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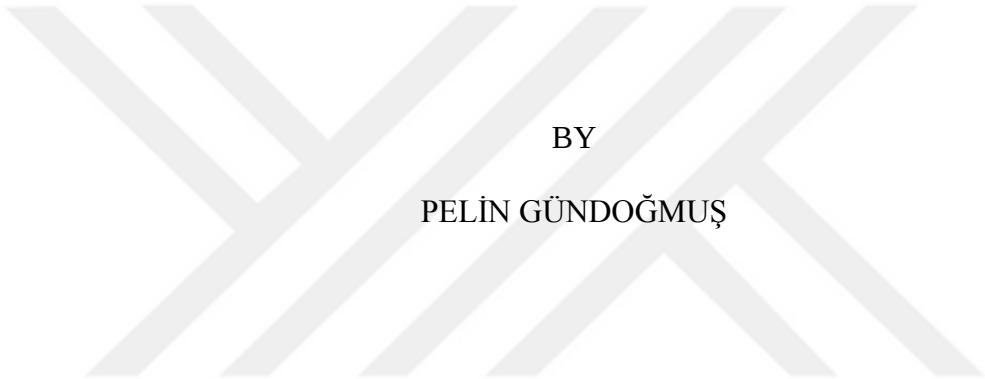
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SYNTHESIS OF $g\text{-C}_3\text{N}_4/\text{TiO}_2$ HETEROJUNCTION COMPOSITES WITH
ENHANCED SOLAR LIGHT PHOTOCATALYTIC ACTIVITY

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY



BY
PELİN GÜNDOĞMUŞ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

JANUARY 2020

Approval of the thesis:

**SYNTHESIS OF g-C₃N₄/TiO₂ HETEROJUNCTION COMPOSITES WITH
ENHANCED SOLAR LIGHT PHOTOCATALYTIC ACTIVITY**

submitted by **PELİN GÜNDOĞMUŞ** in partial fulfillment of the requirements for
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ABSTRACT

SYNTHESIS OF g-C₃N₄/TiO₂ HETEROJUNCTION COMPOSITES WITH ENHANCED SOLAR LIGHT PHOTOCATALYTIC ACTIVITY

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January 2020, 93 pages

The solar light sensitive g-C₃N₄/TiO₂ composites containing various amounts of graphitic carbon nitride (g-C₃N₄) and titania (TiO₂) were prepared by the hydrothermal and sol-gel processes for photocatalytic applications. Hydrothermally derived g-C₃N₄/TiO₂ composites were subjected to regulated heat treatments at temperatures ranging from 350 to 500 °C for 1 h to improve their photocatalytic efficiency. Particle size, crystal structure, morphology, and optical properties of the g-C₃N₄/TiO₂ nanocomposites were investigated and were compared with those of the pristine TiO₂ and g-C₃N₄ powders using particle size analyzer, X-ray diffractometer, Field emission scanning electron microscope, Fourier transform infrared spectroscopy, Raman spectroscopy, diffuse reflectance spectroscopy (DRS) and UV-Vis spectrophotometer. Photocatalytic activity of all powders was assessed by the Methylene Blue (MB) degradation test under solar light illumination. The results revealed that g-C₃N₄/TiO₂ composites exhibited better photocatalytic activity for the degradation of MB than both pristine TiO₂ and g-C₃N₄. Hydrothermally derived and sol-gel derived g-C₃N₄/TiO₂ composites showed 100% and 87.05%, respectively photocatalytic efficiency under 180 min solar light illumination. The enhancement in photocatalytic activity was related to the generation of reactive oxidation species

induced by photogenerated electrons and reduced recombination rate of the electron-hole pairs.

Keywords: Heterojunction, Hydrothermal process, Sol-gel process, g-C₃N₄/TiO₂ composites, Photocatalytic activity.



ÖZ

GELİŞMİŞ SOLAR IŞIK FOTOKATALİTİK AKVİTEYE SAHİP g-C₃N₄/TiO₂ HETEROJONKSİYON KOMPOZİTLERİN SENTEZİ

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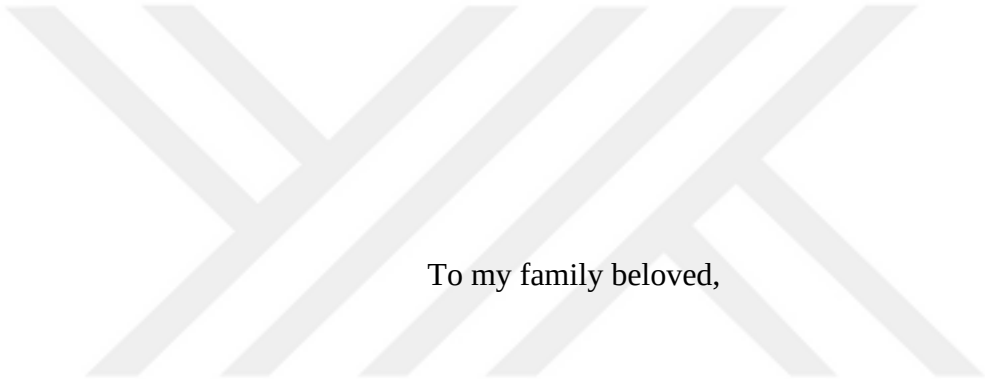
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Farklı miktarlarda grafitik karbon nitrit (g-C₃N₄) ve titanya (TiO₂) içeren solar ışığa duyarlı g-C₃N₄/TiO₂ kompozitleri, hidrotermal ve sol-gel yöntemi kullanılarak fotokatalitik uygulamalar için sentezlendi. Hidrotermal yöntem kullanılarak sentezlenen g-C₃N₄/TiO₂ kompozitleri, fotokatalitik özelliklerini iyileştirmek amacıyla sıcaklığın 350 ile 500 °C arasında değiştiği 1 saatlik ısıtma işlemine tabi tutuldu. g-C₃N₄/TiO₂ kompozitlerinin tanecik büyüklüğü, kristal yapısı, morfolojisi ve optik özellikleri incelendi ve saf TiO₂ ve g-C₃N₄ tozları ile tanecik büyüklüğü analizörü, X-ışını kırınım ölçeri, alan emisyonlu taramalı elektron mikroskopu, Fourier dönüşümlü kızılötesi spektroskopisi, Raman spektroskopisi, Dağınık yansıma spektroskopisi ve UV-vis spektrofotometre kullanılarak karşılaştırıldı. Tüm tozlarının fotokatalitik aktiviteleri solar ışık aydınlatması altında Metilen mavisi (MB) bozunum testi ile değerlendirildi. MB bozunum sonuçları g-C₃N₄/TiO₂ kompozitlerinin saf g-C₃N₄ ve TiO₂ tozlarına göre daha iyi fotokatalitik aktivite sahip olduğunu gösterdi. Hidrotermal ve sol-gel ile üretilen kompozitler 180 dakikalık solar ışık altında sırasıyla %100 ve %87.05 fotokatalitik aktivite gösterdi. Fotokatalitik aktivitedeki artış, fotojenere elektronlar tarafından indüklenen reaktif

oksidasyon türlerinin üretilmesi ve elektron-boşluk çiftlerinin rekombinasyonunun azaltılması ile ilgilidir.

Anahtar Kelimeler: Heterojunction, Hidrotermal yöntem, Sol-gel yöntemi, g-C₃N₄/TiO₂ kompozitleri, Fotokatalitik aktivite.





To my family beloved,

ACKNOWLEDGMENTS

I would like to express my deepest thanks to my supervisor, Prof. Dr. Abdullah Öztürk, for his guidance, advice and endless support. Without his patience and encouragement, this thesis would not have been completed.

I also want to thank my co-supervisor Prof. Dr. Jongee Park for his guidance, criticism, encouragements and positivity insight throughout the research.

This work was financially supported by TÜBİTAK with project number 216M391, and METU BAP with project number YLT-404-2018-3751. These financial supports are appreciated.

I want to special thanks to my lovely friends Merve Nur Doğu, Seren Özer, and Anıl Erdal for their endless support, motivations and not letting me give up. I would like to thank Emel Erdal, İbrahim Aydın, Çağlar Karaoğlu, Tolgahan Ulucan, Doğuhan Sarıtürk, Berk Aytuna, also my laboratory neighbors, Esra Karakaya Sütçü, Çağlar Polat and Elif Yeşilay for their support and helps. I appreciate also to my former and new labmates Asmae Bouziani, Sıtkı Can Akkuş, Nursev Erdoğan, Melis Kaplan, Emre Burak Ertuş, Yiğit Cansın Öztürk, Dilara Çisel Varan, and Merve Begüm Köksal.

I would like to thank my close friends Aydın Albayrak, Ayşemine Semerci, İrem Özge Saraç and Seda Ahi for their unconditional supports and motivations.

I am also grateful for all staff of the Metallurgical and Materials Engineering Department, especially Serkan Yılmaz, Gökhan Polat, and Nilüfer Özel for their help and teaching FESEM and XRD analyses.

My deepest gratitude goes to my mother Hülya, my father Tamer, my sister İpek and my cat Muffin for their unconditional love, understanding and emotional support the whole of my life.

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CHAPTER 1

INTRODUCTION

Energy consumption and environmental pollution are among the two main global problems people face in their daily life in modern societies. In order to solve environmental problems, nowadays semiconductor materials and environmentally friendly processes are practiced [1]. The semiconductors are involved in the production of clean energy by using light for various applications including reduction of carbon dioxide [2], pollutants degradation [3], and hydrogen or oxygen production by water photolysis [4].

In the last three decades, a well-known semiconductor, Titanium dioxide (TiO_2), has received considerable attention from both industry and academia for photocatalytic applications especially for the water remediation processes due to its superior properties including high oxidizing ability, low-cost, long term chemical and biological stability, and non-toxicity [5]. Such highly desirable engineering properties make TiO_2 one of the most commonly practiced photocatalytic materials in both wastewater and air purification treatments. It is also used for the degradation of many organic and inorganic pollutants [6–8]. Despite its pronounced advantages as photocatalytic material, two main drawbacks of TiO_2 restrict its widespread photocatalytic applications. The first one is that it is active only in UV light region of the solar spectrum ($\lambda \leq 388 \text{ nm}$) because of its larger band gap; c.a. 3.2 eV for anatase, 3.02 eV for rutile, and 2.96 for brookite [9]. The large band gap inhibits its photocatalytic activity under sunlight since only a small portion (~5%) of solar spectrum covers UV as compared to visible region (~45%) [10–12]. The second drawback is related to its low photo quantum efficiency. The fast recombination of

photogenerated electron-hole (e^-/h^+) pairs leads to a decrease in the photocatalytic performance [13,14].

Different strategies including doping [15], dye sensitization [16], capping [12] and, semiconductor coupling (coupled/composite TiO_2) [17] have been experienced to improve the photocatalytic efficiency of TiO_2 under sunlight. These strategies are directed towards the enlargement of the absorption wavelength range and enhancement of photocatalytic activity. Among all strategies, semiconductor coupling in other words development of heterojunction with another semiconductor has become very popular in recent years. Heterojunction structure has conjunction between the two semiconductors, and this conjunction inhibits the recombination of e^-/h^+ pairs via transferring photogenerated charge carriers. In heterojunction photocatalysts, the separation of photogenerated e^-/h^+ pairs are promoted through charge transfers between the two semiconductors [18]. Photogenerated holes in the valance band (VB) of TiO_2 transfer to the VB of the other semiconductor and photogenerated electrons in the conduction band (CB) of the other semiconductor transfer to the CB of TiO_2 in TiO_2 based heterojunction composites [19].

Various narrow band gap semiconductors for instance WO_3 [17], ZnO [20], SnO_2 [21], and Fe_2O_3 [22] have been involved to construct heterojunction with TiO_2 . Recently, some of the carbonaceous materials like fullerene [23], carbon nitride [24], graphene [25], and carbon nanotubes [26] have been tried to develop heterojunction composites with TiO_2 .

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) is a narrow band gap semiconductor (ca. 2.7 eV) with applicable properties such as good thermal and chemical stability, lightweight, high absorption and acceptable photocatalytic activity in visible light, non-toxicity and, low cost [24,27]. Moreover, it has absorption in the visible light region and photocatalytic activity in the visible light region of the solar spectrum [28–30]. Like TiO_2 , $g\text{-C}_3\text{N}_4$ has fast recombination rate of e^-/h^+ pairs that restricts its photocatalytic efficiency and limits its photocatalytic applications. However, its band position (–1.3 to +1.4 eV) makes $g\text{-C}_3\text{N}_4$ suitable for the production of a heterojunction with TiO_2

[31]. The CB edge potential of g-C₃N₄ is more negative than that of TiO₂. Hence, the photoinduced electrons on the CB of g-C₃N₄ can easily transfer to CB of TiO₂ via the well-developed g-C₃N₄/TiO₂ interface [19]. Also, the more negative VB edge potential of TiO₂ with regard to that of g-C₃N₄ helps easy transfer from the photoinduced holes on the VB of TiO₂ to the VB of g-C₃N₄. For that reasons, g-C₃N₄ with TiO₂ is very promising to produce oxygen and hydrogen via oxidation of organic products. In addition, g-C₃N₄/TiO₂ heterojunction composites have adequate chemical and thermal stability under ambient conditions [32]. Consequently, construction of g-C₃N₄/TiO₂ heterojunction is a promising way to enhance visible light photocatalytic efficiency of both TiO₂ and g-C₃N₄ [33,34].

Production of g-C₃N₄/TiO₂ heterojunction can be achieved through physical admixing of g-C₃N₄ and TiO₂ powders, growing TiO₂ on g-C₃N₄ powders, and loading g-C₃N₄ on TiO₂ powder [1] by various routes including one-pot method [35], solvothermal method [36], ball-milling [37] sol-gel process [38] and, hydrothermal method [39,40]. Production routes of g-C₃N₄/TiO₂ heterojunction photocatalysts directly affect chemistry and morphology of the resultant product and its photocatalytic activity. Hydrothermal method is preferred because it offers controllable synthesis conditions, feasibility, and good crystallinity in the products. Despite a few publications reporting the outcomes of the studies on the g-C₃N₄/TiO₂ heterojunctions by the hydrothermal process, only little is known for the influence of hydrothermal reaction parameters on the construction of g-C₃N₄/TiO₂ composites.

Hydrothermal synthesis conditions like temperature, dwelling time, rotating speed, and volume of the solution in the vessel, etc., directly affect the composite structure [1]. Interfacial interaction influenced also by the synthesis conditions, which in turn affects the photocatalytic properties. The mechanisms taking place during the hydrothermal evolution of heterojunction composites still remain mysterious. Further research is needed to explore the development mechanism of g-C₃N₄/TiO₂ composites and to upgrade their photocatalytic properties under sun like light that comprises UV and visible light depending on the wavelength experienced.

Therefore, a study directed towards the preparation and photocatalytic activity of solar light sensitive g-C₃N₄/TiO₂ heterojunction photocatalysts has both scientific and technological significance.

The aim of the present study is to synthesize solar light sensitive g-C₃N₄/TiO₂ heterojunction photocatalysts by growing TiO₂ nanoparticles on the surfaces of g-C₃N₄ particles by the hydrothermal and sol-gel processes. The effects of synthesis conditions were kept constant but, g-C₃N₄ content of the composite was varied to get a g-C₃N₄/TiO₂ heterojunction photocatalyst with enhanced photocatalytic activity. The photocatalysts prepared were subsequently heat treated at various temperatures. Impacts of the preparation method, amount of the constituents, and the heat treatment temperatures on the structure and photocatalytic efficiency were studied.

CHAPTER 2

LITERATURE REVIEW

2.1 Photocatalysis Phenomena

An alteration of the chemical reaction rates during light exposure is referred to as photocatalysis that was also defined as acceleration of chemical reaction (generally oxidation and reduction) without consuming a reactant by using light and catalyst [41]. Photocatalytic materials, also known as photocatalysts, are generally semiconductors, which can be alone, or it can combine with metals, organics or inorganics for light absorption. The photocatalytic reactions are categorized to two groups regarding the physical phase of reactants; homogeneous and heterogeneous photocatalysis [27]. When the semiconductor and the reactant have been the same phase that solid, liquid, or gas. This reaction type is named as homogeneous photocatalysis. When the semiconductor and the photocatalysis have been in different states, the reaction type is heterogeneous photocatalysis.

Depending on the band gap (E_g) structures, materials are classified in three main groups; conductors, semiconductors, and insulators. Their band gap energies are schematically shown in Figure 2.1 [42].

In presence of light, semiconductors can act as photocatalysts because they have ability to conduct electricity at room temperature. When photocatalyst is exposed to light by enough energy (desired wavelength), the photons with energy is absorbed by electron (e^-) of the valance band (VB) and it is excited to conduction band (CB) leaving behind the hole (h^+) in VB. At the same time, there is an e^-/h^+ pairs formation in this process [41].

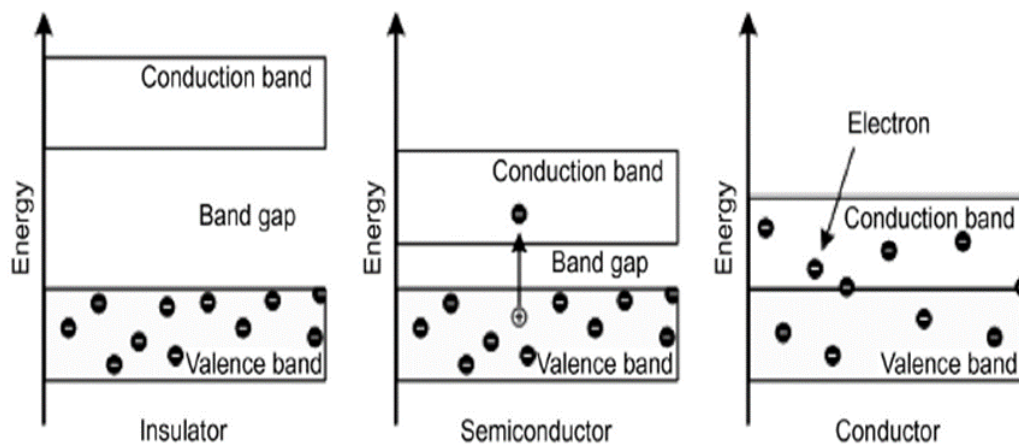


Figure 2.1. Three types of materials as classified regarding their band gap energies [42].

2.1.1 Photocatalytic Materials

Different semiconductors including ZnO [20], Fe₂O₃ [22], g-C₃N₄ [43], SrTiO₃ [44], CdS [45], Ag₃PO₄ [46], BiPO₄ [47], WO₃ [17], and TiO₂ [15] are known as photocatalysts. Band gap energies and the band edge energies of the various semiconductor photocatalysts are tabulated in Figure 2.2. TiO₂ is one of the most commonly practiced photocatalysts due to its powerful ability to degrade many organic and inorganic pollutants resulting from industrial wastes. Because of its superior properties such as high oxidizing ability, low-cost, long term chemical and biological stability, and non-toxicity [5], it is used in special photocatalytic applications to degrade various organic and inorganic pollutants [6–8].

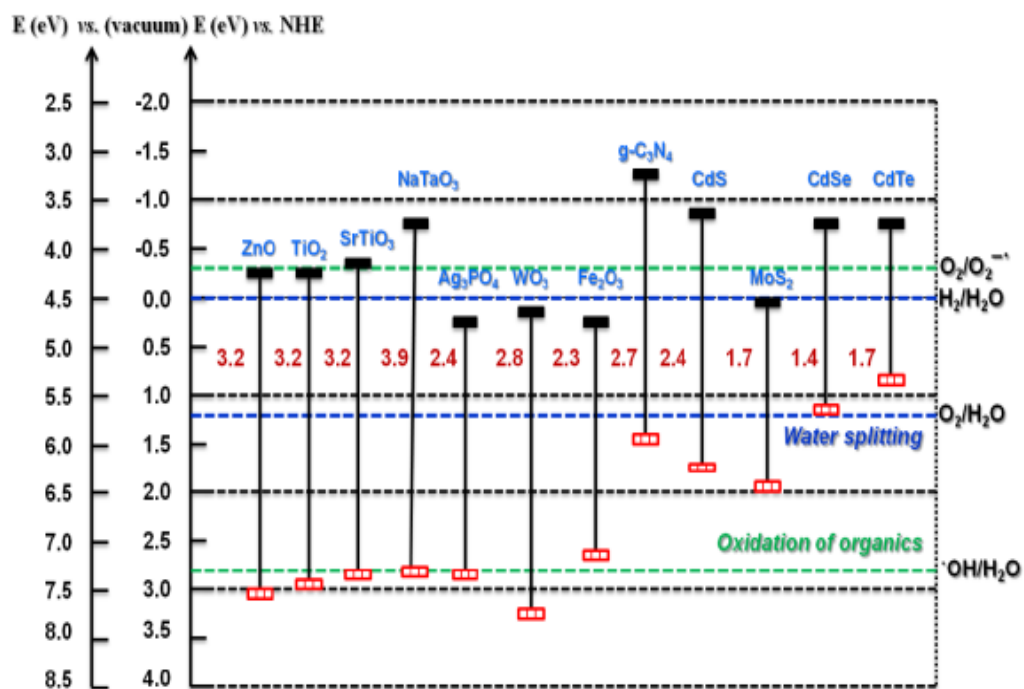


Figure 2.2. Band gap values of selected semiconductors [27].

2.1.1.1 Fundamentals and Mechanism of TiO₂

Photocatalysis is related to the E_g energy of photocatalysts. Irradiation of the photon which is equal to or higher than E_g energy excites the electrons in VB. The excited electrons transfer to CB of the photocatalyst leaving behind the holes. Holes in VB can oxidize donor molecule and react with water molecules to generate hydroxyl radicals which possess strong oxidizing power. At the same time, electrons in VB react with dissolved oxygen for producing superoxide ions. These charge carriers induce the redox reactions [41]. The reactions with the adsorbed components are initiated by the excited e^- and h^+ moving to surface of photocatalyst. The photocatalysis mechanism of TiO₂ in UV/visible light is depicted in Figure 2.3. Hydroxyl ions or adsorbed water can be oxidized from hydroxyl radicals by h^+ in VB. Also, oxygen is transformed to superoxide radicals by helping e^- in CB. Surface of adsorbed molecules degrade by these reactive compounds (superoxide and hydroxyl radicals) [48].

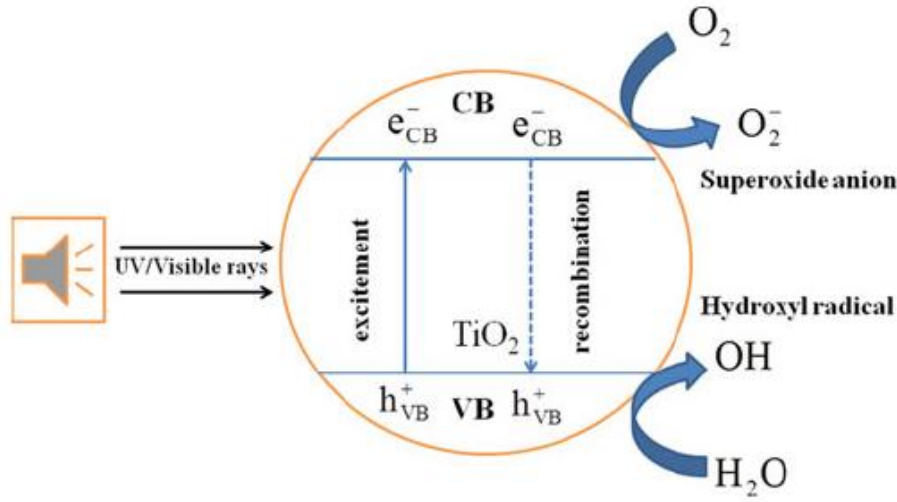
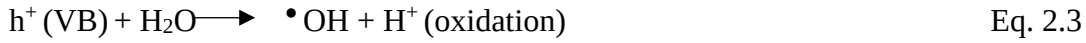


Figure 2.3. Photocatalysis mechanism of TiO_2 under UV/visible light [49].

The redox reactions occurring during photocatalysis phenomena are [48]:



TiO_2 has four polymorphs namely; anatase, rutile, brookite, and $\text{TiO}_2(\text{B})$. Anatase and rutile have tetragonal crystal structure but, brookite and $\text{TiO}_2(\text{B})$ have orthorhombic and monoclinic crystal structure, respectively [12]. Crystal structures of TiO_2 polymorphs are shown in Figure 2.4. All polymorphs consist of TiO_6 octahedra while they are different in terms of their stacking [50].

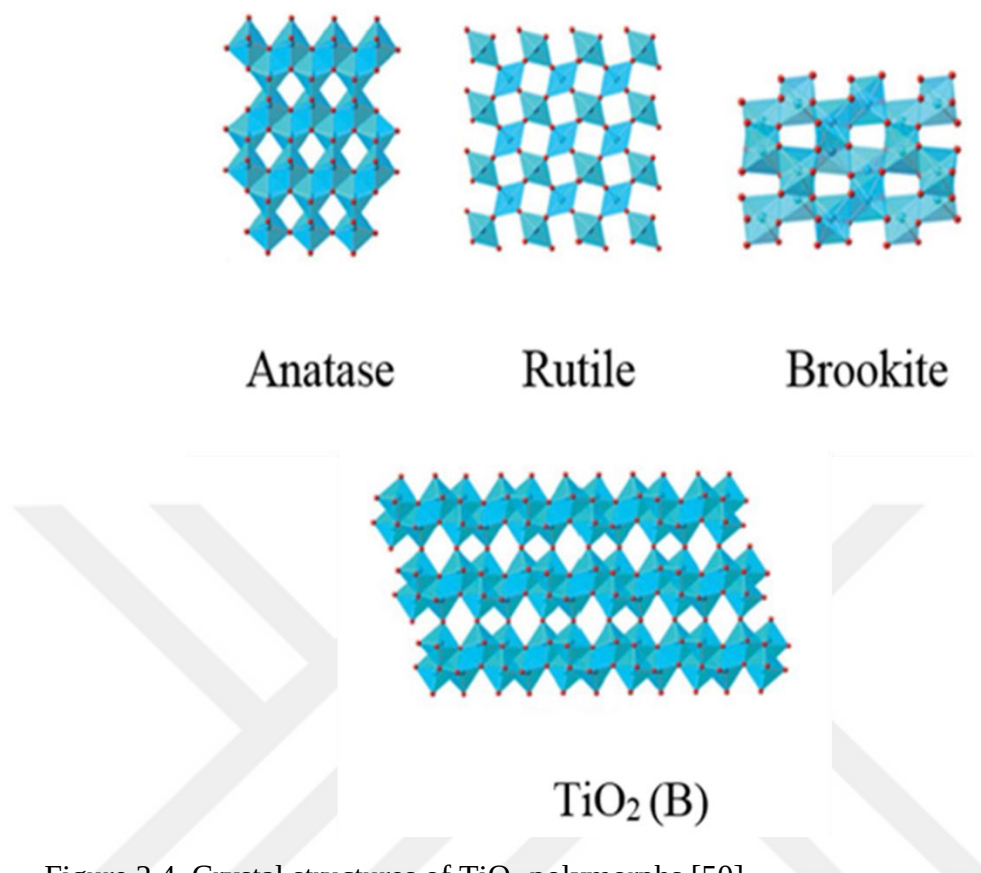


Figure 2.4. Crystal structures of TiO₂ polymorphs [50].

Rutile is thermodynamically the most stable phase. Anatase and brookite are metastable phases, which transform into rutile phase when they are heated [51]. The crystal structure, morphology and particle size of TiO₂ directly affect the properties as well as application areas of TiO₂. Rutile is generally used for pigments, construction, plastic and cosmetic industry, due to its light scattering and reflecting ability, highest density and refractive index [12]. Because anatase crystal structure possesses higher electron mobility and lower density, it is generally used for solar cell and photocatalytic applications. Information about the pure brookite is limited because the synthesis of brookite is extremely difficult [51].

TiO₂ is photoactive only in UV region at wavelengths less than 387 nm because of its large Eg (3.2 eV for anatase) [9,52]. The UV region covers only about 5% of solar spectrum. Also, the photocatalysis efficiency and visible light activation are reduced

by the e^-/h^+ recombination. Various strategies have been applied to improve its solar light photocatalytic efficiency. Some strategies developed to decrease E_g and expand the wavelength ranges of the TiO_2 are;

- Doping
 - ✓ Doping with cations
 - ✓ Doping with anions
 - ✓ Co-doping
- Dye sensitization
- Capping
- Coupled/composite with another semiconductor material

2.2 Ways to Enhance Photocatalytic Effectiveness of TiO_2

2.2.1 Dye Sensitization

Dye sensitization is one of the effective way to enhance solar light efficiency, especially for the wide band gap semiconductors like TiO_2 [53]. This process is generally used for enlarging the range of active spectrum. Dye sensitized TiO_2 degrade hydrazine, phenol, pesticide, chlorophenol, and benzyl alcohol [54]. Transition metal-based dyes are good for electron transfer for the semiconductors. However, they are not cheap and not environmentally friendly. Consequently, organic dyes or complexes are commonly used for this purpose. Photocatalytic reaction is initiated when these dyes or complexes inject electrons to the CB of TiO_2 upon exposure to visible light [42].

2.2.2 Doping

Doping with anions or cations is an effective way to broaden the active spectral range of TiO_2 and enhance solar light photocatalytic efficiency. Doping provides the usage

of main range of solar light and it traps the joining of photogenerated e^-/h^+ pairs [55]. Doping decreases the band gap of semiconductor by adding impurities. Thus, photocatalytic activity enhances [56]. Every impurity has different effect on crystal structures of semiconductors.

2.2.2.1 Cation-doped TiO₂

Doping of TiO₂ with metallic ions decrease E_g , increase the visible absorption edge and redox potential of TiO₂. Thanks to addition of metal oxides, a new energy develops so that the electrons easily move to catalyst's surface and are trapped with noble metals, earth metals, poor metals and, transition metals. At the same time, the e^-/h^+ recombination rate is hindered by keeping the electrons away from the holes. Separation of the electrons from the holes for longer times enhance the quantum efficiency of TiO₂ [48, 57]. Doping of Fe, Zn, Cu, Ni, Ag, Au, Pt, and V narrow the E_g of TiO₂ [56].

2.2.2.2 Anion-doped TiO₂

Carbon [58], Nitrogen [59], Sulphur [60], and Iodine [61] are the most attractive anionic elements for TiO₂ doping. When compared to cationic doping, anionic doping minimizes the center of the recombination. The non-metal ions can be replaced by the oxygen vacancies in TiO₂. Thus, E_g is decreased and the visible light photocatalytic activity is enhanced [62].

2.2.3 Coupled/Composite TiO₂

Coupling of TiO₂ with another semiconductors having dissimilar energy levels is an accepted way to improve visible light photocatalytic activity of TiO₂ [63]. In semiconductor coupling, the large E_g semiconductors are coupled with low E_g semiconductors. Electrons in the low E_g semiconductor, that has more negative E_g ,

transfer to the larger E_g of TiO_2 . This process hampers the recombination of e^-/h^+ pairs. Movement of the photogenerated charge carriers depends on the CB and VB potential difference between the two semiconductors. Only the low E_g semiconductor absorbs the visible light, during visible light irradiation [53].

The most popular couples are TiO_2/CdS , TiO_2/WO_3 , $\text{TiO}_2/\text{SnO}_2$, TiO_2/MO_3 and, $\text{TiO}_2/\text{Fe}_2\text{O}_3$. Nano carbon based photocatalysts like carbon nanotubes (CNT) and graphene have been tried recently. Graphitic carbon nitride (g- C_3N_4) coupled with TiO_2 has been shown to improve visible light photocatalytic activity of TiO_2 . They possess good chemical stability, high mechanical strength, and high specific surface area. These components supply rapid heat and electron transfer. Also, organic compounds were absorbed by these nano carbons in aqueous solutions [26,64].

2.3 Graphitic Carbon Nitride (g- C_3N_4)

Carbon nitride (C_3N_4) has five allotropes namely; α - C_3N_4 , β - C_3N_4 , cubic- C_3N_4 , pseudocubic- C_3N_4 , and graphitic C_3N_4 . Graphitic carbon nitride (g- C_3N_4) is the most stable allotrope of carbon nitride class under ambient conditions [65]. g- C_3N_4 with various structures and properties can be synthesized using various methods like chemical vapor deposition (CVD), physical vapor deposition (PVD), solid state, solvothermal, ionothermal synthesis, thermal condensation, and single step nitration. Among all the synthesizing routes, thermal condensation with nitrogen-rich solutions is the most prevalent method. Some of the nitrogen-rich sources are melamine, urea, thiourea, cyanamide, dicyanamide, triazoles and guanidine which are cheap, accessible and easily producible.

In recent years, g- C_3N_4 has appealed considerable attention for visible light photocatalytic applications. It has superior visible light photocatalytic activity to many metal oxide semiconductors because of its low E_g energy (ca. 2.7 eV) as compared to TiO_2 [66]. It has remarkable properties for example good chemical stability, low density, and high absorption and acceptable photocatalytic activity in

visible light [67]. It is insoluble in water, ethanol and diethyl ether and toluene which are the most popular solvents. It is resistive to acidic and basic medias due to its Van der Waals forces [68]. Dong et al. [18] published that g-C₃N₄ is non-volatile up to 600 °C but, decomposes at 700 °C. Additionally, g-C₃N₄ is non-toxic, cheap, easily fabricated from nitrogen-rich solutions, and available for enhancing electronic and optical properties [69]. Moreover, its E_g position (-1.3±1.4 eV) makes it suitable for heterojunction construction with TiO₂ [30]. Although g-C₃N₄ has good optical and electronic properties, utilization of g-C₃N₄ in photocatalytic applications is limited due to its low photocatalytic efficiency in visible light. Small specific surface area (4-26 m²/g), lower electrical conductivity, and fast recombination of e⁻/h⁺ pairs are other disadvantages restricting the widespread application of g-C₃N₄ in photocatalytic applications [70]. The recombination of photogenerated charge carriers hampers the formation of radical species responsible for the redox reaction during photocatalytic reactions. Smaller specific surface area negatively affects the light harvesting and reduces the separation time of the charge carriers [70,71]. An E_g of 2.7 eV is large for efficient visible light spectrum [72].

In order to improve charge separation and surface area of g-C₃N₄ hence photocatalytic activity, various nanostructures such as nanoribbons, nanobelts, nanoparticles etc. can be engineered [73] or another modification can be applied by using organic dyes and polymers. But, coupling with other semiconductors (construction of a heterojunction) have been among the most popular strategies practiced in recent years [74]. Creation of g-C₃N₄/TiO₂ heterojunction is an encouraging way to improve visible light photocatalytic activity of both TiO₂ and g-C₃N₄ [75].

2.4 g-C₃N₄/TiO₂ Nanocomposite

In heterojunction systems, the separation time for the charge carriers are encouraged through charge transfers between the two semiconductors so that e⁻/h⁺ recombination rate is reduced and photocatalytic activity of the both constituents are enhanced.

Additionally, TiO₂ nanoparticles are combined with the g-C₃N₄ nanosheets by simple and environmentally friendly methods. Because of the enhanced photocatalytic activity and easy production, they have found various promising applications such as production of clean energy and waste water treatment [30,39].

2.4.1 Production Methods of g-C₃N₄/TiO₂ Nanocomposite

Some researchers [30,66,74] have tried different methods to produce g-C₃N₄/TiO₂ nanocomposites. Production techniques of the g-C₃N₄/TiO₂ can be classified into three main groups [1].

2.4.1.1 Physical Mixing of g-C₃N₄ and TiO₂

In this method, g-C₃N₄ and TiO₂ are synthesized separately. After that, these two constituents are mixed by using physical mixing methods like ball mill or solvent evaporation. Yan et al. [75] produced g-C₃N₄ by heating the melamine powder under Ar gas atmosphere, and TiO₂ was synthesized by using TiCl₄ as a precursor. After synthesizing two components individually, g-C₃N₄/TiO₂ heterojunction structure was obtained by ball milling method. Zhou et al. [37] applied the same method to prepare g-C₃N₄/TiO₂ hybrid structure. They first heated melamine to produce layered structure of g-C₃N₄. Then, they utilized the commercial TiO₂ powder, and mixed it with the synthesized g-C₃N₄. By this way, they achieved a highly photoactive g-C₃N₄/TiO₂ heterostructure.

Evaporation of the dispersion solution is another physical method for synthesizing the g-C₃N₄/TiO₂ heterostructure powders. In this method, both components are dissolved in a solvent that is evaporated until a connection between g-C₃N₄ and TiO₂ structures is made [76,77]. TiO₂ nanosheets are synthesized using tetra butyl titanate (TBOT) as a precursor by solvothermal reaction. Urea is calcined to obtain g-C₃N₄. After that, both constituents are dispersed into methanol and the mixture is sonicated

for 30 min to complete dispersion. Later, methanol is evaporated, remaining powder is dried, and heterostructure is obtained.

These physical synthesis methods are easy methods for mass production but, they are not easy for the control of the consequential morphology. Also, connection between the two powders has lower stability compared to the heterojunction catalysts prepared by other methods [1].

2.4.1.2 Loading g-C₃N₄ on TiO₂

First TiO₂ is prepared by any one of the processes. Then, the TiO₂ produced is added into a g-C₃N₄ precursor solution. After washing, filtering, drying and, calcination g-C₃N₄/TiO₂ nanocomposite is obtained. Wang et al. [77] first synthesized TiO₂ nanorods hydrothermally. Then, they produced g-C₃N₄ using melamine as a precursor through CVD. After that, a fluorine doped tin oxide (FTO) glass was coated by TiO₂ in an autoclave. Next, the TiO₂ coated FTO was treated with melamine so that g-C₃N₄/TiO₂/FTO is obtained. This heterojunction shows photocatalytic activity 10 times better than pure TiO₂/FTO under visible light.

Boonprakob et al. [78] utilized Titanium tetra isopropoxide (TTIP) as a TiO₂ precursor. After hydrolysis and condensation of TTIP solution, TiO₂ nanoparticles were obtained. The TiO₂ nanoparticles and melamine were directly mixed to produce g-C₃N₄/TiO₂ films under Ar flow. Their results revealed that the composite containing 50 wt% g-C₃N₄ shows enhanced photocatalytic efficiency

2.4.1.3 Growing of TiO₂ Nanoparticles on g-C₃N₄ Surface

First g-C₃N₄ is synthesized. Then, TiO₂ precursor is introduced to the g-C₃N₄ synthesized for the growth of TiO₂ on the g-C₃N₄ surfaces. Lu et al. [79] applied this routine to produce of g-C₃N₄/TiO₂ hybrid nano composite with higher photocatalytic activity than phase pure constituents under both UV and the visible light. Shen et al.

[80] produced g-C₃N₄/TiO₂ hybridized structure by using template-free method. First, melamine was heated to obtain g-C₃N₄. Then, synthesized g-C₃N₄ was added to titanium sulfate Ti(SO₄)₂ solution. After that, hydrothermal reaction was allowed to produce g-C₃N₄/TiO₂ nanocomposite. Synthesized nanocomposite possesses superior visible light photocatalytic activity.

Growing TiO₂ is an operational way for the construction of g-C₃N₄/TiO₂ hetero structure even though fully dispersion of TiO₂ is difficult on the surface of g-C₃N₄ because of the rapid hydrolysis ability of titanium precursors. Also, the heterojunctions prepared by this way has higher chemical stability [1,81].

There is no difference between resulting structures of the products prepared by the three different methods [1]. Nevertheless, growing of TiO₂ nanoparticles on g-C₃N₄ surface method was chosen in this study to produce g-C₃N₄/TiO₂ heterojunction photocatalysts due to its advantages over the other methods.

2.4.2 Production Routes of g-C₃N₄/TiO₂ Nanocomposites

g-C₃N₄/TiO₂ nanocomposites are produced through different production routes including one-pot method [35], solvothermal method [36], ball-milling [37], sol-gel process [82], and hydrothermal process [83]. In this section a brief information for the sol-gel and hydrothermal processes will be given since these methods were selected to produce g-C₃N₄/TiO₂ nano composites in this study.

2.4.2.1 Hydrothermal Process

Hydrothermal method enables scientists to control mechanisms of diffusion kinetics, crystallinity and purity of the product, and temperature and time of the reaction(s) taking place during processing. The hydrothermal reactions are also affected by pH and viscosity of the prepared solution [83]. Hao et al. [84] prepared g-C₃N₄/TiO₂ heterojunction photocatalysts by dissolving some amount of melamine in DI water

to obtain a homogeneous solution. After that, TiCl_4 solution was added into the mother solution dropwise and the resultant white solution was transferred to an autoclave. Reaction occurred at $180\text{ }^\circ\text{C}$ for 4 h. Following washing and drying process a g- $\text{C}_3\text{N}_4/\text{TiO}_2$ heterojunction composite was produced.

2.4.2.2 Sol-gel Process

Dispersion of colloidal particles in fluid media is referred to as sol. Water, air, organic liquids and aerosol can be fluid media. The sol-gel process can be employed for the production of different products like ceramics, abrasive minerals, membranes, films, and catalysts under ambient temperatures. In sol-gel process, there are five main steps. First, precursor is mixed with sol or solution to allow hydrolysis and condensation reactions. Then, chemical reactions yield gelation that is followed by drying. Finally curing is applied. Some of the main advantages of this process are lower processing temperature, sample purity, easy control of dopant concentrations, and synthesizing multicomponent compositions in various product forms [85,86].

Sun et al. [82] produced g- $\text{C}_3\text{N}_4/\text{TiO}_2$ composites by modified sol-gel process. First, they prepared g- C_3N_4 suspension by mixing g- C_3N_4 powder with ethanol. TBOT was introduced to suspension during magnetic stirring. Then, water and ethanol was added while stirring continues until TiO_2 colloids immobilize onto g- C_3N_4 . After that, the product obtained was dried and exposed to heat treatment.



CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Materials

Titanium tetra isopropoxide (TTIP, 97%) and melamine powder (2,4,6 Triamino-1,3,5-triazine, 99%) were used as TiO_2 precursor and g- C_3N_4 precursor, respectively to prepare g- $\text{C}_3\text{N}_4/\text{TiO}_2$ photocatalysts by the hydrothermal process. Nitric acid (HNO_3 , 70%) was employed as catalyzer. All chemicals were purchased from Sigma Aldrich. Deionized water (DI) was used for the preparation of solutions. Ethanol (96%, Limko) was used as solvent for the sol-gel synthesis. Methylene Blue (MB, 97%) was utilized as a dye for photocatalytic activity measurements. Except HNO_3 , all chemicals were analytical grade and were used without purification.

3.2 Powder Synthesis

Heterojunction photocatalysts were synthesized via hydrothermal and sol-gel routes.

3.2.1 g- $\text{C}_3\text{N}_4/\text{TiO}_2$ Powder Preparation by the Hydrothermal Process

Hydrothermal synthesis of TiO_2 and g- $\text{C}_3\text{N}_4/\text{TiO}_2$ powders were achieved in a Teflon lined vessel made from hast alloy in a high-pressure reactor (ITO Instruments® Imax). The vessel had 300 mL volume. The working principle of the reactor includes various variables such as dwell time, temperature, and pressure. This system involves a magnetic stirrer which is also covered by Teflon. The speed of the magnetic stirrer could be adjusted between 0 to 1500 rpm. Synthesis temperature is set in a range between 0 and 1000 °C. The pressure changes autogenously depending on the temperature, solution type, and solution volume present in the vessel. The

hydrothermal system has also a cooling system to keep the solution in desired temperature. In this study, acidic hydrothermal method was used to produce g-C₃N₄/TiO₂ heterojunction photocatalysts using HNO₃ as catalyzer.

3.2.1.1 Preparation of the g-C₃N₄ Powder

g-C₃N₄ powder was prepared through heat treatment of melamine powder according to the procedure as described by Tong et al. [19]. First, predetermined amount of melamine powder was placed into an alumina crucible and heated to 550 °C at a heating rate of 2 °/min in an electrical furnace. It was kept at this temperature for 4 h then, cooled to room temperature without controlling the cooling rate but turning the power of the furnace off. After that, the resulting yellow agglomerate was collected and ground by using mortar with pestle to obtain g-C₃N₄ powder. The photograph of g-C₃N₄ powder is shown in Figure 3.1 (a).

3.2.1.2 Preparation of the g-C₃N₄/TiO₂ Powder

The g-C₃N₄/TiO₂ heterojunction photocatalysts were synthesized in one step hydrothermal synthesis by growing of TiO₂ nanoparticles on the surfaces of g-C₃N₄ powders. First, necessary amount of g-C₃N₄ powder was mixed with 118 mL of DI water. Then, this mixture was sonicated by ultrasonic liquid processor (Misonix XL2020TM, NY, US) at 20 kHz vibration frequency for 30 min to disperse the size of g-C₃N₄ sheets and to produce homogeneous suspension. Before catalyzer addition, some time was allowed to reduce the temperature of the suspension to room temperature since sonication increased the temperature of the suspension. After cooling to room temperature, the suspension was magnetic stirred at 200 rpm for 0.5 h. Then, 0.833 mL of HNO₃, used as catalyzer, was added into the suspension to get acid molarity of 0.1 M. Next, 6.67 mL of TTIP was introduced to the yellow color suspension dropwise while magnetic stirring. The TTIP was addition was done at 300 rpm for 30 min.

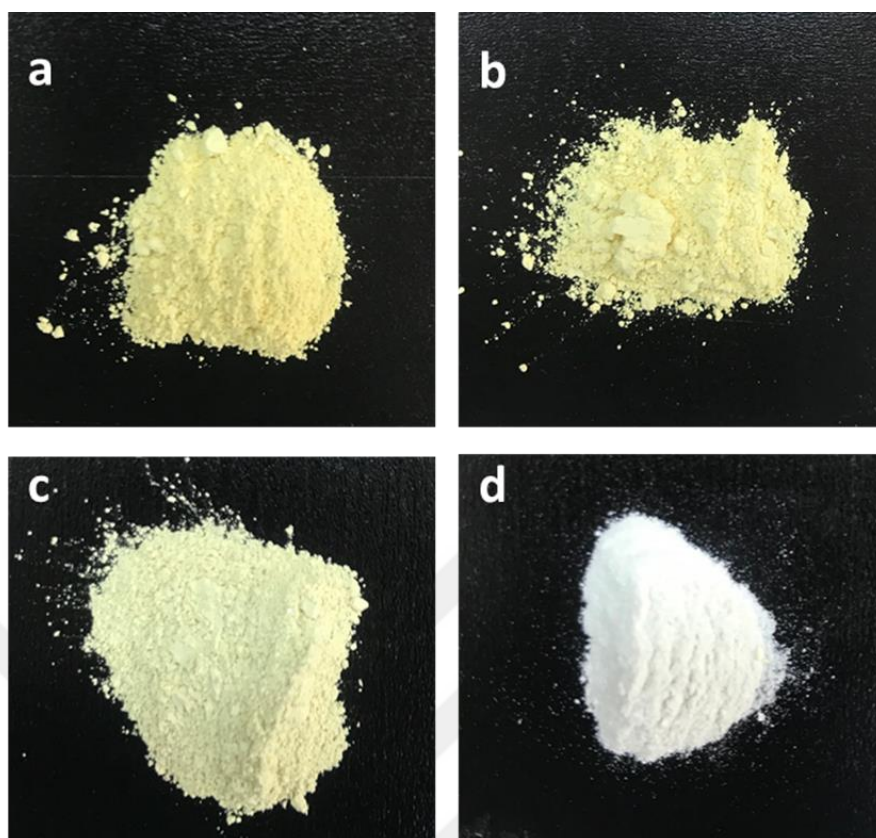


Figure 3.1. Photographs of some of the hydrothermally derived powders. a) $g\text{-C}_3\text{N}_4$, b) TCN-80, c) TCN-20, and d) TiO_2 .

After all, TTIP was dissolved in the suspension, the resultant solution was transferred into the vessel of high-pressure reactor with 300 mL capacity. The hydrothermal synthesis was performed at $110\text{ }^{\circ}\text{C}$ for 1 h. The pressure of the vessel varied autogenously between 0 and 10 bar. After hydrothermal synthesis, the resultant product in light yellow color was collected and washed with DI water several times until the pH become neutral. This product was centrifuged and dried at $80\text{ }^{\circ}\text{C}$ for 24 h. Finally, the dried agglomerates were ground using mortar with pestle to get $g\text{-C}_3\text{N}_4/\text{TiO}_2$ powder. The steps involved in the hydrothermal synthesis of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ powders are shown in Figure 3.2.

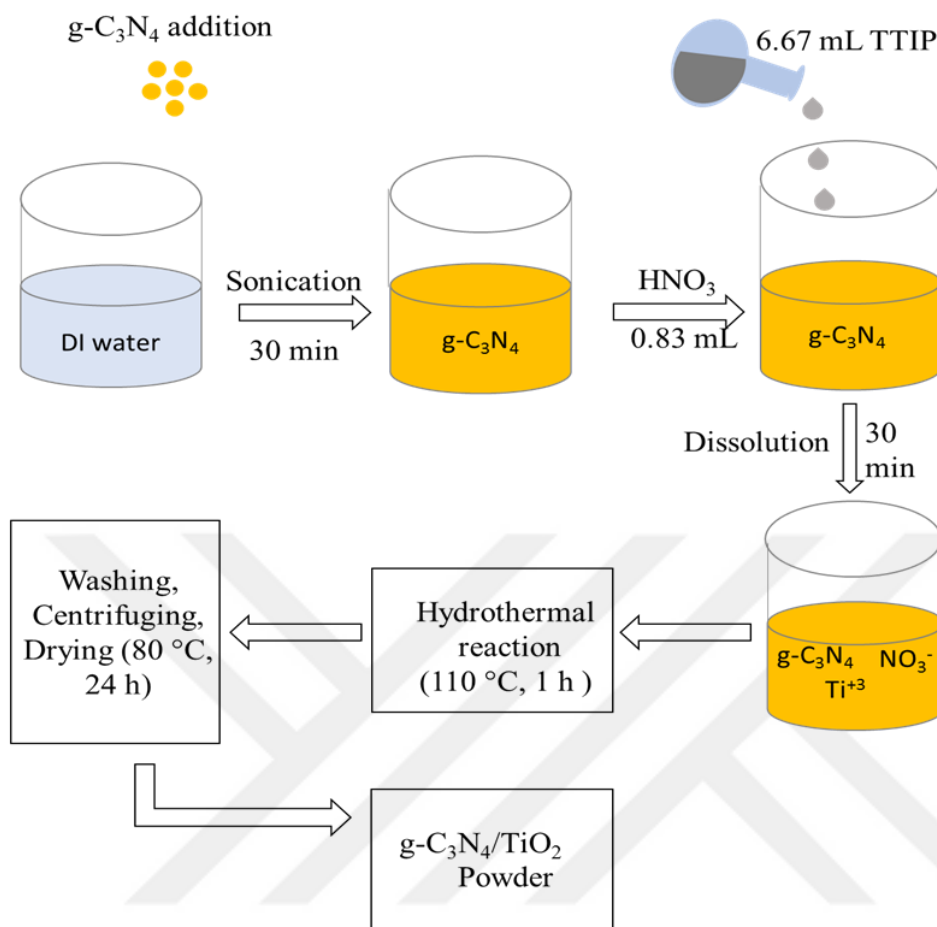


Figure 3.2. Flowchart showing the steps involved in the hydrothermal synthesis of $\text{g-C}_3\text{N}_4/\text{TiO}_2$ powders.

The $\text{g-C}_3\text{N}_4/\text{TiO}_2$ powders synthesized were named based on their $\text{g-C}_3\text{N}_4$ content as TCN-XX, where the last two digits represent the amount (in weight percentage, wt%) of $\text{g-C}_3\text{N}_4$ involved in the powder. The TCN-80 powder was subjected to heat treatment at various temperatures ranging from 350 to 500 °C for 1 h. The heat-treated powders were named with respect to the temperature applied as TCN-80-XXX, where the last three digits represent the temperature applied during heat treatment. Codes of the $\text{g-C}_3\text{N}_4/\text{TiO}_2$ powders synthesized were presented in Table 3.1. Photographs of TCN-20 and TCN-80 powders are shown also in Figure 3.1 (b) and (c).

Table 3.1 Code of the hydrothermally derived g-C₃N₄/TiO₂ powders.

Powder code	g-C ₃ N ₄ content (wt%)	TiO ₂ content (wt%)	Calcination Temperature (°C)
TCN-20	20	80	-
TCN-50	50	50	-
TCN-60	60	40	-
TCN-70	70	30	-
TCN-80	80	20	-
TCN-90	90	10	-
TCN-80-350	80	20	350
TCN-80-400	80	30	400
TCN-80-450	80	20	450
TCN-80-500	80	20	500

3.2.1.3 Preparation of TiO₂ Powder

In addition to g-C₃N₄/TiO₂ powders, TiO₂ powders were hydrothermally synthesized in the same experimental conditions to compare the photocatalytic properties of g-C₃N₄/TiO₂ and TiO₂ powders prepared at the same conditions. First, 0.833 mL of HNO₃ was mixed with 118 mL of DI water to obtain acid molarity of 0.1 M. Then, 6.67 mL of TTIP was added dropwise into the acid solution during magnetic stirring for 30 min. After complete dissolution of the TTIP in the solution, a homogeneous and transparent solution was obtained. This homogeneous solution was transferred into the vessel of the high-pressure autoclave. Then, hydrothermal reaction was allowed to occur at 110 °C for 1 h. After the hydrothermal synthesis, the solution was cooled in the vessel to room temperature. After that it was collected, washed for several times, centrifuged and dried at 80 °C for 24 h in an oven. The synthesized product was TiO₂ powder and was named as TiO₂. Some amount of the TiO₂ powder was exposed to heat treatment at 400 °C for 1 h. The heat treated TiO₂ powder was named as TiO₂-400.

3.2.2 g-C₃N₄/TiO₂ Powder Preparation by Sol-gel Process

3.2.2.1 Preparation of g-C₃N₄/TiO₂ Powder

The first step in the synthesis of g-C₃N₄/TiO₂ powders via sol-gel method was the same as that of TiO₂ powder. First, 54.75 mL of ethanol was diluted with 67.5 mL of DI water and 0.275 mL of HNO₃ was added into this solution. Then, 18.5 mL of TTIP was supplemented dropwise. The solution was stirred until all TTIP was dissolved. Dissolution process took approximately 1 h. After that, predetermined amount of g-C₃N₄ powder that varied according to weight percentages of g-C₃N₄ in the g-C₃N₄/TiO₂ composite was added into the solution. The solution containing g-C₃N₄ powder was mixed at 300 rpm for 48 h using a magnetic stirrer. Later, the solution was washed with DI water for several times until pH became neutral, centrifuged at 6000 rpm for 10 min, and dried at 80 °C for 24 h. The dried agglomerates were collected and ground using mortar with pestle to get g-C₃N₄/TiO₂ powder. The steps involved in the sol-gel synthesis of g-C₃N₄/TiO₂ powders are shown in Figure 3.3.

Some amount of the sol-gel derived g-C₃N₄/TiO₂ powder was exposed to a regulated heat treatment at 400 °C for 2 h. The heating rate was 5 °/min. The g-C₃N₄/TiO₂ powders derived by the sol-gel process were named based on their g-C₃N₄ content as STCN-XX, where the last two digits represent the amount (in weight percentage, wt%) of g-C₃N₄ involved in the powder. All the sol-gel derived powders were heat treated at 400 °C for 1 h. Codes of the sol-gel derived g-C₃N₄/TiO₂ powders are shown in Table 3.2. Photographs of STCN-80 and STCN-20 powders are shown in Figure 3.4 (a) and (b), respectively.

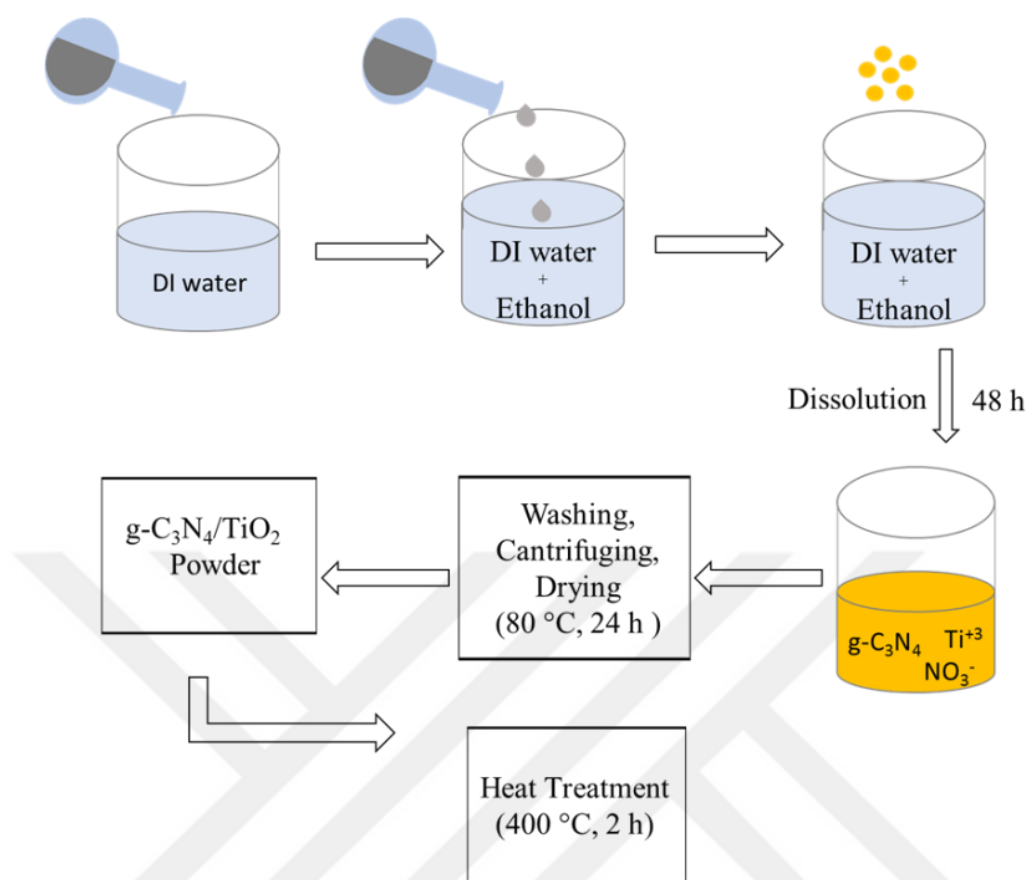


Figure 3.3. Flowchart showing the steps involved in the sol-gel synthesis of g-C₃N₄/TiO₂ powders.

Table 3.2 Codes of the sol-gel derived powders.

Powder code	g-C ₃ N ₄ content (wt%)	TiO ₂ content (wt%)	Calcination temperature (°C)
STiO ₂	-	100	400
STCN-20	20	80	400
STCN-50	50	50	400
STCN-80	80	20	400



Figure 3.4. Photos of some of the sol-gel derived powders. a) STCN-80, b) STCN-20, and c) STiO₂.

3.2.2.2 Synthesis of TiO₂ Powder

In addition to g-C₃N₄/TiO₂ powders, TiO₂ powders were synthesized by the sol-gel process in the same experimental conditions to compare the photocatalytic properties of g-C₃N₄/TiO₂ and TiO₂ powders prepared at the same conditions. First, 67.5 mL of DI water was mixed with 54.75 mL of ethanol in a glass beaker. Then, this mixture was blended during magnetic stirring at 150 rpm for 30 min. Next, 0.275 mL of HNO₃ was added into solution as a catalyzer to get 0.1 M acid molarity. After that, 18.5 mL TTIP was added into the solution dropwise while magnetic stirring at 300 rpm for 48 h. After 48 h, all TTIP dissolved in the solution and a white milky solution was obtained. This solution was washed with DI water several times until pH become neutral. Finally, the resultant solution was filtered and centrifuged at 6000 rpm for 10 min. The agglomerates collected were dried at 80 °C for 24 h in an oven. The

agglomerates synthesized were ground using mortar with pestle. At the end, approximately 3 g of TiO₂ powder was obtained. Some amount of the TiO₂ powder was exposed to a regulated heat treatment at 400 °C for 2 h at a heating rate of 5°/min. The powders had white color after heat treatment and were named as STiO₂ as shown in Figure 3.4 (c).

3.3 Characterization of the Powders

3.3.1 Particle Size Analysis

Particle size analysis of the powders prepared was done using a particle size analyzer (Mastersizer 2000, Malvern Panalytical, Malvern, UK). It measures the size of particles in the range from 0.01 to 3000 µm. It uses both helium neon and solid-state light source for coarser and finer particles, respectively.

3.3.2 X-Ray Diffraction (XRD) Analysis

XRD analysis was done to identify of the phases present in the powders prepared using an X-Ray diffractometer (AXS D8 Advance A25, Bruker, Tokyo, Japan). Powders were scanned in the two-theta range between 10 and 70° at a scanning rate of 2°/min using CuKα radiation at wavelength (λ) of 1.5406 Å. The applied voltage and current were 40 kV and 40 mA, respectively. The peak positions and their intensities for the phases developed were quoted from the Joint Committee on Powder Diffraction Standards (JCPDS) database. The verification of the phase identification was confirmed using Diffrac. Eva. 3.1 software program.

Size of crystallites was calculated from the diffraction line of XRD assuming all the crystallites have spherical shape by using Debye-Scherrer formula [87]:

$$D = \frac{0.9}{\beta \cos \theta} \quad \text{Eq. 3.1}$$

where;

λ : 0.154056 nm and represents the X-ray wavelength from Cu K α radiation

β : full width at half maximum (FWHM).

3.3.3 Field Emission Scanning Electron Microscopy (FESEM) and Elemental Analysis

Size, shape, and morphology of the powders synthesized were examined by field emission scanning microscope (FESEM, Nova, Nanosem) at an operating voltage range between 18 and 20 kV. Before FESEM analysis, all powders were coated by gold using gold sputter (Quorum SC7640, UK) to get desired conductivity. Elemental and compositional analyses were done using an energy dispersive X-ray spectrometer (EDS, JEOL 2100 F, Tokyo, Japan). EDS was operated at 20 kV.

3.3.4 Fourier Transform Infrared Spectra (FT-IR) Analysis

FT-IR analysis was applied to identify chemical structures and molecular interactions of the powders synthesized using an FTIR spectrometer (Perkin Elmer, USA). Before the analysis, the powder was mixed with the conventional KBr powder. The synthesized powder to KBr weight ratio was 3:200. Then, the mixture was uniaxially pressed (~7 tons, for 40 sec) to form pellets. FT-IR data was collected in a range between 4000 cm⁻¹ and 500 cm⁻¹ by using absorbance mode.

3.3.5 Raman Spectroscopy Analysis

Raman spectroscopy analysis was performed to identify crystalline phases present in the powders synthesized using dispersive Raman spectrometer (Renishaw in Via Raman Microscope, UK). Powders were analyzed using ccd detector with an

excitation of 785 nm/300 mW variable diode laser light. Analyses were conducted at a range between 100 cm⁻¹ and 1600 cm⁻¹ Raman shifts.

3.4 Property Measurements of the Powder

3.4.1 Diffuse Reflectance Spectra (DRS) Analysis

The band gap measurements of the powders were performed using a diffuse reflector apparatus attached to the UV-Vis spectrophotometer (Scinco, S-3100, Korea). First, measurement was done at dark. Then, a completely white blank sample was measured to obtain baseline. White blank measurements were applied depending on the USRS-99-010 standard. After these measurements, measurements of the synthesized powders were done. The band gap values of the powders are calculated using following equation [88].

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad \text{Eq. 3.2}$$

where;

α : absorption coefficient

$h\nu$: photon energy

A: constant

E_g : the band gap energy

$n=1$ for direct transition, and $n=4$ for indirect transition.

Absorbance percent versus wavelength graph was transformed to $(\alpha h\nu)^2$ versus $h\nu$ plot. Then, E_g values of the powders were read from the intercept of the tangent point in X axis ($h\nu$) of the graph.

Also, conduction band and valance band potentials of the pristine TiO₂ and the g-C₃N₄ powders were calculated using the formulae given below.

$$E_{VB} = X - E^e + 0.5E_g \quad \text{Eq. 3.3}$$

$$E_{CB} = E_{VB} - E_g \quad \text{Eq. 3.4}$$

where;

E_{VB} and E_{CB} : valance band and the conduction band potentials, respectively

E^e : energy of free electrons on the hydrogen scale which is ~ 4.5 eV

E_g : the band gap values of the semiconductors

X : geometric means of electronegativity values of the components of the semiconductors. X values of TiO_2 and $\text{g-C}_3\text{N}_4$ were taken 5.81 and 4.73 eV, respectively [89].

3.4.2 Photocatalytic Activity Measurements

The photocatalytic activity of the powders synthesized was evaluated through methylene blue (MB) degradation test under 500 W Xenon lamp (XSS-5XD, Shangai Biological Science Inc, China) using a UV-Vis spectrophotometer (Scinco, S-3100). First, an aqueous MB solution was prepared by dissolving 0.01 g of MB powder in 1 L of DI water during magnetic stirring to obtain an initial MB concentration of 10 ppm. MB is affected from the daylight. Thus, this solution was prepared in dark.

For the activity measurements, 0.1 g of the powder synthesized was mixed with 100 mL of the aqueous MB solution. Before exposing the suspension to Xenon light, it was magnetic stirred continuously in dark for 30 min in a homemade wooden box to assure the absorption/desorption equilibrium. Then, 4 mL of this suspension was taken in every 5 min using syringe filters (Millex Millipore, $0.22 \mu\text{m}$) and transferred to the UV-Vis spectrophotometer for measurement. It was recognized that absorption/degradation equilibrium was achieved after 30 min. Accordingly, dark stirring step of the MB degradation test was 30 min for all experiments.

Degradation of DI water was measured using run blank button of the spectrophotometer to get a baseline, then MB solution without any powder addition was measured using run sample button of the spectrophotometer to get a reference. For the MB degradation test of the powders synthesized, 50 mg of the synthesized powder was mixed with 50 mL of the MB solution inside of the wooden box. Prepared suspension was kept for 30 min in dark while magnetic stirring to measure absorbance values. After dark measurement, Xenon lamp was turned on. Then, 4 mL of this suspension was taken in every hour using syringe filters and transferred to the UV-Vis spectrophotometer for measurement. After 1, 2 and 3 h under solar (UV + Vis) light illumination degradation of MB was measured.

UV-Vis spectrophotometer gives absorbance data in a range between 200-800 nm. Top value of the peaks corresponds to 664 nm. Thus, photocatalytic activity calculation was done according to the following equation:

$$\text{Degradation \%} = (C_0 - C)/C_0 \times 100 \quad \text{Eq. 3.5}$$

where;

C_0 : initial concentrations of the MB and

C : concentrations of MB at dark and at different irradiation time, respectively.



CHAPTER 4

RESULTS AND DISCUSSION: PHOTOCATALYTIC ACTIVITY OF THE g-C₃N₄/TiO₂ HETEROJUNCTION COMPOSITES DERIVED BY THE HYDROTHERMAL PROCESS

4.1 General Remarks

In this part of the thesis the results of the hydrothermally derived g-C₃N₄/TiO₂ heterojunction composites were presented and discussed. Hydrothermal method was selected because of the controllable synthesis conditions, feasibility, and good crystallinity in the products. Six different composites with increasing weight percentage (wt%) of g-C₃N₄ from 20 to 90 wt% with 10% increments were prepared. In addition, the composite containing 80 wt% g-C₃N₄ was heat treated at calcination temperatures of 350, 400, 450, and 500 °C. After preparation, effect of the g-C₃N₄ content on g-C₃N₄/TiO₂ composites and the heat treatment temperatures on the microstructure developed were investigated by various characterization techniques. Finally, photocatalytic activity of g-C₃N₄/TiO₂ heterojunction composites were measured and compared with that of TiO₂ and g-C₃N₄ powders along with a commercially available TiO₂ powder. Moreover, the possible photocatalytic mechanism taking place in the g-C₃N₄/TiO₂ nanocomposites upon solar light illumination was outlined.

The g-C₃N₄/TiO₂ nanocomposites prepared were yellow in color. Depending on the g-C₃N₄ content they appeared in light yellow to dark yellow colors as indicated in Figure 3.1. As the g-C₃N₄ content decreases, the yellow color becomes lighter approaching the white color of pristine TiO₂ powder.

4.2 Characterization of the Powders

4.2.1 Particle Size Analysis

Hereafter, the g-C₃N₄ powder prepared will be referred to as pristine g-C₃N₄. The particle size distribution curve of pristine g-C₃N₄ powder is shown in Figure 4.1. The pristine g-C₃N₄ powder has trimodal distribution meaning that the particles are composed of fine, medium, and coarse size of particles. Fine, medium, and coarse particles have the average size of ~0.6, ~10.5, and ~200 μm , respectively. The particle size analysis suggests that size of the g-C₃N₄ particles ranges between 0.28 to 870 μm . The d_{10} , d_{50} , and d_{90} values are 6.2, 98.6, and 278.2 μm , respectively.

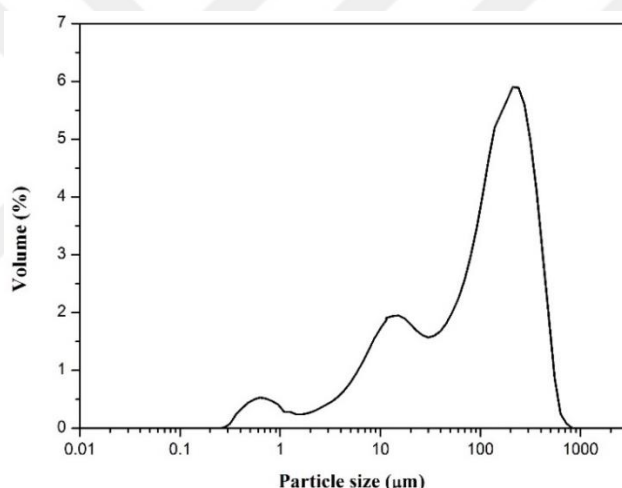


Figure 4.1. Particle size distribution curve of g-C₃N₄ powder.

The particle size distribution curve of the TiO₂ powder prepared, hereafter will be referred to as pristine TiO₂, is shown in Figure 4.2. The pristine TiO₂ powder shows bimodal distribution, meaning that the particles are composed of fine and coarse size of particles. Fine and coarse particles have the average size of ~0.7 and ~57.5 μm , respectively. The particle size analysis suggests that size of the particle's ranges between d_{10} = 3.6 μm and d_{90} =173.6 μm . The average size is 43.6 μm .

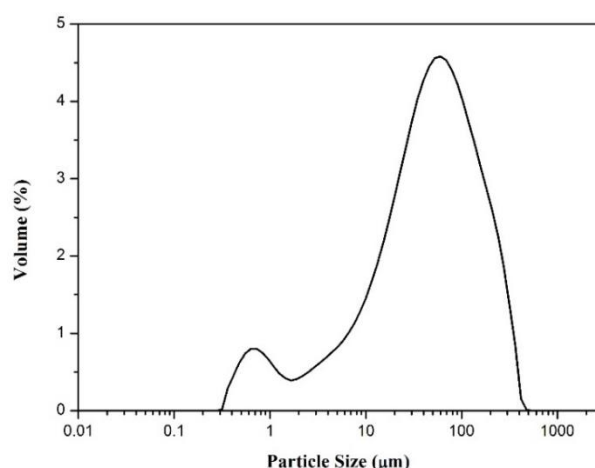


Figure 4.2. Particle size distribution curve of TiO₂ powders.

After this point, the g-C₃N₄/TiO₂ powders prepared will be referred to the codes presented in Table 3.1. The particle size distribution curve of the hydrothermally derived TCN-80 powder is shown in Figure 4.3. The particle size analysis recommends that TCN-80 powder has trimodal distribution. Fine, medium, and coarse particles have the average size of ~0.2, ~0.7, and ~6.4 μm, respectively. A 10% of the particles have sizes smaller than 0.1 μm whereas, a 90% of the particles have sizes smaller than 5.7 μm. Mean size of the particles is 0.2 μm, which is smaller than that of the pristine g-C₃N₄ and TiO₂ powders. Obviously, the hydrothermal treatment at 110 °C for 1 h decreased the particle size and narrowed the particle size distribution range of both pristine g-C₃N₄ and TiO₂ powders.

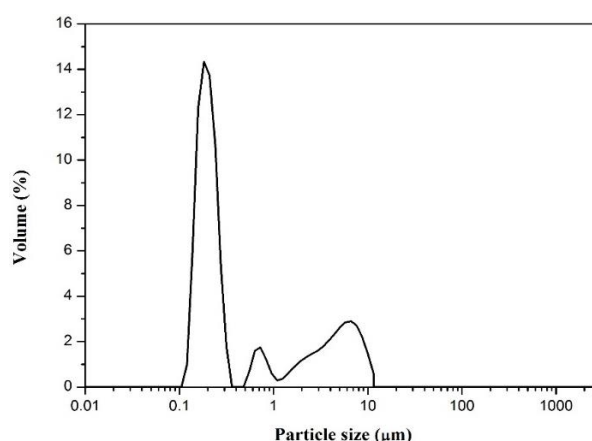


Figure 4.3. Particle size distribution curve of TCN-80 powder.

4.2.2 X-Ray Diffraction (XRD) Analysis

The XRD pattern of pristine g-C₃N₄ is shown in Figure 4.4. The diffraction peaks at 13.0° and 27.4° were attributed to characteristic peaks of (100) and (002) planes of g-C₃N₄ (JCPDS 01-087-1526). The diffraction peaks at 44.5° and 56.5° belong to (201) and (004) planes, respectively of hexagonal g-C₃N₄ (JCPDS 01-087-1526). Moreover, there is a small but visible peak at 17.75° belonging to (020) planes for the leftover carbon phase (JCPDS 01-073-5048). The data imply that pristine g-C₃N₄ is analytically pure.

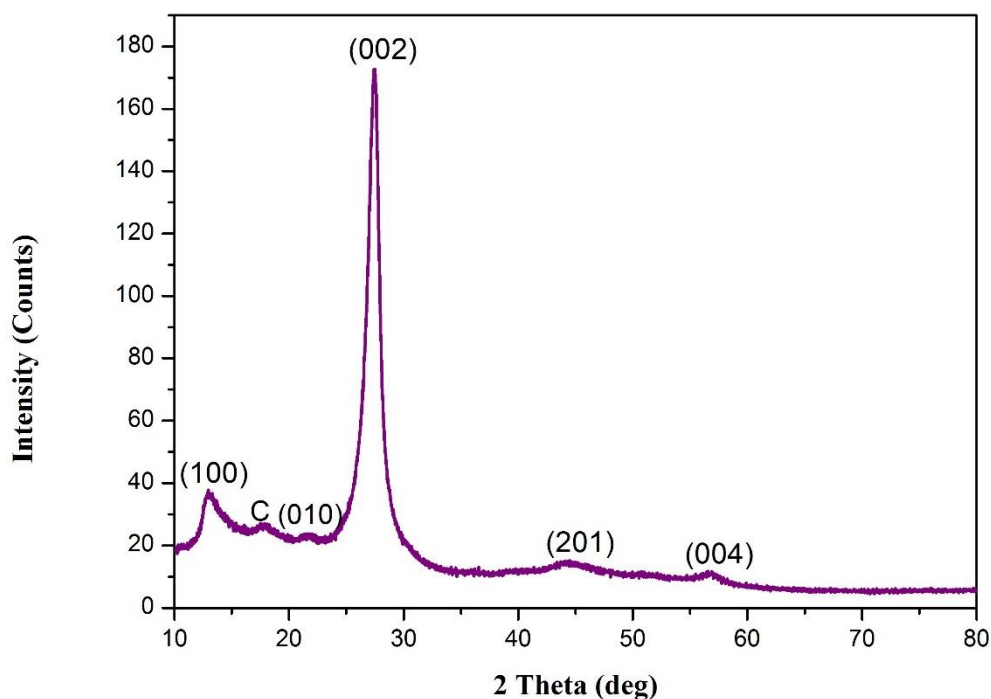


Figure 4.4. XRD pattern of pristine g-C₃N₄ powder.

The XRD pattern of the pristine TiO₂ powder derived by the hydrothermal process is shown in Figure 4.5. The diffraction peaks located at 25.4°, 37.6°, 48°, 54°, and 63° belong to (101), (004), (200), (105), and (204) planes of tetragonal anatase TiO₂ (JCPDS 00-021-1272), respectively. The diffraction peaks located at 25.4° and 30.8° are the characteristic peaks of (120) and (121) planes of brookite TiO₂ (JCPDS 00-029-1360). No diffraction peaks belonging to the other polymorph of TiO₂ (rutile)

or other crystalline phases or contaminations were detected. The data imply that pristine TiO_2 is analytically pure. After this point, the peak angles presented in the text are for the 2θ angles.

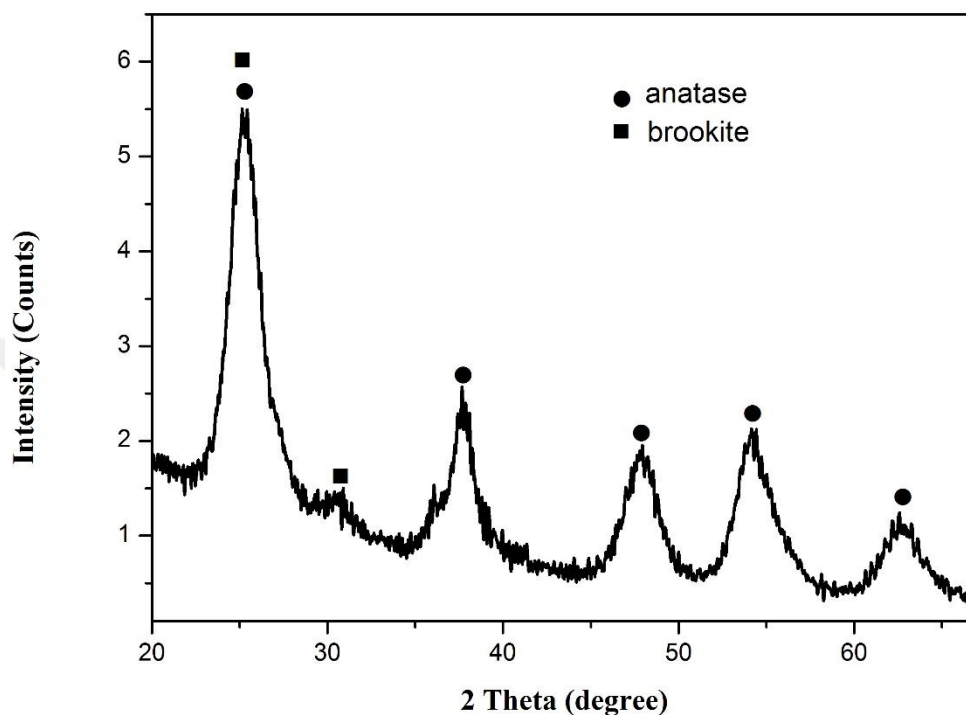


Figure 4.5. XRD pattern of pristine TiO_2 .

The XRD patterns of the TCN powders are shown in Figure 4.6. The XRD patterns of the pristine TiO_2 and pristine $\text{g-C}_3\text{N}_4$ powders are included in Figure 4.6 for better understanding the peak positions in TCN composites. The XRD patterns of all TCN powders exhibit only main diffraction peaks belonging to only characteristic anatase TiO_2 and $\text{g-C}_3\text{N}_4$ crystallites. It is evident that hydrothermal synthesis hindered the development of brookite crystallites during hydrothermal reaction(s). Of course, another possibility is that the amount of brookite phase is very small so that it is below the detection limit of the diffractometer. Hence, XRD analysis may not be capable of detecting the brookite crystallites. Furthermore, because of the low synthesis temperature of 110°C , there is no rutile phase in the prepared TCN powders.

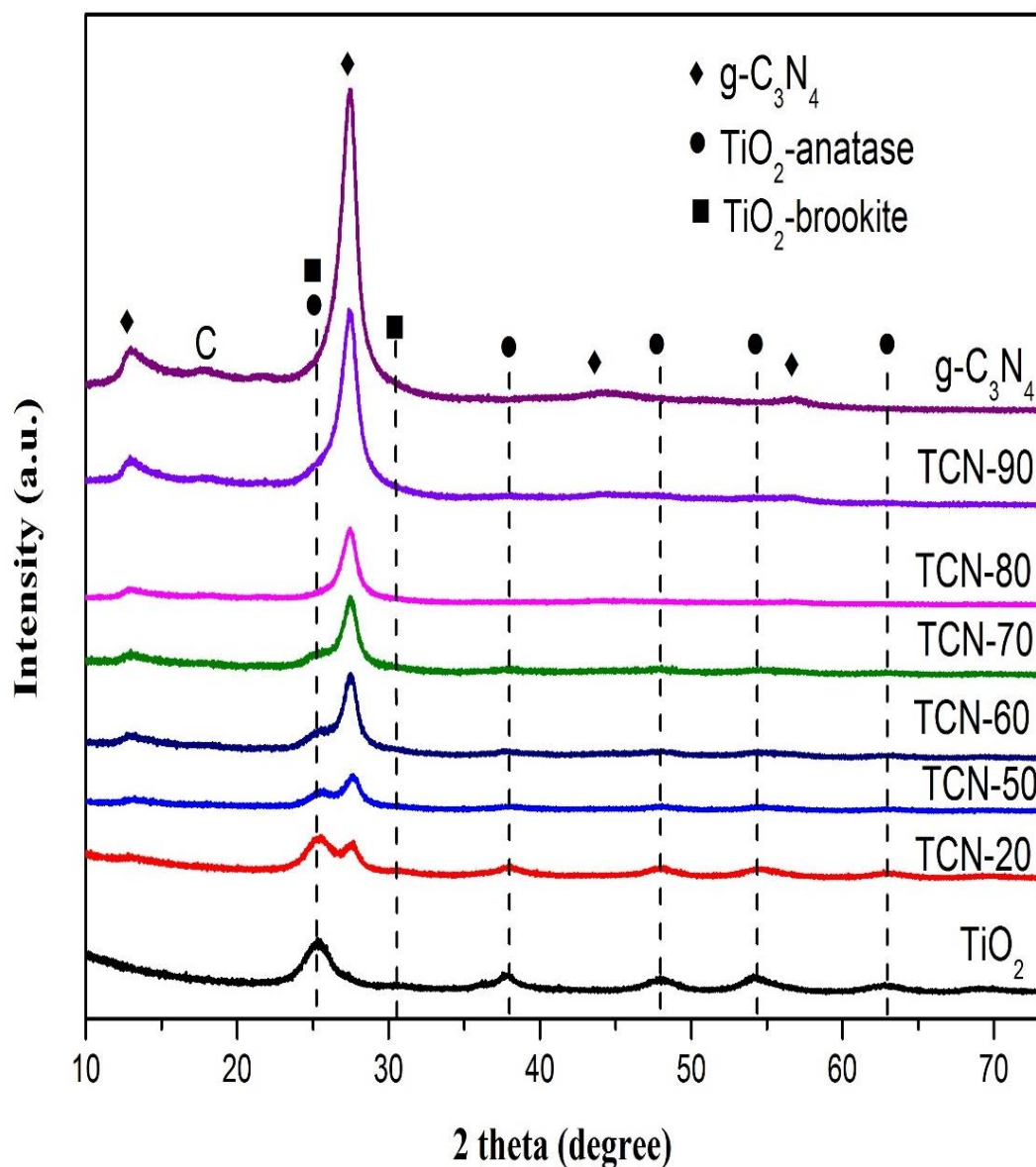


Figure 4.6. XRD patterns of the hydrothermally derived TCN powders together with pristine g-C₃N₄ and TiO₂ powders.

As seen in Figure 4.6, the intensity of the peak of g-C₃N₄ at 27.4° increased as the g-C₃N₄ content in the TCN powders increased without shifting the g-C₃N₄ peak position to higher or lower angles. The intensity of the main characteristic peak of the anatase TiO₂ at 25.4° belonging to 101 planes gradually decreased and eventually disappeared when the g-C₃N₄ content was 50 %. Anatase phase was not detected in

the XRD patterns of the TCN powders containing more than 50 wt% of g-C₃N₄ because of the overlapping of the main characteristic peak of the anatase with the peak of g-C₃N₄. The XRD peaks belonging to the anatase and g-C₃N₄ phases are separated for TCN-20 and TCN-50 powders. Li et. al [82] published similar results. They reported that the intensity of peak at 27.6° belonging to g-C₃N₄ increases while main characteristic peak of TiO₂ at 25.2° decreases as g-C₃N₄ content in the g-C₃N₄/TiO₂ nanocomposite is increased.

Table 4.1 shows the crystallite sizes of the TCN powders together with pristine TiO₂ and pristine g-C₃N₄ powders. The crystallite sizes were calculated by using Debye-Scherrer formula. The anatase crystallites have size of 3.6 nm in pristine TiO₂. This value is almost the same as that 3.9 nm reported by Erdogan et al. [90] for TiO₂ containing only anatase phase. The crystallite size of pristine g-C₃N₄ is 5.01 nm. Svoboda et al. [91] published alike values. g-C₃N₄ powders prepared at different synthesis temperatures have variable crystalline sizes ranging between 4 and 6 nm. It was recognized that the data obtained by the XRD analysis do not agree with the data obtained by the particle size analysis as reported in Section 4.2.1. Because particle size and crystallite size are different from each other. Crystallite size is the smallest crystal in the powder form which is commonly calculated by using Debye-Scherrer formula. However, particle size reports a value for a single crystallite or for an agglomerate of several crystallites. Particle size cannot be smaller than crystallite size but, they may be the same in ultrafine particles [92]. This is an explanation of why the sizes reported in Section 4.2.1 are certainly bigger than the ones presented in Table 4.1. The size of anatase crystallites decreased with increasing g-C₃N₄ content in TCN powders. Because of the insufficient intensity of anatase peak at 25.4° in the XRD patterns of TCN-80 and TCN-90 powders, the anatase crystallite size for these powders could be calculated. The findings are in accord with the results published by Hao et al. [84] who reported that the composite formation provides a tendency to increase anatase TiO₂ phase.

There is no information in the literature related to the crystallite size of the g-C₃N₄ phase present in the g-C₃N₄/TiO₂ heterojunction composites. Some researchers calculated only average crystallite size in the composites [52,84,93] However, when compared to pristine g-C₃N₄ powder, crystallite size of the g-C₃N₄ phase present in TCN powders decreased with small additions of g-C₃N₄, i.e. until the g-C₃N₄ content reaches 60 wt%. When g-C₃N₄ content is more than TiO₂ content in the composites, size of the g-C₃N₄ crystallites present in TCN powders increased. Our fundamental understanding to explain the fluctuations in the size of the g-C₃N₄ crystallites in TCN powders is yet limited. Further investigation is needed to elucidate the reversal in the size of the g-C₃N₄ crystallites with increasing g-C₃N₄ content.

Table 4.1 Size of the crystallites present in the hydrothermally derived powders.

Powder name	Crystallite Size (nm)	
	Anatase	g-C ₃ N ₄
TiO ₂	3.60	-
TCN-20	3.57	4.17
TCN-50	3.12	4.91
TCN-60	3.11	5.55
TCN-70	2.80	5.98
TCN-80	-	6.13
TCN-90	-	5.14
g-C ₃ N ₄	-	5.01

Figure 4.7 shows the XRD pattern of TCN-80 powder together with the XRD patterns taken after heat treating the same composite at various temperatures ranging from 350 to 500 °C. XRD analysis of the TCN powders was performed between at 10 and 70°. The main characteristic peaks belonging to the anatase-TiO₂ and g-C₃N₄ are detected in all TCN powders.

In TCN-80, the main characteristic anatase peak located at 25.4° was not detected due to the overlapping of the anatase and g-C₃N₄ peaks. When heat treatment temperature was increased, the intensity of this main anatase peak increased as seen in Figure 4.7. The anatase peak was distinguished by naked eye clearly especially in the patterns of TCN-80-450 and TCN-80-500 powders. Also, with increasing heat treatment temperature, the XRD peak belonging to the g-C₃N₄ phase weakened due to decomposition of g-C₃N₄. Dong et al. [18] stated that g-C₃N₄ decomposes fully at the temperatures up to 700 °C. In this study the decomposition of g-C₃N₄ started at lower temperatures, which inhibited overlapping of the peaks and reduced the intensity of g-C₃N₄ peak suggesting that the amount of g-C₃N₄ decreased. The reasons why the decomposition of g-C₃N₄ started at lower temperatures need further detailed investigations.

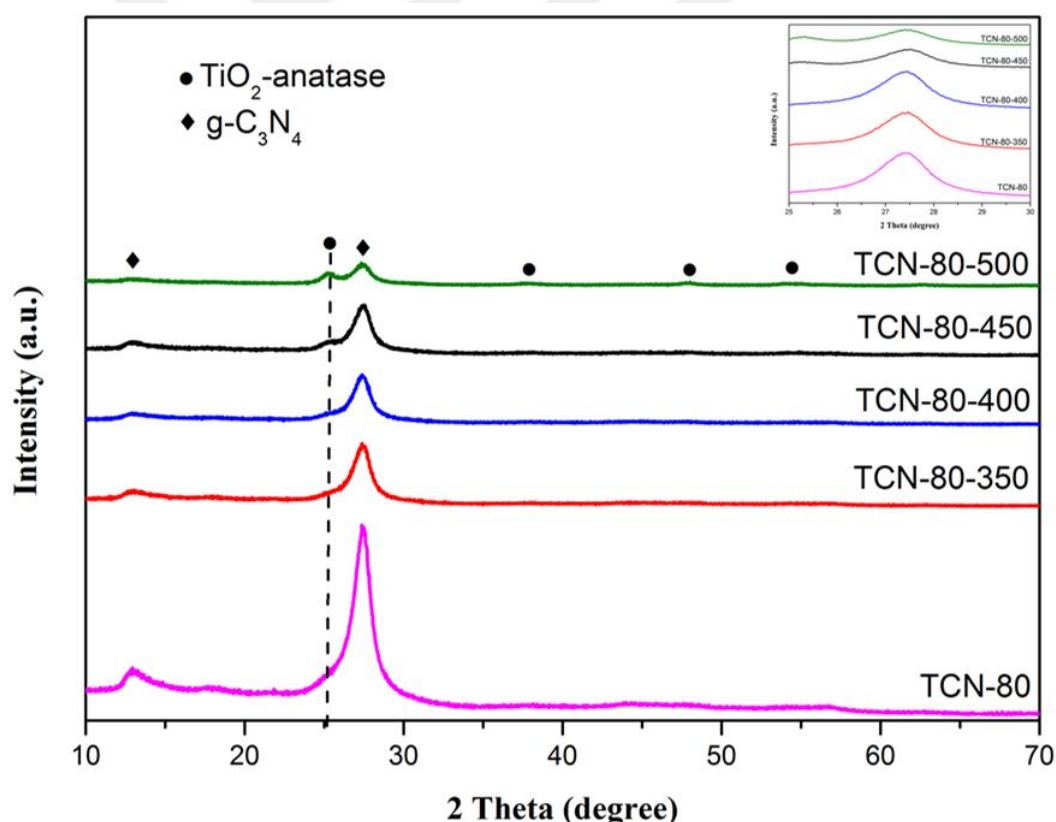


Figure 4.7. XRD patterns of TCN-80 powder before and after heat treatment at various temperatures.

The heat treatment also causes anatase to rutile transition in the temperature range between 600-700 °C [94]. However, in the TCN powders anatase crystallites transformed to rutile crystallites at lower temperatures. The XRD peak at 27.3° corresponding to (110) planes of the main characteristic peak of rutile phase of TiO₂ (JCPDS 00-021-1276) was detected in the pattern of TCN-80-500 powder but, it was not detected in all heat-treated TCN powders in the 25-30° range. Main characteristic peaks of rutile and g-C₃N₄ at 27.3° and 27.4°, respectively are very close to each other and mostly overlaps. Thus, concealment of rutile phase in some of the heat treated TCN powders may be due to the overlapping of the peaks. It is predicted that increasing heat treatment temperature increases the rutile phase. However, the intensity of the peak at 27.4° decreased with increasing temperature as shown in the inset in Figure 4.7. This finding verifies that there is no overlapping between the rutile and g-C₃N₄ particles. The peak present at 27.4° belongs only to g-C₃N₄ phase.

In order to find out whether rutile phase forms in pristine TiO₂ powder during heat treatment or not, pristine TiO₂ powder was heat treated at 400 °C. This powder was named TiO₂-400. Rutile phase was detected clearly in the XRD pattern of TiO₂-400 powder as shown in Figure 4.8. The XRD peaks at 27.3°, 36°, 41.3°, 54.4°, and 62.8° corresponds to (110), (101), (111), (211), and (002) planes of the rutile phase of TiO₂ (JCPDS 00-021-1276). The XRD pattern suggested that the powder also contains anatase and brookite phases of TiO₂.

Table 4.2 presents the crystallite sizes of phases developed in the heat-treated TCN-80 powders. The crystallite size of the anatase phase could not be calculated in the TCN-80 powders heat treated at 350, 400, and 450 °C because of the insufficient intensity of the anatase peak. It is recognized that crystallite size of anatase TiO₂ grows to 5.45 nm upon heat treatment of TCN-80 powder at 500 °C. However, there is a fluctuation in the size of g-C₃N₄ crystallites present in the heat-treated TCN-80 powders. The reason is unknown to us at the present time. Nonetheless, it is believed that the size fluctuation is related to the disintegration of g-C₃N₄ particles that decompose and shrink as the heat treatment temperature increases. It is for sure that

increase in temperature causes a decrease in size of g-C₃N₄ crystallites. See Table 4.2. As mentioned earlier, there is no information reported in the open literature for the crystallite size of the g-C₃N₄ phase present in the g-C₃N₄/TiO₂ powders for comparison.

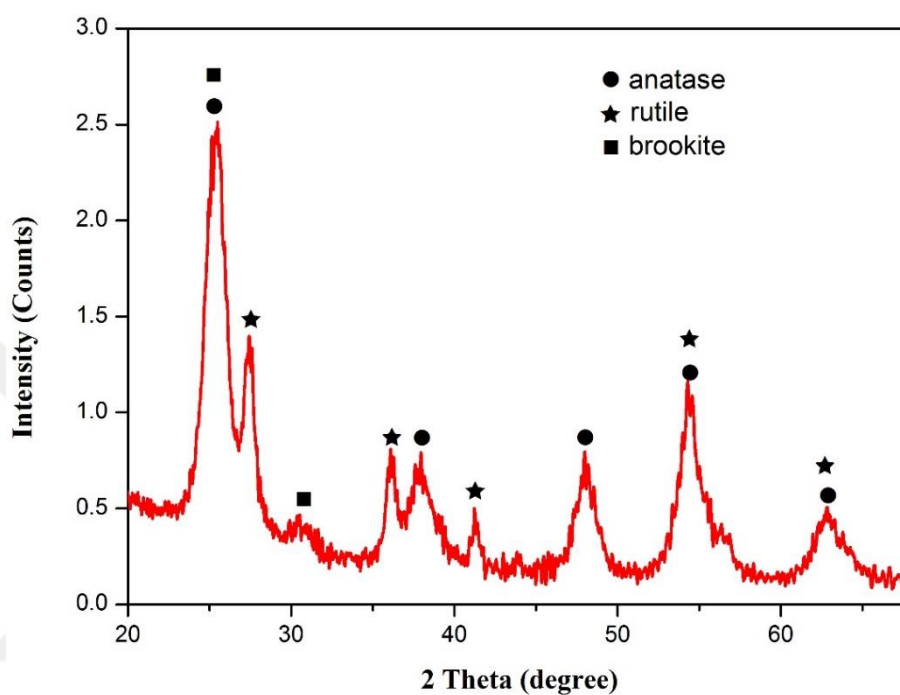


Figure 4.8. XRD pattern of TiO₂-400 powder.

Table 4.2 Crystallite sizes of heat-treated TCN-80 powders.

Powder name	Crystallite Size (nm)	
	Anatase	g-C ₃ N ₄
TCN-80-350	-	5.14
TCN-80-400	-	5.04
TCN-80-450	-	4.98
TCN-80-500	5.45	4.73

4.2.3 Morphological and Elemental Analysis

Figure 4.9 shows the representative FESEM images taken from the surface of pristine g-C₃N₄ and pristine TiO₂ powders together with TCN powders. The effect of TiO₂ content on the morphology of TCN powders was examined in detail. The images for TCN powders were taken at 100000 magnifications. However, the magnification of the image of pristine g-C₃N₄ powder is 10000 though that of pristine TiO₂ powder is 250000. As seen in Figure 4.9 (a), pristine g-C₃N₄ particles consist of a lamellar structure with particles of various sizes ranging from 1 μm to 7 μm . The layers stacked with each other due to thermal polymerization. Also, surfaces of the layers are smooth and flat without irregularities. Size of pristine TiO₂ nanoparticles varies between 12 nm and 32 nm as demonstrated in Figure 4.9 (b). All TiO₂ nanoparticles seem in nearly spherical shape and their morphologies are almost uniform.

The FESEM examinations of TCN powders revealed that lamellar structure of pristine g-C₃N₄ remained in TCN powders but, its surface became rougher as the TiO₂ crystallites grew and attached on their surfaces and covered them as shown in Figure 4.9 (c)-(h). It is remarked that dosing of g-C₃N₄ provides the nucleation and growth of TiO₂ particles on the surfaces of g-C₃N₄ sheets [82]. Obviously, TiO₂ nanoparticles are denser and more uniform than g-C₃N₄ sheets. Because of low amount of TiO₂ in TCN-90, nearly spherical agglomerates of TiO₂ crystallites are shown in the edges of g-C₃N₄ sheets as seen in Figure 4.9 (c). These agglomerates related with the high surface energy of TiO₂ crystallites. Size of the particle's ranges between ~ 0.07 and $0.25 \mu\text{m}$. With increasing TiO₂ content, the surface of TCN powders becomes rougher and the amount and the size of agglomerates increase as shown in Figures 4.9 (d)-(h). Figure 4.9 (f) shows that TiO₂ crystallites covered the g-C₃N₄ layer. Shape of the composite particles is more spherical when TiO₂ content reaches 50 wt% as seen in Figure 4.9 (g). When TiO₂ content was more than g-C₃N₄ content in the composites, more uniform morphology was observed since all g-C₃N₄ particles were covered by TiO₂ and there was excess amount of TiO₂ in the structure

as displayed in Figure 4.9 (h). Additionally, the size of the particles decreased to nanoscale i.e., 20-80 nm. Among all TCN powders, TCN-20 probably had the smallest particles. Conclusively, the TiO_2 content is very effective for the development of the morphology in TCN powders.



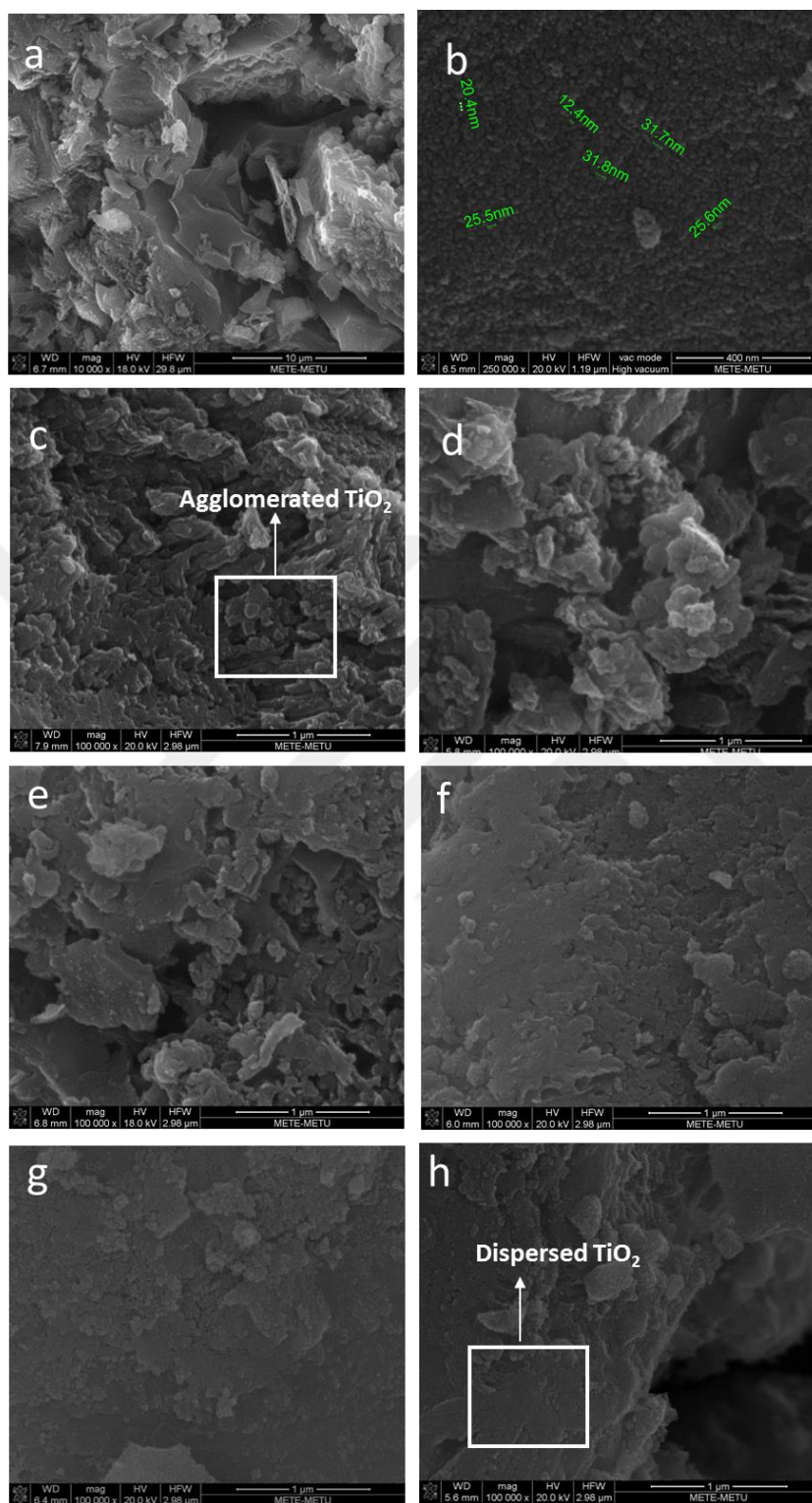


Figure 4.9. FESEM images of the powders a) g-C₃N₄, b) TiO₂, c) TCN-90, d) TCN-80, e) TCN-70, f) TCN-60, g) TCN-50, and h) TCN-20.

The EDS spectra of pristine g-C₃N₄, TCN-50, and pristine TiO₂ powders are depicted in Figure 4.10. Pristine g-C₃N₄ consisted of only C and N elements. Pristine TiO₂ composed of only Ti and O elements. Data agree very well with that obtained from XRD analysis implying that pristine g-C₃N₄ and pristine TiO₂ powders are analytically pure. TCN-50 powder contained the elements present in both pristine TiO₂ and pristine g-C₃N₄ namely; C, N, O, and Ti. The Au element in the spectra comes from sputter coating of the powders to obtain desired conductivity in FESEM analysis.

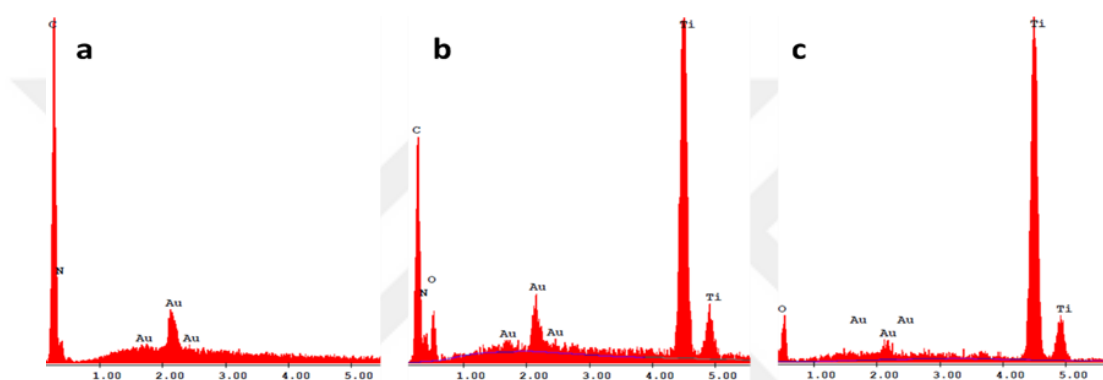


Figure 4.10. EDS spectra of powders a) pristine g-C₃N₄, b) TCN-50, and c) pristine TiO₂.

The EDS analysis data with respect to elemental composition of the powders are listed in Table 4.3 Chemical composition of the powders prepared.. The data reveal that stoichiometric compositions of TiO₂ and g-C₃N₄ were not obtained exactly in TCN powders but, they are very close to desired stoichiometric values. The elements (C, N, O, Ti) present in TCN powders also suggest that there is an interfacial joining between g-C₃N₄ and TiO₂ particles.

Table 4.3 Chemical composition of the powders prepared.

Powder	Composition (wt %)			
	C	N	O	Ti
TiO ₂	0	0	36.35	63.65
TCN-20	8.58	4.38	26.95	60.09
TCN-50	36.41	11.87	15.32	36.40
TCN-60	38.42	15.00	30.55	16.03
TCN-70	39.29	17.42	29.88	13.41
TCN-80	48.25	29.75	3.60	18.40
TCN-90	56.24	40.02	1.06	2.67
g-C ₃ N ₄	48.56	15.79	0	0

The representative FESEM images of the heat-treated TCN-80 powders are shown in Figure 4.11. It is obvious that, the heat-treated TCN-80 powders have similar microstructural features with untreated TCN-80 powder as shown in Figure 4.11 (a)-(c). Microstructure of the heat-treated powders consist of sheets. The shapes of the g-C₃N₄ sheets transformed to curly lamellar porous structure [95]. Upon heat treatment, the surface of the particles became rougher and TiO₂ nanoparticles attached on the g-C₃N₄ sheets. However, the sheets become thinner as compared to the sheets in TCN-80 powder when heat-treatment temperature is increased from 350 to 450 °C. The morphology of TCN-80-500 powder is quite different than the other the heat-treated TCN-80 powders as a result of the decomposition of g-C₃N₄. As explained in XRD and TGA studies, the content of g-C₃N₄ gradually decreased in terms of wt%. When temperature reaches the 500 °C, almost all the g-C₃N₄ disappeared. Table 4.4 tabulates the EDS data for the heat-treated TCN-80 powders. Data revealed that an increase in the heat-treatment temperature causes a decrease in the amount of g-C₃N₄ in the TCN-80 powders.

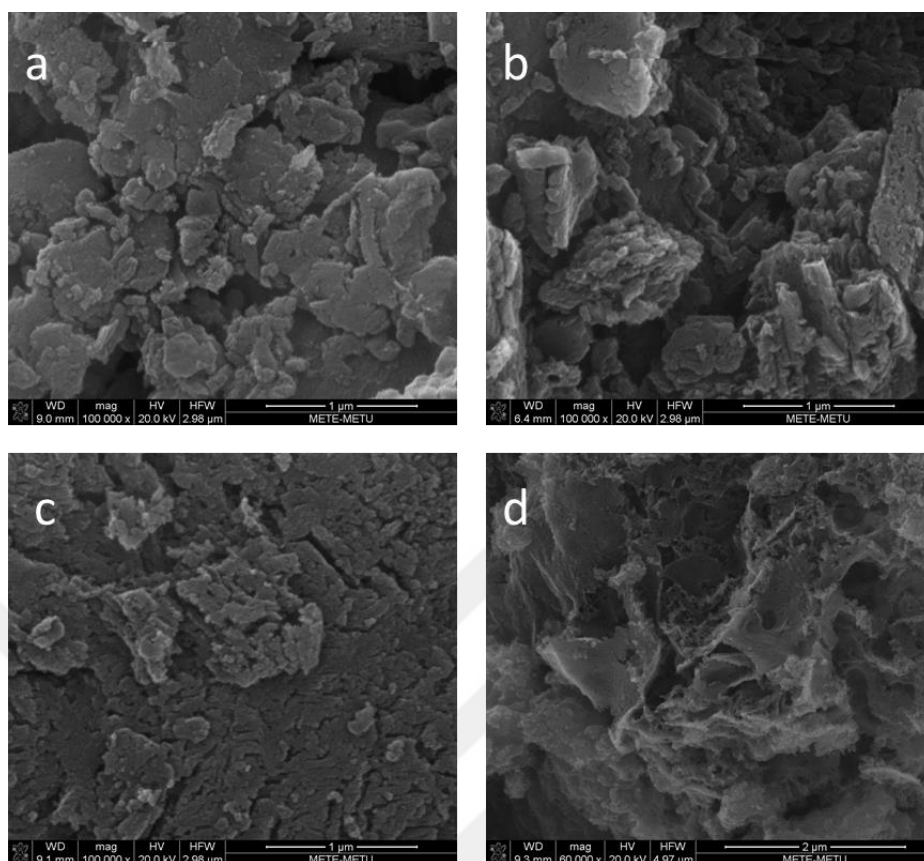


Figure 4.11. FESEM images of powders a) TCN-80-350, b) TCN-80-400, c) TCN-80-450, and d) TCN-80-500.

Table 4.4 Chemical composition of the heat-treated TCN-80 powder.

Powder	Composition (wt %)			
	C	N	O	Ti
TCN-80-350	44.62	31.54	3.47	20.38
TCN-80-400	41.06	27.50	5.39	26.05
TCN-80-450	44.92	19.77	4.08	31.22
TCN-80-500	38.45	17.7	13.57	30.38

4.2.4 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The FT-IR transmission spectra of TCN powders along with those of pristine g-C₃N₄ and pristine TiO₂ powders are shown in Figure 4.12. For pristine TiO₂ powder, the absorption peaks at 400-700 cm⁻¹ and at 1395 cm⁻¹ are attributed to Ti-O and Ti-O-Ti stretching vibrations. The band at 1693 cm⁻¹ shows O-H bending of physisorbed water [96,97]. The broad band at 3142 cm⁻¹ corresponds to hydroxyl group or the absorbed water molecules [40]. In the spectra, the 1232 - 1620 cm⁻¹ range dominates for g-C₃N₄ peak. The bands at 1534 cm⁻¹ and 1620 cm⁻¹ for pristine g-C₃N₄ powder are related to C=N stretching. The 1317 cm⁻¹, 1393 cm⁻¹, and 1534 cm⁻¹ bands correspond to rotating vibration of C-N heterocycles. s-triazine ring vibrations are represented by 806 cm⁻¹ band. When the spectra of TCN powders are compared with that of pristine TiO₂ and g-C₃N₄, they possess the main characteristic spectrum of g-C₃N₄ along with TiO₂ absorption peaks. The intensity of the bands of TiO₂ at 400-700 cm⁻¹ decreases as g-C₃N₄ content in TCN powders increases. Also, the absorption peaks at a range between 1232 and 1620 cm⁻¹ have 6 cm⁻¹ redshifts (movement of the adsorption edge to higher wavelengths).

The results reveal that there is an interfacial construction between g-C₃N₄ and TiO₂, implying composite formation. Similar results have been published by several researchers [39,98]. New bond of g-C₃N₄/TiO₂ interface lead to a decline for long range ordered arrangement of ultrathin g-C₃N₄ layer and the conjugation network structure is also slightly reduced [38].

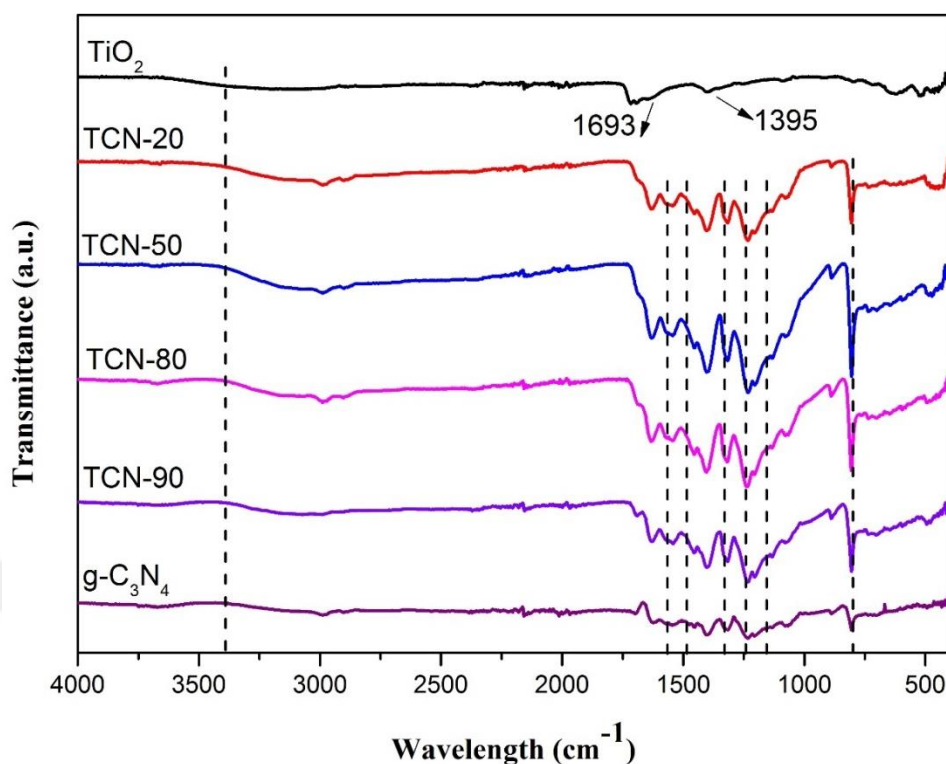


Figure 4.12. The FT-IR transmission spectra of pristine $\text{g-C}_3\text{N}_4$, pristine TiO_2 , and TCN powders.

Figure 4.13 presents the FT-IR transmission spectra of TCN-80 powder and the heat-treated TCN-80 powders. The spectra of pristine $\text{g-C}_3\text{N}_4$ and pristine TiO_2 powders are included in the figure for comparison purpose. The spectra of TCN-80 and the heat-treated TCN-80 powders possess the characteristic absorption peaks of both TiO_2 and $\text{g-C}_3\text{N}_4$. Compared to pristine powders, the characteristic bands of the heat-treated TCN-80 powders redshifted. Redshift is another similarity between the spectra of TCN-80 and the heat-treated TCN-80 powders. Redshift is related with the interaction between TiO_2 and $\text{g-C}_3\text{N}_4$ particles, which prevents recombination of photogenerated electrons and holes. It enhances the photocatalytic activity for the composites, which will be discussed later in Section 4.2.7.

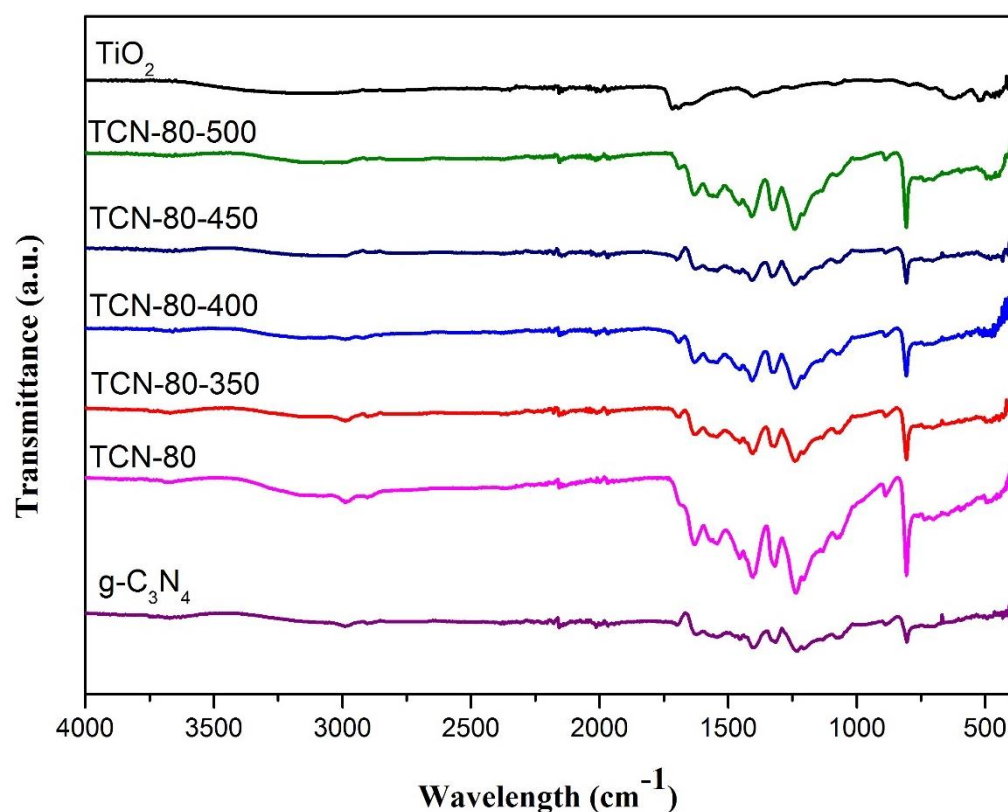


Figure 4.13. FT-IR transmission spectra of TCN-80 and the heat-treated TCN-80 powders together with pristine TiO_2 and $\text{g-C}_3\text{N}_4$ powders.

4.2.5 Raman Analysis

Raman spectra of TCN-80 and TCN-80-400 powders are shown in Figure 4.14. The spectra of both powders include the typical peaks of $\text{g-C}_3\text{N}_4$ at 707 cm^{-1} and 1232 cm^{-1} for TCN-80 powder and at 706 cm^{-1} and 1235 cm^{-1} for TCN-80-400 powder. Raman shift at 706 or 707 cm^{-1} originated from the s-triazine ring in pristine $\text{g-C}_3\text{N}_4$ powder. Also, the peak at 1232 or 1235 cm^{-1} arises from the stretching vibration modes of C-N and C=N cycles [43]. The main anatase peak which is located at 143 and 145 cm^{-1} is seen in the spectra of both TCN-80 and TCN-80-400 powders, respectively. Large degree of $\text{g-C}_3\text{N}_4$ Raman shifts provides a development of new bond alterations at the interface. The interface between $\text{g-C}_3\text{N}_4$ and the TiO_2 proves

that g-C₃N₄/TiO₂ composite was achieved. Therefore, TCN powders and the heat-treated TCN-80 powders henceforward will be called TCN composites and the heat-treated TCN-80 composites, respectively.

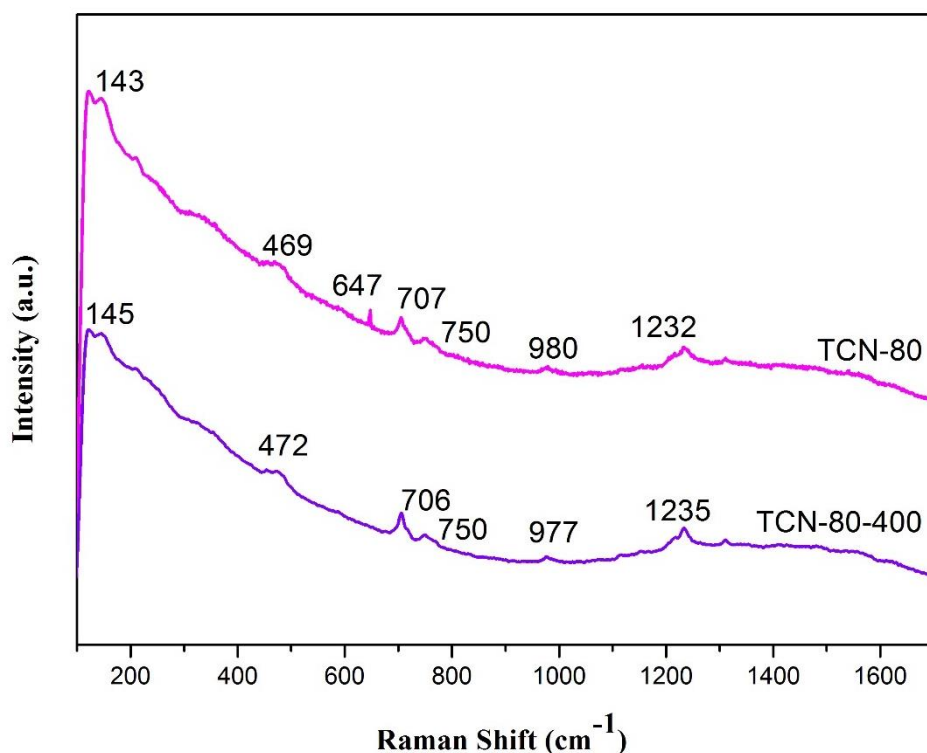


Figure 4.14. Raman spectra of TCN-80 and TCN-80-400 composites.

4.2.6 Diffuse Reflectance Spectra (DRS) Analysis

Figure 4.15 (a) shows absorption thresholds of pristine g-C₃N₄ and pristine TiO₂ powders together with TCN composites. The calculated absorption edge and band gap (E_g) values of the powders prepared are tabulated in Table 4.5. Data revealed that TiO₂ has the absorption edge in the UV-range at 439 nm. However, the absorption edge of g-C₃N₄ is 486.04 nm that involves in both UV and visible regions in solar spectrum. The TCN composites have absorption edge values in between the values of TiO₂ and g-C₃N₄. Also, the TCN composites had redshift to 439 nm. The data suggest that with composite formation, TiO₂ gained considerable extension in

visible light region. When compared to pristine TiO₂, TCN composites have higher absorption intensity. The optical absorption intensity increases with increasing g-C₃N₄ content up to 80 wt%. The absorbance percent versus wavelength graphics shown in Figure 4.15 (a) was transformed to $(\alpha h\nu)^2$ versus $h\nu$ plots as indicated in Figure 4.15 (b) by using Eq. 3.2. Both pristine g-C₃N₄ and TiO₂ have direct band gap. Therefore, the n value was taken as 1 [88]. It is obvious that all TCN composites have an Eg value in between the values of g-C₃N₄ and TiO₂.

Table 4.5 Absorbance edge and the band gap values of the powders prepared.

Powder	Absorbance edge (nm)	Eg (eV)
TiO ₂	439.00	3.08
TCN-20	462.40	2.80
TCN-50	469.98	2.79
TCN-60	470.58	2.77
TCN-70	473.16	2.75
TCN-80	461.12	2.80
TCN-90	466.19	2.78
TCN-80-350	~461	2.80
TCN-80-400	~461	2.80
TCN-80-450	~461	2.80
TCN-80-500	~461	2.80
g-C ₃ N ₄	486.04	2.70

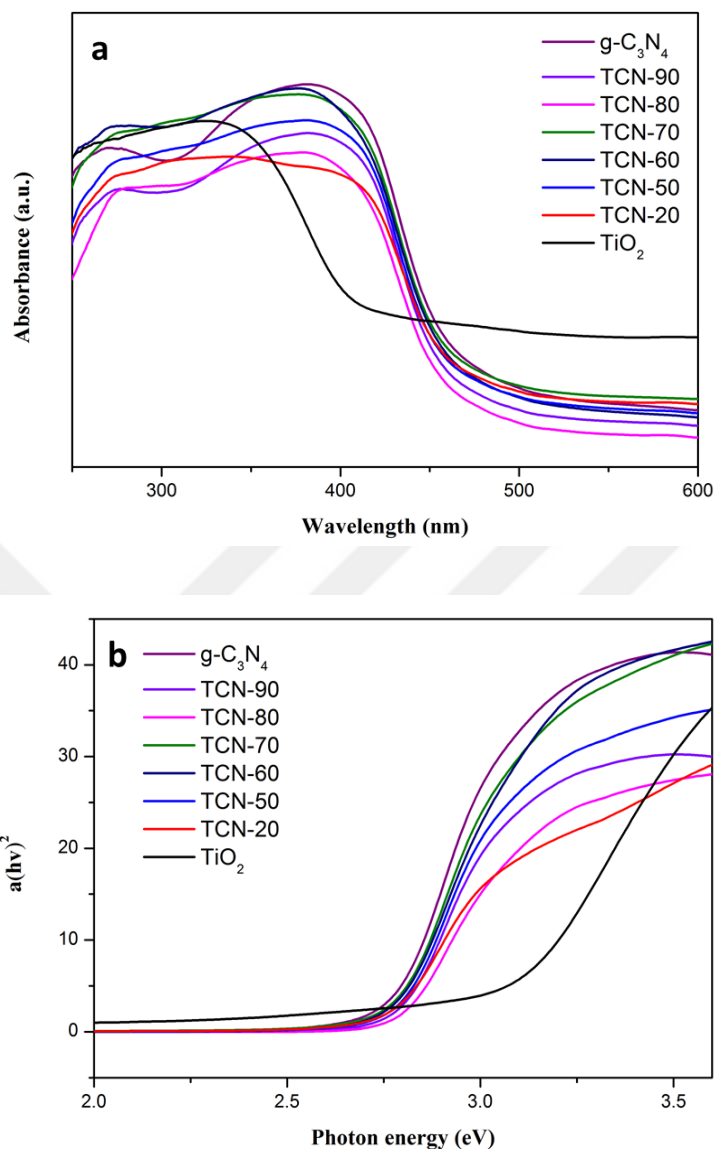


Figure 4.15. a) UV-vis diffuse reflectance spectra and b) $(\alpha h\nu)^2$ vs $h\nu$ plots of the powders prepared.

The E_g values of the powders were calculated by the intersection point between linear part of the related line and x-axis of the graph as shown in Figure 4.16. Pristine TiO₂ has the lowest absorbance edge value. Thus, it has the largest E_g value of 3.08 eV among all the powders prepared. This calculated E_g value is the same as the value reported by Li et al. [83]. The calculated E_g value for pristine TiO₂ is lower than the value for anatase TiO₂ (3.2 eV) since it contains not only anatase but also brookite

phase that has lower E_g (2.96 eV) than anatase [12]. Data revealed that the existence of even small amount of brookite phase in pristine TiO_2 powder affects the E_g value of TiO_2 . g- C_3N_4 has the lowest E_g value of 2.70 eV that match up with the value given by Li et al. [29]. As expected, the E_g values of TCN composites decreased from 2.80 eV to 2.75 eV with increasing g- C_3N_4 content in TCN composites up to 70 wt% g- C_3N_4 additions since g- C_3N_4 has lower E_g value than TiO_2 .

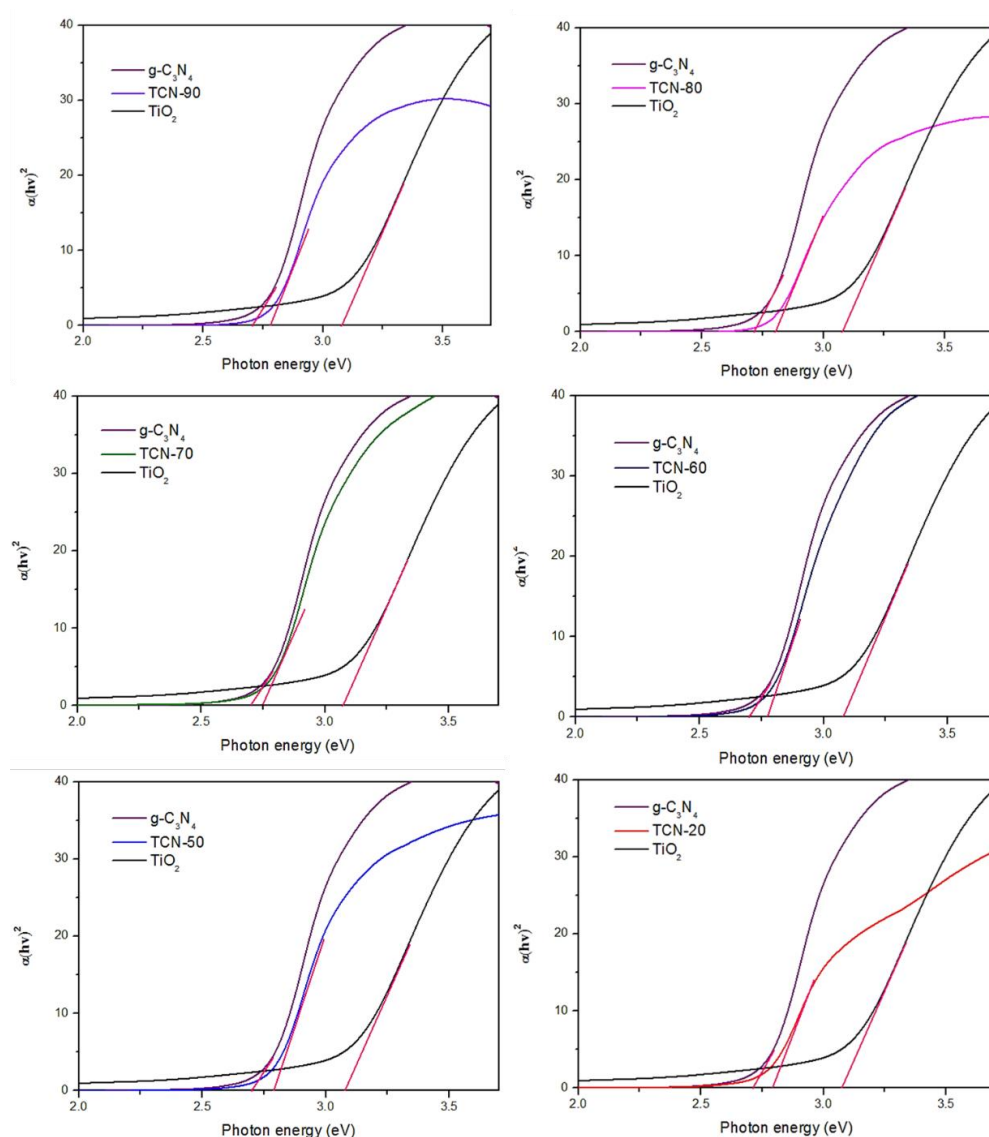


Figure 4.16. Band gaps of TCN composites as compared to pristine TiO_2 and g- C_3N_4 powders.

Although TCN-80 and TCN-90 composites contained more g-C₃N₄ than the other TCN composites, they exhibited the lower E_g values of ~ 2.80 and ~ 2.78 eV, respectively than TCN-70 composite that has E_g value of 2.75 eV. The reason(s) for the inconsistencies in E_g values are beyond our knowledge. However, the inconsistencies between the E_g values are small and within the experimental error limits. The absorbance spectra and the E_g values for the heat-treated TCN-80 composites are depicted in Figure 4.17 (a) and (b). Heat treatment did not have a significant effect on the absorbance edge and the E_g values of TCN-80 composite.

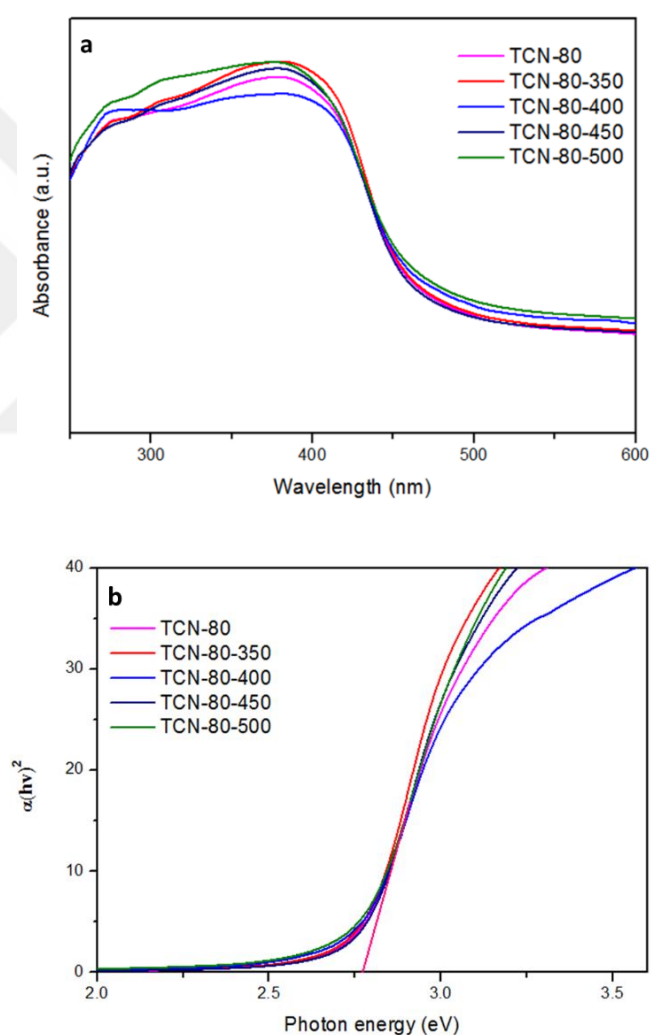


Figure 4.17. a) UV-vis diffuse reflectance spectra and b) band gap of the heat-treated TCN-80 composites.

The E_g configuration and the E_g values of the TCN composites are related with the incident photons, the photoexcitation of the electrons and holes, the transfer charge carriers, and the redox abilities of the electron hole pairs. For this reason, photocatalytic activity of the powder is directly affected by their E_g energies [87,99].

4.2.7 Photocatalytic Activity

Several researchers [7, 100] reported that the absorption-desorption equilibrium for TiO_2 at dark is reached in 30 min. Nonetheless, there is no information in literature reporting the absorption-desorption equilibrium time for TCN composites at dark. The MB degradation tests were performed to find out the absorption-desorption equilibrium time for TCN composites in accord with the procedure as described previously. The measurements were taken in very 5 min at dark for TCN-50 and TCN-80 composites. Results were plotted in Figure 4.18. The last 3 determinations for both composites were almost the same at 30 min and at 60 min.

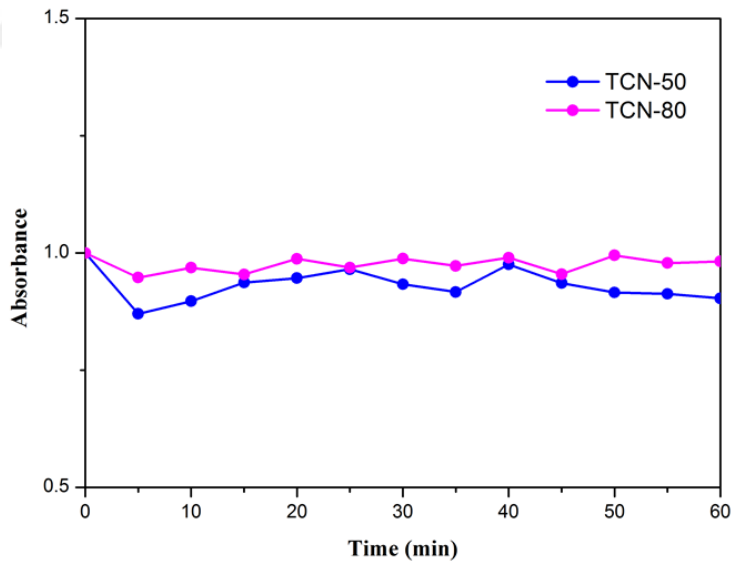


Figure 4.18. Absorption-desorption equilibrium plots for TCN-50 and TCN-80 composites.

It is believed that the absorption-desorption equilibrium was maintained at 30 min. Therefore, holding 30 min at dark was taken as the absorption-desorption equilibrium time for TCN composites and the MB suspensions prepared from TCN composites were kept at dark for 30 min for the photocatalytic activity tests. The photocatalytic activity graphs of pristine g-C₃N₄ and pristine TiO₂ powders together with TCN composites are shown in Figure 4.19. The absorbance and degradation values as calculated under solar light illumination for 180 min are given in Table 4.6. Results revealed that pristine TiO₂ nanoparticles has only 68.8% MB degradation of under 180 min solar light illumination although it had higher absorption (56.9%) at dark in 30 min. The achievement of only small amount of MB degradation is by reason of the wavelength of solar light is not enough for degradation. Pristine g-C₃N₄ particles exhibit lower absorption value (11.6%) than pristine TiO₂. However, it has degradation value of 45.5% under solar light because of its lower E_g (2.7 eV).

Table 4.6 MB degradation values of the powders after solar light illumination.

Powder	Absorbance (%)	MB Degradation (%)		
	(at dark)	(under solar light illumination)		
	30 min	1 h	2 h	3 h
TiO ₂	56.9	60.5	62.4	68.8
TCN-20	11.2	15.1	40.5	54.1
TCN-50	27.3	35.7	51.2	70.7
TCN-60	50.0	66.4	72.2	75.6
TCN-70	19.6	46.9	61.8	77.1
TCN-80	27.4	44.1	61.2	79.7
TCN-90	28.9	40.3	54.4	67.9
TCN-80-350	64.0	73.5	79.2	85.1
TCN-80-400	68.2	86.4	95.3	100
TCN-80-450	54.2	69.6	83.4	89.4
TCN-80-500	59.4	61.2	70.9	84.7
g-C ₃ N ₄	11.6	29.4	39.3	45.5
P25	37.8	49.7	71.5	80.6
MB	1.2	2.7	3.5	5.2

All TCN composites have absorption ability as realized from the decrease in MB concentration at the dark region, and MB degradation ability as understood from the decrease in MB concentration in the UV exposed region in Figure 4.19 (a). It was noticed that the absorbance values for the powders at dark positively affect the amount of MB degradation.

Figure 4.19 (b) demonstrates the variation of absorbance spectra of TCN-80 composite in the MB solution with wavelength. The intensity of absorption peak which has been 664 nm, was decreased gradually with increasing time. TCN-80 composite degraded almost all the MB under 360 min solar light illumination. When the MB degradation values under solar light illumination for 180 min considered, TCN-80 composite exhibited the highest photocatalytic activity among all TCN composites as shown in Figure 4.19 (a). It degraded 79.7% of MB. Except TCN-20

composite, all TCN composites had better MB degradation ability than pristine TiO_2 powder. TCN-20 composite degraded only 54.1% of MB. TCN-80 composite exhibited almost the same photocatalytic activity with P25 powder. See Table 4.6.

When g- C_3N_4 content in TCN composite exceeds 80 wt%, photocatalytic activity decreases. The MB degradation of TCN-90 composite decreased to 67.9%, remarkably. The reason can be, g- C_3N_4 create more surface to coat by the TiO_2 nanoparticles. But, amount of TiO_2 nanoparticles is not enough to cover the surfaces of all g- C_3N_4 sheets. The low amount of TiO_2 coating limits the active sites of the composites. Therefore, transfer of photoinduced carriers and photocatalytic activity decrease [82].

The results reveal that the TiO_2 provides excellent heterojunction effect in TCN composites. The heterojunction effect contributes to the transfer of charge carriers. Therefore, TiO_2 loading enhance photocatalytic activities of the TCN composites [101]. Decreasing crystallite size of the anatase phase in the composites is also accountable for the enhancement in photocatalytic activity.

The variation of photocatalytic MB degradation efficiency of TCN-80 composite and heat-treated TCN-80 composites with solar light illumination time are shown in Figure 4.19 (c). Application of a regulated heat-treatment positively affected the photocatalytic activity of TCN-80 composite. Increasing heat-treatment temperature led to an increase in photocatalytic activity up to 450 °C. One of the reasons for the increase is related to the crystallite size of g- C_3N_4 in the composites. Photocatalytic activity of the TCN composites increased with decreasing crystallite size of g- C_3N_4 . With increasing heat-treatment temperature composite structure began to decompose. See Figure 4.11 (d). Especially for TCN-80-500 composite, amount of g- C_3N_4 decreased. This is the reason why photocatalytic activity decreases after temperature exceeds to 400 °C. Figure 4.11 (d) was drawn to compare the solar light photocatalytic activity of TCN-80-400 composite with control groups. That is, pristine TiO_2 powder, g- C_3N_4 powder, P25 powder, and MB without any photocatalyst addition (blank). TCN-80-400 composite has the highest

photocatalytic activity for the degradation of MB among all TCN composites prepared and controls groups. See Figure 4.11 (c) and (d). TCN-80-400 composite degraded all of MB when exposed to solar light illumination for 180 min. The photocatalytic efficiency of TCN-80-400 composite is 1.5 times higher than pristine TiO_2 powder and 2.2 times higher than pristine TiO_2 .

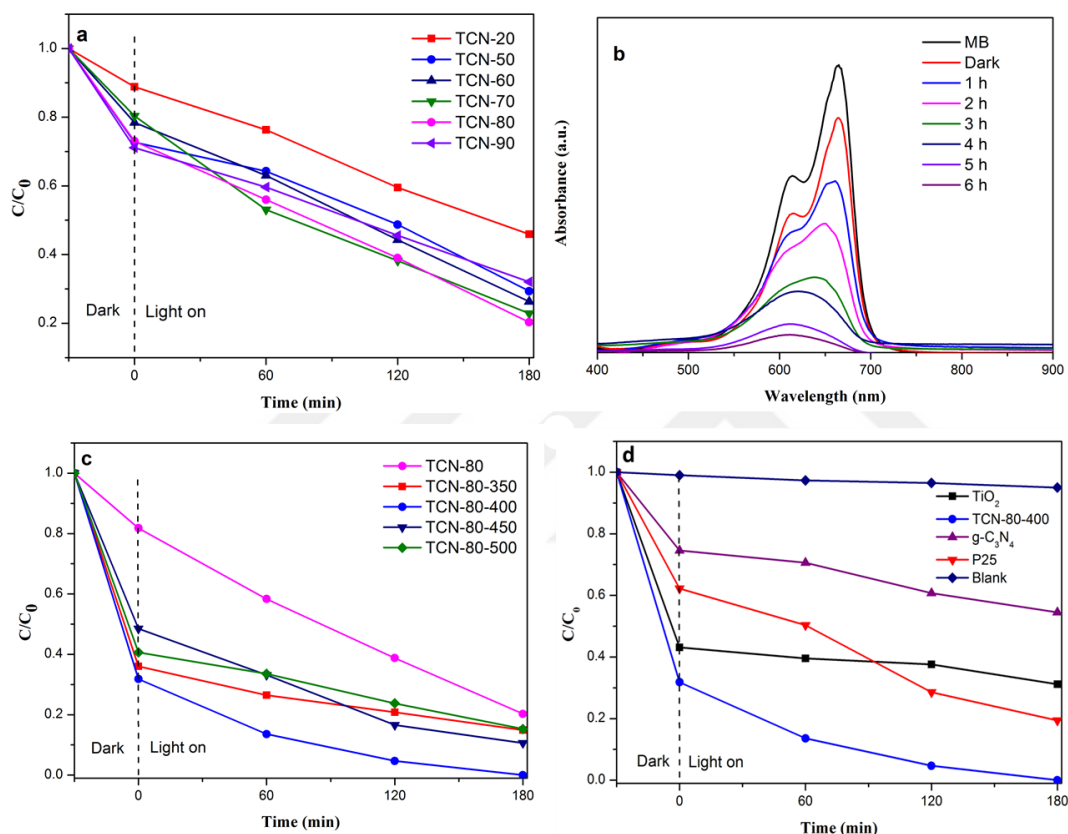


Figure 4.19. a) Solar light photocatalytic efficiencies of TCN composites, b) Absorbance of TCN-80 composite, c) Solar light photocatalytic efficiencies of TCN-80 composite and heat-treated TCN-80 composites, d) Solar light photocatalytic efficiencies of TCN-80-400 composite together with control groups.

The enhancement in the photocatalytic efficiency of TCN-80-400 composite is due to optimum band gap value which provides an extension of longer wavelength. Another reason for improving photocatalytic activity is an effective decrease of the

e^-/h^+ recombination rate. Li et al [82] reported similar results who stated that composites exhibit 80 wt% g-C₃N₄ with 500 °C heat treatment shows the best photocatalytic activity thanks to its smaller grain size and low band gap value.

4.3 Photocatalytic Mechanism

The photocatalysis mechanism proposed for the g-C₃N₄/TiO₂ heterojunction composites is schematically demonstrated in Figure 4.20 where the separation of e^-/h^+ pairs and their transportation are also shown. The VB and CB edge potentials of g-C₃N₄ were calculated by means of the Eqs.3.3 and 3.4 are 1.58 and -1.12 eV, respectively. The estimated VB and CB edge potentials of TiO₂ were 2.85 and -0.23 eV, respectively.

When g-C₃N₄ was exposed to the solar light (UV-vis), it absorbs the light and excites to produce photoinduced electrons as shown in Figure 4.20. First, electrons are transferred from its VB to CB. Then, since the CB edge potential of g-C₃N₄ (-1.14 eV) is more negative than that of TiO₂ (-0.225 eV), photoinduced electrons on the CB of g-C₃N₄ easily transfer to the CB of TiO₂ because of the well-built heterojunction structure [75]. Meantime, TiO₂ absorbs the UV light and excited for producing photoinduced electrons. These photoinduced electrons transfer from its VB to CB. The VB edge potential value of TiO₂ (2.85 eV) is more positive than g-C₃N₄ (1.58 eV). It provides easy transfer of photoinduced holes from TiO₂ to g-C₃N₄ due to heterojunction construction. As a result of this transfer, separation period of e^-/h^+ pairs increases [87]. Thus the photocatalytic activity of the composites to the degradation of MB increases due to the transfer of interfacial charge-reactions [98].

First, to produce $\bullet O_2^-$, oxygen dissolves the collected electrons in the CB of TiO₂. These reactions contributed to produce active $\bullet OH$ radicals. Finally, produced $\bullet HO$ radicals react with the MB molecules. Then, CO₂ and H₂O are the final products. The redox reactions believed to take place are given in Section 2.1.1.1.

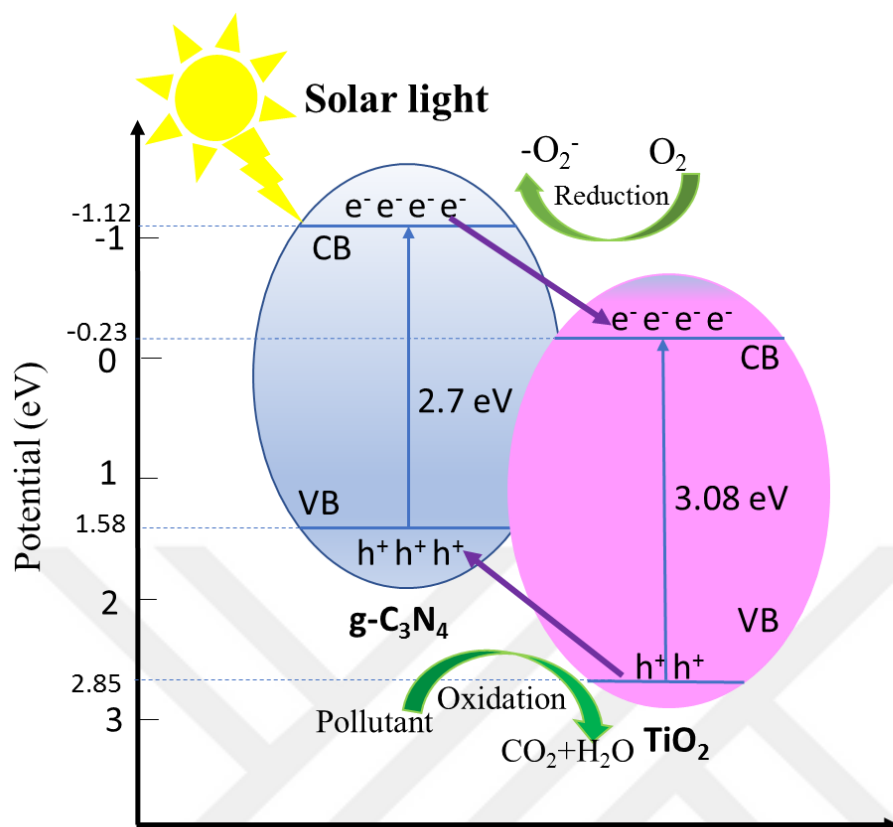


Figure 4.20. Schematic representation of the photocatalysis mechanism of $g\text{-C}_3\text{N}_4/\text{TiO}_2$ heterojunction composite.

CHAPTER 5

RESULTS AND DISCUSSION: PHOTOCATALYTIC ACTIVITY OF THE g-C₃N₄/TiO₂ HETEROJUNCTION COMPOSITES DERIVED BY THE SOL-GEL PROCESS

5.1 General Remarks

In this part of the thesis, the results of the sol-gel derived g-C₃N₄/TiO₂ heterojunction powders, hereafter will be named STCN powders, were presented and discussed. Three different composites with increasing g-C₃N₄ contents of 20, 50, and 80 wt% were synthesized along with pristine TiO₂. The powders were heat treated at 400 °C. After preparation, only the effect of the g-C₃N₄ content in the g-C₃N₄/TiO₂ nanocomposites on the photocatalytic efficiency was investigated. Results were compared with that of the pristine TiO₂ powders as well as a commercially available TiO₂ powder.

Similar to hydrothermally synthesized powders, the g-C₃N₄/TiO₂ nanocomposites derived by the sol-gel process were yellow in color as previously presented in Figure 3.3. Depending on the g-C₃N₄ content, they appeared in light yellow to dark yellow colors. The yellow color becomes lighter approaching the white color of pristine TiO₂ powder with decreasing g-C₃N₄ content.

5.2 Characterization of the Powder Synthesized

5.2.1 Particle Size Analysis

Particle size distribution curve of the sol-gel derived TiO₂ powder, hereafter will be called as STiO₂ powder, is shown in Figure 5.1. STiO₂ particles have bimodal distribution consisting of coarse and fine particles. The mean average size of fine

particles are 0.54 μm and that of coarse particles are 23.6 μm . The particle size distribution of particles ranges between $d(0.1)=0.953\ \mu\text{m}$ and $d(0.9)=39.43\ \mu\text{m}$. The average particle size of all powders is 14.24 μm . When a comparison is made, STiO₂ powder consists of particles smaller than the hydrothermally synthesized pristine TiO₂ powders. See Figure 4.2. It is assumed that the calcination of STiO₂ powders at 400 °C reduces the particle size.

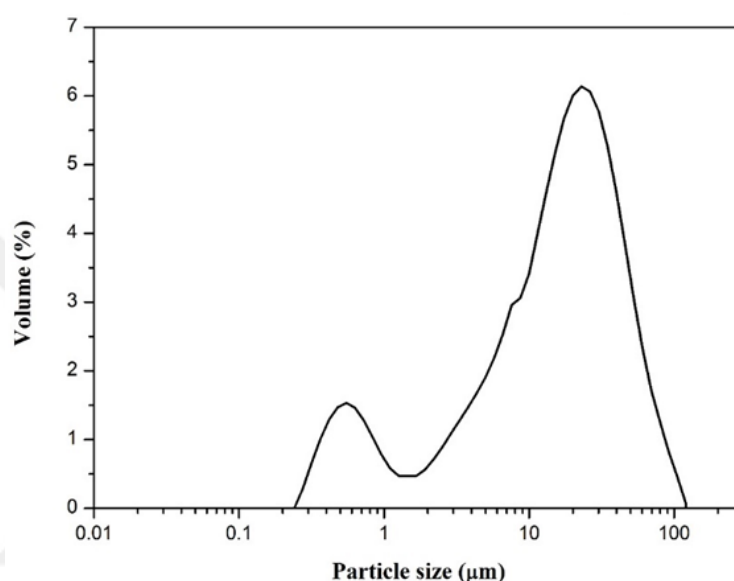


Figure 5.1. Particle size distribution curve of the STiO₂ powders.

The STCN powders will be referred to the codes given in Table 3.1. The particle size distribution curve of STCN-50 powder is demonstrated in Figure 5.2. The particle size analysis of this powder reveal that particles range between 0.3 μm and 200 μm . The average particle size of the particles is 18.11 μm . Similar to STiO₂ powder, it has bimodal distribution. Fine and coarse particles have average of 0.6 μm and 2.4 μm sizes, respectively. 10% of the particles is smaller than 3.2 μm while 90% of the particles is smaller than 48.8 μm . It is clear that STCN-50 powder has smaller particles than both constituents. That is, pristine g-C₃N₄ (Figure 4.1) and STiO₂.

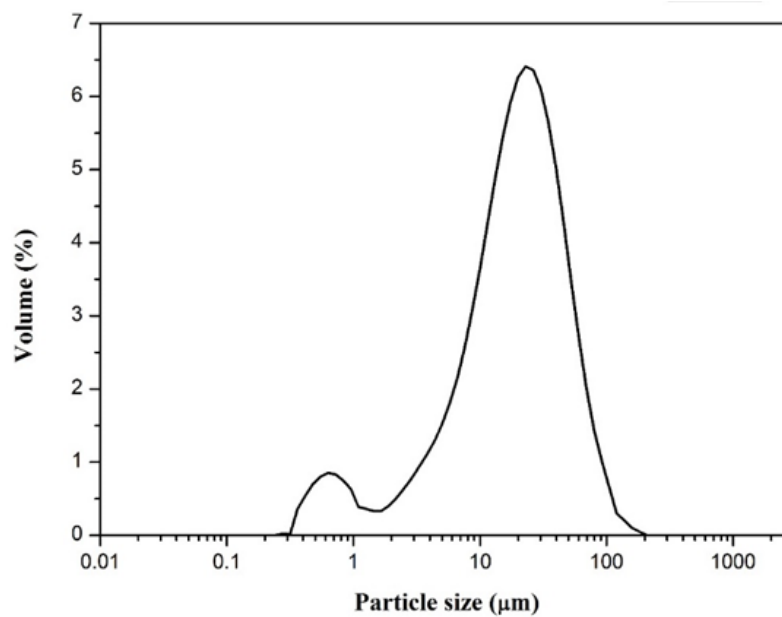


Figure 5.2. Particle size distribution curve of the STCN-50 powders.

5.2.2 X-Ray Diffraction (XRD) Analysis

XRD pattern of STiO₂ powder is demonstrated in Figure 5.3. The diffraction peaks located at 25.4°, 37.8°, 48°, 54°, 55°, 63°, and 69° corresponds to (101), (004), (200), (105), (211), and (204) of tetragonal anatase TiO₂ (JCPDS 00-021-1272), respectively. Additionally, main characteristics peak of brookite TiO₂ diffracting from (121) is situated at 30.8° (JCPDS 00-029-1360). There is an overlapping between brookite (120) and anatase (101) peaks at 25.4°. Similar results were reported previously by other researchers [15, 102].

As stated previously in Section 4.2.2, heat treatment leads to transformation of anatase to rutile or brookite to rutile. However, STiO₂ powder was consisted of only anatase phase even after the heat treatment at 400 °C. Rutile and contaminations were not observed. Brookite peak located 30.8° in STiO₂ powder, more visible than that present in pristine TiO₂, can be originated from long synthesizing durations of the sol-gel derived powders. Paola et al. [51] stated that brookite can be synthesized generally at low temperatures (110-220 °C) and for long synthesis times (24-48 h).

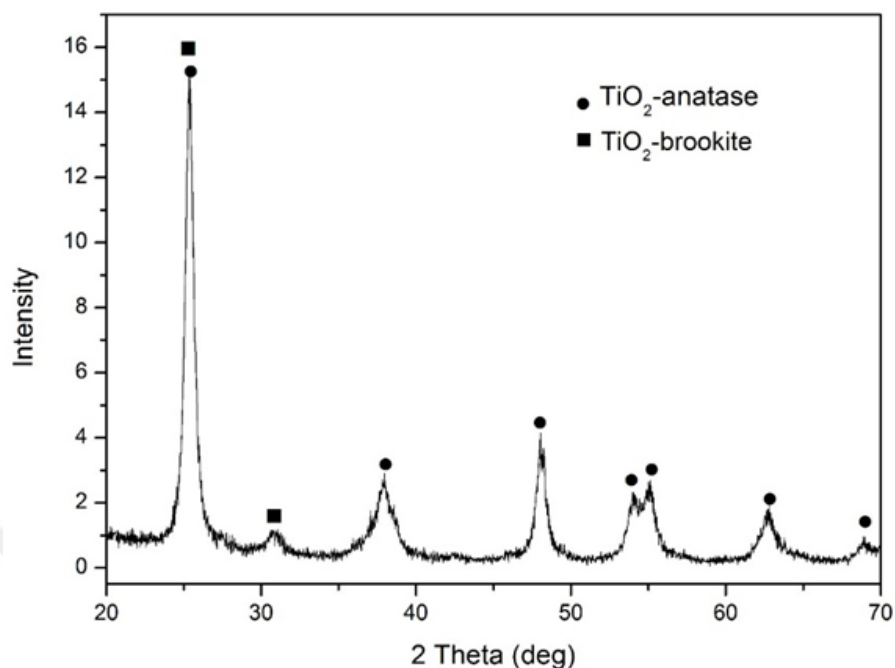


Figure 5.3. XRD pattern of STiO₂ powders.

Phases present in the STCN powders were identified by XRD analysis. Figure 5.4 shows the XRD patterns of the STCN powders together with g-C₃N₄ powder and STiO₂ powder. Except STiO₂ powder, all powders have diffraction peaks at 13.0° and 27.4° corresponding to (100) and (002) of g-C₃N₄ (JCPDS 01-087-1526) [83]. There is a graphitic like structure [33]. No other peak belonging to g-C₃N₄ was observed in the XRD of the STCN powders. Moreover, all of the STCN powders possessed the phases present in STiO₂ at almost the same peak positions of the phases. Tetragonal anatase peaks located at 25.4°, 37.8°, 48°, 54°, 55°, 63°, and 69°, corresponding to (101), (004), (200), (105), (211), and (204), respectively (JCPDS 00-021-1272) were detected. Unlike the TCN powders, the brookite peaks (JCPDS 00-029-1360) corresponding to (120) and (121) were observed at 25.4° and 30.8°, respectively in the XRD of the STCN powders. Also, addition of g-C₃N₄ hampered the formation of rutile phase despite calcination [85].

Intensity of g-C₃N₄ peaks in the STCN powders increased gradually as g-C₃N₄ content increased without shifting the peaks to lower or higher angles. Tough, the peak intensities for the anatase and brookite phases decreased. Wang et al. [33]

published akin results. It is obvious that the (101) peaks of anatase at 25.4° became distinct when TiO_2 content is 80 wt%. Other anatase peaks become clearer, too.

When the XRD patterns of the STCN powders are compared with each other, brookite TiO_2 phase is more visible in STCN-20. Unlike hydrothermal synthesis, the composite formation by the sol-gel process does not hinder brookite formation. Li et al. [29] detected brookite phase after the formation of $\text{g-C}_3\text{N}_4/\text{TiO}_2$ powders by the sol-gel process. Gunnar et.al [103] reported that anatase and brookite nano crystals formed as a result of low temperature and low pH synthesis conditions. It is believed that a 48 h mixing time and room temperature synthesis facilitate the brookite formation.

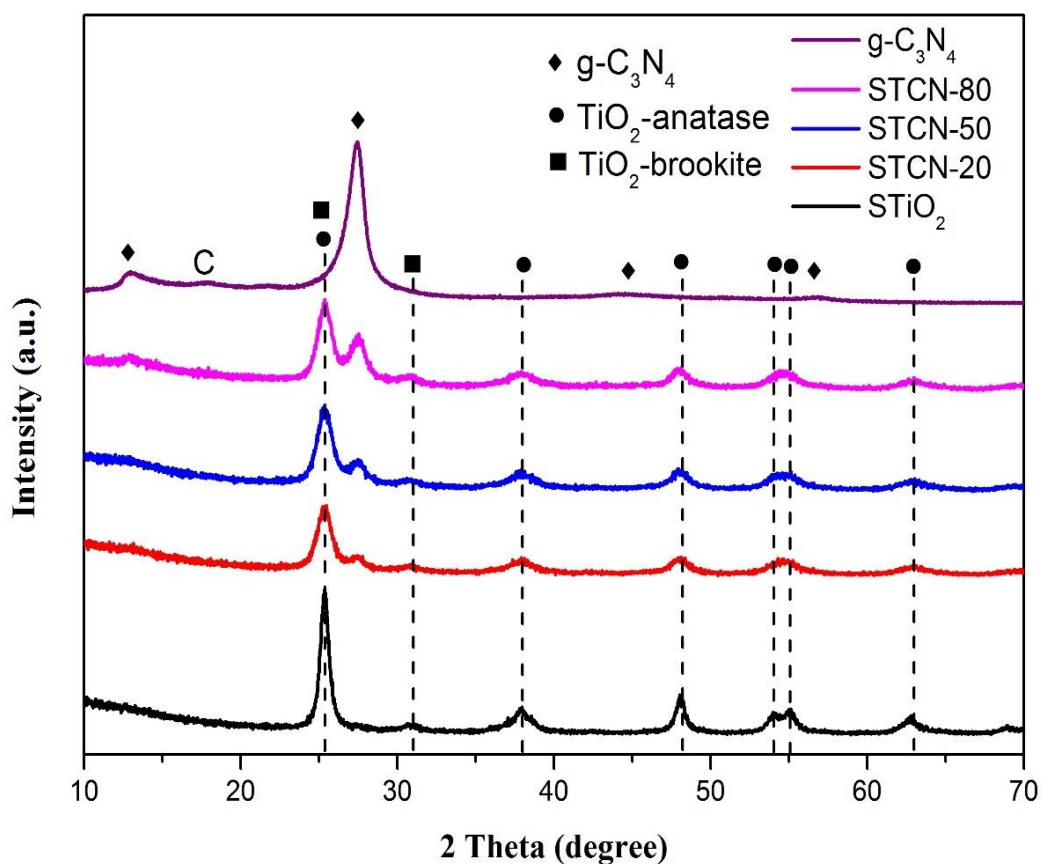


Figure 5.4. XRD patterns of the STCN, STiO_2 , and $\text{g-C}_3\text{N}_4$ powders.

Table 5.1 lists the crystallite sizes of the STCN and STiO₂ powders as calculated by Debye-Scherrer formula. Anatase crystallite size in the STCN powders is bigger than that in STiO₂ powder. Average size of anatase crystallites was 10.76 nm. With increasing g-C₃N₄ content in the STCN powders, anatase crystallite size decreased from 6.98 nm to 6.56 nm. These results reveal that g-C₃N₄ hinders the growth of anatase crystals [85].

As mentioned in Section 4.1.2, no data related to the crystallite size of g-C₃N₄ in the composites is available in literature. The crystallite size of pristine g-C₃N₄ is 5.01 nm as presented in Table 4.1. Crystallite size values of the STCN powders are closer to the size of g-C₃N₄ crystallites rather than that of anatase crystallites, which range between 4.46 and 5.52 nm. As seen in Table 5.1, g-C₃N₄ addition leads to the growth of g-C₃N₄ crystals.

The measured particle sizes reported in Section 5.2.1 is very different from the calculated crystallite sizes for both TiO₂ and g-C₃N₄ particles since they are different terms as discussed in Section 4.2.2.

Table 5.1 Crystallite sizes of the STCN powders.

Powder name	Crystallite Size (nm)	
	Anatase	g-C ₃ N ₄
STiO ₂	10.76	-
STCN-20	6.98	4.46
STCN-50	6.68	5.35
STCN-80	6.56	5.52

5.2.3 Morphological and Elemental Analyses

Representative FESEM images of the STCN powders are shown in Figure 5.5. Effect of g-C₃N₄ content on the morphology developed in the powders was investigated.

All images were taken at 100000 magnification but the image for the STiO₂ powder was taken at 400000 magnification as depicted in Figure 5.5 (a). Similar to pristine TiO₂ powder, STiO₂ powder consists of nearly spherical particles with a diameter of ranging from 8 to 33 nm. g-C₃N₄ powder was in a lamellar structure and its surface was flat as demonstrated in Figure 4.9 (a) but, the STCN powders comprised irregular shaped particles as shown in Figure 5.5 (b-d). The surface of g-C₃N₄ sheets became rougher because of the growth of TiO₂ particles [52]. Almost all g-C₃N₄ sheets were covered by the nano size TiO₂ particles. As seen in Figure 5.5 (b), STCN-20 powder includes some agglomerated TiO₂ particles with 11 to 37 nm particle size. There is no distinct difference in the morphologies between STCN-20 and STCN-50 powders. See Figure 5.5 (c). Particle sizes and shapes are more or less the same in both powders. Nonetheless, TiO₂ nanoparticles in STCN-50 powder are more uniform representing good heterojunction formation. Figure 5.5 (d) shows the image of STCN-80 powder. Although TCN-80 powder includes particles as big as micrometer in size, STCN-80 powder comprises smaller particles in the range from 13 to 35 nm in size. The microstructure of this powder is a bit different from the other particles. It is observed that TiO₂ nanoparticles with an average diameter of 35 nm are agglomerated on some edges or corners of the g-C₃N₄ sheets.

All of the STCN powders are in the nano size range hence, they are named nanopowders based on the FESEM images. When the morphologies of STCN-50 and STCN-80 nanopowders are compared with each other, the dispersity of TiO₂ nanoparticles were higher in STCN-50 powders which directly affect the photocatalytic activity [83].

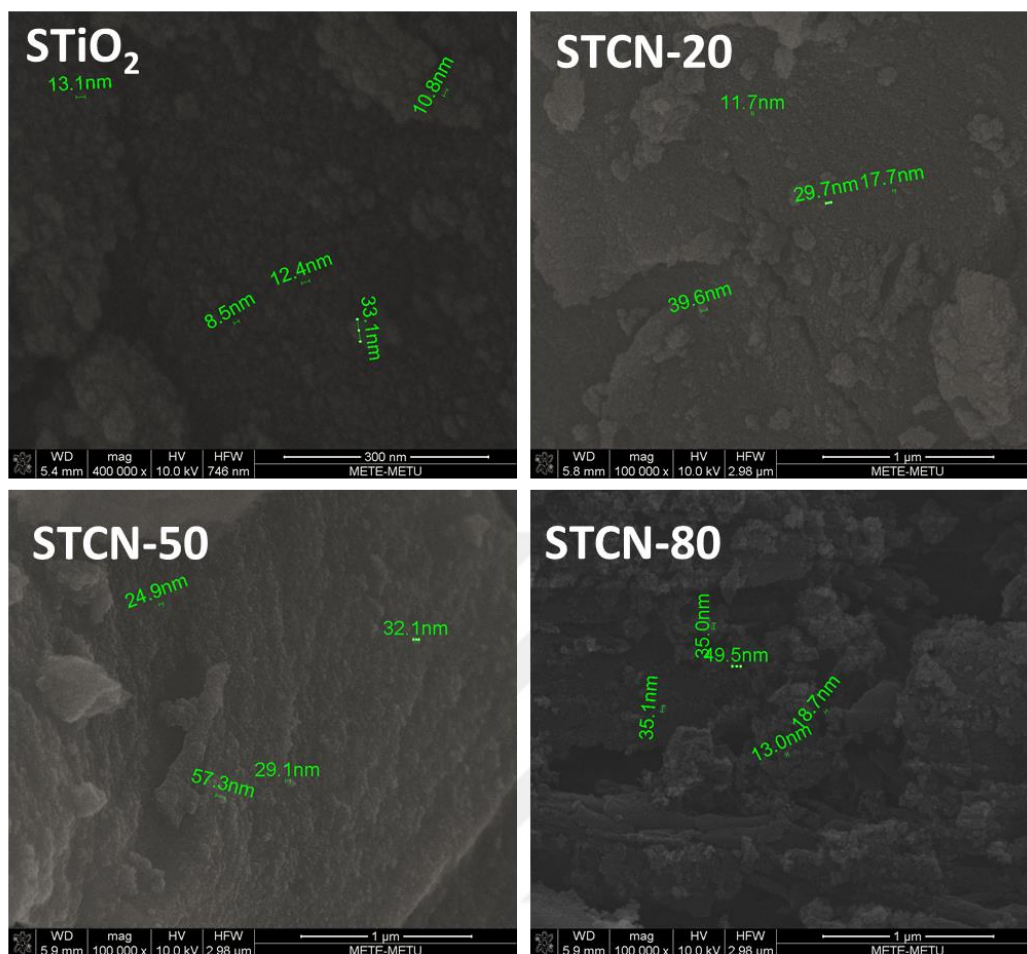


Figure 5.5. FESEM images of a) STiO₂ powders, b) STCN-20, c) STCN-50 and d) STCN-80 powders.

The EDS spectra of STiO₂ and STCN-50 powders are shown in Figure 5.6. STiO₂ powder composed of only Ti and O whereas, STCN-50 nanopowder contains C and N in addition to Ti and O. Au is detected due to Au coating of the powders.

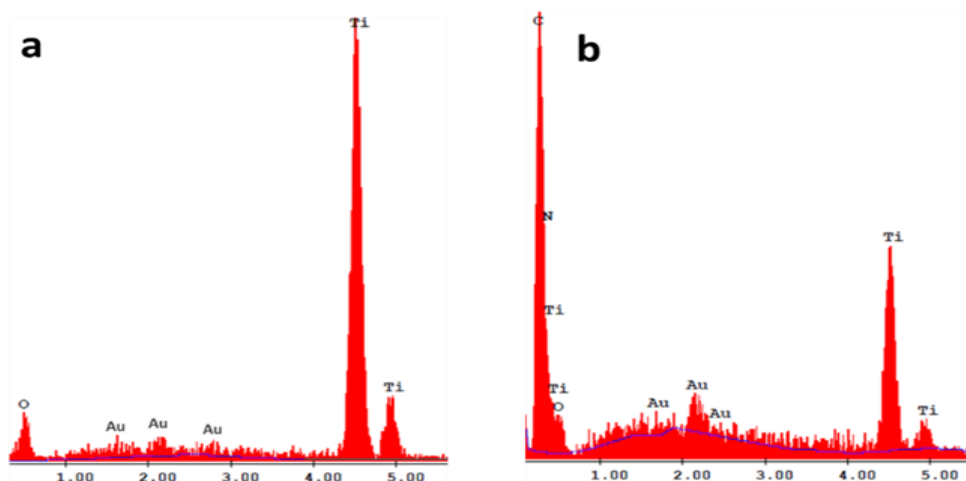


Figure 5.6. EDS spectra of a) pristine STiO₂ and b) STCN-50 powders.

EDS data in terms of elemental composition for the STCN powders are given in Table 5.2. The findings confirmed that the STCN powders attained the desired quantity of the expected elements in terms of chemical composition. For example, STCN-50 powder has 55.77 wt% g-C₃N₄ and 44.23 wt% TiO₂. Moreover, the STCN powders consist of C, N, O and Ti. The EDS data suggest that there is an interfacial connection between TiO₂ and g-C₃N₄.

Table 5.2 Elemental analysis data for the STCN powders.

Powder	Composition (wt %)			
	C	N	O	Ti
STiO ₂	0	0	32.61	67.61
STCN-20	11.35	6.12	26.51	59.07
STCN-50	45.39	10.38	8.54	25.52
STCN-80	47.41	24.33	6.02	22.23

5.2.4 Diffuse Reflectance Spectra (DRS) Analysis

Absorption threshold plots of the STCN powders together with pristine g-C₃N₄ powder are shown in Figure 5.7 (a). Estimated absorption edge values of the STCN

powders are listed in Table 5.3. Similar to pristine TiO_2 , STiO_2 powder has the absorption edge value of 431.4 nm that is in the UV-range. As previously described in Section 4.2.1, the absorption edge of $\text{g-C}_3\text{N}_4$ powder is 486.04 nm which is in the solar spectrum range. As anticipated, heterojunction formation extended operational wavelength region of STiO_2 powder. These nanopowders have an absorption range between 473.8 and 486.04 nm that is closest to value of $\text{g-C}_3\text{N}_4$. Growing STiO_2 nanoparticles on the $\text{g-C}_3\text{N}_4$ sheets improved the visible light absorption ability of TiO_2 . [104]. Therefore, the STCN nanopowders exhibit a redshift when compared to STiO_2 nanopowder and they have absorption ability in both UV and visible light zone. This visible light absorption ability decreases the e^-/h^+ recombination with increasing oxidation and reduction reactions [83].

Absorbance versus wavelength graph shown in Figure 5.7 (a) was transformed into $(\alpha h\nu)^2$ versus photon energy plot using Tauc's transformation formula and depicted in Figure 5.7 (b). This plot provides a calculation of E_g values using an extrapolation of the linear part of the x vs y-axis. Calculated E_g values are listed in Table 5.3.

The STCN powders exhibit larger absorption edge values than the TCN powders whose absorption edge values were given previously in Table 4.5. They have lower E_g values than the TCN powders since the STCN powders still have some amount of brookite phase that has lower E_g value and decreases the E_g value of the STCN powders.

Table 5.3 Absorbance edge and band gap values of sol-gel synthesized powders.

Powder	Absorbance edge (nm)	E_g (eV)
STiO_2	431.4	3.10
STCN-20	473.8	2.75
STCN-50	479.2	2.72
STCN-80	481.2	2.71

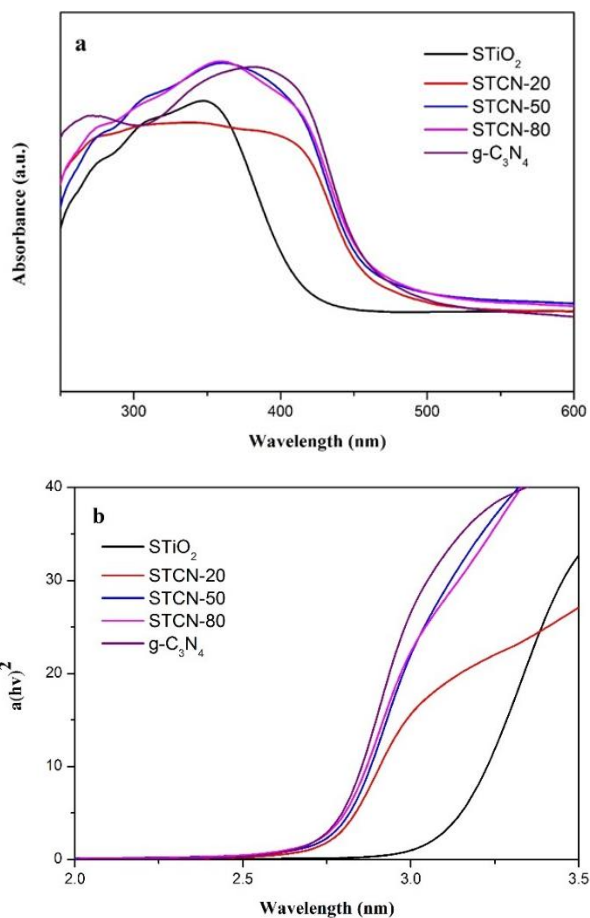


Figure 5.7. a) Absorbance edge spectra, b) $(\alpha h\nu)^2$ versus photon energy ($h\nu$) graph of the STCN powders.

5.2.5 Photocatalytic Activity of the Powders

Photocatalytic performances measured for the STCN powders and for some control groups under 3 h solar light irradiation is shown in Figure 5.8. The absorption and MB degradation values of the STCN powders in terms of percentage are presented in Table 5.4.

STiO₂ powder has a lower MB absorption value (3.92 %) in dark while the degradation value of STiO₂ powder is 49.10% under solar light illumination. As mentioned in Section 4.2.7, pristine g-C₃N₄ has 11.6% absorption and 45.5% MB degradation ability. All of the STCN powders exhibit higher absorption degradation

value than STiO₂ powder and pristine g-C₃N₄ powder. See Figure 5.8 (a). STCN-20 powder has 82.63% MB degradation. By comparison of the MB degradation value of TCN-20 powders (see Table 4.6), STCN-20 powder exhibits quite higher photocatalytic activity. Data implies that there is a well-defined heterojunction between the g-C₃N₄ sheets and TiO₂ nanoparticles in the STCN powders as a result of long synthesizing time i.e, 48 h. Additionally, heat treatment is beneficial for photocatalytic activity [96]. Figure 5.8 (b) demonstrates the absorbance spectra of SCTN-50 nanopowder in the MB solution upon exposure to solar light for 180 min. Absorption peak intensity located at 664 nm decreased gradually with increasing exposure time. Increasing g-C₃N₄ content is beneficial for the MB degradation value of the STCN powders to some extent. STCN-50 powder has higher degradation value (87.05%) than STCN-80 powder that has a degradation value of 83.96%. The reason may be low content of TiO₂ nanoparticles limit the coated sites of the surface of the g-C₃N₄ [88].

Although their E_g values are closest the each other, their microstructures are different from each other which is another effect for photocatalytic activity. TiO₂ nanoparticles in STCN-50 powder are more dispersive than in STiO₂ powders. This dispersity of TiO₂ nanoparticles accelerates the movement of photogenerated carriers and affects the photocatalytic activity of the powders positively [83].

Figure 5.8 (c) demonstrates the photocatalytic activity of STCN-50 powder with a comparison between the control groups namely; STiO₂ powder, g-C₃N₄ powder, blank (MB), and P25 powder. As stated previously, STiO₂ powder have 49.1% MB degradation ability under solar light. This result is very higher when compared to pristine TiO₂ powder. See Table 4.6. The calcination at temperature of 400 °C and higher amounts of brookite may affect the degradation ability positively.

These results reveal that STCN-50 powder have better photocatalytic ability than pristine g-C₃N₄ powder under solar light illumination. Photocatalytic activity of STCN-50 powder (87.05%) almost two times better than pristine g-C₃N₄ (45.5%). Furthermore, this nanopowder has better photocatalytic activity than P25 powder

(80.58%). See Table 4.6. P25 owns the better photocatalytic activity regarding to literature thanks to its special structure that contains both anatase and rutile phases [105].

STCN-50 powder has higher degradation ability than TCN-50 powder (70.7%). The higher degradation ability is attributed to different reasons. Lower E_g value of STCN-50 powder may be the one of the reasons, which increase the photogenerated charge carriers. Also, calcination applied to STCN-50 powder is beneficial for photocatalytic activity.

When compared to the TCN powders, most of the STCN powders exhibit better degradation ability due to their nano size effect. Yu et al. [106] proved that anatase and brookite mixture exhibits the higher photocatalytic activity than P25 powder. The STCN powders consist of anatase, brookite and $g\text{-C}_3\text{N}_4$ mixture. Thus, interaction between these three phases may affect the photocatalytic activity.

Table 5.4 Absorbance and MB degradation results of sol-gel synthesized powders.

Powder	Absorbance (%)	MB Degradation (%)		
	(at dark)	(under solar light illumination)		
	30 min	1 h	2 h	3 h
STiO ₂	3.92	9.81	26.68	49.10
STCN-20	34.35	57.75	72.66	82.63
STCN-50	19.03	58.03	79.82	87.05
STCN-80	40.98	61.43	75.72	83.96

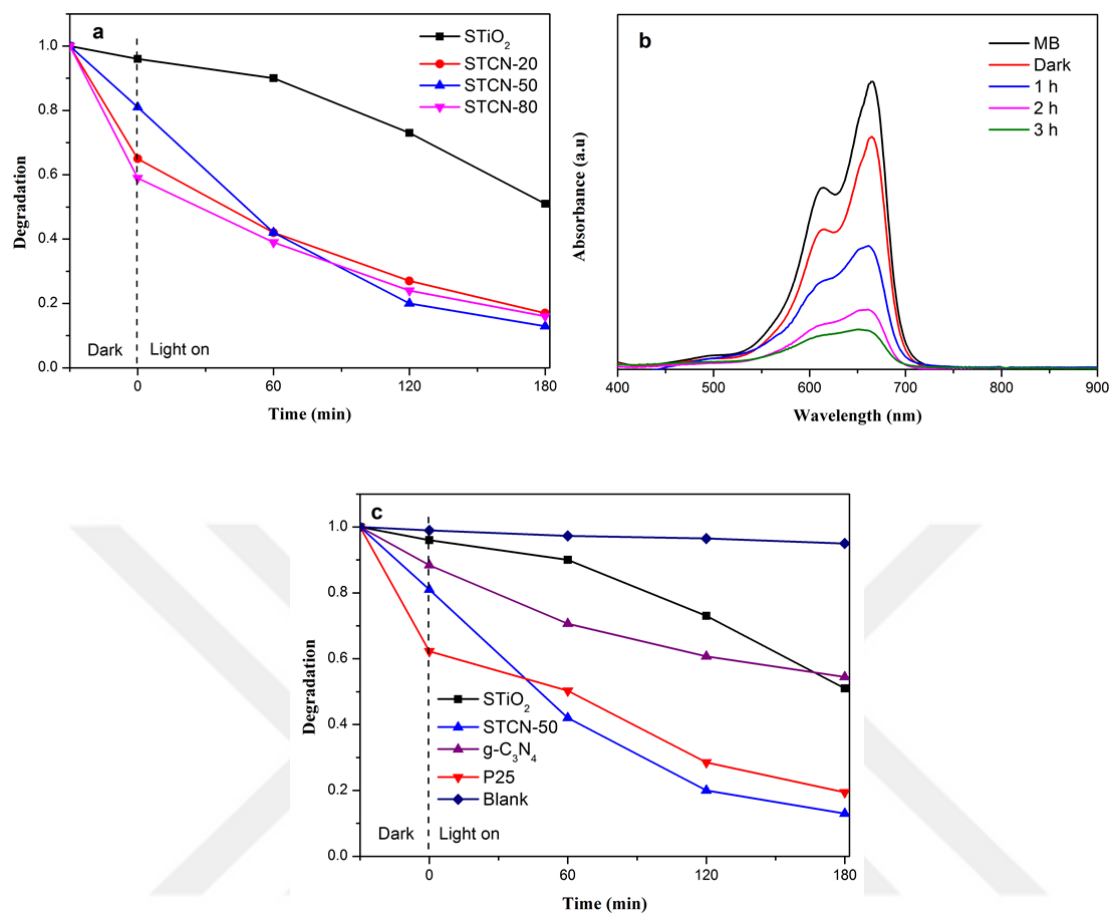


Figure 5.8. a) Photodegradation values of STCN powders, b) UV-vis absorption spectra of STCN-50 powder, c) photodegradation of STCN-50 powder compared with control groups.

CHAPTER 6

CONCLUSIONS

The solar light sensitive g-C₃N₄/TiO₂ composites containing various amounts of graphitic carbon nitride (g-C₃N₄) and titania (TiO₂) are successfully prepared by the hydrothermal and sol-gel processes for photocatalytic applications. FESEM and EDS analyses revealed that all composites prepared are in nano size range and developed through deposit of TiO₂ nanoparticles on g-C₃N₄ sheets via hydrothermal or sol-gel reactions. An interface between the constituents of the nanocomposites was evidenced through the XRD, FTIR, and Raman analyses. The heterojunction construction among g-C₃N₄ and TiO₂ powders extends the absorption edge of pristine TiO₂ powders by redshifting. The redshift of visible light regions improves separation time of the photogenerated charge carriers. All g-C₃N₄/TiO₂ composites exhibit the photocatalytic ability to degrade aqueous Methylene Blue (MB) solution under solar light illumination. Except for the hydrothermally derived g-C₃N₄/TiO₂ composite containing 20 wt% g-C₃N₄, all g-C₃N₄/TiO₂ composites exhibit superior photocatalytic activity for the degradation of MB to both pristine TiO₂ powder and pristine g-C₃N₄ powder. Among all hydrothermally prepared composites, the g-C₃N₄/TiO₂ composite containing 80 wt% g-C₃N₄ shows the best photocatalytic activity. The photocatalytic efficiency of the hydrothermally derived g-C₃N₄/TiO₂ composites are improved if they are subjected to regulated heat treatments at temperatures ranging from 350 to 500 °C for 1 h. Hydrothermally derived and sol-gel derived g-C₃N₄/TiO₂ composites exhibited good photocatalytic efficiency in 180 min solar light illumination. The composite containing 80 wt% g-C₃N₄ and heat-treated at 400 °C for 1 h exhibited MB photodegradation efficiency ~2.2 times better than pristine g-C₃N₄ powder besides ~1.5 times better than pristine TiO₂ powder. The enhancement in photocatalytic activity was related to the creation of reactive

oxidation species encouraged by photogenerated electrons and reduced recombination rate of the e^-/h^+ pairs.

The sol-gel derived g-C₃N₄/TiO₂ composite containing 50 wt% g-C₃N₄ showed better photocatalytic efficiency than pristine g-C₃N₄ and P25 powders. This composite shows the photocatalytic efficiency ~1.8 times better than pristine TiO₂ powder and ~2.2 times better than pristine g-C₃N₄ powder.

Hydrothermally synthesized composites exhibit 100% while sol-gel prepared exhibits 87.05% photocatalytic activity under 3 h solar light illumination.



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