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Synthesis and characterization of nanostructured magnesium oxide powders for composite layers – NANOMAGLAY

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The topic of the proposed project corresponds to the new and current field of nanotechnologies and focuses specially on the study of nanostructured layers. The sol-gel process allows the synthesis of nanocomposite layers starting from MgO nanopowders, with a more elaborate structure in terms of composition, purity, size and dimensional distribution. The project proposal submitted is a component of a multiannual research programme of the Regional Research and Development Centre for Innovative Materials, Products and Processes for the Automotive Industry (RR&DC-AUTO) from University of Pitesti in which the team carries out the research activities. The knowledge of the nanocomposite layers obtained using nanopowders is a necessity for the industry in Romania and, from scientifically point of view, for us. The choice of magnesium and titanium oxides as an object of study is well justified as nanostructured oxides presents multiple properties and configurations at nanometric scale and are used in varied modern applications; thus, the scientific interest is increasing year after year.

The proposed project is considered as a multiannual research programme, with components of fundamental research, industrial and experimental development in order to elaborate some methods for technological transfer. An important manufacturer SITEX 45 is an industrial SME interested for production of new photocatalysts, with high efficiency in the visible spectrum is interested able to decompose hazardous pollutants in the aqueous environment. (http://www.sitex45.com).

By developing the technique of sol-gel, as proposed in the project, such as method of preparation of nanostructured composites, starting from SPVD-nanopowders, the researches, in the field of elaboration and characterization of nanostructures, continue. The project is based on the experience gained by experiments so far by the team members.

The technique sol-gel is not an actual coverage, as in the case of plasma spraying, but using nanopowders like precursors modifies the structure and chemical composition of the surface layer of the base material. This has the advantage that the newly formed layer has an excellent adhesion to the substrate. Final layer properties (thickness, surface chemistry, crystallinity) can be controlled through the following process parameters: current density, rotations, nature and concentration of conductive salts, nature of the electrolyte, temperature.

The developing of a new technique for obtaining nanostructured MgO/TiO_2 composite layers, starting from nanopowders obtained by SPVD, with good interface quality and high photocatalytic properties due to the synergy of the two oxides, is a novelty in the Romanian and European research area and may create favorable following approaches that would target in particular the development of procedures / equipment / test nanostructured layers. The microstructural characterization of nanostructured powders and coatings will be estimate by using specific techniques based on X-Ray Diffraction and Scanning Electron Microscopy. We'll use a Rigaku ULTIMA IV diffractometer, PDF 4+ database, PDXL 2.0 XRD software and a Hitachi SU5000 FESEM with EDS, WDS and EBSD detectors. The sol-gel synthesis will be performed with a spin-coater. The surface specimen's

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preparation will be done by a Hitachi Ion Milling IM4000Plus system. The reasearch infrastructure is presented at: https://erris.gov.ro/CENTRUL-REGIONAL-DE-CERCETAR

The global objective *is the elaboration and characterization of nanostructured composite layers MgO /TiO2 by sol-gel synthesis using MgO nanopowders obtained by SPVD.*

The concrete objectives are:

O.1.*The development of new methodology for synthesis of nanostructured composite layers MgO/TiO_2 by sol-gel synthesis*

O.1.1. *Elaboration of pure or doped MgO nanopowders by SPVD;*

O.1.2. *Development of new methodology for synthesis oxides using solar energy*

O.2 *Elaboration and characterisation of MgO/TiO_2 layers by sol-gel technique, using MgO nanopowders to obtain composite layers.*

O.2.1. *Elaboration of MgO/TiO_2 layers by sol-gel technique*

O.2.2. *Morpho and structural characterization of pure and doped MgO nanopowders*

O.2.3. *Study and modelling of morpho-structural characterization*

O.3. Physical-chemical characterization of structural layers

O.3.1. Establishing of correlation parameters of process-structure-properties;

O.3.2. Modelling of nucleation and growth processes in order to control the morphology of nano-structured layers

O.4. *Dissemination of results*

O.4.1. International conferences participation

O.4.2. Preparing ISI paper

The main objectives to developed at CNRS, Promes – Odeillo are:

- *O1.1 Elaboration of nanostructured MgO pure or doped powders*
- *O.1.2. Development of new methodology for synthesis under solar energy. This are detailed in the work plan of the project.*

From MgO nanopowders prepared by SPVD, it follows elaboration of MgO/TiO2 coatings by sol-gel technique at RR&DC-AUTO, University of Pitesti (corresponding to O.2, O.3 and O.4).

The activities are:

- *- Elaboration of MgO/TiO2 coatings by sol-gel technique at RR&DC-AUTO*
- *- Caracterization of nanopowders and coatings at RR&DC-AUTO by XRD, SAXS, STEM, EDS, FTIR (most of these characterizations will be performed in Auto laboratory: Physico-chemical characterization of structural layers;*
- *Establishment of correlation parameters of process-structure-properties;*
- *Study and modelling of dopants distribution, modelling of structure defects;*
- *Modelling of nucleation and growth processes in order to control the morphology of nano-structured layers;*
- *Modelling the influence of composition and morphology on optical and photocatalytic properties;*
- *Establishing of models for the study of the correlation between synthesis parameters-microstructure-properties.*

The study of their electrical conductivity and of their optical properties will be completed in collaborations of institutional partners.

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DETAILED WORK PLAN

The high potential of the vaporisation-condensation process in solar reactor to grow nanocrystalline pure and doped ZnO as whiskers (10 to 50 nm large and several microns long) or as small particles with mean crystallite sizes of 5 nm has been demonstrated.

Recent experiments have shown that MgO nanopowders obtained by different methods opens the way for important fundamental results on the electronic, magnetic and optical properties of nanopowders, nanocrystalline dense MgO ceramics or thin films.

The main objectives to developed at CNRS, Promes – Odeillo are:

O1.1 Elaboration of nanostructured MgO pure or doped powders

O.1.2. Development of new methodology for synthesis under solar energy

Following these, the main scientific and technological activities to do in the CNRS infrastructure are:

- *Preparing pure MgO and doped targets Mg1-MxO (M=Al, Zn);*
- *Synthesis of Mg1-MxO (M=Al, Zn) nanopowders under solar energy;*
- *Establishing of models for the study of the correlation between synthesis parameters- in the solar reactor under oxidizing gas mixture flow*

This process is a top-down technique, because under solar energy the process (evaporation) starts with a block of material that is brought to the desired shape (condensation). The whole synthesis need a controlled gas flow and depends of solar flux.

Team members for the 1st stay:

- *Electronics engineer: - has used the installation Heliotron and Nanosol;*
- *Chemist, physicist, researcher - has not used the installation;*
- *Engineer physicist, reasercher - has not used the installation.*

For the first stay is required the participation of 3 members of the team to initiate experimental works. The electronics engineer & chemist are in charge of coordinating organization of the laboratory experiments. It will be responsible for establishing the composition of the doped targets considering the expertise in the field of obtaining oxidic nanopowders by SPVD. The physicist is responsible for determining the experimental parameters and thermodynamic conditions (gas pressure, temperature) and to establish the correlation the solar flux - parameters conditions. The engineer is needed for setting up the installation (positioning, fixing).

Team members for the 2nd stay:

- *electronics engineer: - has used the installation Heliotron and Nanosol;*
- *physicist, researcher: has used the installation;*
- *chemist, phD student: has not used the installation.*

The 2nd visit is necessary for continuing the elaboration of nanopowders at established concentration of dopants. The two researchers involved in the project will be tutors for the doctoral student member on the team. The physicist will decide the experimental parameters, based on the previous experiments made by the first team. The engineer is needed for setting up the installation and to decide if modifications are necessary. The PhD student will carry out the composition of targets and will take part in the experiments.

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WHY

In recent years, numerous reports on the synthesis of nanocrystalline oxides with large surface areas and high reactivity have been presented. Magnesium oxide (MgO) is an interesting basic oxide that has many applications. For example, MgO with ultrafine, nanoscale particles and high specific surfaces area has shown great promise as destructive adsorbent for toxic chemical agents. Nanoscale MgO exhibits unique optical, electronic, magnetic, thermal, mechanical, and chemical properties, due to its characteristic structures. Therefore, nanoscale MgO has been extensively used in catalysis, toxic waste remediation, and refractory materials industries based on its versatile properties.

Using the most recent reactors: the "heliotron" or "nanosol", it's posible to associates the two processes: collection by trapping on a cold finger and pumping through a filter, which decreases the phenomena of condensation on the walls of the balloon and increases the effectiveness of the collection. The production rate of the nanopowders depends on the vapor pressure of the material. In the best cases, it can reach several hundred milligrams per hour.

The necessity of solar furnace is for the following procedure:

- *In the first phase the oxide target evaporates*
- *In the second step the vapours condense on a cold support (cooper) and on a nanoporous filter, to obtain a powder with a very fine microstructure;*
- *Collection of the final powder.*

The devices needed are: solar reactors constituted by glass balloons, 2kW solar furnaces (HELIOTRON or NANOSOL), nanoporous ceramic filters, pump vacuum. One person from technical staff of the lab. is needed to set-up the equipment's in the first day. Some common tools are also necessary.

During the years *the oxide nanopowders obtained were formed by one type of nanophases or by a mixture of them: ZrO2-x, SnO2-x, MgO, gadolinium doped ceria Ce1-xGdxO2-δ, yttrium doped zirconia Zr1xYxO2-δ, TiO2 (Anatase or Rutile) and pure or doped zinc oxide nanophases : Zn1-xInxO, Zn1-xSbxO, Zn1-xAlxO, Zn1-xCoxO, Zn1-xBixO, β-Bi2O3-δ. /Rouanet et al., 1993 ; Rouanet et al., 1995 ; Monty et al., 1998 ; Boulares et al., 2004 ; Monty, 2002 ; Monty, 2005 ; Kouam et al, 2008/ but also, starting from targets made by sintering ZnO and Bi2O3, mixtures of (Zn1-xBi$_x$O) and (Bi1-yZny)$_2$O$_3$-z. nanophases /Ait Ahcene et al., 2007.*

By developing the technique of coating by sol-gel starting from MgO nanostructured powders obtained by SPVD, such as method of preparation of nanostructured composites, the researches, in the field of elaboration and characterization of nanostructures, continue. The technique is not an actual coverage, as in the case of plasma spraying, but modifies the structure and chemical composition of the surface layer of the base material. This has the advantage that the newly formed layer has an excellent adhesion to the substrate. Final layer properties (thickness, surface chemistry, crystallinity) can be controlled through the following process parameters.

RESULTS

The degree of pollution reduction constitutes a real challenge for sustainable and durable development. In this context, the realization of nanostructured composite layers starting from nanopowders with photocatalytic properties can allow selective oxidative decomposition and degradation of organic substances and inorganic from aqueous environment, is a field of scientific interdisciplinary research of great actuality. Do to their photocatalytic properties; the developments

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of nanostructured layers of MgO/TiO_2 have interesting perspectives for the development of the detection devices for the environment protection and monitoring the control of foodstuffs. The developing of a new technique for obtaining nanostructured MgO/TiO_2 composite layers pwith good interface quality it and high photocatalytic properties due to the synergy of the two oxides, is a novelty in the Romanian and European research area and may create favorable following approaches that would target in particular the development of procedures / equipment / test nanostructured layers. The results will be compared to those obtained on coatings and thin films prepared by other methods: R-F sputtering (collaboration with INFLPR Bucharest) and electrophoresis of dispersed nanopowders in aqueous and organic solvents (collaboration with IMNR Bucharest). Financing the project opens of new doctoral research themes: elaboration of nanostructured layers by plasma electrolytic oxidation or laser plasma deposition and increase the research portofolio services.

TEAMS:

Members of the teams from the University of Pitesti

No. crt.	Name and surname	Faculty	Department	Research unit	Function
1	Oproescu Mihai	FECC	DECIE	*CRC&D-Auto NanoBioMat*	MANAGER /
2	Plaiasu Gabriela	FMT	DFMI	*CRC&D-Auto NanoBioMat*	MEMBER
3	Ducu Catalin	FMT	DFMI	*CRC&D-Auto NanoBioMat*	MEMBER
4	Moga Sorin	-	-	*CRC&D-Auto NanoBioMat*	MEMBER

BUGETUL CONTRACTULUI

Category of receipts	***Value***
The total value of the research contract	26 000 euro managed by PROMES-CNRS
The total value of the amount collected from the competition budget / contract beneficiary	-
Total amount of co-financing for the contract (if applicable)	-