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Review

*Dedicated to Dr. Maria Zaharescu
on the occasion of her 80th anniversary*

A SHORT HISTORY OF THE SOL-GEL PROCESSES INITIATED IN INSTITUTE OF PHYSICAL CHEMISTRY

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The challenge for materials science is to find a processing method in which the crystalline phase as well as the size and morphology of nanomaterials can be controlled. The sol-gel method is the most used and studied among the nonconventional processes for the preparation of oxide materials, being unanimously recognized for the uniqueness of its advantages in synthesis of tailor made materials (films, monolithic gels, fibers, powders) with high homogeneity and purity and remarkable properties (optic, electric, magnetic, catalytic, etc). The present work describes some researches in this field initiated in the Institute of Physical Chemistry and which have been published starting with 1983 in national and international journals.

$$M(OR)_n + xH_2O \rightarrow M(OH)_n(OR)_{n-x} + xROH$$

$$\text{-M-OH + HO-M-} \rightarrow \text{-M-O-M-} + H_2O$$

$$\text{-M-OH + RO-M -} \rightarrow \text{-M-O-M- + ROH}$$

$$\text{-M-OR + RO-M -} \rightarrow \text{-M-O-M- + ROR}$$

1. GENERAL OVERVIEW

1.1. Sol-gel processes

Solution chemistry offers many possible routes for "chemical manipulation" and allows various combinations in the synthesis of solids of diverse structures, compositions and morphologies.[1] The motivation for sol-gel processing is primarily the potentially higher purity and homogeneity and the lower processing temperature associated with sol-gels compared with traditional glass melting or ceramic powders methods.[2] At the very beginning, sol-gel chemistry was designed to obtain glasses[3-6] and ceramic materials[3, 7-9] after hydrolysis, condensation and gelation of alkoxides precursors, $M(OR)_n$ or of metal complexes in aqueous solution.[1,10] Molecular precursors are transformed into an oxide network by hydrolysis and condensation reactions. Two routes are currently used depending on the nature of the molecular precursors: metal alkoxides in organic solvents or metal salt in aqueous solutions.[11] Ward and Ko[12] consider the sol-gel method as a versatile means in developing catalytic materials, as well as an important experimental tool in understanding their physical and chemical properties.

The advantages of the sol-gel method in the preparation of mono-component materials refer to the very high purity due to the quality of the available precursors and to the possibility to tailor the textural properties of the product, especially the

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surface area and the pore size distribution. For the multi-component systems the following specific advantages can be mentioned: the ability to control both structure and composition at molecular level, the possibility to introduce several components in a single step, and the power to impose kinetic constraints on a system and thereby stabilize metastable phases. Furthermore, the controlled shape and size (usually, mono-disperse), and the nanometer size of the particles must be mentioned.

1.2. The connection between nanomaterials and sol-gel process

Nanomaterials science is a growing area of multidisciplinary studies that attracts great interest, investment and efforts in research and development around the world. Nanoscale is fascinating because it is on this scale that atoms and molecules interact and assemble into structures that possess unique properties, which are dependent on their size. It is at this scale that molecular interactions, processes, and phenomena can be controlled and directed to form the desired geometries of the materials building blocks with desirable properties.[13]

Most of the research in the broad field of nanoscience is dedicated to the development of synthesis routes to nanoparticles and nanostructures. These efforts gave access to nanomaterials with a wide range of compositions, monodisperse crystallite sizes, unprecedented crystallite shapes, and with complex assembly properties.[14] Nanoparticles and nanomaterials represent an evolving technology that has the potential to have an impact on an incredibly wide number of industries and markets: energy, healthcare, engineering.[15] There are many novel properties and applications of nanoparticles demonstrated: from catalysis, environmental remediation, biomedical to information displays, and electronics.

The development of high-speeed computing (and hence modeling), of advanced characterization techniques (such as atomic force microscopy and scanning tunneling microscopy) and of synthesis routes (such as sol-gel processing) made possible to design nanomaterials. Due to the possibilities of leading the chemical reactions occuring in solution through the sol-gel procedure, the obtaining of nanosized materials with predetermined properties is relatively new technology. Among the advantages of the preparing of oxide materials by the sol-gel method is the possibility to control their microstructure and to obtain homogeneous materials. Considered as unique and fascinating from both a scientific, and practical point of view, the sol-gel process has gained in the last years, more and more importance in the materials science field, being unanimously recognized for the uniqueness of its advantages in preparing some special materials and biomaterials with remarkable properties (electric, magnetic, optic or of sensing, etc), as films or nanopowders.

2. SOL-GEL PROCESSES – ACHIEVEMENTS IN THE INSTITUTE OF PHYSICAL CHEMISTRY

The first researches in the sol-gel field in Romania were accomplished in the Laboratory of Oxide Compounds and Materials Science from the "Ilie Murgulescu" Institute of Physical Chemistry of the Roumanian Academy, under the coordination of Acad. Dr. Maria Zaharescu and were published starting with 1983 in national and international journals.[16] The TiO_2 based nanomaterials field has also been initiated by the same team which brought original contributions related both to formation mechanisms and complex characterization of mono-, binary-, ternary- and quaternary powders and nanostructured films obtained by the sol-gel process.

2.1. Sol-gel films

Obtaining sol-gel films represents one field of the applicative science which extended rapidly due to the special properties of the coatings such as mechanical resistance, materials with pre-established refractive index, luminescent solar concentrators, environment sensors and devices for non-linear optics. The sol-gel method is suitable to obtain high purity and homogeneous films. These ones are obtained by the reaction of the essential components at molecular level, in solution.

The growing interest to obtain and characterize the sol-gel films is mainly due to:

- multiple applications field, the most important being: optics (protective and antireflective coatings, interferential filters, fluorescent films), microelectronics (waveguides, voltaic effect joints, pollutants sensors) and catalysis (membranes);
- low cost fabrication, comparatively with the classical methods;
- possibility of controlled doping;
- facility to obtain films with expected optical and electrical properties, by modifying the

technological fabrication parameters: the thermal treatment subsequent to the deposition, the substrate, the type and the quantity of the dopants included in the oxide matrix.

In comparison to the conventional methods to obtain films, as CVD, evaporation or sputtering, the sol-gel films require considerable less equipments and are more convenient economically. Supplementary, the ability to control accurately the microstructure of the deposited film must be mentioned.

Table 1 presents the most representative applications of the sol-gel coatings.

As Table 1 shows the work of the team have been the object of numerous scientific internal and international communications and have been published in prestigious journals.[16-63] Our researches in the sol-gel field have had as a purpose obtaining some new materials, with special properties as coatings and monolitic materials (mono- and policomponent), and scientific original contributions in order to clarify the reaction mechanisms that take place in both stages of the sol-gel process (transition from solutions to gels and from gels to glass or crystallized materials). If I made an incursion in time, I would stop in 1986 year, when in an article published in Silikattechnic[19] the authors highlighted the titanium in tetrahedral coordination on the sol-gel films obtained in our laboratory. The infrared spectra were recorded on a IR SPECORD 75 spectrophotometer between 1800-400 cm^{-1}. A total attenuated reflexion (ATR) apparatus with 14 reflexions, equipped with a KRS 5 single crystal with an angle of 45°, has been used. Since then, TiO_2 has always been in the attention of researchers. The nananostructured feature of the coatings has been pointed out by atomic force microscopy (AFM), a new world investigation method for that period, the results being presented in the paper.[29] AFM was used to study the influence of the thermal treatment on the structural and textural properties of the sol-gel TiO_2 films and informations about the thickness and roughness of the films were obtained. The vanadium doped sol-gel TiO_2 coatings[30] have been tested as sensors for redox potential measurements in electrochemical process with the functional performances comparable with those of the platinum electrode.These papers[29, 30] included under the title *"TiO_2 based nanomaterials obtained by sol-gel method"* have received "Gh. Spacu" award of the Roumanian Academy in 1998. Research continues with new approaches in various systems with multiple applications.

Table 1

The applications of the sol-gel coatings

Field	Composition	References
Optical coatings		
- protective coatings for solar mirrors	TiO_2	18, 19, 26
- coloured (electrochromic)	SiO_2/transitional metal; TiO_2/transitional metal; SiO_2-TiO_2-CeO_2 (high absorption in UV);	23
- reflective	TiO_2-Pd, TiO_2-Au, TiO_2-Ag	43, 47
- antireflective	SiO_2-TiO_2	38, 40
- waveguides	TiO_2:Eu^{3+}; TiO_2:La^{3+}; TiO_2 (Rhodamine G); SiO_2-TiO_2:Er^{3+}, SiO_2-TiO_2-Al_2O_3:Er^{3+}, SiO_2-TiO_2, SiO_2-ZrO_2	34, 38, 56
- nonlinearoptic	SiO_2-Nb_2O_5, SiO_2-Nd_2O_3; TiO_2-PEG	38, 54
Coatings for electronics		
- photoanodes	TiO_2-V_2O_5, TiO_2	29, 30, 93, 103
- conductive	ITO-SnO_2-In, ITO, V_2O_5, SnO_2; SnO_2-TiO_2-ZrO_2, $LiCoO_2$; ZnO, TiO_2-Nb_2O_5; TiO_2-Pd	37, 48, 49, 51, 52, 59, 61
- sensors	TiO_2-V_2O_5, TiO_2-Nb_2O_5, SiO_2-TiO_2, SiO_2-ZrO_2,	30, 39, 41, 58, 60, 62,
- dielectric coatings for semiconductors	SiO_2; TiO_2	20, 21, 22, 24
- ferro-electro-optical	$BaTiO_3$, BZT, PLZT	50
Protective coatings		
- chemical corrosion resistent	SiO_2; TiO_2; TiO_2-CeO_2; B_2O_3-SiO_2; $2SiO_2 \cdot 3Al_2O_3$	16, 17
- mecanicanical resistent	$2SiO_2 \cdot 3Al_2O_3$; Al_2O_3	33
-electronic passivation	SiO_2	16
Depollution coatings	TiO_2, TiO_2-S, TiO_2-Pd, TiO_2-Fe, TiO_2-Co, TiO_2-Ni, TiO_2-Ag, TiO_2-Au, ZnO	31, 32, 35, 43, 44, 45, 46, 47, 53, 57
Porous coatings (catalysts)	Al_2O_3, SiO_2, TiO_2, ZrO_2, Al_2O_3-Mn, SiO_2-Mn	25, 27, 28, 33, 42, 63
Different coatings	TiO_2-Fe_2O_3; TiO_2/Al_2O_3, hidroxy-apatite; Fe_2O_3	36, 38, 55

Table 2

The oxide systems studied

Oxide system	References
Al_2O_3	67, 70, 92, 114
SiO_2	67, 70, 92, 119, 132
TiO_2	63, 64, 67, 70, 92, 103, 108, 114, 117, 118, 126-129, 132, 133, 135, 140, 142, 143, 147
ZnO	141, 144, 145
ZrO_2	125, 134
Al_2O_3-TiO_2	65, 67, 72, 74, 78, 88, 91, 99, 131
Al_2O_3-SiO_2	66, 81
Al_2O_3-MgO	69, 74
Al_2O_3-NiO	122
BaO-TiO_2	136
BaO-ZrO_2	97
La_2O_3-CoO	123, 124
Li_2O-CoO	83, 138, 139
MO-Nd_2O_3 (M = Ca, Sr, Ba)	112, 115, 116, 146
MgO-TiO_2	130
SiO_2-Fe_2O_3	71, 76, 77, 79, 84, 86, 87, 94, 95, 98, 100-102, 105-107, 110, 111
SiO_2-TiO_2	109
V_2O_5-CeO_2	120, 121
WO_3-C	96
Al_2O_3-MgO-TiO_2	69, 73-75
Al_2O_3-SiO_2-TiO_2	66, 73
Al_2O_3-Fe_2O_3-MgO-TiO_2	104
Al_2O_3-MgO-SiO_2-TiO_2	82, 85, 89

2.2. Sol-gel oxide nanopowders

The importance of the sol-gel powders results from their numerous practical applications influenced by: their controlled shape and size (usually mono-disperse), their homogeneity at the molecular scale, increased purity and reactivity (which leads to lower processing temperatures) and the nanometer size of the particles. They serve as components for the high technique polycrystalline ceramics, pigments, catalysts, abrasive materials, chromatographic supports and constituents of electro-optic and magnetic devices. The dependence relationship between the properties of the molecular precursors used in the sol-gel synthesis and the characteristics of the final macromolecular obtained materials allow the extension of new expectations regarding the applications. The most studied sol-gel oxide powders belong to the silica and titania systems, respectively. Due to their scientific and technological importance, their study was extended from mono- to bi- and poly-component systems, obtained by doping. The possibility to control both nucleation and growth of the particles during the preparation process allows the preparation of special powders with a much more complex distribution of dimensions. Thus, the drawbacks of the high costs, long processing time and low yield characteristic to the sol-gel method can be surpassed.

The obtained results have been also the object of numerous scientific internal and international communications and have been published in prestigious journals.[64 - 147]

The oxide systems studied in which the powders were obtained are presented in Table 2.

Our team has also experience in obtaining sol-gel composite materials resulted from embedding organic molecules (fullerene)[90] and some biomolecules (enzymes – alkaline and neutral proteases, glucose oxidase)[80] in SiO_2 matrix. The collection of papers *"Bionanocomposites obtained by the sol-gel method"* has received "Gh. Spacu" Roumanian Academy award in 2002.

The sol-gel domain is viable (see our references in the period 1986 – 2017). In a review published in 2008 in the Surface Science Report, Fujisima *et al.*[148] showed that 2400 papers in the field of heterogeneous photochemistry were published in that year, and 80% of them refer to TiO_2. The subject remains in vogue and now because of the growing applicative potential, which justifies the subject of publications: photocatalytic water splitting and hydrogen production, photoelectrochemistry, dye sensitization and solar energy conversion, reactor design and process kinetics, and photochemical air and water treatments.[149] In this context, the first PhD thesis[150] and the most recently presented one[151] at the institute, at a significant time interval, both having as theme of TiO_2-based materials and coordinated by Acad. Dr. Maria Zaharescu, are conclusive.

CONCLUSIONS

A short history of the sol-gel processes initiated in the Institute of Physical Chemistry was accomplished. The possibilities offered by sol-gel method to design the nanomaterials (films and powders) with special properties were mentioned. The review is mainly focused on nanocomposites, TiO_2 films and nanopowders, but also other oxide systems were investigated.

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