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PhD Thesis

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Nanomaterials with Applications in Photocatalysis

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Introduction

The paper focuses on the use of photocatalysis, a light-activated process in which titanium dioxide (TiO_2) accelerates redox reactions without being consumed, for the degradation of organic pollutants in water. TiO_2 is appreciated for its stability and efficiency, especially in the anatase form, but it is mainly active under UV radiation. To extend its activity into the visible spectrum, strategies such as doping, nanostructuring, and combining with conductive materials are employed.

In this context, emerging pollutants such as paracetamol, ibuprofen, 17β-estradiol, amoxicillin, and sulfamethoxazole are analyzed—compounds frequently detected in wastewater that can have negative effects on both human health and ecosystems. The paper emphasizes the need to develop efficient water purification technologies to reduce the impact of these contaminants.[1]

Nanocomposite preparation

In this study, several photocatalytic nanocomposites based on titanium dioxide in the form of nanoparticles (TiO_2NP) and nanotubes (TiO_2NT) were obtained, functionalized with noble metals or metal oxides (Ag, Au, Pt, Cu_xO, NiO) and various forms of graphene derivatives (GO, trGO, NGr). The materials were synthesized using different methods, such as wet impregnation, thermal reduction in a controlled atmosphere, and hydrothermal synthesis, with the aim of producing efficient compounds for photocatalytic applications under visible light.

Graphene oxide was obtained using the modified Hummers method and was subsequently thermally reduced (trGO) or nitrogen-doped (NGr) in order to optimize its electronic and charge transfer properties. TiO_2NT were synthesized via hydrothermal methods, while the TiO_2NP form was chemically prepared from organometallic precursors. The metals were deposited onto the support by impregnation and reduction, using the corresponding metal salts ($HAuCl_4$, H_2PtCl_6, $AgNO_3$, $Cu(NO_3)_2$, $Ni(NO_3)_2$).[1] The composites were combined with graphene through mixing and subsequent thermal treatments, either to reduce the graphene or to stabilize the final structure. The resulting products were lyophilized to preserve their morphology and subjected to thermal treatments in a controlled atmosphere for activation and crystallization. Following these steps, various types of hybrid nanocomposites were obtained, which were subsequently characterized and tested for the degradation of emerging pollutants in water, demonstrating variable photocatalytic activity depending on the nature of the support, the metal, and the form of graphene used.

TiO_2 Nanoparticles decorated with Ag and nitrogen-doped graphene

The morphology of the Ag-TiO_2NP-NGr nanocomposite was analyzed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), revealing its complex structure. TEM images showed a non-uniform distribution of particles and the presence of agglomerations, while SEM revealed a three-dimensional porous surface. The integration of nitrogen-doped graphene oxide (NGr) into the composite enhances mechanical stability and conductivity, facilitating charge transfer and reducing electron–hole pair recombination. Silver nanoparticles increase visible light absorption through the plasmonic effect, and nitrogen doping extends the photocatalyst's sensitivity into the visible spectrum.[2]

Characterization of the Ag-TiO_2NP-NGr composite using XRD, XPS, and UV-Vis techniques confirm the successful synthesis and reveals significant improvements in photocatalytic properties. XRD analysis highlights the formation of crystalline phases and the effective interaction between TiO_2NP, Ag, and NGr, which enhances photocatalytic performance. XPS spectroscopy indicates a modification in the electronic structure due to the presence of NGr, facilitating charge transfer and extending light absorption into the visible range. UV-Vis analysis shows that the NGr-doped material exhibits superior absorption across the entire visible spectrum, due to the synergistic effects between components, making it a promising candidate for environmental purification applications.

The combination of these characterizations confirms that the material possesses an extended active surface area, high porosity, and a complex composition—key factors for photocatalytic applications, water purification, and solar energy conversion. The presence of Ag nanoparticles and nitrogen doping improves photocatalytic performance, while the graphene oxide component stabilizes the structure and enhances electrical conductivity.[2]

Nanomaterials with TiO_2 nanoparticles decorated with Cu_2O/CuO and graphene Derivatives

The Cu_2O/CuO-TiO_2NP-trGO nanocomposite was characterized using morphological, structural, chemical, and optical analyses, highlighting its photocatalytic potential. SEM images revealed a complex morphology, with spherical nanoparticles unevenly distributed on the surface of thermally reduced graphene oxide (trGO), which stabilizes the structure and prevents excessive agglomeration. XRD analysis confirmed the presence of the anatase phase and the effective decoration with copper oxide, while XPS analysis indicated the successful reduction of graphene oxide and improved conductivity, favorable for charge transfer.
UV-Vis spectroscopy demonstrated enhanced absorption in the visible range, especially for the thermally treated composite (Cu_2O/CuO-TiO_2NP-trGO300), due to the narrowing of the band gap (Eg) and the synergistic effect among the components. Composites with 2% Cu_2O/CuO showed the best balance between stability and optical performance, and were therefore selected for advanced photocatalytic applications under natural light conditions.[3]

Nanomaterials with TiO_2 nanotubes decorated with gold and graphene derivatives

Caracterizarea nanocompozitelor pe bază de TiO_2NT, aur și oxid de grafenă (GO/trGO) a evidențiat o morfologie poroasă, uniformă și bine organizată, conform analizelor TEM și SEM. Utilizarea oxidului de grafenă redus termic (trGO) favorizează formarea unor structuri compacte și stabile, cu interfețe extinse între componente, ceea ce îmbunătățește transportul sarcinii și eficiența fotocatalitică. Analiza XRD confirmă integrarea cu succes a componentelor și păstrarea stabilității cristaline, în timp ce XPS atestă prezența aurului în formă metalică și compatibilitatea cu fazele carbonice. Spectroscopia UV-Vis relevă o absorbție eficientă în domeniul vizibil și o reducere a benzii interzise (E_g), în special la compozitele cu Au și trGO, ceea ce le face promițătoare pentru aplicații în fotocataliză și conversie fotochimică. [4]

Nanomaterials with TiO_2 nanotubes decorated with Pt and graphene derivatives

The nanocomposites based on Pt-TiO_2NT and NGr/trGO were characterized morphologically, structurally, chemically, and optically, demonstrating high potential for photocatalytic applications. TEM and SEM analyses revealed a uniform distribution of platinum nanoparticles on TiO_2NT and their effective integration into stable nanostructured networks with an extended active surface area. The presence of trGO enhances the mechanical stability and conductivity of the material.

XRD analysis confirmed the presence of crystalline phases of anatase and metallic platinum, highlighting the influence of graphene oxide on crystallite size and metal distribution. XPS spectroscopy showed that thermal treatment at 650°C leads to the complete reduction of Pt species to their metallic form (Pt^0), which is essential for catalytic efficiency.

UV-Vis spectroscopy demonstrated extended absorption in the visible range due to the presence of Pt and NGr, while Tauc analysis indicated a significant decrease in the band gap (Eg) for the samples containing Pt and nitrogen-doped graphene. This reduction promotes the absorption of lower-energy photons, optimizing photocatalytic performance under natural light.

Nanomaterials with TiO_2 nanotubes decorated with NiO and graphene derivatives

The nanocomposites based on NiO-TiO_2NT and trGO/NGr were characterized using morphological, structural, chemical, and optical analyses, revealing promising performance for photocatalytic applications. TEM and SEM analyses showed a uniform distribution of NiO nanoparticles on TiO_2NT, with effective interactions between the active phases. Functionalization with trGO or NGr resulted in three-dimensional porous networks with good dispersion of graphene sheets, although with a slight tendency toward agglomeration.[3]

XRD analysis confirmed the stability of the anatase phase of TiO_2NT and the presence of nickel oxide, without affecting the crystalline structure, while the absence of specific graphene reflections suggests efficient dispersion and low content. XPS spectroscopy revealed differences between trGO and NGr regarding the interaction between NiO and TiO_2NT, with a more effective binding observed in the case of trGO. [3]

UV-Vis analysis demonstrated radiation absorption in the visible range and a significant reduction in the band gap energy (Eg) in the presence of trGO, which enhances solar light absorption and improves charge transfer—key properties for boosting photocatalytic activity.[3]

Evaluation of the photocatalytic activity of the prepared nanomaterials for various emerging contaminants

Photocatalytic degradation of sulfamethoxazole in the presence of Ag-TiO_2NP-NGr

This chapter focuses on evaluating the performance of the Ag-TiO_2NP nanocomposite modified with nitrogen-doped graphene (NGr) in the photocatalytic degradation of sulfamethoxazole (SMZ) under visible light. Through an integrated approach that includes adsorption studies, kinetic analysis, identification of reactive species, and testing under natural light, the advantages brought by structural modifications on photocatalytic efficiency are highlighted. The study contributes to a deeper understanding of the mechanisms involved in photocatalytic depollution processes and supports the potential of this type of nanocomposite for real-world water treatment applications.

Reducing the band gap (Eg) below the threshold of 3.1 eV is essential for the efficient activation of photocatalysts in the visible range. The integration of nitrogen-doped graphene oxide (NGr) into the Ag-TiO_2NP composite led to a decrease in Eg to 2.5 eV, enabling the absorption of photons in the 420–700 nm spectrum and resulting in a significant enhancement of photocatalytic activity. This effect was confirmed by the photocatalytic degradation tests of sulfamethoxazole (SMZ), where the Ag-TiO_2NP-NGr nanocomposite achieved an efficiency of 83% under visible light, compared to only 5% for the material without NGr. [2]

The adsorption isotherm analysis of SMZ highlighted the importance of the initial interaction between the contaminant and the nanomaterial surface, with the adsorption step being crucial for initiating the photodegradation process. A slight increase in the amount adsorbed was observed with increasing pollutant concentration, without reaching saturation, suggesting the presence of a large number of active sites available on the surface of the composite.[2]

In the adsorption modeling analysis, the Langmuir model proved particularly useful for practical interpretation, providing insights into the maximum adsorption capacity and the material's efficiency under high-concentration conditions. Although the photocatalytic degradation efficiency did not vary significantly at low SMZ concentrations, a slight improvement was observed at 250 µg/L, reaching a degradation rate of approximately 80%.[2]

The study on the influence of photocatalyst dosage showed that a concentration of 1.33 mg/mL of Ag-TiO_2NP-NGr provides the best results, significantly accelerating the photodegradation process. The reaction kinetics followed the Langmuir model, supporting the idea that the reaction rate is proportional to the surface coverage of the catalyst. Investigations into the reactive species confirmed the involvement of hydroxyl radicals (•OH) as the primary agents responsible for degradation, followed by photogenerated holes (h^+), while superoxide radicals ($•O_2^-$) played a less significant role.[2]

The proposed action mechanism highlights the essential role of NGr in promoting charge transfer and inhibiting charge carrier recombination, leading to efficient photodegradation under visible light. The energy band diagram supports this hypothesis, showing both kinetic and energetic favorability for electron transfer from the conduction band of TiO_2NP to NGr and subsequently to dissolved oxygen, resulting in the generation of reactive species.[2]

By comparison, under UV-A irradiation, the Ag-TiO_2NP composite exhibited superior catalytic activity due to the strong effect of silver nanoparticles. However, under natural light (sunlight) exposure, the NGr-containing composite outperformed it, achieving a degradation rate of over 90% in just 60 minutes—a performance that clearly highlights the advantages of integrating nitrogen-doped graphene into the catalyst structure.[2]

In conclusion, the efficiency of photocatalytic systems is influenced not only by the amount of catalyst and the nature of the radiation but also by the type of carbon-based support used. The Ag-TiO_2NP-NGr nanocomposite stands out for its high performance under visible and natural light, making it a promising candidate for sustainable water purification applications under real environmental conditions.[2]

Photocatalytic degradation of methylene blue and amoxicillin in the presence of Cu_2O/CuO-TiO_2NP-trGO

In this study, the photocatalytic performance of hybrid composites based on Cu_2O/CuO-TiO_2NP and graphene oxide with various degrees of reduction (trGO200/trGO300) was evaluated for the removal of methylene blue (MB) and amoxicillin (AMX) under visible light. The results revealed remarkable efficiency of the combined adsorption and photodegradation process, particularly during the first 150 minutes, followed by a stabilization phase.

Among the tested materials, Cu_2O/CuO-TiO_2NP-GO exhibited the highest photocatalytic activity, a behavior attributed to the ability of graphene oxide to facilitate charge transfer and extend light absorption into the visible range. These observations were further supported by the degradation tests of amoxicillin, where the materials containing GO or trGO outperformed the composite without graphene oxide.

The proposed photocatalytic mechanism involves the formation of a type II heterojunction, which enables efficient separation of photoinduced charge carriers and the generation of reactive oxygen species required for contaminant degradation. The favorable positioning of the energy bands allows for effective migration of electrons and holes, even in the absence of graphene oxide, ensuring sustained catalytic activity.[3]

These results confirm the potential of hybrid nanocomposites based on Cu_2O/CuO-TiO_2NP for advanced treatment applications of emerging pollutants. They also highlight the importance of the structural and energetic phase of photoactive materials in optimizing performance under real lighting and environmental conditions. [3]

Photocatalytic degradation of 17*β*-estradiol in the presence of Au-TiO_2NT-GO/trGO

This chapter investigated the efficiency of Au-TiO_2NT-based nanocomposites in the photodegradation of 17β-estradiol, an emerging pollutant with significant endocrine-disrupting effects. The study compared the base material with variants functionalized with graphene oxide (GO) and reduced graphene oxide (trGO), highlighting the impact of these modifications on photocatalytic performance.
In the absence of light, the efficient adsorption of the pollutant onto the catalyst surfaces demonstrated the crucial role of this step in initiating the photocatalytic process. Among the tested materials, the Au-TiO_2NT-GO composite exhibited the highest efficiency, followed by the material containing trGO. These differences

are correlated with the ability of graphene oxide to enhance charge transfer and reduce electron–hole recombination, thereby promoting oxidation processes.[4]

The reaction kinetics followed a first-order model, with a linear progression of pollutant degradation over time. The GO-functionalized material exhibited the best performance, supporting the use of graphene oxide as an effective strategy for enhancing photocatalytic efficiency.
To better understand the mechanism of action, reactive species scavengers were employed. The experiments showed that photogenerated holes (h^+) play a major role in the oxidation process, while hydroxyl (•OH) and superoxide ($•O_2^-$) radicals contribute in a complementary manner. GO significantly improved overall efficiency without altering the fundamental reaction mechanism. [4]

The proposed mechanism involves the generation of electron–hole pairs on the catalyst surface under visible light, followed by the formation of reactive species capable of degrading 17β-estradiol. Electrons from the conduction band of TiO_2 reduce dissolved oxygen, generating active radicals, while holes in the valence band oxidize water or hydroxide ions. Additionally, the favorable alignment between the HOMO level of 17β-estradiol and the valence band of TiO_2 thermodynamically supports the degradation process. [4]

In conclusion, the results confirm that the addition of graphene oxide, particularly GO, significantly enhances the efficiency of the photocatalysts and makes these compounds promising solutions for the treatment of water contaminants, especially under visible light conditions.[4]

Photocatalytic degradation of acetaminophen and ibuprofen in the presence of Pt (5%)-TiO_2NT-NGr/trGO

This chapter describes the photocatalytic performance of Pt-TiO_2NT-based nanocomposites, with and without the addition of graphene oxide (NGr or trGO), in the degradation of two pharmaceutical contaminants of interest: acetaminophen and ibuprofen, under visible light irradiation. The tests revealed high degradation efficiency for all materials, particularly during the initial stages of irradiation, with near-complete removal of the pollutants.

First-order kinetics were confirmed for both contaminants, indicating a linear progression of the degradation process. The integration of nitrogen-doped graphene oxide led to a slight improvement in catalytic efficiency, attributed to its ability to reduce charge recombination and facilitate electron transfer. However, the differences between the graphene oxide-modified materials and the unmodified one were moderate, suggesting that the influence of the carbon-based support is limited under the applied testing conditions.

In conclusion, the Pt-TiO_2NT composite proved to be effective even in the absence of graphene oxide, and the tested materials can be considered promising candidates for water purification applications under visible light. Further research is needed to clarify the extent to which graphene oxide significantly contributes to the optimization of these hybrid systems and to explore possible synergies under varying environmental and contamination conditions.

Photocatalytic degradation of 17*β*-estradiol, acetaminophen, and ibuprofen in the presence of NiO-TiO_2NT-NGr/trGO

This chapter investigated the photocatalytic performance of NiO-TiO_2NT-based nanocomposites functionalized with different forms of graphene oxide (trGO and NGr) in the degradation of emerging pharmaceutical contaminants: 17β-estradiol, acetaminophen, and ibuprofen. The main objective was to identify materials capable of performing efficiently under visible light.

The results showed that the base material (NiO-TiO_2NT) exhibited low photocatalytic activity, while functionalization with graphene oxide led to significant improvements. The composite with trGO demonstrated the best performance, followed by the one with NGr, in the degradation of both 17β-estradiol and acetaminophen. These improvements were attributed to the ability of graphene oxide to facilitate charge transfer and reduce electron–hole recombination.

The photocatalytic degradation processes followed first-order kinetics, and experimental data confirmed that trGO had the greatest impact on the degradation rate. However, in the case of ibuprofen, none of the tested materials exhibited significant catalytic activity. This observation highlights the need to optimize both materials and experimental conditions according to the nature of the contaminant. Furthermore, the analysis of energy band alignment revealed the influence of graphene oxide on the electronic properties of the composites. It was found that thermally reduced graphene oxide has a more pronounced effect on facilitating electron transfer, while nitrogen-doped graphene oxide exerts a more moderate impact.

In conclusion, the integration of different forms of graphene oxide into the NiO-TiO_2NT nanocomposite structure represents a promising strategy for enhancing photocatalytic efficiency. The obtained results support the use of these materials in water purification processes, with the caveat that selecting the appropriate type of graphene oxide and adjusting reaction conditions are essential for performance optimization.[5]

General conclusions

This study aimed to develop and evaluate advanced photocatalytic nanocomposites based on titanium dioxide (TiO_2), with the goal of removing emerging pollutants from water through an eco-friendly process activated by sunlight. Materials based on TiO_2 nanoparticles (TiO_2NP) and nanotubes (TiO_2NT) were synthesized and functionalized with metals (Ag, Au, Pt, Cu, Ni) and various forms of graphene oxide (GO, trGO, NGr) to enhance performance in the visible light range and reduce charge carrier recombination. The results highlight the high efficiency of several composites, such as:

- **Au-TiO_2NT-GO**, which demonstrated excellent interaction between the catalyst and graphene oxide;
- **NiO-TiO_2NT-trGO**, with more efficient charge transfer than the nitrogen-doped graphene oxide variant;
- **Pt-TiO_2NT** and **Cu_2O/CuO-TiO_2NP**, which showed high activity even in the absence of graphene oxide.

It was found that photocatalytic efficiency is correlated with both the energy alignment between the catalyst and the pollutant, and the structural properties of the material. Additionally, the use of graphene oxide significantly improved charge separation and extended light absorption into the visible range. Overall, the study provides a solid foundation for the development of sustainable and efficient water purification systems, demonstrating the high potential of TiO_2-based nanocomposites in addressing pharmaceutical and hormonal pollution under real lighting conditions.

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