Abstract on the PhD thesis

Contributions to the synthesis, characterization and photocatalytic activity of nanomaterials oxide

~ English version ~

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Introduction

The main subject of the present PhD thesis is based upon one of the greatest humanity problems, caused by a continous accumulation of non-biodegradable organic substances in the environment. The dyes have represented compounds with complex structures and claimed on biodegradation resistance and toxicity issues. Taken into account different legislative constraints appeared as a real necessity in order to solve the wastewater discharged into the environment matters, a good motivation that could rise on a research focused on the development of new treatment processes lesser polluting may be fundamental. The heterogeneous photocatalysis is a favorable method with a promising potential that opens new favourable expectations in the photodegradation of different organic substances presented in industrial wastewater. The nanostructured materials with a photocatalyst role may have several components: metal oxides - support and dopants - metal ions deposited on the substrate.

Nanostructured materials oxide powders have the ability to effectively degradate pollutants by encapsulating them without the possibility of returning back into the filtered medium. Nanostructured oxide powders are innovative materials obtained by new synthesis processes. The novelty element lies on the reactants used and on the capability of generating new properties, making them highly efficient. The optimization of photodegradation process represents a high research subject area related to analysis and synthesis of new materials with specific properties (surface area, crystallite size, crystallinity, etc.). Based on porosity as one of important properties, oxide nanostructured materials have been confirmed to be a real support for determining the role of doping metal ions or tandem photocatalysts.

Main objectives

The PhD thesis having the title "**Contributions to the synthesis, characterization and photocatalytic activity of nanomaterials oxide"** addresses to a wide range of topical issues on the study and application by new materials synthesis with specific properties. In this regard, nanostructured oxide powders were synthesized having its applications in photocatalytic processes. There were applied chemical synthesis methods (precipitation, sonication, hydrothermal method, template method) to obtain nanostructured oxide powders of high purity.

Materials that possesed structural, textural and morphological properties underly on the treatment of wastewater containing synthetic organic dyes (methylene blue, Nile blue, methyl orange, eosin Y) by using photocatalytic processes.

The main objectives proposed in this work were:

O1. Obtaining of new nano oxide undoped with a high efficiency in photocatalytic degradation of dyes. The objective was achieved through the following activities:

- identify of new optimal methods to the synthesis of ZnO and SnO_2 powders;
- characterization of new products by modern methods (RDX, adsorption / desorption of N2 at 77K, Fourier transform infrared spectroscopy, scanning electron microscopy);
- photodegradation of organic dyes in the presence of metal oxide powders;
- determination of the photocatalysis kinetic parameters.

O2. Obtaining of new nano metal oxide doped with a high efficiency in photocatalytic degradation of dyes:

- choosing of appropriate metal oxides with photocatalytic properties;
- choosing of appropriate chemical methods for synthesis of new oxide products;
- characterization of new products by modern methods (RDX, adsorption / desorption of N2 at 77K, Fourier transform infrared spectroscopy, scanning electron microscopy, local EDX analysis);
- determination of the metal ion doping influence on structural, morphological and composition properties for the samples;
- optimization of doping conditions: precursors, ion mass percentage of dopant;
- evaluation upon the photocatalytic activities of representative organic dyes

degradation.

O3. Obtaining of new nanomaterials coupled to a second semiconductor by having high efficiency in photocatalytic degradation of dyes:

- choosing a metal oxide with a high photocatalytic performance;
- choosing of appropriate chemical methods for synthesis by new coupled oxides;
- characterization of new products by modern methods (RDX, adsorption / desorption of N2 at 77K, Fourier transform infrared spectroscopy, scanning electron microscopy, local EDX analysis);
- optimization of coupling conditions: precursors, mass percentage of couplant oxide;
- determination of second semiconductor coupling influence on morphological, structural and optical properties;
- evaluation upon the photocatalytic activities in the degradation of eosin Y;
- determination of the photocatalysis kinetic parameters.

O4. Optimization of the photodegradation process of eosin Y on photo-catalytic systems obtained by a second semiconductor coupling:

- identification and optimization of the photocatalysis process specific parameters (initial concentration of dye, type and amount of catalyst, influence of the wavelength in the photocatalysis, influence of pH);
- new modeling methods based on simple and stacked neural networks applied to obtain supplimentary predictions on the evolution of photocatalytic process parameters;
- selection of suitable parameters useful for simple neural networks by using a sensitivity analysis method.

Structure of thesis

The present work includes issues related to the synthesis, characterization and applications of nanostructured oxide powders in wastewater treatment. From the structural point of view, the thesis consists of nine chapters, in which Chapter 1 represents the

introduction, Chapter 2 and 3 highlights theoretical foundations aspects and the other ones expose original contribution brought to the specific field of research. Each chapter is finishing with a section of conclusions. The last chapter contains general conclusions.

Chapter 1 presents some general aspects upon an introduction to the content of the present work, a list of general objectives and the structure from the thesis.

Chapter 2 is the state-of-art in the field of water pollution, dyes, advanced oxidation processes and nanostructured materials in photocatalytic processes. Generally, there are reviewed aspects related to dyes and their classification and inorganic oxides used in photocatalysis processes.

Chapter 3 presents aspects related to classification, synthesis and state-of-art on the physico-chemical properties of metal oxide nanomaterials. At the same time, the synthesis methods are presented based on metal oxides and modern experimental techniques for characterization.

Chapter 4 describes the original studies in a comparative manner upon the synthesis of nanostructured oxide powders by different "bottom-up" chemical methods: precipitation method, hydrothermal method, template-mediated method and sonication method, specifying the caracteristics on the work flow and operational parameters in order to make decision on the optimal one.

Chapter 5 deals with the synthesis and structural, textural and morphological characterization of zinc oxide and tin oxide nanostructured powders, which were used as supports for metal ions deposition. Zinc oxide was deposited on textile supports. The purpose of this study was based on finding a chemically and facile method in terms of versatility, convenience and reproducibility of preparation. The photocatalytic study activity of undoped oxides pursued against performance catalysts prepared by three different chemical methods.

Chapter 6 reveals the encapsulation of metal ions on zinc oxide has improved the photocatalytic properties on dyes degradation processes. The synergistic effects of the oxide nanocomposites were distinguished by high specific surfaces, optimal concentrations of catalysts, as well as other operational parameters.

However, in **Chapter 7** there are obtained doped tin oxide exhibiting photocatalytic metal by the hydrothermal method. The oxide powders were morphological and structural characterized. They indicate improved properties of the new doped tin oxide. The new products by photocatalytic processes performances were evaluated using synthetic solutions of eosin Y.

Chapter 8 is focusing on the synthesis and characterization of tandem photocatalysts obtained by the co-precipitation method. The study takes into account the influence of the photocatalytic activity of the catalyst type and initial concentration of dye, the pH of the solution and the effect of the wavelength degradation. Meanwhile, there are included methods of modeling of experimental data in order to obtain supplimentary predictions by using a multilayer perceptron neural network or an ensamble of neural networks aggregated into a stack. Sensitivity analysis is adopted as a strategy to eliminate of certain parameters.

Chapter 9 resumed the principal aspects performed in the present work. The thesis is finalised with a bibliography of 409 references that represent the own and the consulted papers.

Conclusion

The study from this thesis brings different and important contributions to the improvement of nanostructured semiconducting oxide materials field. Also, it proves a deepen experimental knowledge of the photocatalysis processes.

The original part of the present work is based on experimental studies in a comparative matter on the analysis and economical ways to obtain the following efficient photocatalytic systems: ZnO and SnO_2 nanostructured oxides; nano-oxide powders doped by introducing ions of silver, cerium and cobalt as doping agents; photocatalytic tandem systems based on the coupling of Fe_2O_3 / SnO_2 and ZnO / SnO_2 nano-oxides, applicable in the process photocatalytic degradation of textile dyes (methylene blue, Nile blue, methyl orange and eosin Y) of the synthetic wastewater and for improving the quality of textile fibers.

In an original and comparative manner there were been described the synthesis of nanostructured oxides by: so called "bottom-up" chemically precipitation method,

hydrothermal method, template-mediated method, specifying the work flow and operational parameters specific to identify the optimal method of synthesis.

The effectiveness of each method was evaluated on the basis of morpho-structural and textural characterization of powders obtained and performed by modern methods. Comparative analysis of morphological characteristics and weaves emphasizes the superiority of template-mediated synthesis method.

Based on the idea that the increasing hydrophilicity of a textil represents the key to the user's comfort, a study approach is reflected by nano-oxide composite materials - cellulose (textile) by improving the ZnO synthesis in situ. This aspect is leading to an increase in hydrophilicity of textiles and maintaining the characteristics after repeated washing cycles. Also, there is presumed an increasing in durability of textiles, in wearing comfort or an improving in hygienic properties.

The structural, textural and morphological properties of these nano-oxides were the basis for making decision for the optimal photocatalysts and the photocatalytic processes analysis on the treatment of wastewater containing synthetic organic dyes. Comparative analysis of ZnO/SnO_2 photocatalytic systems behaviors in the degradation of eosin Y, were performed at assessing the influence of process parameters on the photodegradation efficiency of eosin Y.

There was performed a methodical and original approach, in which the following operational parameters involved in photocatalysis process: type of catalyst; the initial concentration of eosin Y dye (10 mg / L and 20 mg / L); the catalyst dose (0.5, 1.0 or 2.0 g / L); the pH of the dye solution (pH 4, pH 6, pH 8, pH 10); the photocatalysis wavelength used (254 nm, 365 nm) were studied.

I appreciate that my study has led to the development of news doped oxide nanostructures and new tandem oxide nanostructures, which behaved as photocatalytic systems with improved properties. The band gap energy decreases significantly by decreasing the molar ratio Fe / Sn, and by using Pluronic P123 surfactant in the synthesis as a consequence of the changes produced in the conditions analyzed of some structural morphological features, such as increased surface area and volume of the pore size and the crystallites decrease.

The research has led to the obtaining of new types of nano oxides, that possesed superior photocatalytic activity properties. They have a high potential to be applied in the degradation of organic dyes on the basis of doping metal ions (silver, cerium and cobalt) of inorganic oxides (ZnO and SnO2), and coupling by a second semiconductor (ZnO / SnO_2, and Fe2O3 / SnO2).

Adopting of new methods of mathematical modeling by using simple MLP neural network types or associated in stacks to obtain optimal parameter values of the photocatalytic processes of ZnO and SnO_2 coupled oxide represent an original contribution in a relatively new field of scientific knowledge.

Dissemination of results

My own research results of the thesis are reflected in: three ISI papers, two ISI Proceedings papers, three BDI papers, one published in-extenso paper in a national conference, one book chapter, 20 different conferences, in which 10 national conferences and other 10 international conferences.

- **ISI papers**

1. **Tanasă D.E.**, Piuleac C.G., Curteanu S., Popovici E., Photodegradation process of Eosin Y using ZnO/SnO_2 nanocomposites as photocatalysts: experimental study and neural network modeling, Journal of Materials Science, 48(22), 8029-8040, 2013. **(I.F.=2.305)**
2. Vrinceanu N., **Tanasă D.,** Hristodor C.M., Brinza F., Popovici E., Gherca D., Pui A., Coman D., Carsmariu A., Bistricianu I., Broasca G., Synthesis and characterization of zinc oxide nanoparticles, Journal of Thermal Analysis and Calorimetry, 111(2), 1107-1119, 2013. **(I.F.=2.206)**
3. **Tanasă D.,** Vrinceanu N., Nistor A., Hristodor C.M., Popovici E., Bistricianu I.L., Brinza F., Chicet D.L., Coman D., Pui A., Grigoriu A.M., Broasca G., Zinc oxide-linen fibrous composites: morphological, structural, chemical and humidity adsorptive attributes, Textile Research Journal, 82 (8), 832-844, 2012. **(I.F.=1.135)**

- **ISI Proceedings indexed papers**

1.Hristodor C.M., Vrinceanu N., Pui A., Brinza F., Copcia V.E., **Tanasă D.**, Popovici E., Study of nanosized clay- SnO_2 compounds used in degradation of Eosin Y dye, ModTech 2012 - New face of TMCR, Proceedings, vol.I, ISSN 2069-6736, p. 445-448, 2012.

http://www.modtech.ro/publication_2012.php?index=H

2.Vrinceanu N., Hristodor C.M., **Tanasă D.**, Popovici E., Brinza F., Toma S., Coman D., Cirsmariu A., Broasca G., Approach regarding the potential of different nanophotocatalysts onto a model textile dye, ModTech 2012 - New face of TMCR, Proceedings, vol. II, ISSN 2069-6736, p. 1057-1060, 2012.

http://www.modtech.ro/publication_2012.php?index=V

- **BDI papers**

1. Vrinceanu N., Coman D., Popovici E., Hristodor C.M., **Tanasă D.**, Laboratory methods used in photocatalytic degradation of dyes in aqueous solution using sol-gel coated cotton fibrous substrate, PTCONF, The Third International Proficiency Testing Conference, Iasi, Romania, ISSN 2066-737X, 2011.

2. **Tanasă D.**, Vrinceanu N., Hristodor C.M., Popovici E., Coman D., Brinza F., Bistricianu I., Chicet, D., A Comparative Approach of Degradative Potential of Two Different Nanophotocatalysts onto a Model Textile Dye, The Annals of "Dunarea de Jos" University of Galati. Fascicle IX. Metallurgy and Materials Science, 3, ISSN 1453 – 083X, 71-75, 2011. http://www.fmet.ugal.ro/Anale/Anale%203-2011.pdf;

3. Vrinceanu N., Hristidor C.M., **Tanasă D.**, Popovici E., Gherca D., Pui A., Carsmariu A., Bistriceanu I., Study concerning the synergetic effect of synthesis agents onto the surface crystallinity of some fibrous substrates coated with nano-oxides, with direct implication onto thermal protection, Tehnical Textile-Present and Future, ISBN 978-973-730-908-2, Iasi, Romania, 272-280, 2012.

- **Papers published in-extenso at national conferences**

1. **Tanasă D.**, Popovici E., Activitatea fotocatalitică a nanocompozitelor ZnO/SnO_2 în degradarea eozinei Y, Analele Ştiinţifice ale Universităţii "Alexandru Ioan Cuza" Iaşi, ACTA CHEMICA Iaşi – supliment SCSSMD 2011, pp. 30-31, 2011.

- **Chapter book**

1. Vrinceanu N., Hristodor C.M., Popovici E., Coman D., Pui A., **Tanasă D.**, Petre B.A., Zinc oxide-linen fibrous composites: morphological, structural, chemical, humidity adsorptive and thermal barrier attributes, in cartea Modern Surface Engineering Treatments, Editura Intech Open, ISBN 980-953-307-959-7, Editors: Mahmood Aliofkhazraei, Tarbiat Modares University, Iran, 2013.

http://www.intechopen.com/myprofile/index/dashboard

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