following that, the mixture was carefully stirred until it reached a uniform texture. To establish uniformity, Al₂O₃, WO₃, ZnO, CNT, and SiNT were mixed in comparable proportions with TiO₂. The mixture was stirred again. At room temperature, the solution solidified for 24 hours. Following the gelation method, the gel was dried at 100⁰C for 12 hours to ensure that all solvent had been removed. Extensive study shows that heating the dried gel at 550⁰C for six hours yields the greatest TiO₂ production results. The composite was ready for use after the calcination step and subsequent cooling to room temperature. This novel approach manufactures TiO₂ composites with suitable nanocrystalline material utilizing a sol-gel process.

2.3 Characterization Techniques

X-ray diffraction (XRD) was used to analyze the phase composition and crystal structure of the TiO₂ nanocomposite. We used a Cu-K α radiation diffractometer to get XRD patterns. The samples were scanned at a constant rate of one degree per minute throughout a 2 θ range of 10 to 70 degrees. We investigated the optical properties of the TiO₂ nanocomposite using UV-vis spectroscopy. This approach allows for the assessment of the sample's light absorption and transmission at various wavelengths. BET measurements assessed the surface area and pore size distribution of the TiO₂ nanocomposite. BET analysis may be used to assess the surface area and pore size distribution by measuring the quantity of gas (often nitrogen) adsorbed onto the sample's surface at different pressure levels.

3. Result and Discussion

3.1. X-Ray Analysis

The mixed anatase-rutile nanocrystalline TiO₂ nanoparticles were analysed structurally using the XRD technique. X-ray diffractometer measurements using a BROOKER D8 employed Cu K α irradiation ($\lambda = 0.154$ nm). The diffraction spectra of the (101) anatase and (110) rutile peaks were obtained with a step width of 0.1 degrees during survey scans ranging from 20° to 80°.

3.2 X-Ray Analysis for TiO₂ Composites

This work explored the X-ray diffraction patterns of TiO₂ composites consisting of SiNT, CNT, WO₃, Al₂O₃, and ZnO. The ideal temperature and time were found to be 550 °C and 6 hours, respectively. The composites' X-ray diffraction patterns were measured and evaluated. Figure 3 shows the X-ray diffraction pattern of the TiO₂-Al₂O₃ composite, revealing the existence of the Al₂O₃ phase alongside TiO₂'s anatase and rutile phases. Figure 4 depicts the XRD patterns of the remaining composites, as seen in Figure 7. The composite materials of ZnO, CNT, and SiNT include both anatase and rutile phases of TiO₂. The research found that the sol-gel technique is successful for producing TiO₂ composites from diverse materials. The calcination parameters have a considerable influence on the crystallite morphologies and phases of the final composite.

3.2.1 TiO₂-Al₂O₃ Composite

The TiO₂-Al₂O₃ composite consists of TiO₂ anatase, rutile, and Al₂O₃ phases. The composite contains a higher concentration of anatase TiO₂ compared to the pure TiO₂ sample. Al₂O₃ functions as a nucleating agent, enhancing the presence of the anatase phase in composites. According to the XRD pattern, the composite contains Al₂O₃, as indicated by a peak at 37.6°. At an angle of 65.9°, there is evidence of a combination of aluminum and titanium oxides. This indicates the possibility of a solid solution or composite between titanium dioxide (TiO₂) and aluminum oxide (Al₂O₃). Al₂O₃ has formed on the surface of TiO₂ in the mixed oxide system. Al₂O₃ exhibits higher surface energy compared to TiO₂, resulting in accelerated surface growth.

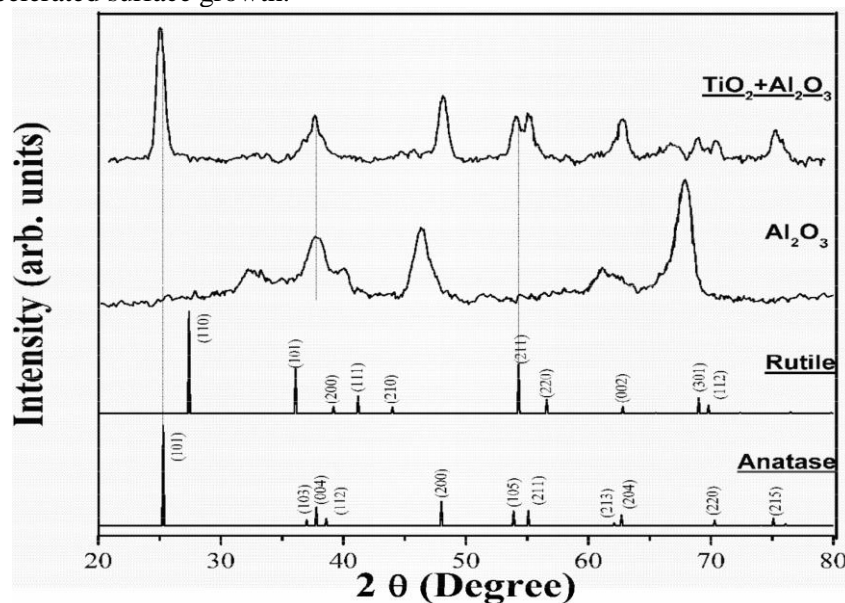


Figure 1. XRD pattern of an Al₂O₃ and TiO₂ composite.

Our study using the Scherrer formula reveals that the TiO₂ crystallite size in the composite material corresponds to 18.1 nm. These crystals have a somewhat lower size than pure TiO₂, suggesting that Al₂O₃ inclusion in the compound could stop TiO₂ crystal development. X-ray diffraction investigations reveal that the TiO₂-Al₂O₃ composite has a unique crystal structure that distinguishes it from both pure TiO₂ and pure Al₂O₃.

3.2.2 Composite TiO₂-WO₃

Figure 2 shows the X-ray diffraction (XRD) pattern of the TiO₂-WO₃ composite, thereby exposing the main component as the anatase phase of TiO₂. Moreover, the composite has quite high concentrations of rutile phase of TiO₂. The composite exhibits a maximum intensity of anatase TiO₂, greater than that of the pure TiO₂ sample, suggesting that WO₃ facilitates the development of the anatase phase. Obviously, the highest peak in the anatase phase points in the (101) plane for anatase TiO₂. The XRD

pattern shows a clear peak at 54.3° suggesting the likely presence of the WO_3 phase in the composite material. The observations suggest that W and Ti are present in a mixed oxide environment. The maximum noted at 62.66° points to the location of this system near the border between WO_3 and TiO_2 . This suggests the surface of TiO_2 has developed WO_3 . An essential system in the field as this composite has the ability to greatly increase its photocatalytic activity.

Our investigation utilizing the Scherrer formula and looking at the full width at half-maximum (FWHM) of the diffraction peak indicates that the TiO_2 crystallite has a size of 15.26 nm. By providing a larger surface area for reactions, the small dimensions of the TiO_2 crystallites in the composite have benefits in photocatalytic uses. The WO_3 phase shows as larger particles or aggregates with a crystallite size of 27.1 nm, higher than that of TiO_2 .

Generally, in this study the TiO_2 - WO_3 composite analysis demonstrates the presence of both W and Ti at the two phase contact. WO_3 addition into the system raises the anatase phase production of TiO_2 . Improved photocatalytic activity of the composite may be explained in part by WO_3 inclusion and TiO_2 crystal small size.

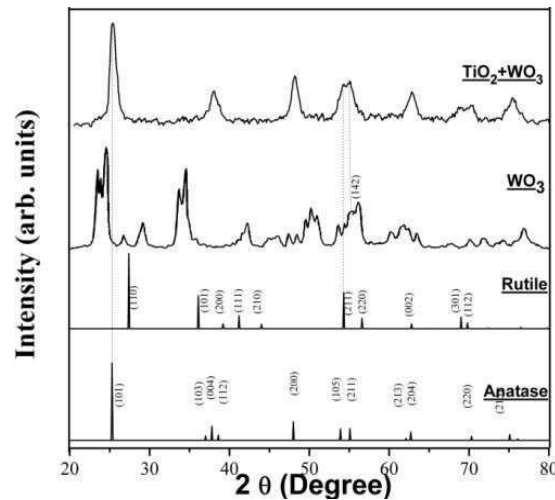


Figure 2. XRD pattern of TiO_2 and WO_3 composite.

3.2.3 Composite TiO_2 - ZnO

Figure 3 shows the XRD pattern of a Zn-containing TiO_2 composite, indicating the existence of the anatase and rutile phases of TiO_2 . Compared to pure TiO_2 samples, this sample shows a higher concentration of the rutile phase. One may deduce that the rutile phase has developed in the TiO_2 based on the intensity of the peak in the (110) planes. The composite contains ZnO , as evidenced by the peak at 36.3° . Based on the observed peaks at various angles, it appears that the sample contains a mixed oxide system, which likely includes Zn and Ti. These peaks indicate that ZnO is forming on the surface of TiO_2 .

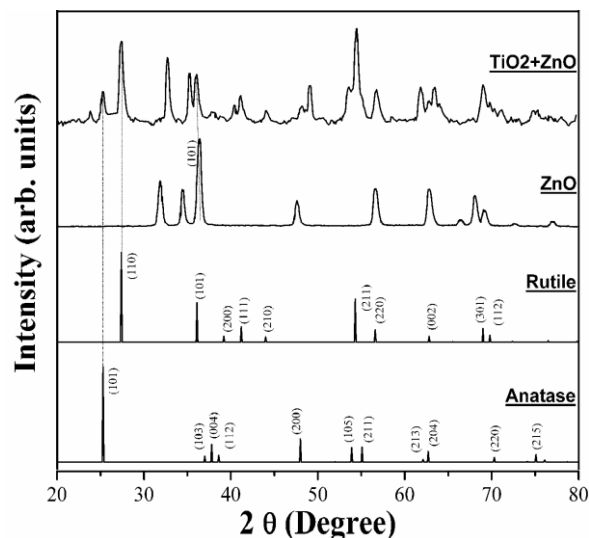


Figure 3. XRD pattern of TiO_2 and ZnO composite

The Scherrer formula calculation for the TiO_2 in the composite produced a crystallite size of 27.71 nm. Remarkably, in composites with Al_2O_3 and WO_3 , this size is greater than the crystallite size of TiO_2 . Findings revealed that the ZnO crystallite size in the composite is 55.72 nm, a considerable increase above the crystallite sizes of Al_2O_3 and WO_3 in their respective TiO_2 composites. According to XRD studies, the insulator material selection affects the development of mixed oxide systems at the interface between insulator materials and TiO_2 . In composite materials, the insulator material selection affects the crystallite size as well.

3.2.4 TiO_2 -CNT composite

Figure 4 shows TiO_2 's XRD pattern in combination with a carbon nanotube (CNT) insulating material. Whereas the two bottom contours of the third graph show the X-ray diffraction peaks of TiO_2 's anatase and rutile phases, the X-ray diffraction of CNT with a crystallite size of 20.4 nm is shown here. The XRD pattern of the as-synthesized TiO_2 -CNT composite is illustrate in the upper graph. The XRD pattern of the composite demonstrates a substantial increase in the quantity of anatase TiO_2 . Suggesting the formation of the anatase phase, the (211) planes exhibit the maximum intensity peak. The XRD pattern confirms the presence of CNT in the composite by exhibiting a CNT peak at 26° . Additionally, the peak at 63.3° suggests that the sample contains titanium oxide and carbon. It is anticipated that this system will emerge at the interface of CNT and TiO_2 , indicating that CNT growth has taken place on the surface of TiO_2 .

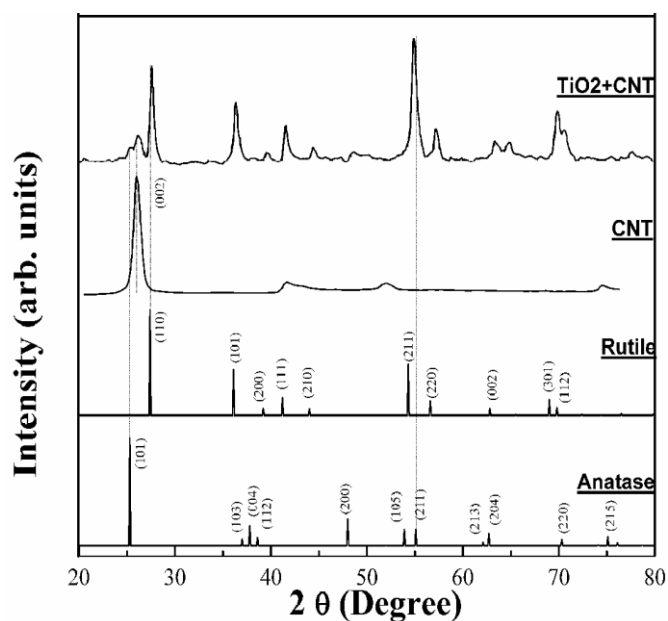


Figure 4. XRD pattern of TiO_2 - CNT composite

The crystallite size of TiO_2 , which is 26.32 nm, is calculated from its full width at half maximum (FWHM) using the Scherrer formula. The XRD pattern of the TiO_2 -CNT composite is crucial for confirming the effective synthesis of the molecule since it provides details on the crystalline phases and sizes present.

3.4.5 TiO_2 -SiNT composite

Figure 5 shows the XRD pattern of TiO_2 by use of silicon nanotubes (SiNT), the insulator material. The X-ray diffraction of SiNT is shown in the third graph. The XRD peaks of anatase and rutile phases of TiO_2 are shown in the bottom two graphs. The XRD pattern of TiO_2 that was generated using SiNT is depicted in the upper graph. According to the XRD pattern, the composite has experienced a substantial increase in the quantity of anatase TiO_2 . The anatase phase is evident in the peak of maximum intensity for the (101) planes. The XRD pattern's peak at 48.7° provides evidence that SiNT is present in the composite. Peaks at 23° indicate the existence of a silicon-titanium oxide system in the sample. This system most likely developed at the interface between SiNT and TiO_2 , indicating that SiNT has grown on TiO_2 's surface.

The crystallite size of TiO_2 is determined from the FWHM using the Scherrer formula, which yields 11.15 nm. This value suggests that the composite contains relatively small TiO_2 particles. The XRD pattern of the TiO_2 -SiNT composite is essential for determining the crystalline phases and sizes present in the composite, thereby verifying the effective synthesis. SiNT may provide the composite with

supplementary properties, such as enhanced electronic conductivity, which could be advantageous in a variety of industries, including solar energy conversion and photocatalysis.

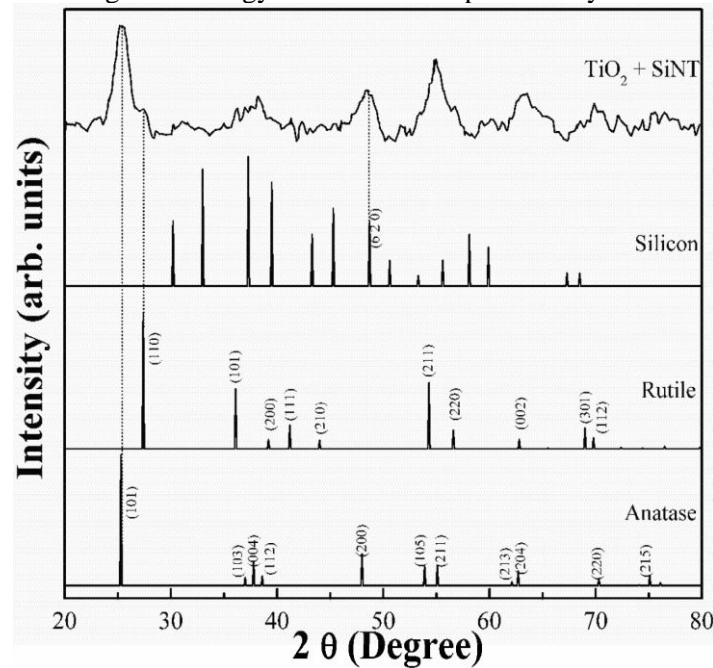


Figure 5. XRD pattern of the TiO₂-SiNT composite

3.2 BET ANALYSIS

Table 1 shows the effective surface area of the composites, calculated using the BET technique from nitrogen adsorption measurements. The samples were tested to establish the specific surface area and average crystallite size. The composite material has a specific surface area of 32.1 m²/gm and average crystallite size of 18.09 nm. TiO₂ + WO₃ has a higher specific surface area (51.4 m²/gm) and a slightly smaller average crystallite size (15.36 nm). The TiO₂ + ZnO combination has the largest and lowest specific surface areas, with an average crystallite size of 27.71 nm and 15.2 m²/gm. The composite material has a specific surface area of 33.2 m²/gm and average crystallite size of 26.32 nm. The combination of TiO₂ + SiNT has the largest specific surface area (93.1 m²/gm) and the shortest average crystallite size (11.15 nm).

The results indicate that including CNT and SiNT in TiO₂ reduces the average crystallite size and increases the specific surface area. The special structure of the nanotubes, marked by their porous character and large surface area, most likely explains this phenomena. Specifically, this structure helps TiO₂ nanoparticles to accumulate. Reducing the average crystallite size of TiO₂ was shown to be equivalent depending on WO₃ and Al₂O₃. Their influence on the particular surface area was really negligible, however. Still, adding ZnO caused an average crystallite size to rise and specific surface area to drop. The larger particle size of ZnO compared to TiO₂ could potentially provide an explanation for this phenomenon. According to BET's investigation, the inclusion of nanotubes, specifically SiNT, in TiO₂ composites has the potential to greatly enhance their specific surface area.

Table 1 Surface area and crystallite size for different TiO₂ Composites.

Sr.	Sample	Avg. Crystallite	Specific Surface
1	TiO ₂ +Al ₂ O ₃	18.09	32.1
2	TiO ₂ +WO ₃	15.36	51.4
3	TiO ₂ +ZnO	27.71	15.2
4	TiO ₂ +CNT	26.32	33.2
5	TiO ₂ +SiNT	11.15	93.1

Recent research has revealed exciting advancements in enhancing the photocatalytic activity and surface area-based applications of composites, as indicated by several studies [11, 15, 22, 32].

3.3 UV-VISIBLE Composites Analysis

Figure 6 displays the UV-vis absorption spectra of the synthesized TiO₂ composites. The table displays the band gap values of different composites containing TiO₂. In comparison to TiO₂, composites display larger band gaps, indicating reduced photocatalytic activity. When comparing TiO₂ alone to combinations of TiO₂ + Al₂O₃ and TiO₂ + SiNT, it is evident that the latter two exhibit a larger band-gap value. This suggests that they possess higher levels of photocatalytic activity. These substances have

the potential to decrease electron activation, thereby inhibiting photocatalytic processes. This might happen because these materials increase electron-hole pairs and photocatalytic processes [7].

Based on an investigation, scientists have shown that the $\text{TiO}_2 + \text{WO}_3$ Composite exhibits the lowest band gap value and the maximum photocatalytic activity [29]. Studying the strong electron affinity of WO_3 can help us understand the occurrence of electron-hole pair generation. As a materials scientist, one can observe a significant enhancement in the photocatalytic activity. Based on the UV analysis findings, the addition of specific materials to TiO_2 can have a significant impact on its photocatalytic activity. Thus, it is crucial to thoroughly assess the characteristics of various materials and how they interact with TiO_2 before drawing any conclusions. The graph displays the band gap values derived from the data in Table 2.

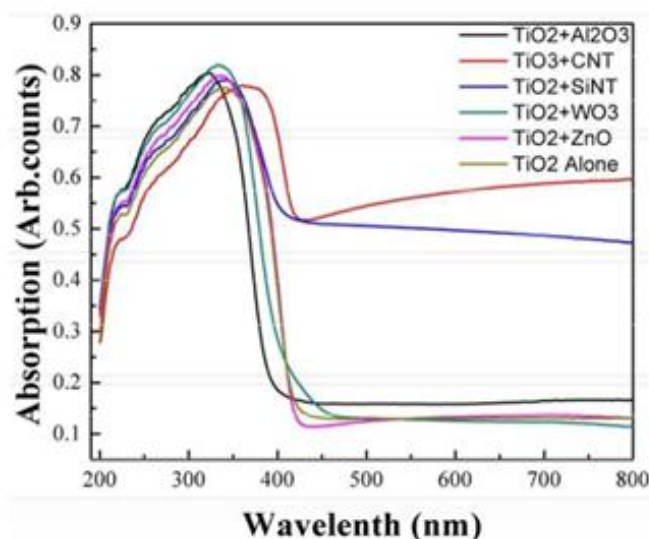


Figure 6. The UV-vis spectra of TiO_2 composites.

Table 2. Band gap values of different composites with TiO_2

TiO_2 Composites	Support Materials	Crystallite Size (nm)	Specific Surface Area (m^2/gm)	Band Gap (eV)
TiO_2	-	15.26	44.08	3.00
$\text{TiO}_2\text{-Al}_2\text{O}_3$	Al_2O_3	18.09	32.1	3.10
$\text{TiO}_2\text{-WO}_3$	WO_3	15.36	51.4	3.01
$\text{TiO}_2\text{-ZnO}$	ZnO	27.71	15.2	3.05
$\text{TiO}_2\text{-CNT}$	CNT	26.32	33.2	3.03
$\text{TiO}_2\text{-SiNT}$	SiNT	11.15	93.1	3.14

Combining titanium dioxide (TiO_2) with other elements helps to produce materials known as TiO_2 compounds that improve their characteristics. They work in fields like photocatalysis and energy storage. Among the many composite support materials included in the data are Al_2O_3 , WO_3 , ZnO , CNTs, and SiNTs. The features of the material depend much on the range of crystallite sizes (15.26 to 16.7 nm). From 44.08 to 93.1 m^2/g , the range of particular surface areas seen in the research is very large. This large spectrum points to the existence of a noteworthy surface area ready for many kinds of responses. Electrical conductivity and light absorption are substantially affected by the range of band gaps, which runs from 3.00 to 3.14 eV. TiO_2 composites have a wide spectrum of characteristics that one may change to fit different uses.

3.4 Photocatalytic Dye Degradation

The photocatalytic degradation of methylene blue (MB) was assessed by monitoring its UV-Visible absorbance at 664 nm. TiO_2 samples calcined at different temperatures were tested under UV light for 30 minutes, with TiO_2 calcined at 550°C showing the highest degradation, as indicated by the steepest drop in absorbance in Figure 7. The absorbance reduced from 1.0 to 0.15, demonstrating enhanced crystallinity, reduced defect states, and increased catalytic sites in the anatase phase.

Further analysis of calcination time at 550°C revealed that TiO_2 calcined for 6 hours exhibited the most effective MB degradation, as shown in Figure 8. The absorbance decreased from 1.0 to 0.08, confirming that this duration optimizes the crystalline phase and surface area without excessive grain growth, ensuring maximum photocatalytic efficiency, as supported by studies on nanocomposite photocatalysts.

The use of TiO₂ composites with support materials such as WO₃ and SiNT further improved photocatalytic performance. Figure 9. illustrates that the TiO₂-WO₃ composite achieved the highest degradation, with absorbance decreasing from 1.0 to 0.05, followed by TiO₂-SiNT at 0.10. This enhancement is due to the lower bandgap of WO₃, which improves visible light absorption and charge transfer.

Photocatalysis in TiO₂ occurs through photon absorption, exciting electrons to the conduction band and generating electron-hole pairs. These pairs initiate redox reactions, forming superoxide (O₂^{•-}) and hydroxyl radicals (•OH), which effectively break down MB into non-toxic products. However, charge recombination can reduce efficiency, highlighting the importance of materials that promote charge separation for enhanced photocatalytic applications.

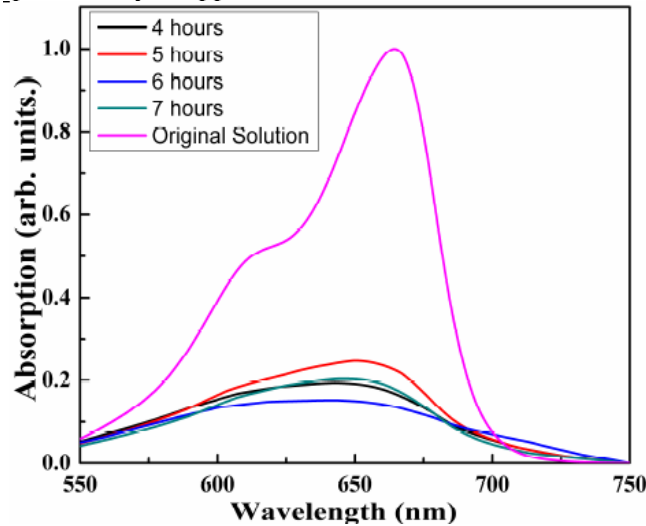


Figure 7. UV-Visible Absorption graph of MB after degradation using as synthesized TiO₂ samples calcined for different times

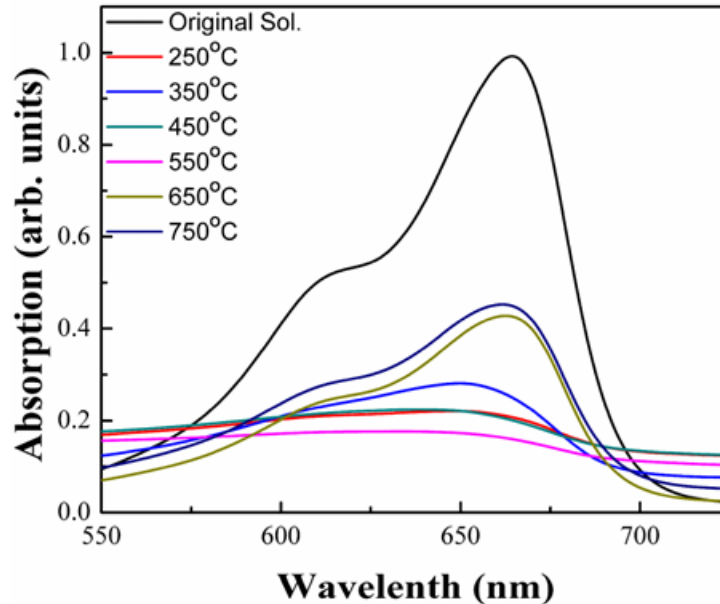


Figure 8. UV-Visible Absorption graph of MB after degradation using as synthesized TiO₂ samples calcined at different temperatures

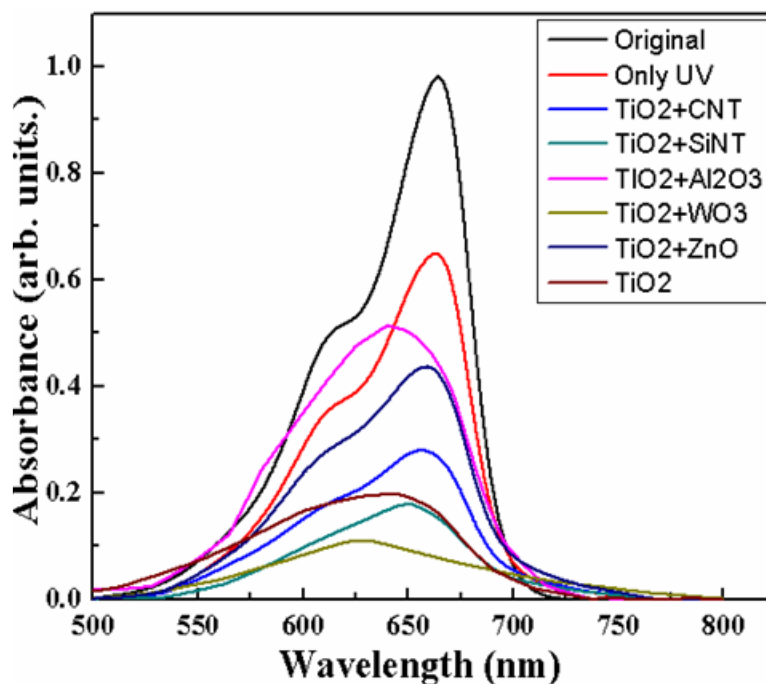


Figure 9. UV-Visible Absorption graph of MB after degradation using as synthesized composites of TiO₂

4. Conclusion

In this study, the Sol-Gel technique was successfully employed to evaluate the effects of various additives and optimize the band gap characteristics of TiO₂ composites. Comprehensive investigations confirmed the phase formation, crystal size, and band structure of TiO₂-based compounds, particularly focusing on Al₂O₃, WO₃, ZnO, and SiNT additives. The results revealed that different chemical additions to TiO₂ compounds resulted in diverse crystal structures and lattice parameters, which significantly influenced their properties and potential applications.

After extensive testing, it was found that the ideal calcination temperature for TiO₂ was 550°C for six hours. The formation of mixed oxide systems such as TiO₂-Al₂O₃ and TiO₂-WO₃ composites was confirmed, indicating the presence of separate components on the surface of TiO₂. Variations in crystal size, ranging from 15.26 nm to 18.1 nm, demonstrated the impact of different additives on crystal morphology. Notably, the TiO₂-SiNT composite exhibited a remarkable specific surface area of 93.1 m²/g, highlighting its potential for high-resolution applications.

The TiO₂ composites displayed varying band gap values, with TiO₂-Al₂O₃, TiO₂-WO₃, TiO₂-ZnO, and TiO₂-SiNT composites showing a band gap of 3.14 eV, compared to the pure TiO₂, which had a band gap of 3.00 eV. These variations in band gap were attributed to the different additives incorporated into the composites. Furthermore, the absorption spectrum analysis revealed significant modifications in the band structure of the TiO₂ composites, opening avenues for new applications in materials science.

In conclusion, this work contributes significantly to the understanding of TiO₂ composites, enhancing our knowledge of their practical applications. Future research should prioritize the practical use and further assessment of these composites, fostering the development of innovative and versatile materials for a wide range of applications.

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