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School of Advanced Studies of the Romanian Academy

Institute of Physical Chemistru „Ilie Murgulescu”

SUMMARY OF Ph.D. THESIS

SYNTHESIS AND CHARACTERIZATION OF TiO_2-BASED PHOTOACTIVE MATERIALS WITH APPLICATIONS IN DEPOLLUTION AND ENERGY

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CONTENT

*Note: The numbering of the content corresponds to that used in the doctoral thesis.

***Keywords*:** oxide nanomaterials, sol-gel method, noble metals, oxidative photodegradation, gas-phase ethanol

« The mechanisms of life are structured as
atomic arrangements, in relation to all the
movements of the universe.»

(Louis Pasteur)

THESIS OBJECTIVES

In the present PhD thesis the main theoretical aspects and personal contributions related to the preparation of oxide materials by the sol-gel method with applications in depollution technologies are presented.

The theoretical part deals with methods of preparation and characterization of oxide nanomaterials, with emphasis on the influence of composition and method of synthesis on photocatalytic properties.

The personal contributions include the controlled synthesis of TiO_2 nanopowders, but also lanthanum and titanium based perovskites modified with noble metals, obtained both *in-situ* and by post-synthesis impregnation, followed by their complex structural, morphological and optical characterization.

The applicability of the synthesized materials was demonstrated by specific analyses: Fourier-transform coupled infrared spectroscopy (FT-IR), thermal analysis (DTA/DTG/TG), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), BET specific surface area determination, UV-Vis spectroscopy and gas chromatography (GC-FID/TCD).

The synthesized nanopowders were used in depollution applications by ethanol degradation in gas phase and under simulated solar light irradiation. The obtained results revealed the influence of the noble metal, the method of modification of the oxide support, and the post-synthesis treatments on the photocatalytic efficiency, highlighting the dominant reaction pathways and the essential role of the structure and texture of the materials in their performance.

STRUCTURE OF THE THESIS

This thesis contributes to the study of photocatalytic materials based on titanium dioxide (TiO_2) and lanthanum-titanium-based perovskites ($La_2Ti_2O_7$), modified with noble metals, for air depollution applications through the gas-phase photodegradation of ethanol under simulated solar light (SSL) irradiation.

The main research directions focused on synthesizing these materials using the sol-gel method, both *in-situ* and by post-synthesis impregnation, with and without chemical reduction, followed by detailed characterization of their properties.

The photocatalytic activity was evaluated by monitoring the reaction products generated during light-induced oxidation processes. The influence of composition and preparation method on photocatalytic efficiency was investigated, along with the underlying reaction mechanisms.

The results provide new insights into optimizing oxide nanomaterials for environmental applications, demonstrating the effectiveness of the sol-gel method combined with chemical treatments in obtaining catalytically active and stable materials.

This thesis is structured into four chapters and addresses the synthesis, characterization, and photocatalytic applicability of the synthesized nanomaterials:

Chapter 1 offers a general introduction regarding the importance of oxide nanomaterials in the context of environmental and energy-related applications.

Chapter 2 discusses the fundamental theoretical aspects related to synthesis methods (particularly sol-gel and post-synthesis impregnation) and characterization techniques used to assess the physicochemical, structural, morphological, and optical properties of the obtained materials.

Chapter 3 represents the experimental part, where the original contributions are presented.

Subchapter 3.1 describes the objectives of the current PhD thesis.

Subchapter 3.2 focuses on the TiO_2 system modified with Au and Pt, analyzing the effect of the preparation method (*in-situ* and post-synthesis impregnation, with or without reduction) on the material properties.

Subchapter 3.3 addresses the mixed oxide system TiO_2-La_2O_3, emphasizing its photocatalytic behavior and the influence of platinum on the stability and efficiency of the materials.

The final section of the thesis, *Chapter 4*, presents the general conclusions, highlighting the original contributions related to synthesis optimization and the correlation between material structure and photocatalytic performance. Future research perspectives are also outlined.

The references section is preceded by a list of the author's publications and a series of appendices containing tabulated data.

„In nature,

nothing is lost,

nothing is gained,

everything

is transformed.”

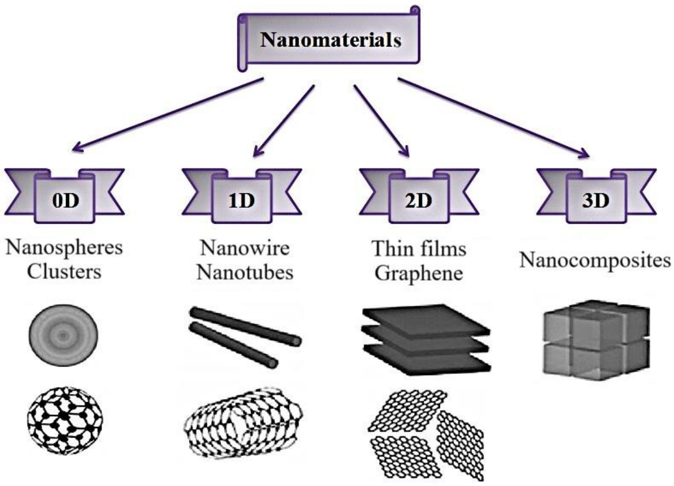
~ Antoine Lavoisier~

INTRODUCTION

Nanoscale materials have become a field of interdisciplinary research of great interest due to their unique nanoscale properties (1-100 nm), including chemical reactivity, electrical conductivity, mechanical resistance, and optical behavior [1-3].

The applications of nanomaterials are diverse and constantly expanding, including areas such as medicine, energy, electronics, and environmental protection. However, they also raise challenges related to synthesis, characterisation, and assessment of health and environmental impacts [4-6].

These materials can have various shapes and are classified by size (0D-3D). Metallic oxides are extensively studied for their remarkable properties and diverse applications, including energy storage and conversion, gas sensors, photocatalysis for environmental purification, and even antimicrobial systems in biomedicine [7-9].



SYNTHESIS AND CHARACTERIZATION OF NANOMATERIALS

The synthesis of oxide nanomaterials is a key area in materials science due to its direct influence on the final properties of materials. The main methods include physical methods (evaporation-condensation, laser pyrolysis) [10-11], chemical methods (sol-gel, hydrothermal, precipitation) [12-16], and biological methods (using microorganisms or plant extracts) [17]. In this work, two methods were used: sol-gel and post-synthesis impregnation.

The sol-gel method is appreciated for its fine compositional control, the possibility of doping with noble metals, and obtaining porous materials with a large specific surface area - essential features in photocatalysis. This involves chemical transformations in the solution, followed by drying and heat treatment of the gel [18-20].

Post-synthesis impregnation consists of adding active species (such as Au or Pt) to an already formed oxide support by treating it with a metal precursor, followed by drying and reduction. The method allows the surface to function without altering the structure of the support and provides precise control over the location of metals, being effective in improving photocatalytic activity by promoting the separation of photo-generated charges [21-22].

The characterization of nanomaterials was achieved through a series of complementary techniques. FT-IR identified functional groups, thermal analysis (TG/DTA/DTG) provided information about thermal stability, SEM-EDX and TEM evaluated particle morphology, size, and composition, and XRD determined the crystalline structure. The XRF and BET techniques provided data on elemental composition and specific surface area, while UV-Vis allowed the estimation of the width of the forbidden band (Eg), relevant to the photocatalytic activity. The efficiency of catalysts was assessed by gas chromatography (GC-FID/TCD), used for the analysis of ethanol degradation compounds [23-31].

The photocatalytic activity of oxide nanomaterials is based on the generation of electron-hole pairs under irradiation, followed by the formation of reactive species (•OH, $O_2^{\bullet-}$) involved in redox processes. Properties such as particle size, structure, noble metal modification, and porosity have a major impact on process efficiency. Materials such as TiO_2, ZnO, Fe_2O_3, or WO_3 are widely used for their stability and high potential in purification and conversion applications [32-36].

THE TiO_2 SYSTEM

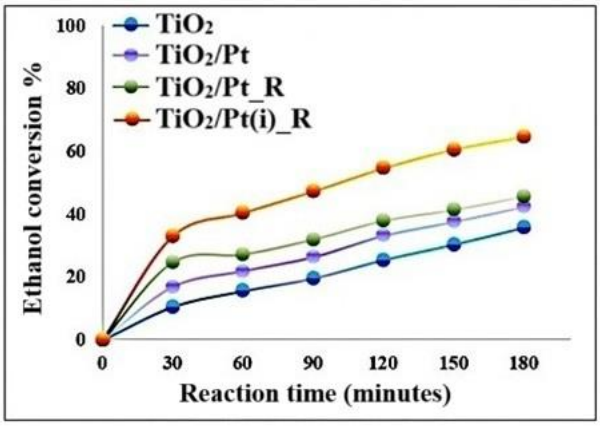
Titanium dioxide (TiO_2) is one of the most studied metal oxides in the field of photocatalysis, due to its stable semiconductor properties, high availability, chemical and thermal resistance, as well as its ability to generate reactive oxygen species (ROS) under UV irradiation. TiO_2 crystallizes in three main forms: anatase, rutile, and brookite, of which anatase is the most active photocatalytic. In this paper, the synthesis, modification, and detailed characterization of TiO_2 in the form of nanopowders were followed, in order to use them in the process of photocatalytic degradation of ethanol in the gas phase [37-42].

TiO_2-based nanomaterials have been obtained by the sol-gel method, a versatile chemical technique that allows precise control of composition and homogeneity on a nanoscale. The modification with noble metals (gold and platinum) was made in three ways: (i) *in-situ* modification, (ii) *in-situ* modification followed by reduction with sodium borohydride ($NaBH_4$), and (iii) post-synthesis impregnation followed by reduction. These methods followed the efficient dispersion of metallic nanoparticles on the TiO_2 surface, with the aim of improving the separation of photogenerated charges and extending absorption into the visible range.

The materials obtained were characterized by a series of complementary techniques:

- *FT-IR* has highlighted the presence of hydroxyl, carbonate, and Ti-O oxide network-specific groups, as well as interactions between noble metal and TiO_2;
- *TEM* confirmed the nanocrystalline structure of TiO_2 and the uniform dispersion of Au and Pt nanoparticles, with dimensions between 3-40 nm, depending on the modification method;
- *XRD* showed that all heat-treated samples keep the crystalline phase of anatase stable, with small variations in network parameters and crystal sizes (11-14 nm);
- *XRF* confirmed the incorporation of noble metals in quantities of 0.5-1.1% in the matrix of the oxide support, without significant contamination;
- *BET* demonstrated that the TiO_2 modifying method influences the porosity and specific surface area, the impregnation samples having more developed porosity (S_{BET} up to 49 m^2/g);

- *UV-Vis* highlighted the effect of the modification with noble metal on optical behavior, especially by the occurrence of plasmonic absorption for gold nanoparticles and the slight reduction of the bandgap value to 3.32-3.36 eV, indicating increased potential for radiation absorption in the visible area.



Synthesized powders have been photocatalytically tested for the degradation of ethanol in the gaseous phase under solar-simulated light (SSL) irradiation. The results showed an increase in activity following the change with Pt, with ethanol conversion increasing from 35.84% (pure TiO_2) to 64.82% for the TiO_2/Pt(i)_R sample, obtained by post-synthesis impregnation followed by a reduction process. This material has also demonstrated the best performance in CO_2 formation, indicating superior mineralization and outstanding catalytic efficiency.

The study of reaction intermediates (CH_3CHO and HCOOH) allowed a detailed assessment of the oxidation mechanism, confirming that the process is carried out in successive steps and that the presence of platinum facilitates not only the conversion of ethanol but also the degradation of intermediates.

Oxidative degradation of ethanol in the gaseous phase under solar-simulated light irradiation involves the use of molecular oxygen (O_2) in the air. The process leads to the formation of acetaldehyde (as the majority product), formic acid, and carbon dioxide as the final oxidation product [43-45].

$$\text{(a) } TiO_2 + h\nu \rightarrow e^-_{BC} + h^+_{BV}$$

$$\text{(b) } e^-_{BC} + Pt \rightarrow Pt^-$$

<u>General reactions</u>

$$C_2H_5OH + ½ O_2 \rightarrow CH_3CHO + H_2O$$

$$CH_3CHO + 2\ O_2 \rightarrow HCOOH + CO_2 + H_2O$$

$$HCOOH + ½ O_2 \rightarrow CO_2 + H_2O$$

The photocatalytic degradation of ethanol is improved by the modification of TiO_2 with platinum, by the reduction of recombination of electrons, and by the specific action of platinum as a co-catalyst. Platinum facilitates the transfer of electrons to the organic substrate and accelerates the reaction speed. The main oxidation pathway of ethanol involves its transformation into acetaldehyde, followed by the formation of formic acid, and finally carbon dioxide.

In conclusion, the modification of titanium dioxide with noble metals, especially by the post-synthesis impregnation method, significantly improves the photocatalytic performance. TiO_2/Pt(i)_R has proven to be the most effective, both in terms of conversion and mineralization, which recommends it as a promising material for air purification and degradation applications of volatile organic compounds under solar light irradiation.

The results obtained on TiO_2 powder synthesized by the sol-gel method and on platinum-modified powders, both *in-situ* and post-synthesis impregnation, has been valued by publishing an article in an ISI article [46] and presented at several 4 international conferences (3 posters and an oral presentation).

THE TiO_2-La_2O_3 SYSTEM

The $La_2Ti_2O_7$ oxide system belongs to the class of layered perovskites with *Ruddlesden–Popper* or *Aurivillius-like* structure, being characterized by the lamellar architecture of octahedra [TiO_6] and their intercalation with layers of La^{3+}. This structure generates a marked anisotropy and favorably influences the mobility of tasks, the separation of e^-/h^+ carriers, and structural stability, critical aspects for photocatalysis applications. The electronic and photocatalytic properties of $La_2Ti_2O_7$ can be improved by doping with transition metals or noble metals such as platinum [47-49].

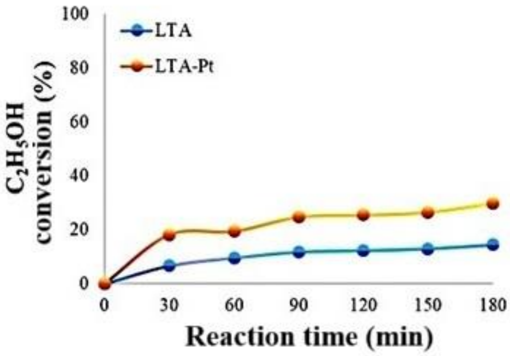
$La_2Ti_2O_7$ was synthesized by the sol-gel method, using lanthanum nitrate and titanium isopropoxide as metal precursors, in the presence of acetic acid and isopropyl alcohol. The resulting gel was heat treated progressively, establishing by thermogravimetric analysis (TGA) and FT-IR spectroscopy that the formation of the oxide network occurs at temperatures >700°C. The crystallized powders were obtained at 900°C, generating a white powder (LTA), subsequently modified with platinum (LTA-Pt) by post-synthesis impregnation and chemical reduction with $NaBH_4$.

The materials obtained were characterized by a series of complementary techniques:

- *FT-IR* highlighted the emergence of Ti-O-Ti, Ti-O and La-O vibration-specific bands, between 400-800 cm^{-1}, confirming the formation of a well crystallized octahedral network;
- *SEM* microscopy showed irregular, rough and slightly agglomerated particles for LTA, while LTA-Pt exhibited more uniform and compact morphology;
- *TEM* highlighted an average particle size of ~70 nm and a homogeneous distribution of Pt nanoparticles on the oxide surface, suggesting effective coverage of the active phase;
- *EDX* and *XRF* have confirmed the elemental composition, indicating about 1-1.8% mass proportions in the platinum modified material;
- *XRD* showed that both samples crystallize in the pure $La_2Ti_2O_7$ phase, without the appearence of other secondary phases, even after impregnation with Pt, which attests a substructural or amorphous dispersion of platinum;
- *BET* - the average size of the crystallite has been estimated at 14 nm for LTA and 15 nm for LTA-Pt. The specific surface was modest (10.1 m^2/g for LTA and 8.8

m^2/g for LTA-Pt), specific to high-temperature treated stratified compounds with a stable mesoporous texture characterised by IV-type isotherms and H3 hysteresis loops;

- Optical properties, investigated by *UV-Vis* spectroscopy, indicated a predominant UV absorption for LTA (bandgap 3.78 eV), with an expansion to visible in LTA-Pt (bandgap 3.83 eV) due to platinum-induced d-d transitions and absorption-enhancing effect;
- LTA-Pt has also demonstrated more efficient photogeneration of the superoxide anion ($O_2•^−$), determined by the XTT method, confirming the co-catalytic role of Pt in activating reactive oxygen species.



The gas photocatalytic tests under solar-simulated irradiation (AM 1.5) demonstrated superior efficiency for the LTA-Pt sample in the oxidative degradation of ethanol, with a conversion of 29.75% versus 14.29% for LTA. The main products of the reaction were acetaldehyde and formic acid as intermediates and CO_2 as the final product of mineralization. Also, the production of H_2 was doubled in the case of LTA-Pt, reflecting improved efficiency in redox surface processes. The reaction speed constant (k) was 0.0016 min^{-1} for LTA-Pt and 0.0008 min^{-1} for LTA, supporting improved process kinetics.

The proposed mechanism involves the generation of $e^−/h^+$ pairs following the absorption of photons, followed by the transfer of electrons to Pt, the reduction of oxygen to $O_2•^−$, and the oxidation of ethanol via holes (h^+), according to a sequence of reactions leading to the formation of acetaldehyde, formic acid, and CO_2. Impregnation with Pt plays a key role in reducing the recombination of carriers and facilitating redox reactions [50-54].

$$\text{(a) } La_2Ti_2O_7 + h\nu \rightarrow e^- + h^+$$

$$\text{(b) } Pt + e^- \rightarrow Pt^-$$

$$\text{(c) } O_2 + e^- \rightarrow O_2^-{}_{(ads)} \rightarrow [O] \text{ (oxigen activ)}$$

General reactions

$$C_2H_5OH + h^+ \rightarrow CH_3CH_2O• + H^+$$

$$CH_3CH_2O\bullet + [O] \rightarrow CH_3CH_2OO\bullet$$

$$CH_3CH_2OO\bullet + h^+ + e^- \rightarrow CH_3CHO + H_2O$$

$$CH_3CHO + [O] \rightarrow HCOOH + H_2O$$

$$HCOOH + [O] \rightarrow CO_2 + H_2O$$

$$C_2H_5OH \xrightarrow{\text{slowly}} CH_3CHO \rightarrow HCOOH \xrightarrow{\text{rapidly}} CO_2$$

This mechanism highlights how ethanol is degraded in a gaseous phase under solar-simulated light irradiation in the presence of $La_2Ti_2O_7$ photocatalysts.

In conclusion, the $La_2Ti_2O_7$ system, synthesized by the sol-gel method and modified with noble metal, proves to be an effective photocatalyst for the degradation of ethanol in the gaseous phase and has valuable potential in atmospheric depollution applications under solar irradiation.

The results obtained are being valued by publishing an article in an ISI article [55] and presented at an international conference (poster).

GENERAL CONCLUSIONS

This doctoral thesis aimed to develop and investigate two TiO_2-based photocatalytic systems for applications in air depollution by degradation of volatile organic compounds (VOC). The two systems (TiO_2 and $La_2Ti_2O_7$), both in their pure forms and modified with noble metals, were synthesized by the sol-gel method.

In the first described system, pure TiO_2 nanostructured powders were obtained, but also modified with gold or platinum, by three distinct methods: (a) *in-situ* synthesis, (b) *in-situ* synthesis followed by chemical reduction, and (c) post-synthesis impregnation. The results showed that the modification method significantly influences the distribution and size of the metal nanoparticles, directly affecting the structural, morphological, and photocatalytic properties of the materials. The powders obtained showed a crystalline phase of anatase, nanometric sizes ranging from 11-14 nm, good dispersion of metals, and extensive absorption in the visible region, especially in the case of materials with Au (plasmonic effect).

Photocatalytic tests on TiO_2 powders showed a significant increase in ethanol conversion in the presence of noble metals, particularly in the TiO_2/Pt(i)_R sample, where a conversion of 64.82% was achieved, compared to 35.84% for pure TiO_2. In all cases, acetaldehyde formation as the primary intermediate and complete mineralization to CO_2 was observed. The results demonstrate the superior efficiency of the change with Pt, especially when it is achieved through post-synthesis impregnation followed by reduction, due to the formation of accessible active centres and an efficient separation of photo-induced loads.

In the TiO_2-La_2O_3 system, the synthesis and photocatalytic behavior of lanthanum titanate ($La_2Ti_2O_7$), a material with a stratified perovskite structure, subsequently modified with Pt, was investigated. Structural and morphological characterization confirmed the achievement of the pure $La_2Ti_2O_7$ phase, well crystallized, with crystallized sizes of about 14-15 nm, and the uniform distribution of Pt nanoparticles on the surface of the oxide support. The system showed high thermal stability and strong absorption in the UV region, with a slight expansion to the visible range following the change with Pt.

From a photocatalytic point of view, the LTA-Pt sample ($La_2Ti_2O_7$ modified with Pt) showed superior activity to the pure sample (LTA), both in terms of ethanol conversion (29.75% versus 14.29%) and in the formation of the final product of mineralization, namely CO_2. The proposed mechanism involves a sequence of progressive oxidation of ethanol and the formation of reactive oxygen species, with a determinant role of superoxide anion ($O_2•^−$).

In comparison, the TiO_2-La_2O_3 system is remarkable by a balanced photocatalytic behavior, which favors both the mineralization of pollutants and the production of H_2, while the simple TiO_2 system has a more intense oxidative activity and increased selectivity towards CO_2. Both systems highlight the advantages of noble metal modification strategies and morphological optimization in the direction of developing effective photocatalysts in ambient conditions.

Overall, the thesis demonstrates that the integration of noble metals in TiO_2 oxide networks leads to the achievement of high-performance photoactive materials, adapted for environmental applications, especially in air pollution technologies. Through the applied methodology, correlations were made between synthesis, structure, optical properties, and catalytic performance, thus contributing to the development of fundamental and applied knowledge in the field of oxide nanomaterials for photocatalysis.

Future perspectives for this research include the extension of experimental studies on the photocatalytic activity of the modified TiO_2 system with Au, which demonstrated promising potential, particularly through plasmonic effects in the visible region, but which require further investigation to optimize composition and stability under reaction conditions.

It is also proposed to develop the TiO_2-La_2O_3 system using alkoxide precursors, which can provide superior control over the homogeneity and morphology of the resulting materials, with potential impact on photocatalytic performance.

Not in the least, the catalytic activity of TiO_2-based materials could also be tested for other types of reactions with depollution applications, such as phenol photo-oxidation or methanol photodegradation, to assess the versatility and stability of these materials in various catalytic contexts.

ARTICLES PUBLISHED

1. A. Sandulescu, C. Anastasescu, F. Papa, M. Raciulete, A. Vasile, T. Spataru, M. Scarisoreanu, C. Fleaca, C.N. Mihailescu, V.S. Teodorescu, N. Spataru, M. Zaharescu, I. Balint (**2021**) *Advancements on Basic Working Principles of Photo-Driven Oxidative Degradation of Organic Substrates over Pristine and Noble Metal-Modified TiO_2. Model Case of Phenol Photo Oxidation*, Catalysts 11 (4), 487. 10.3390/catal11040487
2. E. Goncearenco, I.P. Morjan, E. Dutu, M. Scarisoreanu, C. Fleaca, L. Gavrila-Florescu, F. Dumitrache, A.M. Banici, V.S. Teodorescu, C. Anastasescu, A. Sandulescu, I. Balint (**2022**) *The effect of noble metal addition on the properties of oxide semiconductors nanoparticles*, J. Solid State Chem. 307, 122817. 10.1016/j.jssc.2021.122817
3. M. Raciulete, C. Anastasescu, F. Papa, I. Atkinson, C. Bradu, C. Negrila, D.I. Eftemie, D.C. Culita, A. Miyazaki, V. Bratan, J. Pandele-Cusu, C. Munteanu, G. Dobrescu, A. Sandulescu, I. Balint (**2022**) *Band-Gap Engineering of Layered Perovskites by Cu Spacer Insertion as Photocatalysts for Depollution Reaction*, Catalysts 12 (12), 1529. 10.3390/catal12121529
4. E. Goncearenco, I.P. Morjan, C.T. Fleaca, F. Dumitrache, E. Dutu, M. Scarisoreanu, V.S. Teodorescu, A. Sandulescu, C. Anastasescu, I. Balint (**2023**) *Titania nanoparticles for photocatalytic degradation of ethanol under simulated solar light*, Beilstein J. Nanotechnol. 14, 616-630. 10.3762/bjnano.14.51

ARTICLES IN THE PROCESS OF PUBLICATION

1. A. Ilie (Sandulescu), L. Predoana, C. Anastasescu, J. Pandele-Cusu, S. Preda, A. Rusu, D.C. Culita, V. Bratan, V.A. Maraloiu, V.S. Teodorescu, I. Balint, M. Zaharescu (**2025**) *PHOTOCATALYTIC DEGRADATION OF ETHANOL DRIVEN BY PRISTINE AND METAL-MODIFIED TiO_2 OBTAINED BY SOL-GEL METHOD*, RRC_2025/66
2. A. Ilie, L. Predoana, C. Anastasescu, S. Preda, D.C. Culita, V. Bratan, I. Balint, M. Zaharescu (**2025**) *Layered perovskite $La_2Ti_2O_7$ obtained by sol-gel method with photocatalytic activity*, Applied Sciences MDPI. accepted for publication-ID:applsci-3698820

NATIONAL CONFERENCES

1. A. Sandulescu, C. Anastasescu, F. Papa, M. Raciulete, A. Vasile, N.D. Scarisoreanu, T. Spataru, M. Scarisoreanu, N. Spataru, M. Zaharescu, Ioan Balint (**27-28 Mai 2021**) *PHOTO OXIDATIVE DEGRADATION OF ORGANIC SUBSTRATES OVER NOBLE METAL-MODIFIED* TiO_2, NeXT-Chem III-2021 – Oral presentation

INTERNATIONAL CONFERENCES

1. A. Ilie, C. Anastasescu, L. Predoana, J. Pandele-Cusu, A. Rusu, S. Preda, D. Culita, I. Balint, M. Zaharescu (**14-15 Noiembrie 2024**) *PHOTO DEGRADATION OF ORGANIC COMPOUNDS DRIVEN PRISTINE AND Pt-MODIFIED* TiO_2, Physics of Materials (PM-8) – Poster
2. A. Ilie, C. Anastasescu, L. Predoana, J. Pandele-Cusu, A. Rusu, S. Preda, D. Culita, I. Balint, M. Zaharescu (**27-29 Noiembrie 2024**) *Ethanol photo degradation on noble metals-modified* TiO_2 *obtained by sol-gel method*, NanoBioMat 2024 – Oral presentation
3. A. Ilie, C. Anastasescu, L. Predoana, J. Pandele-Cusu, A. Rusu, S. Preda, D.C. Culita, V. Bratan, V.A. Maraloiu, V.S. Teodorescu, I. Balint, M. Zaharescu (**23-25 Aprilie 2025**) *Noble metal-modified* TiO_2 *obtained by the sol-gel method: Ethanol photodegradation*, ECCS - The 3rd International Electronic Conference on Catalysis Sciences – Poster
4. A. Ilie, C. Anastasescu, L. Predoana, A. Rusu, S. Preda, D.C. Culita, V. Bratan, V.A. Maraloiu, V.S. Teodorescu, I. Balint, M. Zaharescu (**05-07 Mai 2025**) *PRISTINE AND Pt-MODIFIED* TiO_2 *DRIVEN ORGANIC COMPOUNDS PHOTODEGRADATION*, IECME - The 2nd International Electronic Conference on Metals – Poster
5. A. Ilie, L. Predoana, C. Anastasescu, S. Preda, V. Bratan, D.C. Culita, I. Balint, M. Zaharescu (**08-10 Septembrie 2025**) $La_2Ti_2O_7$ *doped with Pt, obtained by sol-gel method, with photocatalytic activity in the oxidative degradation of ethanol*, IOCTO - The 2nd International Online Conference on Toxics – Poster

PATENT APPLICATIONS

1. Patent application registered at OSIM with number A/00578/2020 - Development of pigment solar cells (DSSC) based on copper oxide modified mesoporous TiO_2 (CuOx) that become more efficient with the time of use. Authors: Anastasescu Crina, Săndulescu Elena-Alexandra, State Răzvan Nicolae, Pavel Monica, Scărișoreanu Gina-Monica, Scărișoreanu Nicu Doinel, Balint Ioan.
2. Patent application registered at OSIM with number A/00680/2020 - Synthesis of glutathione-stabilized ZnSe nanoparticles modified with Au or Ag, generators of reactive bactericidal oxygen species under illumination in the visible range. Authors: Anastasescu Crina, Atkinson Irina, Brătan Veronica, Preda Silviu, Săndulescu Alexandra, Balint Ioan, Zaharescu Maria, Anastasescu Mihai.
3. Patent application registered at OSIM with number A/00518/2021 - Obtaining a GeO_2-based photocatalyst for the mineralization of gas-phase ethanol under monochromatic light irradiation on the wide spectral range (360-620 nm). Authors: Anastasescu Crina, Săndulescu (Ilie) Elena-Alexandra, Papa Florica, Vasile Anca, Scărișoreanu Gina-Monica, Scărișoreanu Nicu Doinel, Balint Ioan.
4. Patent application registered at OSIM with number A/00801/2024 - The process of obtaining hydrogen by splitting water on wide-band forbidden oxides with photoactive defects. Authors: Anastasescu Crina, Ilie Elena-Alexandra, Anastasescu Mihai, Balint Ioan.

SELECTIVE BIBLIOGRAPHY

1. Nasrollahzadeh, M. et al. (**2019**) *Chapter 1 - An Introduction to Nanotechnology*, Interface SciTech. 28:1-27.
2. Malik, S. et al. (**2023**) *Nanotechnology: A Revolution in Modern Industry*, Molecules 28 (2):661.
3. Rickerby, D. & Morrison, M. (**2007**) *Nanotechnology and the environment: A European perspective*, Sci. Technol. Adv. Mater. 8 (1-2):19.
4. Nasrollahzadeh, M. et al. (**2019**) *Chapter 4 - Applications of Nanotechnology in Daily Life*, Interface SciTech. 28:113-143.
5. Paras, M.K. (**2024**) *Nanotechnology and its applications: An overview*, Int. J. Phys. Appl. 6 (2):179-185.
6. Altammar, K.A. (**2023**) *A review on nanoparticles: characteristics, synthesis, applications, and challenges*, Front. Microbiol. 14:1155622.
7. Mekuye, B. & Abera, B. (**2023**) *Nanomaterials: An overview of synthesis, classification, characterization, and applications*, Nano Select 4 (8):486-501.
8. Joudeh, N. & Linke, D. (**2022**) *Nanoparticle classification, physicochemical properties, characterization, and applications: a comprehensive review for biologists*, J. Nanobiotechnol. 20 (262).
9. Saleh, T.A. (**2020**) *Nanomaterials: Classification, properties, and environmental toxicities*, Environ. Technol. Innov. 20:101067.
10. Khan, S. et al. (**2020**) *Gas-Phase Synthesis for Mass Production of TiO_2 Nanoparticles for Environmental Applications*, Springer, Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications, pp 1-21.
11. Lungu, I.I. et al. (**2023**) *Laser Pyrolysis of Iron Oxide Nanoparticles and the Influence of Laser Power*, Molecules 28 (21):7284.
12. Parashar, M. et al. (**2020**) *Metal oxides nanoparticles via sol–gel method: a review on synthesis, characterization and applications*, J. Mater. Sci.: Mater. Electron. 31:3729-3749.
13. Chang, C. et al. (**2023**) *Review of the sol–gel method in preparing nano TiO_2 for advanced oxidation process*, Nanotechnol. Rev. 12 (1):20230150.

14. Divya, G. et al. (**2023**) *Microwave assisted sol–gel approach for Zr doped TiO_2 as a benign photocatalyst for bismark brown red dye pollutant*, RSC Advances 13:8692-8705.

15. Tazim, T.Q. et al. (**2025**) *Hydrothermal synthesis of nano-metal oxides for structural modification: A review*, Next Nanotechnol. 7:100167.

16. Ba-Abbad, M.M. et al. (**2022**) *Synthesis of Fe_3O_4 Nanoparticles with Different Shapes Through a Co-Precipitation Method and Their Application*, JOM 74:3531-3539.

17. Shakeel, N. et al. (**2025**) *Green Synthesis of Titanium Dioxide Nanoparticles: Physicochemical Characterization and Applications: A Review*, IJMS 26 (12):5454.

18. Tseng, T.K. et al. (**2010**) *A Review of Photocatalysts Prepared by Sol-Gel Method for VOCs Removal*, Int. J. Mol. Sci. 11 (6):2336-2361.

19. Sakka, S. (**2013**) *Sol-gel process and aplications*, Handbook of Advanced Ceramics, Elsevier Inc. 883-910.

20. Kessler, V. & Seisenbaeva, G.A. (**2023**) *Molecular mechanisms of the metal oxide sol-gel process and their application in approaches to thermodynamically challenging complex oxide materials*, JSST 107 (1):1-11.

21. Sescu, A.M. et al. (**2021**) *TiO_2 Doped with Noble Metals as an Efficient Solution for the Photodegradation of Hazardous Organic Water Pollutants at Ambient Conditions*, Water 13 (1):19.

22. Barrino, F. (**2024**) *Hybrid Organic–Inorganic Materials Prepared by Sol–Gel and Sol–Gel-Coating Method for Biomedical Use: Study and Synthetic Review of Synthesis and Properties*, Coatings 14 (4):425.

23. Griffiths, P.R. & de Haseth, J.A. (**2006**) *Fourier Transform Infrared Spectrometry*, Wiley-Interscience, 2nd Edition, pp 1-95.

24. Pigłowska, M. et al. (**2020**) *Kinetics and Thermodynamics of Thermal Degradation of Different Starches and Estimation the OH Group and H_2O Content on the Surface by TG/DTG-DTA*, Polymers 12 (2):357.

25. Rades, S. et al. (**2014**) *High-resolution imaging with SEM/T-SEM, EDX and SAM as a combined methodical approach for morphological and elemental analyses of single engineered nanoparticles*, RSC Advances 4 (91):49577.

26. Li. N. et al. (**2025**) *In situ transmission electron microscopy characterization and manipulation of the morphology, composition and phase evolution of nanomaterials under microenvironmental conditions*, Chem. Sci. 16:9604-9637.

27. Adams, F. (**2005**) *X-RAY ABSORPTION AND DIFFRACTION | Overview*, Encyclopedia of Analytical Science, Second Edition, pp 365-377.

28. Lemelle, L. et al. (**2017**) *Analytical requirements for quantitative X-ray fluorescence nano-imaging of metal traces in solid samples,* TrAC Trends Anal. Chem. 91:104-111.

29. Nayan, M.B. et al. (**2019**) *Comparative Study on the Effects of Surface Area, Conduction Band and Valence Band Positions on the Photocatalytic Activity of ZnO-M_xO_y Heterostructures*, JWARP 11 (3):357-370.

30. Sultana, M. et al. (**2023**) *Strategic development of metal doped TiO_2 photocatalysts for enhanced dye degradation activity under UV–Vis irradiation: A review*, CRGSC 7:100383.

31. Budiman, H. et al. (**2015**) *Comparison between GC-TCD and GC-FID for the determination of propane in gas mixtur*, Procedia Chem. 16:465-472.

32. Greco, E. et al. (**2025**) *Nanomaterials in Photocatalysis: An In-Depth Analysis of Their Role in Enhancing Indoor Air Quality*, Appl. Sci. 15 (3):1629.

33. Cheng, Q. et al. (**2024**) *Clarifying the Direct Generation of •OH Radicals in Photocatalytic O_2 Reduction: Theoretical Prediction Combined with Experimental Validation*, J. Phys. Chem. Lett. 15 (34):8650-8659.

34. Hassaan, M.A. et al. (**2023**) *Principles of Photocatalysts and Their Different Applications: A Review*, Top. Curr. Chem. 381 (6):31.

35. Mohamadpour, F. & Amani, A.M. (**2024**) *Photocatalytic systems: reactions, mechanism, and applications*, RSC Adv. 14:20609-20645.

36. Arumugam, M. et al. (**2023**) *Noble metals (Pd, Ag, Pt, and Au) doped bismuth oxybromide photocatalysts for improved visible light-driven catalytic activity for the degradation of phenol*, Chemosphere 324:138368.

37. Navidpour, A.H. et al. (**2023**) *Investigation of Advanced Oxidation Process in the Presence of TiO_2 Semiconductor as Photocatalyst: Property, Principle, Kinetic Analysis, and Photocatalytic Activity*, Catalysts 13 (2):232.

38. Pelaez, M. et al. (**2012**) *A review on the visible light active titanium dioxide photocatalysts for environmental applications*, Appl. Catal. B: Environ. 125:331-349.

39. Ghamarpoor, R. et al. (**2023**) *Investigating the use of titanium dioxide (TiO_2) nanoparticles on the amount of protection against UV irradiation*, Sci. Rep. 13:9793.

40. Wang, Y. et al. (**2014**) *Review of the progress in preparing nano TiO_2: An important environmental engineering material*, J. Environ. Sci. 26 (11):2139-2177.

41. Luong, G. & Ku, Y. (**2021**) *Selective Oxidation of Benzyl Alcohol in the Aqueous Phase by TiO_2-Based Photocatalysts: A Review*, Chem. Eng. Technol. 44 (12):2178-2190.

42. Shariatinia, Z. & Karimzadeh, Z. (**2025**) *Recent advances on oxidation of alcohols over various types of materials as effective catalysts: An overview*, Coord. Chem. Rev. 526:216372.

43. Shayegan, Z. et al. (**2017**) *TiO_2 photocatalyst for removal of volatile organic compounds in gas phase – A review*, Chem. Eng. J. 334:2408-2439.

44. Katsiev, K. et al. (**2017**) *Mechanism of Ethanol Photooxidation on Single-Crystal Anatase TiO_2(101)*, J. Phys. Chem. C 121 (5):2940-2950.

45. Sanusi, I. & Almquist, C.B. (**2023**) *ZnO/TiO_2 Composite Thin-Film Photocatalysts for Gas-Phase Oxidation of Ethanol*, Catalysts 13 (8):1203.

46. Ilie, A. et al. (**2025**) *PHOTOCATALYTIC DEGRADATION OF ETHANOL DRIVEN BY PRISTINE AND METAL-MODIFIED TiO_2 OBTAINED BY SOL-GEL METHOD*, RRC. - în curs de publicare

47. Jha, S.K. & Priyadarshi, P.K. (**2024**) *Structural and Functional Insights into ABO_3 Perovskites: Tailoring Properties for Advanced Technological Applications*, IJESI 13 (10):40-44.

48. Pérez, G.M.H. et al. (**2014**) *Layered-structural monoclinic-orthorhombic perovskite $La_2Ti_2O_7$ to orthorhombic $LaTiO_3$ phase transition and their microstructure characterization*, Mater. Charact. 89:13-22.

49. Abe, Y. & Laine, R.M. (**2020**) *Photocatalytic plate-like $La_2Ti_2O_7$ nanoparticles synthesized via liquid-feed flame spray pyrolysis (LF-FSP) of metallo-organic precursors*, J. Am. Ceram. Soc. 103 (9):4832-4839.

50. Xiong, L. & Tang, J. (**2021**) *Strategies and Challenges on Selectivity of Photocatalytic Oxidation of Organic Substances*, Adv. Energy Mater. 11 (8):2003216.

51. Tan, Y. et al. (**2017**) *Charge-compensated (Nb, Fe)-codoped $La_2Ti_2O_7$ photocatalyst for photocatalytic H_2 production and optical absorption*, J. Alloys Compd. 709:277-284.

52. Al-Madanat, O. et al. (**2021**) *TiO_2 photocatalysis: Impact of the platinum loading method on reductive and oxidative half-reactions*, Catal. Today 380:3-15.

53. Mamaghani, A.H. et al. (**2017**) *Photocatalytic oxidation technology for indoor environment air purification: The state-of-the-art*, Appl. Catal. B: Environ. 203:247-269.

54. Vorontsov, A.V. & Dubovitskaya, V.P. (**2004**) *Selectivity of photocatalytic oxidation of gaseous ethanol over pure and modified* TiO_2, J. Catal. 221 (1):102-109.

55. Ilie, A. et al. (**2025**) *Layered perovskite* $La_2Ti_2O_7$ *obtained by sol-gel method with photocatalytic activity*, Applied Sciences. accepted for publication-ID:applsci-3698820