MINISTRY OF EDUCATION AND TRAINING

VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY

GRADUATE UNIVERSITY SCIENCE AND TECHNOLOGY

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RESEARCH ON SYNTHESIS OF NANOCOMPOSITE MATERIALS ON THE BASIS OF TiO_2 - GRAPHENE OXIDE (GO) APPLICATION-ORIENTED IN WATER TREATMENT

SUMMARY OF DISSERTATION ON SCIENCES OF MATTER

Major: Inorganic Chemistry

Code: 9 44 01 13

Ha Noi - 2025

The dissertation is completed at: Graduate University Science and Technology, Vietnam Academy Science and Technology

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PREAMBLE

1. The urgency of the thesis *(reasons for choosing the topic, scientific and practical basis)*

Water pollution remains a critical challenge for humanity in the 21st century, particularly in developing countries. Contaminated water, laden with organic substances, heavy metals, and pathogenic bacteria, poses direct risks to human health and causes long-term ecological damage. Traditional water treatment methods, such as chemical disinfection, adsorption using activated carbon, and mechanical filtration, exhibit limitations including inconsistent efficacy and environmental degradation through the generation of toxic by-products. Consequently, there is an urgent need to research and develop advanced materials that can disinfect water effectively and in an environmentally friendly manner.

Photocatalytic materials have shown significant potential in water treatment, particularly in decomposing recalcitrant organic substances and disinfecting bacteria. TiO_2 is among the most extensively researched photocatalytic materials due to its high chemical stability, effectiveness under UV light, and affordability. When activated by light, TiO_2 generates free radicals such as •OH and $•O_2^-$, which possess strong oxidizing properties that help break down complex organic compounds and eradicate microorganisms. However, anatase TiO_2, the most prevalent crystalline form, has a large band gap of approximately 3.2 eV, which confines its activity to the ultraviolet region—a mere 3–5% of sunlight. Furthermore, the rapid recombination of electrons and holes notably diminishes its photocatalytic efficiency.

Graphene oxide (GO), a two-dimensional material with a large surface area and rich in oxygen-containing functional groups such as hydroxyl (-OH), carboxyl (-COOH), and epoxy (-O-), is considered an ideal substrate for combination with TiO_2. GO enhances the adsorption of organic pollutants through π-π interactions and improves electron transport efficiency, thereby reducing the electron-hole recombination rate in TiO_2 [1-4]. The integration of TiO_2 with GO has led to the development of composite materials with enhanced photocatalytic performance, particularly in the visible light region. However, previous studies have indicated that the bonding between TiO_2 and GO is often uneven, which can lead to suboptimal photocatalytic efficiency [5-7]. Moreover, conventional TiO_2/GO composites still face challenges with recovery after use, which hampers their reusability and increases processing costs.

To address the aforementioned limitations, this study proposes the development of multifunctional composite materials by incorporating a third component, such as silver nanoparticles (Ag) or magnetic particles (Fe_3O_4). Silver nanoparticles not only provide robust antibacterial properties but also enhance photocatalytic efficiency through the formation of plasmonic hot spots under visible light. Conversely, Fe_3O_4 magnetic particles improve material recovery and support applications in mobile or automated water treatment systems. The integration of TiO_2, GO, and either silver nanoparticles or magnetic particles is expected to yield materials with superior photocatalytic properties, enhanced stability, and easy reusability, fulfilling contemporary water disinfection needs. However, the

fabrication of these three-component composites presents challenges, particularly in achieving a strong interconnection among the components to meet performance criteria. To address this, the following specific solutions are proposed:

i) Increase the contact area between the two component materials and GO;

ii) Employ a suitable method to bond the component materials to GO.

Utilizing advanced synthesis methods such as gamma irradiation or chemical treatment, the study aims to ensure uniform bonding across the components. Two approaches include: (a) synthesizing spherical TiO_2 nanoparticles and Fe_3O_4 on GO using a chemical method; (b) bonding TiO_2 nanotubes and silver nanoparticles to GO via γ ^{60}Co irradiation. The physical and chemical properties of the materials, including structure and surface area, were rigorously examined to assess their water disinfection efficacy. Furthermore, the photocatalytic performance of the materials in decomposing organic dyes and eliminating bacteria was tested under natural light conditions, verifying their practical application.

2. Research objectives of the thesis

This research focuses on the development and fabrication of nanocomposite materials, including spherical TiO_2 nanoparticles and magnetic iron oxide on graphene oxide (GO-Fe_3O_4-TiO_2, denoted as GMT), synthesized chemically, and TiO_2 nanotubes with silver nanoparticles on graphene oxide (GO-AgNPs-TNTs, denoted as GAT), synthesized via γ ^{60}Co irradiation. The synthesized materials are intended for use in water disinfection applications, specifically

for the photochemical degradation of Rhodamine B dye and the antibacterial treatment against *E. coli*.

3. The main research content of the thesis

The thesis consists of two parts:

+ Part 1: Synthesis and characterization of individual nanomaterials.

i. Synthesis and characterization of GO;

ii. Synthesis and characterization of TNTs;

iii. Synthesis and characterization of AgNPs.

+ Part 2: The main content of the thesis is presented in the illustration diagram below:

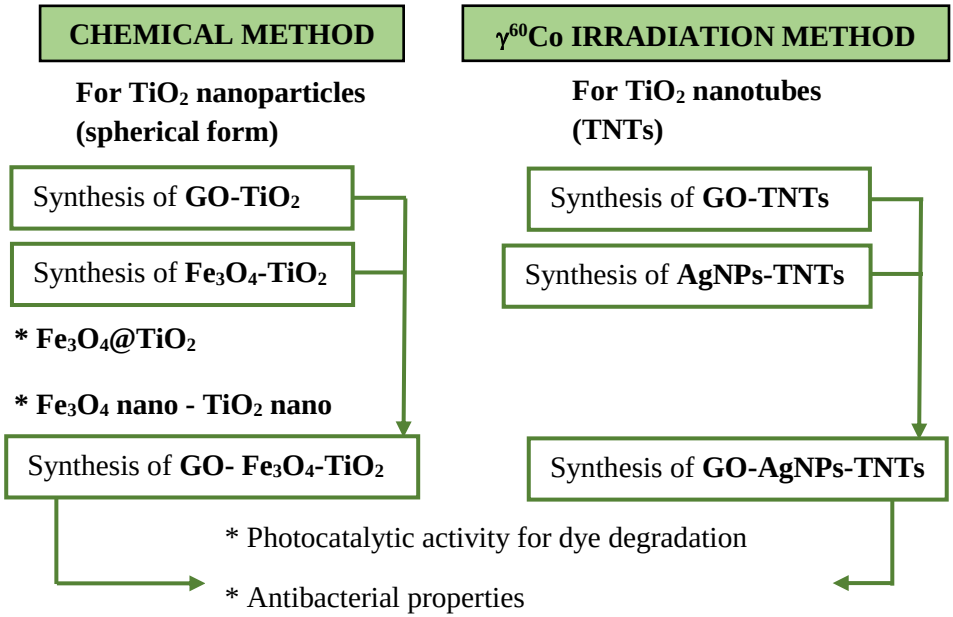
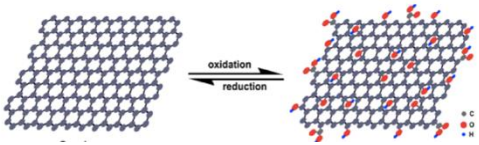


Diagram 1. Two main research contents of the thesis

Chapter 1. RESEARCH OVERVIEW

1.1. Graphene oxide (GO) material

Graphene oxide (GO), as shown in Figure 1.1, is produced by oxidizing graphite using various reagents. The structure of GO is distinguished by the presence of oxygen-containing functional groups (OFGs), which greatly enhance its hydrophilicity. This increase in hydrophilicity makes GO more dispersible in various solvents.



Graphene **Graphene oxide**

Figure 1.1. Structural model of graphene and graphene oxide [1].

1.2. TiO_2 (TO) material

TiO_2 nanoparticles (spherical)

Titanium dioxide (TiO_2, TO) (Figure 1.2) [5] have effective photocatalytic activity. TO is also a good antibacterial photomaterial, thanks to its ability to release electrons and holes.

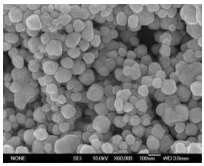


Figure 1.2. TiO_2 nanoparticles [5].

TiO_2 nanotubes (TNTs)

TiO_2 nanotubes (TNTs) feature a hollow structure. Compared to TiO_2 nanoparticles, TNTs possess a larger specific surface area, which enhances their photocatalytic activity. The integration of TNTs with metal or metal oxide nanoparticles has garnered considerable research interest. Examples of such combinations

include TNTs with Co_3O_4, Cu_2O, MnO_2, In_2O_3, Ag_2O, among others [23].

1.3. Material Fe_3O_4 (FO)

Nano Fe_3O_4, known for its outstanding magnetic properties, has many important applications due to its high chemical stability and biocompatibility. Fe_3O_4 has been extensively researched and utilized to address the challenge of recovering TiO_2 in environmental applications.

1.4. Silver nanoparticles (AgNPs)

AgNPs, known for their outstanding properties, have been extensively researched and applied across various fields, including optoelectronics, environmental treatment, and medicine [33].

1.5. Composite materials synthesis

Based on recent research, chemical and irradiation methods have been selected for the synthesis of ternary composite materials. Specifically, the GO-Fe_3O_4-TiO_2 composite was synthesized using chemical methods, while the AgNPs-TNTs-GO composite was synthesized using irradiation methods.

1.5.1. Chemical method

When synthesizing GO-Fe_3O_4-TiO_2 ternary composites, the conventional hydrothermal method was employed. Temperature changes during this process promoted more effective material bonding compared to other chemical methods starting from precursors.

1.5.2. Irradiation method

In this study, GO sheets, AgNPs particles, and TNTs tubes were combined into composite materials using a gamma irradiation

process with varying radiation doses to form the GO-AgNPs-TNTs composite.

Chapter 2. RESEARCH SUBJECTS AND METHODS

2.2. Materials synthesis process

2.2.1. Synthesis of GO material

The GO material was synthesized using the traditional Hummers method as described by Hummers et al. [4]. Throughout the project, GO was also produced using the modified Hummers method and the synthesis process proposed by Marcano et al. in their 2010 report [16]. The variations in synthesis efficiency of GO were experimentally recorded and subsequently published [77]. However, due to the large quantities of GO required for this project and to match the experimental conditions of our research group, the synthesis was predominantly conducted using the Hummers method.

2.2.2. Synthesis of GO-Fe_3O_4-TiO_2 composite materials by chemical method

The desired material system to be prepared includes GO, TiO_2 and Fe_3O_4.

Synthesis of core-shell Fe_3O_4@TiO_2 material: The desired core-shell Fe_3O_4@TiO_2 material (denoted as MT@) was synthesized following the process described by Q. Zhang and colleagues, published in 2013 [45].

Synthesis of Fe_3O_4-TiO_2 material from nanoparticles: Fe_3O_4-TiO_2 material was synthesized based on the procedure of D.Du and colleagues, published in 2013 [79]

Synthesis of GO-TiO_2: GO-TiO_2 composite material were synthesized according to the publication of Jiang et al. [80]. The two

components, GO and TiO_2, were combined in three different mass ratios to produce three products: GOTO 21, GOTO 11 and GOTO 12. In addition to exploring the ratios of GO and TiO_2, the effect of processing temperature on the properties of the GO-TiO_2 composite (at the best ratio) was investigated at three distinct temperatures: 100^oC, 150 ^oC and 200 ^oC.

Synthesis of GO-Fe_3O_4-TiO_2 (GMT) composite materials: The combination of Fe_3O_4-TiO_2 and GO materials was conducted based on the process for integrating TiO_2 nanomaterials with GO, as reported by Y. Jiang et al. in 2014 [11].

2.2.3. Synthesis of GO-AgNPs-TNTs composite materials by irradiation method

The desired material system to be prepared includes: GO, TiO_2 nanotubes (TNTs) and Ag nanoparticles (AgNPs).

Synthesis of AgNPs: AgNPs materials were synthesized based on the process published by D. Aherne et al. [83], where polysodium styrene sulfonate (PSSS) was replaced by polyethylene glycol (PEG).

Synthesis of TiO_2 nanotubes (TNTs): TNTs materials were synthesized based on the process published by M. A. L. Zavala et al. in 2017 [84].

Synthesis of Ag-TiO_2 nanomaterials (AgNPs-TNTs): After separate synthesis, AgNPs and TNTs materials were dispersed in PEG solution 0.5 $mg.L^{-1}$, ultrasonicated and irradiated with γ radiation doses of 5 kGy and 15 kGy. Similar to other composite materials, three different w/w ratios between AgNPs and TNTs were

investigated, denoted as AgNPs-TNTs 1:1, AgNPs-TNTs 1:2 and AgNPs-TNTs 2:1, respectively.

Synthesis of GO-TiO_2 nanotubes materials (GO-TNTs): The GO-TNTs composite materials were synthesized from individual GO and TNTs in three ratios (1:1, 1:2, 2:1) based on the publication of G. Jiang et al. [65]. These were then dispersed in 0.5 $mg.L^{-1}$ PEG solution. After dispersion, the GO-TNTs suspension was thoroughly stirred and irradiated with γ radiation doses of 5 kGy and 15 kGy. Following irradiation, the solution was vacuum freeze-dried to obtain the final product.

Synthesis of GO-AgNPs-TNTs composite materials: First, separately disperse GO and TNTs in 0.5 $g.L^{-1}$ PEG solution using ultrasonication for 30 minutes. Then, add the AgNPs solution and continue dispersion with ultrasonication for another 30 minutes. Following this, the solutions were irradiated with 60Co γ rays with doses of 5 kGy, 10 kGy, 15 kGy, 20 kGy, 25 kGy.

2.3. Characterization of the structure, morphology and properties of composite materials

+ X-ray diffraction (XRD): The solid post-synthesis sample was measured using a D2 Phaser-2ndGen, Bruker, Germany device at Customs Inspection Department 3, Ho Chi Minh City.

+ Fourier transform infrared spectroscopy (FTIR): Solid samples were prepared with KBr salt, compressed into pellets and analyzed using an Equinox 55 FTIR, Brucker, Germany at the Institute of Applied Materials Science. Operating parameters: measured at 25ºC, covering a spectral range 400 cm^{-1} – 4000 cm^{-1}. Repeatability was ensured with 3 measurements per sample.

+ **Raman Spectroscopy:** Solid samples post-synthesis were analyzed using a Raman Microscope System (Model: HORIBA Xplora One 532 nm) at the Institute of Applied Materials Science. Repeatability: 3 measurements per sample.

+ **Inductively Coupled Plasma Mass Spectrometry (ICP-MS):** The GO-AgNPs-TNT composite sample was converted into a soluble form using a mixture of 65% HNO3 and 10% HF (following PerkinElmer's recommended procedure) and analyzed with a PerkinElmer NexION 2000® instrument at the Institute of Applied Materials Science.

+ **Scanning Electron Microscope (SEM):** Solid post-synthesis samples were imaged using a FE-SEM S-4800 (Hitachi, Japan) at the Nanotechnology Laboratory - High-Tech Park.

+ **Transmission electron microscopy (TEM):** Samples were imaged using a JEM-1400 device at Ho Chi Minh City University of Technology.

+ **UV-Visible absorption spectroscopy method:** Liquid samples were analyzed using a Shimadzu UV-1800 instrument at the Institute of Applied Materials Science. Repeatability: 3 measurements per sample.

+ **Thermogravimetric analysis (TGA):** Samples for thermosolid analysis were measured using a METTLER TOLEDO TGA-DSC 3+ instrument at the Institute of Applied Materials Science.

2.4. Characterization of the properties of composite materials

2.4.1. Photocatalytic activity and durability test

The photocatalytic activity of the composite material was evaluated by assessing the degradation of RhB dye under natural sunlight,

following the method described by Nagaraja et al. [68]. High-performance liquid chromatography (HPLC) was employed to analyze the RhB solution post-reaction, demonstrating the material's capability to photodegrade RhB

2.4.2. Antibacterial activity test against E. coli

The antibacterial activity of the material was investigated using the direct contact method on E. coli bacteria, according to the AATCC 100 standard test procedure: Assessment of Antibacterial Finishes on Textile Materials, established by the American Association of Textile Chemists and Colorists (AATCC). The procedure and experiments to evaluate the antibacterial activity of the GMT materials were conducted at the Laboratory of Animal Biotechnology, Faculty of Biology and Biotechnology, University of Natural Sciences, Vietnam National University, Ho Chi Minh City.

2.5. Data processing

The data in the study were processed and analyzed using characteristic spectra such as FTIR, UV-Vis, XRD, Raman, and TEM/SEM images to evaluate the synthesis efficiency and structural properties of the materials. The verification and reliability of the spectral data were ensured through:

a) Repeatability assessment: Each spectrum (FTIR, Raman, UV-Vis) was measured repeatedly at least three times to ensure consistency.
b) Verification with reference materials: Peak positions or material parameters were compared with standard data (JCPDS for XRD, spectral libraries for FTIR and Raman).

Chapter 3. RESULTS AND DISCUSSION

3.1. Graphene oxide (GO) material

The raw graphite powder is fine and black (see Figure 3.1a). After the oxidation reaction, the resulting GO product is a light, porous, brown powder (see Figure 3.1b).

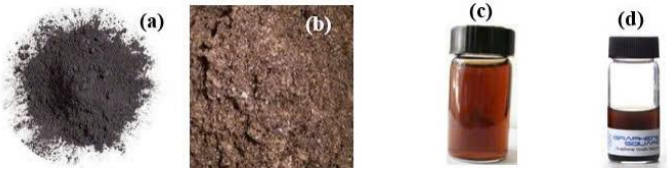


Figure 3.1. (a). Graphite powder, (b). Synthesized GO product, (c) GO solution in distilled water, (d) GO of Graphene Square Inc.

The GO product was tested for water solubility by dissolving a small amount in distilled water and vigorously shaking, resulting in a brown solution without any precipitate (see Figure 3.1c). This indicates a significant increase in solubility compared to the original graphite, demonstrating that the reaction successfully introduced polar functional groups such as OH, CO, and COOH onto the graphene surface. The appearance and state of the product solution resemble the descriptions in the report by Marcano et al. [16] and a commercial GO water solution from Graphene Square Inc. (Korea) (see Figure 3.1d), confirming the successful synthesis of the GO

3.1.1. Results of structural analysis of GO material

The resulting product exhibits a GO structure synthesized via the Hummers method.

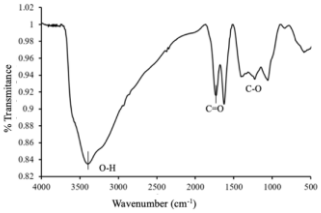


Fig. 3.2. FTIR spectrum of GO

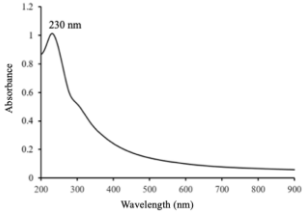


Fig. 3.3. UV-Vis spectrum of GO

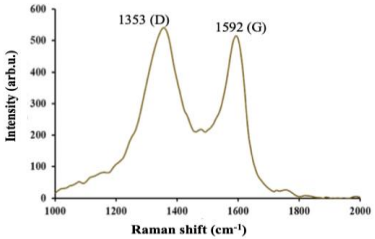


Fig 3.4. Raman spectrum of GO

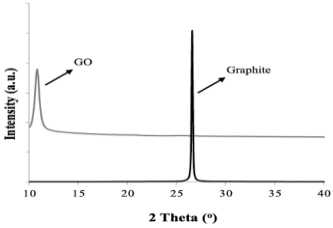


Fig 3.5. XRD pattern of GO and its graphite precursor.

3.1.2. Surface morphology analysis reults of the GO material

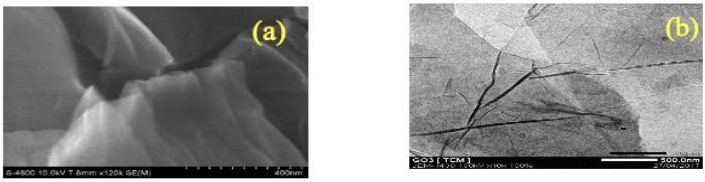


Fig 3.6. SEM (a) and TEM (b) images of the GO

The surface parameters was analyzed using the BET equation, yielding a surface area of 565,1984 $m^2.g^{-1}$, a pore size of 29,9680 nm and a pore volume of 3,7600 $cm^3.g^{-1}$.

3.1.3. Thermal property analysis results of the GO material

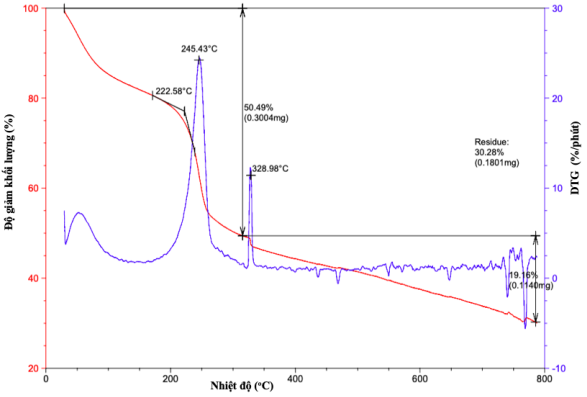


Fig 3.7. TGA curve of the GO.

Based on the obtained results, the GO material was successfully synthesized with suitable physicochemical properties, serving as a promising precursor for further synthesis steps.

3.2. GO-Fe_3O_4-TiO_2 composite material (GMT)

Based on the synthesis investigation of the two individual components, Fe_3O_4-TiO_2 and GO-TiO_2, the ternary GO-Fe_3O_4-TiO_2 composite was examined at three different ratios, ensuring equal proportions of GO-TiO_2 or Fe_3O_4-TiO_2, designated as GMT (111, 211, 212). The synthesized GO-Fe_3O_4-TiO_2 material appeared as a dark gray powder.

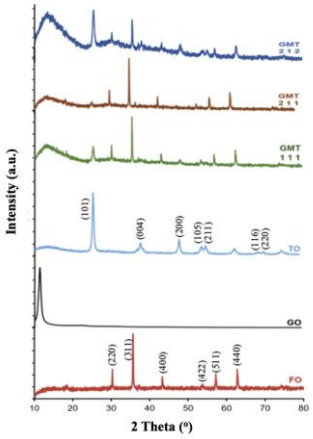


Fig 3.8. XRD patterns of GMT 111, GMT 211, GMT 212 compared with anatase TiO_2 nanoparticles (TO), Fe_3O_4 nanoparticles (FO), and GO.

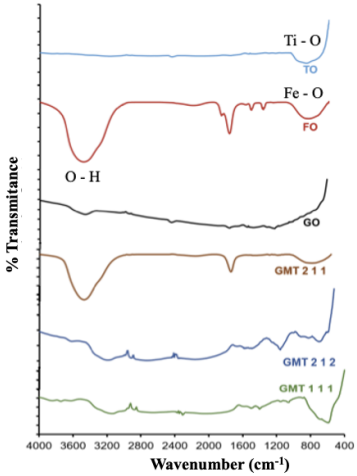


Fig 3.9. FTIR spectra of GMT 111, GMT 211, and GMT 212, compared with anatase TiO_2 nanoparticles (TO), Fe_3O_4 nanoparticles (FO), and GO

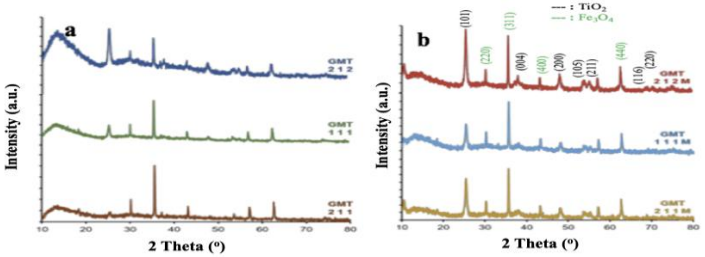


Fig 3.10. XRD patterns of GMT samples (a) and the mechanically mixed sample (GMT M) (b)

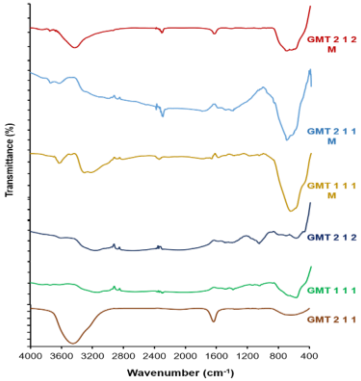


Fig 3.11. FTIR spectra of the mechanically mixed samples (GMT M) and GMT samples.

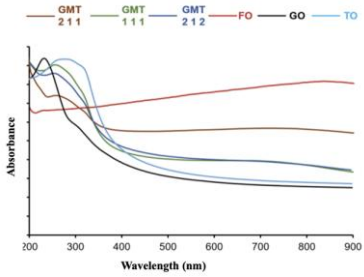


Fig 3.12. UV-Vis spectra of GMT 111, GMT 211, and GMT 212, compared with anatase TiO_2 nanoparticles (TO), Fe_3O_4 nanoparticles (FO), and GO.

3.3. GO-AgNPs-TNTs composite material (GAT)

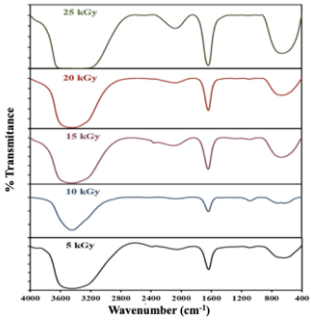


Fig 3.13. FTIR spectra of GO-AgNPs-TNTs samples irradiated at doses of 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 25 kGy.

Through the synthesis investigation of the GO-Fe_3O_4-TiO_2 composite material using chemical methods, the involvement of secondary factors and by-products affects material evaluation and

homogeneity. Therefore, precise control is required to ensure its suitability for future applications

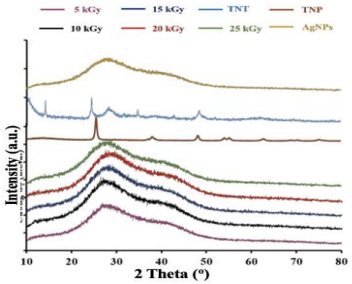


Fig 3.14. XRD patterns of GO-AgNPs-TNTs samples irradiated at doses of 5, 10, 15 , 20, and 25 kGy, along with irradiated TiO_2 nanotube material, initial TiO_2 nanopowder, and irradiated AgNPs solution.

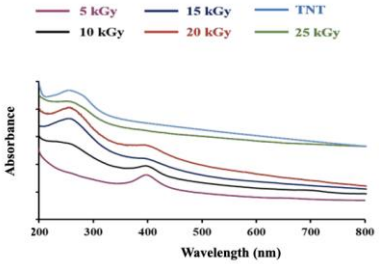


Fig 3.15. UV-Vis spectra of GO-AgNPs-TNTs samples irradiated at doses of 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 25 kGy, along with the separate TNTs material

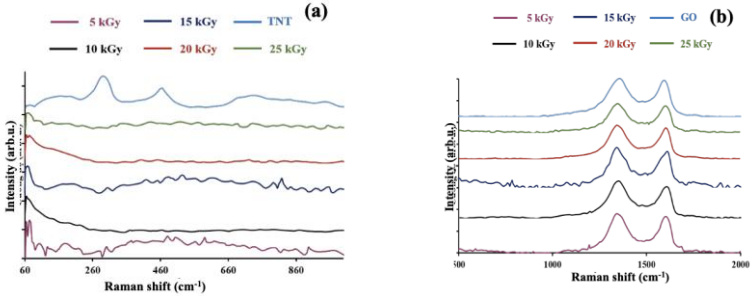


Fig 3.16. Raman spectra of GO-AgNPs-TNTs samples irradiated at doses of 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 25 kGy (a), and the individual GO material (b)

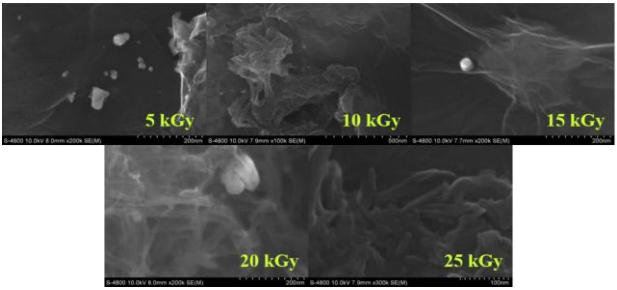


Fig 3.17. SEM images of GO-AgNPs-TNTs composite samples irradiated at doses of 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 25 kGy.

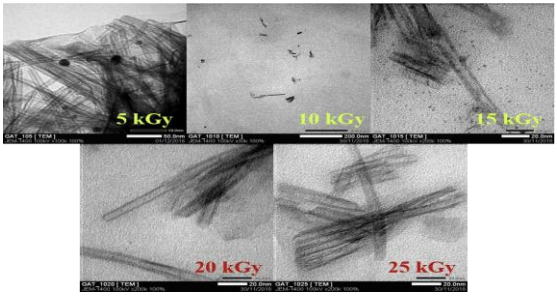


Fig 3.18. TEM images of GO-AgNPs-TNTs composite samples irradiated at doses of 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 25 kGy.

Silver nanoparticles (AgNPs) were used as a substitute for Fe_3O_4 to enhance compatibility with TNTs. Several studies have demonstrated the combination of AgNPs, GO, and TNTs. Based on the synthesis of individual binary components, the combination of GO, AgNPs, and TNTs at a 2:2:1 ratio was investigated under γ-irradiation using a ^{60}Co source at various radiation doses. During the γ-irradiation synthesis of the GO-AgNPs-TNTs composite, increasing the irradiation dose significantly enhanced the crystallization of TiO_2 while also promoting the aggregation of Ag nanoparticles at

excessively high doses. The optimal irradiation dose for maintaining the integration of GO, AgNPs, and TNTs was determined to be 10 kGy and 15 kGy, consistent with findings from studies on binary composite materials.

3.4. Photocatalytic activity testing of the materials

3.4.1. Photocatalytic activity of the GMT composite material

Table 3.1. DE (%) value of the raw materials and synthesized materials

Nº	Materials	C (ppm)	C_o (ppm)	DE (%)
1	GMT 111	7,44	10	**25,60**
2	GMT 211	6,14	10	**38,40**
3	GMT 212	4,71	10	**52,90**
4	GO	4,78	10	**52,20**
5	TiO_2	7,95	10	**27,20**
6	Fe_3O_4	8,49	10	**24,10**

The adsorption and retention of RhB within the GO pores only reduce its concentration without altering its chemical nature, whereas photocatalytic degradation completely decomposes RhB into degradation products. After the photocatalytic reaction, RhB solutions were analyzed using high-performance liquid chromatography (HPLC) equipped with a UV-Vis detector to identify degradation products. The chromatograms in Figures 3.63 and 3.64, corresponding to the initial 10 ppm RhB solution and the post-reaction solution with GMT 212, confirm that RhB was indeed degraded rather than merely adsorbed and retained within the GO pores.

Investigation of catalyst stability: The investigation results indicate that the synthesized GMT material exhibits relatively good photocatalytic activity compared to conventional TiO_2 and possesses

magnetic recoverability. Furthermore, its high stability suggests promising potential applications. The findings also reveal that the ratio of GO, TiO_2, and Fe_3O_4 significantly influences the photocatalytic activity of the composite, with the 212 ratio yielding the most catalytically stable material. These experimental results align well with the structural morphology analysis and other physicochemical property evaluations.

3.4.2. Photocatalytic activity of the GAT composite material

Table 3.2. Component contents and DE values of GAT composite samples irradiated at 5 kGy, 10 kGy, 15 kGy, 20 kGy, and 25 kGy.

GAT samples	% GO	% AgNPs	% TNT	DE (%)
GAT-5	67,40	$0{,}003E^{-4}$	32,60	31,69
GAT-10	**69,12**	**4,90**	**25,98**	**81,21**
GAT-15	72,31	$0{,}01E^{-4}$	27,69	28,55
GAT-20	64,84	$0{,}01E^{-4}$	35,16	36,87
GAT-25	88,90	$0{,}002E^{-4}$	11,10	61,18

The photocatalytic reaction experiments of GAT composite samples and individual component materials yielded promising results: the composite materials exhibited superior photocatalytic activity compared to their individual components. The combination effectively harnessed the advantages of GO, AgNPs, and TNTs, facilitating chemical reactions that degraded RhB dye under natural sunlight irradiation.

3.5. Antibacterial activity testing of the composite materials against *E. coli*

3.5.1. Antibacterial activity of the GMT material against E. coli

Table 3.3. Antibacterial activity of the GMT composite materials and the precursors against *E. coli*.

COLONY FORMATION RESULTS AGAINST *E. coli*				
Samples	Colony count	A	B	% Bacterial reduction (R)
TO	30 45	75		53,99
FO	30 38	68		58,28
GMT 111	52 72	124		23,93
GMT 211	70 78	148		9,20
GMT 212	36 53	89		45,40
Control sample	74 89		163	

Through the evaluation of *E. coli* antibacterial activity under natural sunlight exposure, the GMT composite materials exhibited antibacterial properties comparable to TiO_2 and Fe_3O_4.

3.5.2. Antibacterial activity of the GAT composite material against E. coli

Table 3.4. Antibacterial activity against *E. coli* for GAT samples irradiated at 5, 10, 15, 20, and 25 kGy, along with the control.

COLONY FORMATION RESULTS AGAINST *E. coli*				
Samples	Colony count	A	B	% Bacterial reduction (R)
5 kGy	0 3	5		**99,33**

	2			
10 kGy	3	11		**98,53**
	5			
	3			
15 kGy	7	22		**97,07**
	8			
	7			
20 kGy	0	1		**99,87**
	1			
	0			
25 kGy	1	3		**99,60**
	1			
	1			
AgNPs	0	0		**100**
	0			
	0			
TNTs	25	90		**88,00**
	35			
	30			
Control sample	250		750	
	250			
	250			

Through the evaluation of *E. coli* antibacterial activity under natural sunlight exposure, the GO-AgNPs-TNTs composite materials exhibited excellent antibacterial performance, surpassing TNTs and comparable to AgNPs.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

*** Synthesis of Materials and Characterization:** The constituent nanomaterials, including graphene oxide (GO),

titanium dioxide nanotubes (TNTs), and silver nanoparticles (AgNPs), were successfully synthesized with structural morphology and physicochemical properties suitable for composite fabrication. Binary composite materials such as GO-AgNPs, GO-TNTs, and AgNPs-TNTs were synthesized via γ-irradiation using a ^{60}Co source to determine the optimal component ratios. The identified ratios, GO:TNTs = 2:1 and AgNPs:TNTs = 2:1, served as the foundation for developing the ternary composite material GO-AgNPs-TNTs.

*** Morphological and Structural Properties of the GO-AgNPs-TNTs composite:** The ternary GO-AgNPs-TNTs composite was synthesized via γ-irradiation at a dose of 10 kGy from its individual components. Structural morphology analysis revealed a uniform distribution of AgNPs on TiO_2 nanotubes and scattered over GO sheets. Additionally, TiO_2 nanotubes were observed on the GO surface, forming a strong interfacial network among the components.

*** Photocatalytic and Antibacterial Activities**

- Photocatalytic Activity: Rhodamine B degradation experiments under natural sunlight demonstrated that GO-AgNPs-TNTs exhibited superior photocatalytic performance compared to individual materials and binary composites.

- Antibacterial Activity: The antibacterial efficacy of GO-AgNPs-TNTs against *E. coli* surpassed that of standalone TiO_2 and was comparable to AgNPs, highlighting the synergistic effect in the ternary composite.

- Advantages of the GO-AgNPs-TNTs Composite: Compared to GO-Fe_3O_4-TiO_2, the GO-AgNPs-TNTs composite demonstrated

higher suitability for antibacterial applications due to stronger interfacial interactions and enhanced photocatalytic efficiency.

Recommendations

In future studies, the following questions should be explored and addressed:

+ Investigate the binding mechanism among the three components under γ-irradiation by employing advanced characterization techniques to analyze the relationships between C–C, C–O, C–Ti, C–Ag, and Ti–Ag bonds (e.g., XPS, XRD, and pulse irradiation treatments for individual materials).

+ Examine the effect of γ-ray dosage on the integration of GO, AgNPs, and TNTs to achieve controlled synthesis of the GO-AgNPs-TNTs composite with tunable component interactions.

+ Study the kinetics of the photocatalytic degradation of dyes and evaluate the adsorption behavior of the synthesized GAT material.

+ Assess the antibacterial activity of the GO-AgNPs-TNTs composite against various microorganisms (e.g., bacteria, fungi) to expand its potential applications. Additionally, optimize the dispersion stability of GO-AgNPs-TNTs solutions and incorporate additional components to explore applications in post-harvest agricultural preservation.

NEW CONTRIBUTIONS OF THE THESIS

- **Scientifically:** The GO-AgNPs-TNTs composite with a composition ratio of GO:TNTs = 2:1 and AgNPs:TNTs = 2:1 was successfully synthesized via γ-irradiation at a dose of 10 kGy, exhibiting effective photocatalytic and antibacterial activities. The irradiation process did not completely reduce GO to rGO, preserving

oxygen functional groups on the GO surface, which facilitated strong interactions with AgNPs and TNTs..

- **Synthesis Methodology:** The γ-irradiation technique overcomes the limitations of conventional chemical synthesis methods by minimizing side reactions and residual by-products. During this process, irradiation-generated active species activate the nanomaterial surfaces, promoting strong interfacial bonding among components and enhancing synergistic effects.
- **Application Potential:** The GO-AgNPs-TNTs composite demonstrates not only high efficiency in dye degradation but also significant antimicrobial activity, offering promising applications in environmental remediation and advanced purification technologies.

LIST OF THE PUBLICATIONS RELATED TO THE DISSERTATION

i) ***Journal of Nanoscience and Nanotechnology***. Title: Graphene Oxide and Graphene Oxide-TiO_2 Nanocomposites: Synthesis, Characterization, and Rhodamine B Photodegradation Investigation, Số đăng và trang: (2021) 21(3), 1507–1516. Authors: Duy Khang Vu Nguyen, **Thuy Loan Thi Pham**, My Hanh Thi Tran, Tuong Vi Tran, and Dang Khoa Nguyen Vo.

ii) ***Applied NanoScience***. Title: Silver nanoparticles-assembled graphene oxide sheets on TiO_2 nanotubes: synthesis, characterization, and photocatalytic investigation. Số đăng và trang: (2020) 10, 3735-3743. Authors: **Thuy Loan Pham Thi**, Duy Khang Nguyen Vu, Phuong Anh Nguyen Thi, Dang Khoa Vo Nguyen.

iii) ***Journal of BioTechnology***. Title: Synthesis of Graphene oxide-TiO_2 nanotubes-silver nanoparticles nanocomposite by gamma irradiation for antibacterial and post-harvest preservation purposes. Số đăng và trang: (2019) 17(4), 1-8. Authors: Nguyen Thi Phuong Anh, **Pham Thi Thuy Loan**, Nguyen Vu Duy Khang, Vo Nguyen Dang Khoa.