# Highlights of the R&D activities in the nanotechnology area performed by the Italian Interuniversity Consortium on Materials Science and Technology (INSTM)

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## ABSTRACT

The Italian Interuniversity Consortium on Material Science and Technology (INSTM) is actually participated by 44 Italian Universities thus realizing an integrated scientific network among the community of chemists and engineers. INSTM is involved in many strategic areas for innovative devices development, such as: molecular materials for electronics and photonics; polymeric, composite, metallic and ceramic materials for structural and/or functional applications; nano-materials; nano-bio-materials and protective coatings. Research and development activities are performed through projects funded by public and private Italian institutions and International institutions, such as the European Commission. In the recent years much effort has been put to develop fundamental and applied knowledge in the area of nanotechnology and nanostructured materials. In this frame INSTM is actually coordinating three European Networks of Excellence and is participating in different Integrated Projects. A summary related to some of the on-going R&D activities is reported.

***Keywords***: magnetic materials, polymer nanocomposites, catalytic materials, ceramics

## 1 INTRODUCTION

Among the most relevant INSTM actions in the framework of nanotechnology and nanostructured materials they can be evidenced:

- activities related to molecular approach to nanomagnets and multifunctional materials, performed by partners grouped in the network of excellence MAGMANet, funded by the EU in the 6$^{th}$ Framework programmme;

- activities related to nanostructured and functionally polymer-based materials and nanocomposite, performed by partners grouped in the network of excellence Nanofunpoly, funded by the EU in the 6$^{th}$ Framework programme;

- activities related to integrated design of catalytic nanomaterials for a sustainable production, performed by partners grouped in the network of excellence Idecat, funded by the EU in the 6$^{th}$ Framework programme;

- activities related to structural ceramic nanocomposites for top-end functional applications, performed by partners inside the integrated project Nanoker, funded by the EU in the 6$^{th}$ Framework programme.

An overview of the main objectives for the above mentioned projects will be reported, together with some relevant obtained results. The aim is to give a contribution to the state of the art knowledge on nanotechnology, to define future scenarios and directions of R&D strategies.

## 2 NANOMAGNETS AND MULTIFUNCTIONAL MATERIALS

MAGMANet is a Network of Excellence which connects more than 20 nodes from 10 different European countries (Italy, France, Germany, Spain, Portugal, Switzerland, The Netherlands, UK, Poland and Romania). Leading institution of the network is INSTM. The goal is that of integrating the participating Laboratories in order to make them more competitive in the field of "Molecular approach to Nanomagnets and Multifunctional Materials", it is a recent research area which is well inserted in the frame of molecular materials. Information can be obtained at the following address: http://www.magmanet-eu.net. The main research topics are collected in Fig. 1.

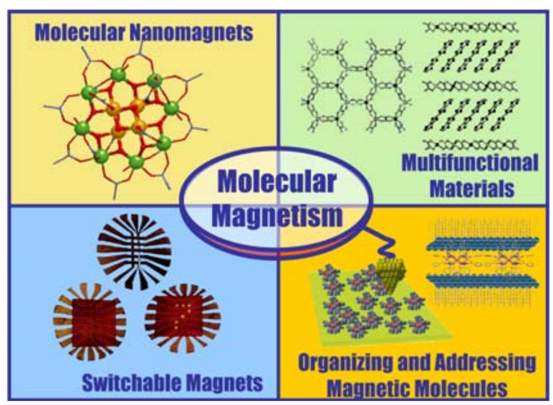


Fig. 1 Research topics of MAGMANet

### 2.1 Some highlights of R&D activities [1-2]

One of the key features of MAGMANet is the development of the so called Single Molecule Magnets, SMM, and Single Chain Magnets, SCM. The former are individual molecules which at low temperature behave as tiny



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magnets, and the latter are polymers whose magnetization relaxes slowly at low temperature. One of the possible uses, beyond advancement of basic science, is as memory elements. In order to do this it is necessary to organize the SMM on suitable surfaces. Encouraging results have been obtained using Langmuir Blodgett films, self assembled monolayers and dispersion in polymers. The relative efficiencies of the three techniques have been evaluated using magneto-optics techniques, which have shown how the environment dramatically influences the magnetic properties of the organized molecules. Magneto-optical techniques have also been used on metal alloys nanoparticles, showing that the magnetic properties can be tuner by interaction with visible light opening exciting perspectives. Other interests are addressed to the development of magnetic nanoparticles using molecular techniques. For instance it has been reported the use of undecanoic acid for the formation of monolayers of Cobalt Ferrite on silicon.

## 3 NANOCOMPOSITES AND NANOSTRUCTURED POLYMERS

The main objective of NANOFUN-POLY (http://www.nanofun-poly.com) is to generate a Network of Excellence designed to become the European organization on Multifunctional Nanostructured Polymers and Nanocomposite Materials. This objective will be reached through a trans-disciplinary partnership of 120 scientists combining excellence in different scientific areas, where the synergy of international excellence and multidisciplinary approaches will lead to develop and spread knowledge in innovative functional and structural polymer-based nanomaterials and their sustainable technologies. Applications that will benefit from NANOFUN-POLY concern strategic industrial sectors which can be competitive only by using advanced technologies: optoelectronics and telecommunications, packaging, agriculture, building construction, automotive and aerospace, etc. The NANOFUN-POLY Consortium consists of 29 partners (12 core partners, 17 Satellite Partners). Leading institution of the network is INSTM.

### 3.1 Some highlights of R&D activities: carbon nanotubes and nanocomposites [3-4]

Electrophoretically deposited single-walled carbon nanotube (SWCNT) films on a transparent conducting surface are used as electrodes for the electrodeposition of a π-conjugated polymer formed by the oxidative coupling of fluorine units. This method provides a uniform coverage of the conducting surface with respect to SWCNTs chemically assembled on a gold substrate.

The conductivity of the PF/C-SWCNTs/FTO sample increases and becomes ohmic with the thickness of the SWCNTs (Fig. 2). This result is consistent with a better percolation of the deposited carbon nanotubes.

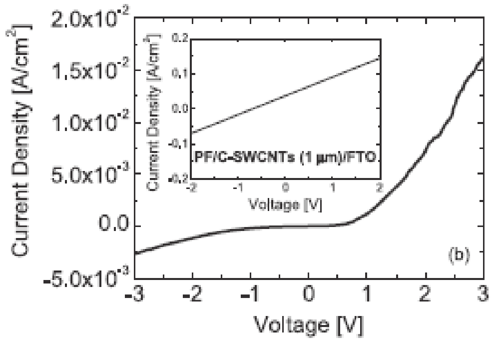



Figure 2. I–V characteristic of PF/C-SWCNTs/FTO (inset for PF/C-SWCNTs (≈1μm)/FTO sample)

Such enhanced conductivity of polymeric chains can be attributed to the entrapped nanotubes and nanotube bridging (Fig.3). The one-dimensional structure of CNTs may also induce and promote oriented polymerization, hence yielding an enhanced supramolecular order and higher conductivity. By combining the attractive properties of SWCNTs and polyfluorene, these nanocomposites open additional opportunities to achieve electrical contacts in nano-to micro-devices.

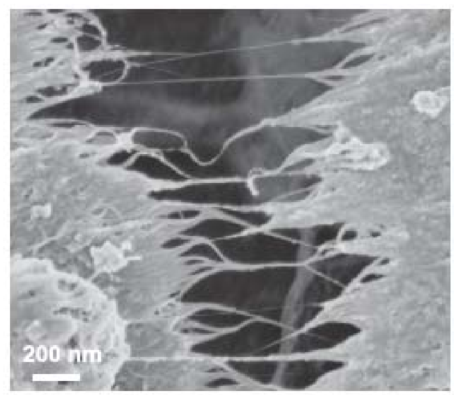
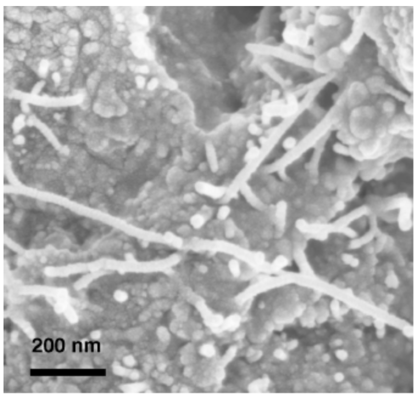



Figure 3. PF deposited on the C-SWCNTs/FTO electrode.

In the area of nanocomposite fabrication, a methodology showing how plasma fluorinated single-walled carbon nanotubes (SWNTs) reacted with a primary aliphatic amine (i.e.butylamine, BAM) hardener (BAM-SWNTs) was investigated, in order to prepare an integrated nanotube composite material. The grafting of butylamine onto CF4 plasma treated SWNTs was used to obtain a cross-linked epoxy nanocomposite. This methodology allowed to obtain a BAM-SWNTs/epoxy nanocomposite (Fig. 4) and experimental results showed that BAM-SWNTs acted as a catalyst, with interactions of cross-linking between the epoxy and amino-functionalized SWNTs during the cure reaction. Amino functionalized nanotubes had a better dispersion in the polymer matrix and the obtained nanocomposites presented an improvement in mechanical strength with respect to those prepared with un-functionalized SWNTs.

(a)



(b)

Fig.4. (a) BAM-SWNTs/epoxy and BAM-u-SWNTs/epoxy nanocomposites; (b) image of BAM-SWNTs/epoxy nanocomposites

# 4 CATALYTIC NANOMATERIALS

The development of high-performance and conceptually innovative catalytic nanomaterials is of high impact for industry and for Europe sustainable future. In Europe, several excellent research teams exist in catalysis. IDECAT Network of Excellence (http://idecat.unime.it) aims are related to the creation of a coherent framework of research, know-how and training between the various catalysis communities (heterogeneous, homogeneous, bio-catalysis) with the objective of achieving an integration between the main European Institutions in the area. IDECAT integrates into a more general strategy of restructuring/reshaping the catalysis research in Europe and focuses its research actions on synthesis and mastering of nano-objects, the materials of the future for catalysis, integrating the concepts common also to other nanotechnologies, bridging the gap between theory and modeling, surface science, and kinetic\applied catalysis as well as between heterogeneous, homogeneous and biocatalytic approaches, integrated design of catalytic nanomaterials. The structure of IDECAT is based on a group of 37 laboratories from 17 Institutions, gathering over 500 researchers with a broad multidisciplinary expertise covering most of the aspects of catalysis. Leading institution of the network is INSTM.

## 4.1 Some highlights of R&D activities: catalytic membranes [5-6]

The use of layered materials (layered perovskite, anionic clays, pillared clays) in catalytic reactions, with their structure consisting of stacked sheets, represent an interesting opportunity for developing new materials with a tailored nanodesign, controlled accessibility to the site sand properties, tuneable pore size and volume, and high surface area. The evaluation of the scientific literature over the period 2000–2006 (English written), evidences that nearly 20,000 papers have been published on clays, layered perovskites (LP) pillared clays (PILC) and hydrotalcite (HT) materials, of which about 85% were dealing on catalysis. From an additional analysis it can be concluded that the LP and PILC materials are still mainly at the lab scale development stage, while HT and especially clays find a broad range of applications. They can offer possibility to develop new processes for environmental protection, selective oxidation and refinery/biorefinery and thus are subject of R&D investigations.

# 5 NANOCERAMICS AND n-COATINGS

The main objective of the Integrated Project NanoKer [7] (http://www.nanoker-society.org) is to find ceramic material solutions which allow the industrial application of knowledge-based nanoceramics and nanocomposites for top-end functional and structural applications. The industrial exploitation of nanostructured ceramics rely to the successful consolidation of these materials which preserve their nanostructure. Traditional processing techniques still show strong limitations in retaining conventional nanoparticles as the starting materials. Therefore, in addition to new material solutions, the full added-value chain of ceramic manufacturing has to be revisited. The technological objectives and expected breakthroughs of IP NANOKER will consist of new multifunctional materials with outstanding hardness, fracture resistance and fracture toughness operating in chemically and physically aggressive environments, and of new multifunctional materials processed into knowledge-based, industrially applicable nanoceramics and nanocomposites with added multifunctionality, e.g. biocompatible functions and very long lifetime, optical properties, tribochemical functions and excellent electrical conductivity, nanostructured coatings with tribological and barrier functions, etc.

IP Nanoker is carrying out research activities in many strategic fields of industrial application, such as Hip, knee and dental implants with life spans superior to the actual ones; new-concept bone substitutes; radiation windows for satellite guidance; satellite mirrors with high stability and reduce surface roughness; polycrystalline lasers of high efficiency; components and nanostructured coatings for engine in aeronautics; conductive nanoceramics to be machined by EDM technologies; metal-ceramic materials of extreme hardness for cutting tools and finally high-creep resistant ceramic nanocomposites.

22 European Partners are involved in this project and 5 of them are Italian. INSTM is a partner of the project.

## 5.1 Ceramic oxide-oxide nanocomposites development [8]

The research aim is to develop micro-nano and nano-nano alumina-based composites, in particular yttrium-aluminium garnet (YAG)–alumina nanocomposites which are promising materials for optical, electronic and structural applications. INSTM research units are involved in the wet chemical synthesis of nanocomposites powders whose full densification as a nanoscaled material is pursued by using conventional sintering routes coupled to particular mechanical and/or thermal powder pre-treatments. One of the main results up to now achieved is the production of an alumina-YAG (50 vol%) nano-nanocomposite material by coupling an optimised powder pre-treatment to an extensive mechanical activation, performed by a conventional wet milling. The set-up of this procedure allowed the Consortium INSTM to deposit an Italian Patent and now an European Patent is pending. After that powder compacts fully sintered (>98%) at very low sintering temperature, ranging between 1370 and 1420°C. As a consequence, a very fine microstructure was obtained in which α-alumina and YAG grains were lower than 300 nm in size (Fig.5).

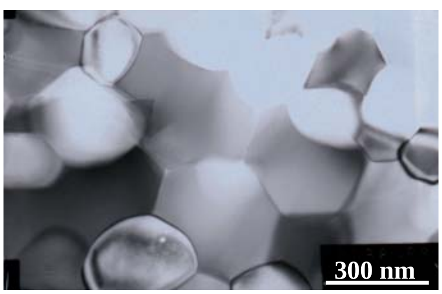



Fig.5 - TEM micrographs of a 50 vol% alumina-YAG composite, after natural sintering.

## 5.2 New scaffolds for bone substitution based on hydroxyapatite (HAp) nanopowders [9]

This activity is aimed at finding possible solutions for the increasing need for advanced ceramic scaffolds for bone substitution, showing improved mechanical performances and biological properties in terms of cell adhesion and bone ingrowth. One of the major objectives is to achieve a suitable control of the porosity features in terms of total porosity, pore size distribution, pore distribution from the surface to the bulk of the component from the nano up to the micro-scale. To reach this goal, first of all, it is necessary to produce and characterize HAp nanopowders and then to control their sintering behavior in order to control the final nano-microstructural features. Hydroxyapatite (HAp) nanopowders were synthesised following different precipitation routes and the pivotal role of the type of the preparation process on the thermal stability of HAp powders as well as on their sintering behavior and final fired microstructure (Fig.6) was clearly pointed out during the preliminary study through nanostructured scaffolds.

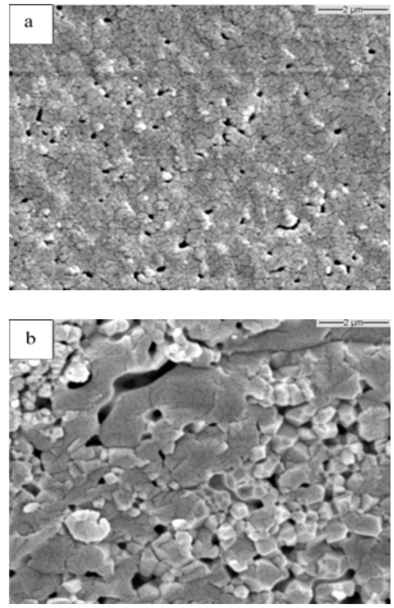



Fig. 6 – HAp materials prepared by precipitation (a) from calcium hydroxide and phosphoric acid solution and (b) from calcium nitrate and diammonium hydrogen phosphate solutions, and then sintered at 1050°C for 3 hrs.

## 5.3 Synthesis of pure YAG nanopowders [10]

Although a lot of investigations on pure alumina preparation have underlined the strong influence of some process parameters (temperature, pH, rate of addition and nature of the precipitation agent) on the phase evolution and on the properties of the synthesized alumina, when wet chemical syntheses and particularly precipitation are used, similar studies on pure yttrium-aluminium garnet (YAG) were lacking in the literature. YAG powders were therefore synthesized using a reverse-strike precipitation, by adding an aqueous solution of yttrium and aluminium chlorides to dilute ammonia while monitoring the pH to a constant value of 9. After precipitation, the gelly product was washed several times; precipitation and washing procedures were performed at three different temperatures, namely at 5, 25 and 60°C. After drying, the powders were calcined at different temperatures and times. Phase evolution was investigated by X-ray analysis; the evolution of crystallites formation and growth as a function of the temperature was followed by TEM observations (Fig. 7).

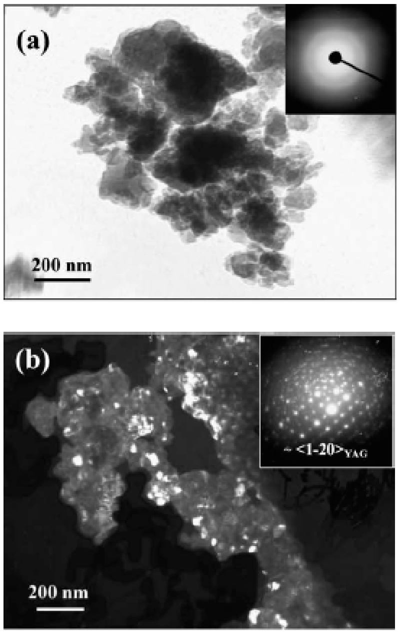



Fig. 7 - TEM of YAG powder synthesized at 25°C: (a) dried at 60°C, (b) pre-treated at 950°C

From this investigation it was possible to demonstrate a relevant influence of the co-precipitation temperature on the phases appearance, crystallization path and final homogeneity of these powders.

## 5.4 Coatings by nanostructured powders [11]

Three main deposition methods are actually under investigation: high velocity oxy-fuel (HVOF), suspension plasma spraying (SPS) and air plasma spraying (APS), for fabrication of wear and/or high temperature resistant coating. In the case of APS the materials under investigation are $Al_2O_3/TiO_2/ZrO_2$, $Y_2O_3/ZrO_2$, $CaO/ZrO_2/SiO_2$, $Cr_2O_3$. With respect to coatings fabricated with the same methodology but with conventional microstructured powders improvements in terms of microhardness, fracture toughness, wear resistance and thermal cycling resistance have been observed. An example of coating microstructure is reported in Fig. 8.

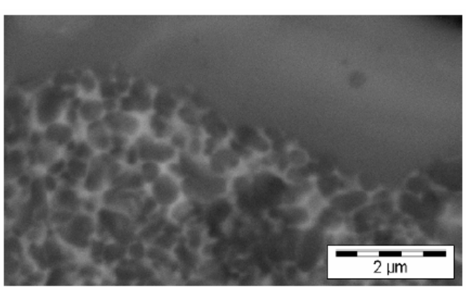



Fig. 8 – SEM cross section of a coating by APS based on $Al_2O_3/TiO_2/ZrO_2$ powders.

Even in the case of WC-Co HVOF coatings, improvements in terms of fracture toughness, microharndess and wear resistance have been observed. In both cases, a strict control of spraying temperature distribution, injection properties as well as jet properties is required in order to retain nanostructured areas inside the coatings. For these reasons an off-line modeling procedure of the jet and of the particle-jet interactions has been developed to address processing parameters optimization.

## 6 CONCLUSIONS

INSTM is actually involved in different research topics dealing with nanotechnology and nanostructured materials. National, European and International collaborations has been established not only on the scientific and/or academic side, but with the participations of industries and potential end-users. Results obtained up to now are relevant in terms of new generated knowledge. The transfer phase is just at the beginning and will be the area to which efforts will be finalized in the near future.

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