

Perspectives of application for nanoparticles prepared by CO₂ laser pyrolysis: from ceramic nanocomposites to nanofluids

R. D'AMATO⁽¹⁾(*), M. FALCONIERI⁽²⁾, F. FABBRI⁽¹⁾ and E. BORSELLA⁽¹⁾

⁽¹⁾ *C. R. ENEA Frascati - Via E. Fermi 45, 00044 Frascati (RM), Italy*

⁽²⁾ *C. R. ENEA Casaccia - Via Anguillarese 301, 00060 Rome, Italy*

ricevuto il 9 Marzo 2013

Summary. — Nanoparticles are one of the main ingredients for the realization of a wide range of nanostructured materials and devices with potential applications in several research areas and industrial sectors, hence their synthesis is a critical step in the development of nanotechnologies. Here we report on the preparation of several types of nanoparticles by laser pyrolysis of gas phase or vapour phase precursors, a very flexible and scalable synthesis route. A critical insight is given into the perspectives of practical applications of these nanoparticles in a number of fields ranging from the fabrication of ceramic nanocomposites to wear resistant coatings, from fluorophores for bio-imaging to nanofluids for efficient thermal management, from nanocoatings for cultural heritage preservation to the realization of a new class of inks for ink-jet printing applications.

PACS 81.07.-b – Nanoscale materials and structures: Fabrication and characterization.

PACS 81.07.Wx – Nanopowders.

PACS 76.67.Bf – Optical properties of low-dimensional, mesoscopic, and nanoscale materials and structures.

PACS 87.85.Qr – Nanotechnology design.

1. – Introduction

Nanomaterials or nanostructured materials possess properties that considerably differ from the corresponding bulk material, thereby making them attractive for a number of structural and functional applications [1]. The possibility to use nanomaterials in such applications often requires the development of methods for the production of nanoparticles with strict control over size, shape and crystalline structure.

(*) E-mail: rosaria.damato@enea.it

Nowadays, nanoparticles of a wide range of chemical composition and phases can be prepared by a variety of “top-down” and “bottom-up” methods. The first type of approach consists in the division of a massive solid into smaller nanometric parts, as in ball milling, attrition etc. [1]. On the other hand, the bottom-up method of nanoparticle synthesis is mostly based on the condensation of atoms, molecules or radicals in the gas phase or solution [2, 3]. One method of achieving in the gas phase the supersaturation necessary to induce homogeneous nucleation and growth of nanoparticles is based on the infrared (CO_2) laser-induced excitation and dissociation of reactants [4]. Compared to other methods, this technique, usually denominated laser pyrolysis, allows for highly localized heating and rapid cooling of reactants, which results in the formation of nanoparticles with controllable composition, high-purity, small-size and narrow-size distribution [4, 5]. Moreover, laser pyrolysis is a scalable route for the production of large volumes of nanoparticles as requested for the fabrication of several types of nanomaterials needed for practical applications [6].

The technique of laser pyrolysis of gas phase reactants has been applied at ENEA to the synthesis of a large variety of oxide (TiO_2 , SiO_2 , Al_2O_3 , Fe_2O_3) and non-oxide (Si, SiC, Si_3N_4 , Si/C/N, Si/Ti/C, MoS_2) nanopowders [4]. Here we will present a comprehensive description of this preparation technique, of the post-synthesis processing and of the properties of several nanopowders of interest for a wide range of functional and structural applications. In particular, we will give a critical insight into the perspectives of exploitation for Si and Si-based nanopowders in several R&D fields. Moreover, we will report on recent progress in the synthesis of TiO_2 and SiO_2 nanopowders for applications in the energetic sector and cultural heritage preservation.

2. – Experimental methods

2.1. Process description. – The CO_2 laser pyrolysis technique is a vapour phase synthesis process for the production of nanoparticles. In this class of synthesis routes, nanoparticle formation starts abruptly when a sufficient degree of supersaturation of condensable products is reached in the vapour phase [2, 3]. Once nucleation occurs, fast particle growth takes place by coalescence/coagulation rather than further nucleation. At sufficiently high temperatures, particle coalescence (sintering) is faster than coagulation and spherical particles are formed. At lower temperatures, coalescence slows down and partially sintered, non-spherical particles and/or loose agglomerates of particles are formed [2]. It follows that to prepare small, spherical particles it is necessary to create a high degree of supersaturation for inducing the formation of a high density of nuclei and then quickly quench the particle growth either by removing the source of supersaturation or by slowing down the kinetics.

In the process of CO_2 laser pyrolysis, the condensable products result from laser induced chemical reactions at the crossing point of the laser beam with the molecular flow of gas or vapour phase precursors (fig. 1). The pre-requisite for energy coupling into the system, leading to molecular decomposition, is that at least one of the precursors absorbs through a resonant vibrational mode the infrared (IR) CO_2 laser radiation at about $10\ \mu\text{m}$ [4]. Alternatively, an inert photo-sensitizer is added to the vapour phase mixture. The high power of the CO_2 laser induces the sequential absorption of several IR photons in the same molecule, followed by collision-assisted energy pooling leading to a rapid increase in the average temperature of the gas through V-T (vibration-translation) energy transfer processes, often accompanied by the appearance of a flame in the interaction

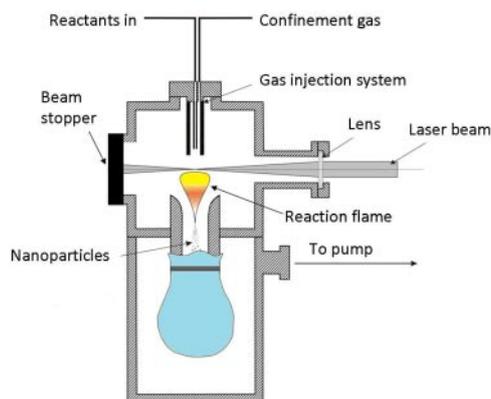


Fig. 1. – Scheme of the set-up for laser synthesis of nanoparticles from gas phase reactants.

volume [4]. If the molecules are excited above the dissociation threshold, molecular decomposition, eventually followed by chemical reactions, occurs with the formation of condensable and/or volatile products.

Compared with other vapour phase synthesis methods [2, 3], it is fairly evident that laser pyrolysis permits highly localized and fast heating (leading to rapid nucleation) in a volume that can be limited to a few hundred mm^3 , followed by fast quenching of the particle growth (in a few ms). As a result, nanoparticles with average size ranging from 5 to 30 nm and narrow size distribution are formed in the hot region [4-6]. Unavoidable agglomeration, however, occurs when the nanoparticles leave the high-temperature region since coalescence becomes much slower than coagulation.

2.2. Experimental set-up. – A scheme of the ENEA set-up for the production of nanopowders by CO_2 laser pyrolysis is shown in fig. 1. The CW CO_2 laser beam ($\lambda = 10.6 \mu\text{m}$) is focused by a lens at the centre of the reaction chamber where it orthogonally intersects the reactant gas flow. The maximum laser power is 1.2 kW and the laser beam intensity in the focal region can be varied in the range 2–4 kW/cm^2 . Reactant gases enter the chamber through the inner tube of a coaxial stainless-steel nozzle. An inert gas (helium or argon) flows through the outer tube with the purpose of confining and cooling the particles. The pressure in the reaction chamber is kept constant by a throttle valve and measured by a capacitance gauge. Typical cell pressures are in the range $6.7\text{--}80 \times 10^3 \text{ Pa}$.

In the laser pyrolysis process, the reactants are most often in the gas phase, however in some cases, liquid precursors are either the only choice or the most advantageous from an economical point of view. For this reason, an evaporation system has been recently developed at ENEA to use liquid precursors in the laser pyrolysis set-up and increase the range of nanopowders that can be synthesized. The use of liquid precursors is made possible by bubbling the inert gas, or one of the gas phase reactants, through a heated jar containing the liquid precursor to carry out its vapour into the chamber (fig. 2).

After leaving the hot reaction zone, the produced particles are driven by the gas flow through a chimney into a removable bag, located in a tank between the reaction chamber and the vacuum pump.

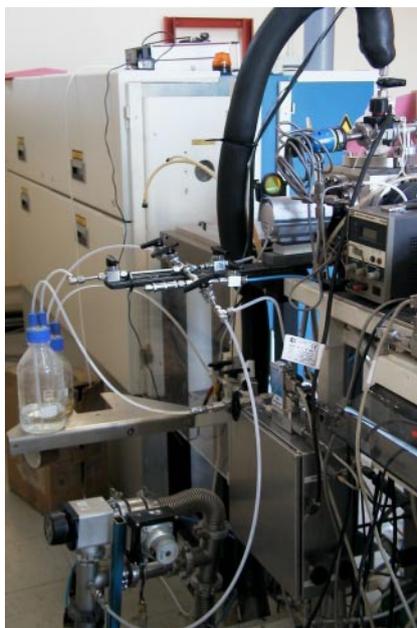


Fig. 2. – Picture of the gas injection system for use of liquid precursors in the laser pyrolysis set-up.

2.3. Nanopowders preparation and properties. – The technique of laser pyrolysis of gas phase reactants is applied at ENEA to the preparation of nanoparticles of a wide range of chemical compositions, including multi-component and doped materials [4, 7].

In this context, Si and Si-based nanoparticles are the most widely investigated for two main reasons: i) silane gas (SiH_4), a common precursor for Si radical formation, has a very high absorptivity for the emission line of an untuned, multimodal CO_2 laser (at $10.6\ \mu\text{m}$); ii) the enormous importance of Si and Si-based nanoparticles for a multitude of applications, as discussed in detail in the following paragraphs. In fig. 3, TEM images of typical crystalline Si nanoparticles are reported [8]. Si nanoparticles are formed as a result of the laser induced dissociation of pure silane, whereas silicon carbide (SiC) and silicon nitride (Si_3N_4) are formed by addition to silane of small hydrocarbons or ammonia,

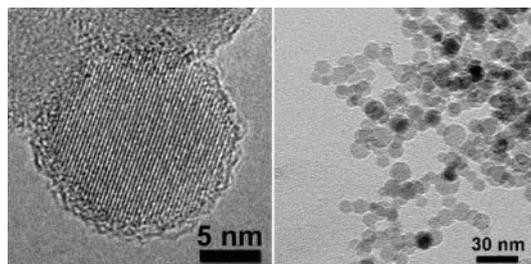


Fig. 3. – TEM images of Si nanoparticles produced by CO_2 laser pyrolysis of silane. Courtesy of Prof. G. Mattei and Dr. V. Bello, University of Padua, Italy [8].

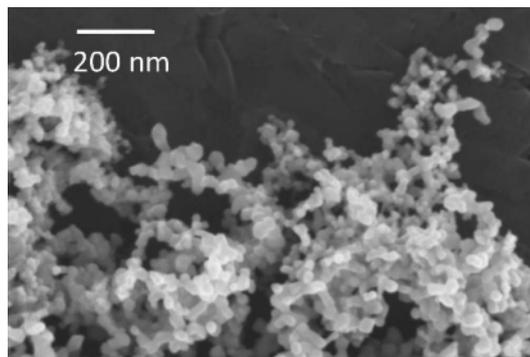


Fig. 4. – SEM image of TiO_2 nanoparticles produced by CO_2 laser pyrolysis of TTIP, after annealing in air to remove the contaminants.

respectively [4, 7]. Compound nanoparticle formation takes place through collision and coalescence between radicals formed in the flame after reactant dissociation. Typical productivity values range between 80 and 100 g/h.

The flexibility of the laser pyrolysis technique has also made possible to synthesize ternary composite Si-based nanopowders like Si/C/N and Si/Ti/C with a different, controllable composition, by acting on the ratio between the reactants in the gas mixture [7, 9, 10]. Moreover, nanopowders can be doped by controlled addition of a small amount of a dopant precursor to the gas mixture. For example B-doped SiC nanoparticles are obtained by addition of a low percentage of diborane to silane and acetylene gas mixture in the reaction chamber.

In case of silica (SiO_2) nanopowder formation, however, it is necessary to use a precursor different from silane gas, that reacts violently with oxygen and can cause an explosion. A good precursor is tetraethoxysilane (TEOS), a liquid at room temperature, with a vapor pressure of about 200 Pa, in which Si atoms are already oxidized. The aerosol is produced by bubbling Ar gas in the liquid precursor bottle and carried to the reaction chamber by the Ar flow passing through a liquid evaporator (fig. 2). Ar gas can also be used as a diluent for the reagents. Titania (TiO_2) nanoparticles can also be synthesized by laser pyrolysis of an aerosol of a liquid precursor, *i.e.* titanium tetraisopropoxide (TTIP). Both silica and titania nanoparticles have been successfully prepared by use of the new liquid evaporation system. In both cases, ethylene gas (C_2H_4) was chosen as reaction sensitizer to increase the coupling of the laser energy in the system. A problem often encountered when sensitizers are needed for the reaction, is the presence of contaminants in the final products, deriving from unwanted partial dissociation of the sensitizer. Annealing of nanoparticles is used to remove contaminants with volatile oxides (as carbon), trying to keep a moderate heating temperature to avoid grain growth. A SEM image of titania nanoparticles after heating treatment in air (at $T = 500^\circ\text{C}$ for 3 h) is reported in fig. 4. Negligible increase of the nanoparticle size was observed.

The mean nanoparticle size can be varied by acting on the process parameters like the residence time of the particles in the flame, the total pressure in the reaction chamber and the reaction temperature T . This explains the flexibility of laser pyrolysis with respect to other synthesis techniques. However, as in other vapour phase synthesis methods, one of the major obstacles to the widespread use of pyrolytic nanoparticles is the formation of chained agglomerates of small particles, rather than spherical particles (fig. 3).

High-power ultrasonic treatment and/or ball milling are effective in reducing the nanoaggregate mean size by disaggregation of soft-agglomerates, whereas partially sintered aggregates can only be eliminated by centrifugation or filtration, with significant material loss. Stabilization of nanoparticles dispersed in liquids is usually achieved by using surfactants, that is, surface active agents adsorbed on the nanoparticle surface [1,2].

3. – Structural and functional applications of nanopowders prepared by laser pyrolysis

In the following we will report on the preparation and processing of Si and Si-based nanopowders that have been tried for a variety of applications in challenging research fields and competitive industrial sectors.

3.1. *Nanocomposite materials.* – The class of nanophase ceramic materials started to attract wide and considerable interest for high-temperature structural applications mainly as a consequence of the impressive mechanical performances reported for these materials by Niihara and his co-workers [11]. In this context, SiC nanopowders produced at ENEA by laser pyrolysis were used i) as second phase for the fabrication of ceramic nanocomposites like $\text{Al}_2\text{O}_3/\text{SiC}$, ii) as filler of the polycarbosilane precursor for the production of SiC Ceramic Matrix Composites (CMC) and for iii) preparing fiber reinforced CMC by electrophoretic infiltration of two-dimensional woven carbon fiber fabrics [12]. However, it has been recognized that conventional processing routes are not efficient to fabricate structural materials from nanophase constituents. This conclusion pushes, on the one hand, towards the development of new processing and forming techniques and, on the other, towards the development of nanocomposites for applications where the sensitivity to defect population is not very critical (like abrasion resistance, polymer reinforcement by addition of nanoparticles etc.) or specific functions are required (optical, magnetic, electrical, thermal etc.).

In this context, there is now a considerable demand for protective coatings with improved resistance to highly aggressive environments in order to extend drastically the safe service life of industrial objects. Nanocomposite films can be fabricated through electrochemical deposition of the matrix material from a solution containing suspended nanoparticles of various chemical composition, such as oxides, carbides, nitrides and metal powders. This technique has been applied successfully to produce nanocomposite coatings containing SiC nanoparticles prepared at ENEA by laser pyrolysis. Two different types of coatings were prepared: nickel-SiC and bronze-SiC nanocomposites [13]. The mean size of the SiC nanoparticles was of about 20 nm. The co-deposition of nickel with SiC nanoparticles brought to the formation of a more uniform deposit with smaller, rounder nickel grains conferring better mechanical and anticorrosive properties to the coating [13]. This promising result led towards a scaling-up of the electrodeposition process for the realization of corrosion and wear resistant Ni/SiC nanocomposite coatings on ship propeller models and real scale propeller profiles as well as on train axles [13].

3.2. *Development of Si and Si-based nanoparticles for photonics and bio-imaging.* – In recent years, research on nanomaterials has been mainly stimulated by the discovery of their novel properties as compared to bulk materials, which open up possibilities for a variety of applications, beyond the field of structural and mechanical applications. In particular, a great interest has been attracted by the “quantum confinement” effect

which results in the possibility to tune the optoelectronic properties of the semiconductors by changing the particle size [1]. In this framework, the discovery of room temperature visible photoluminescence (PL) emission from nanostructured, porous Si (p-Si) [14], has arisen a great scientific and technological interest for the perspective of developing all-silicon optoelectronics and photonics due to the intrinsic compatibility of efficient Si-based light emitters with existing silicon based electronic technologies [15]. One attempt to merge the world of optoelectronics and photonics with silicon technologies is related to doping Si with Er atoms [16]. In this way the Er emission at the $1.54\ \mu\text{m}$ telecommunication wavelength could be attained in a silicon-based material. Use of nanostructured Si was expected to produce a novel device scheme where Si nanoparticles act as sensitizers of nearby Er ion emission, *i.e.* transfer to the ion the energy absorbed after optical excitation [16]. To this purpose, Si-based nanopowders were prepared by laser pyrolysis [17] and integrated in an Er-doped silica glass by standard dispersion procedure and sol-gel processing. Photoluminescence measurements on a glass sample containing 5 at.% of Si-based nanopowders and 0.5 at.% of Er revealed that Er ions emit at $1.54\ \mu\text{m}$ not only by direct pumping, but also under out-of-resonance excitation, thus confirming the activation of the energy transfer mechanism [16, 17] and the functionality of silicon and silicon-based nanoparticles as antennas or sensitizers.

Another option for a new generation of optoelectronic devices that could be fabricated with minimal disturbance to conventional silicon technology is represented by the exploitation of luminescent Si nanocrystals [15]. However, as-synthesised Si nanoparticles are scarcely luminescent. A strong luminescence enhancement is obtained by using a wet chemical oxidation process on silicon nanopowders produced by laser pyrolysis [6]. We have shown that surface oxidation has the effect of both increasing the PL emission intensity and modifying the spectral profile of the emission band. These results pushed us to investigate in more detail the interplay between localized defects at the Si/SiO₂ interface and the quantum confinement of photogenerated carriers. In a recent paper [18] we have reported on the spectroscopic properties of the same sample as-prepared by laser synthesis (Si nanocrystals, Si-nc) and after chemical oxidation (amorphous silica nanoparticles, a-SiO₂), providing unambiguous direct comparison of their luminescence properties. The similarity of the spectral and time dependent features of the red PL emission band in both systems strongly suggests that this emission is due to the same kind of defect states, likely non-bridging oxygen centres (NBO) [18]. Consequently, the possibility of using Si-nc luminescence for new technologies rests on the control of the crystallite size and the structural and chemical properties of the surface, targets still to be fully achieved.

Although strongly influenced by material properties and surface effects, an interesting option for the exploitation of luminescent Si-nc is represented by fluorescence bio-imaging [19, 20]. In fact Si is an intrinsically inert, non-toxic material, and is in principle more suitable than II-VI quantum dots for *in vivo* studies. Other appealing characteristic of the Si-nc photoluminescence is its long decay time (order of several tens of microseconds) which provides the possibility of using gating techniques for rejection of the short-lived biological background fluorescence [19]. In this context, we have demonstrated [21] the possibility of two-photon luminescence excitation of Si-nc, that is a very interesting property for advanced imaging techniques which call for photo-excitation in the red-near infrared band falling in the transparency window of living tissues [19].

In order to exploit their potential for bio-medical applications, Si-nc should remain highly luminescent and well dispersed in water and biological fluids over a wide range of pH and salt concentrations. This is a particularly hard task since the ionic strength

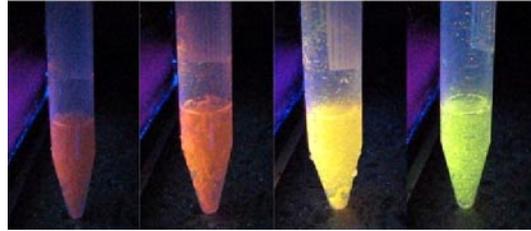


Fig. 5. – Dispersions of fluorescent Si-nc emitting at different colours after HF/HNO₃ etching. From left to right the etching time is 3 min (red emission), 3.5 min (orange emission), 4 min (yellow emission) and 9 min (green emission), respectively. Courtesy of Prof. D. Wang, Univ. of South Australia [19].

in physiological fluids is high enough to decrease the electrostatic repulsion between Si-nc, which normally prevents aggregation [19]. Disaggregation of dried powders to well-dispersed Si nanoparticles in water using both acid etching and alkali etching procedures results problematic, but successful results can be achieved by a combined alkali-etching procedure terminated by the addition of H₂O₂. The use of HF/HNO₃ mixture as etching agent can make the Si-nc photoluminescent with various emission colors depending on the etching time (fig. 5), however the stability of the emission still needs to be enhanced [19]. To prevent the formation of large aggregates, Si-nc can be coated with a biocompatible polymer in order to improve biodistribution. Colloidally stable and biocompatible Si-nc have been fabricated by grafting hydrophilic polymer chains, such as polyethyleneglycol (PEG), on the Si-nc. It was found that the PEGylated Si-nc remain stable in water for weeks. Moreover, negligible cytotoxicity of PEGylated Si-nc was observed by vitality tests on epithelial cell lines known to be fairly sensible to noxious agents, *i.e.* A30 cells (located at the air/blood barrier) [19, 20, 22].

Although promising results have been obtained in the functionalization of pyrolytic Si-nc and first *in vivo* bio-imaging tests have been done on guinea pigs [19], the objective of assessing a stable and reliable preparation route for Si-nc to be effectively used as bio-markers is still to be reached.

Using the past experience on Er sensitization by Si-nc, a different approach was recently experimented to get tuneable and stable photoluminescence from Si-based nanocrystals, *i.e.* binding a rare-earth ion to the nanocrystal surface [23]. Si-nc can be effectively excited at all the photon energies above the band gap and subsequently transfer their energy to the linked rare-earth ion which decays emitting photons at their characteristic transition energies. In principle, it should be possible to get different well-defined emission wavelengths, over a narrow spectral range, by linking the Si-nc to different rare-earth ions and by using the same excitation wavelength, thus allowing for multicolour labelling of cells. This approach was first tried on Yb ions, by exploitation of the aptitude of this ion to form complexes with amino groups which are easily linkable to the surface of pyrolytic Si-nc [23]. A sharp PL emission peak at about 980 nm, due to the presence of Yb ions, was observed under excitation of the surface functionalized Si-nc at 532 nm, a wavelength where Yb ions do not absorb. This demonstrates that the excitation of rare-earth ions takes place through the desired energy transfer from Si-nc [23]. The procedure is based on a wet-chemistry approach which does not require high temperature annealing for luminescence emission activation and could be extended to other lanthanide ions in order to produce Si-based nanocrystals emitting

at different wavelengths in a rainbow of colours. It should be mentioned that toxicity tests recently performed on epithelial cells and fibroblasts demonstrate that Yb-doped Si-nc in concentration suitable for luminescent labelling do not affect significantly the cell viability [23].

3.3. Development of nanofluids for enhanced heat exchange. – Nanofluids are a new class of highly performing nanotechnology-based coolants engineered by dispersing and stably suspending in base fluids a limited amount of nanoparticles (metallic or nonmetallic) with typical size on the order of 10–250 nm. An assessment of enhanced heat transfer coefficient in nanofluids with respect to conventional coolants would push towards their industrial exploitation for a variety of applications ranging from cooling of electronic components, transformer oil and heat-exchange devices to development of better performing chillers, domestic refrigerators-freezers and more [24]. In this framework, nanopowders for the preparation and testing of selected nanofluids have been produced at ENEA by CO₂ laser pyrolysis. An enhancement in the thermal conductivity (with respect to distilled water) was observed in all the nanofluids based on ENEA pyrolytic nanoparticles (TiO₂, SiO₂ and SiC) dispersed at different concentrations in water. The thermal conductivity of nanofluids was determined either with conventional methodologies (at the University of Birmingham-UK and the Royal Institute of Technology-SW) or with an optical, laser-induced grating set-up, realized at ENEA, which provides the possibility for *in situ* monitoring of coolant performances [25]. On this premise, evaluation tests of the heat transfer performance of water based nanofluids containing either TiO₂ or SiC pyrolytic nanoparticles (in different concentrations) were conducted at ENEA by use of an experimental facility designed to allow for direct comparison with distilled water [26]. Using the Reynolds number as a reference parameter, it has been found that the heat transfer coefficient for the nanofluids is higher than for the basic fluid. This result has been attributed to the higher viscosity of the nanofluids which for the same Reynolds number corresponds to a higher velocity, thus allowing for a better heat transfer performance [26]. However, due to the higher velocity, for the same Reynolds number pressure drops associated with nanofluids are higher than those typical of the basic fluid. This conclusion has to be taken into account when considering the perspectives for exploitation of nanofluids in practical applications.

3.4. Development of nanocomposites for cultural heritage preservation. – In the last few years, there was a surge of interest for the application of nanocomposites to restoration and conservation of artworks. In fact, it has been found that the addition of inorganic oxide nanoparticles, such as silica and titania, improves the performances of materials used in the conservation field. SiO₂ and TiO₂ nanoparticles, as produced by CO₂ laser pyrolysis with mean size of about 15 nm, were added as nanometric fillers to acrylic and siloxane polymeric dispersions. Nanosilica and nanotitania were chosen for their physical properties, such as the improved water repellent. The preservation properties of our nanocomposites were tested by the application on two different litotypes, very common in outdoor cultural heritage: white marble (statuary and veined Carrara) and travertine [27]. To this purpose different solutions of an acrylic resin and a silicon-based polymer with dispersed silica and titania nanoparticles were prepared. Artificial aging processes, both in climatic chamber and in solar box, were carried out to simulate real degradation processes in terms of photo-thermal effects and mechanical damage. The relative durability of the two different consolidants as modified by nanoparticles was evaluated comparatively by means of several diagnostic techniques. The results demonstrate that nanoparticles enhance the efficacy of consolidant and protective materials

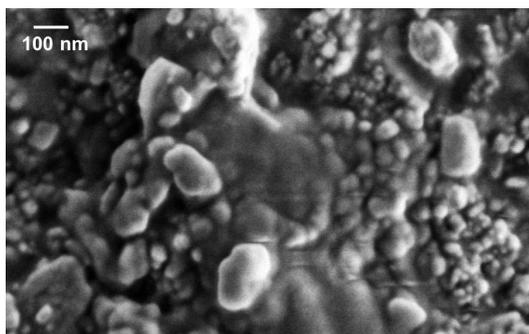


Fig. 6. – High-magnification SEM image of grey Carrara marble treated with Paraloid B72/TiO₂ (0.2% w/v): the nanoparticles induces a micro- and nano-scale roughness at the acrylic surface. Courtesy of L. Pilloni, ENEA.

because they induce substantial changes of surface morphology of the coating layer (see fig. 6) and hinder the physical damage observed during artificial weathering, especially in alkylsiloxane products [27].

3.5. Development of nc-based inks for ink-jet printing applications. – Recently, particular attention has been devoted to the deposition and patterning of films by TiO₂-nc solution processing to obtain substrates covered by nanoparticles to be employed as self-cleaning surfaces, antibacterial agents, working electrodes for dye-sensitized solar cells, insulator layers in electronic applications, water and air purification, optical applications, and waveguides [28]. In particular, substitutional N doping was found to be quite effective in decreasing the band gap of the anatase phase and, consequently, in improving the optical absorption and photocatalytic activity of TiO₂ nanoparticles under visible light [28]. On account of this remarkable property, the possibility of dispersing N-doped TiO₂ in solution might provide new inputs for the fabrication of scattering layers and in the photocatalytic and photovoltaic research sectors. In addition, stable N-doped TiO₂-based solutions could further extend the application field up to innovative deposition methods in the ink-jet printing (IJP) technique suitable for the realization of defined patterns. N-doped TiO₂ nanoparticles were dispersed in solution through the use of polyethylenimine (PEI), a polycation polymer, to manufacture inks for IJP applications [28]. NaTiO₂/PEI/EtOH suspensions at different PEI concentrations were prepared, and a study of the effect of the dispersant content on the ink printability was performed. The suspensions were characterized in terms of viscosity, surface tension, particle size, and time stability. The results of the analyses indicated that all of the prepared samples have the appropriate chemico-physical properties for employment as inks [28].

4. – Conclusions and perspectives

The laser pyrolysis method for the synthesis of nanoparticles has proven to be a very flexible and versatile technique which permits to cope with several challenges in different sectors of nanotechnology and applied physics. Here, applications in the field of structural nanoceramics, wear resistant coatings and functional nanomaterials for opto-electronics, photonics and bio-imaging have been described. Moreover, preliminary results have

been reported on new challenging applications like the preparation of nanofluids for improved thermal management, the development of doped and pure TiO₂ nanoparticles for ink-jet printing, the realization of protective nanocomposite coatings for cultural heritage preservation. In most cases, a critical outlook has been given on the real potentialities of pyrolytic nanopowders for practical applications.

* * *

We wish to thank Dr. R. FANTONI and Dr. R. GIORGI for helpful and valuable discussions on the process of nanoparticle formation; Dr. M. CARPANESE and Dr. F. RONDINO for their contribution in different phases of the experimental activity on the synthesis and processing of nanoparticles; Prof. G. MATTEI, Dr. V. BELLO, Dr. R. PILLONI and Dr. E. SERRA for significant support and insight into the characterization of nanopowders with electron microscopy; Dr. E. TRAVE for long lasting cooperation in the study of the optical properties of Si nanoparticles; Dr. L. CANEVE and Dr. F. PERSIA for collaboration in the activity on the development of nanocomposites for cultural heritage preservation. A special thank to Mr. G. TERRANOVA for his skillful and indispensable technical support in running the experimental facility. Funding for our research in this field came from EC funded Projects: FP5-IST-SINERGIA, FP6-Life-Science-BONSAI and FP7-Large-Scale-Collaborative-HENIX (NanoHex) Project. We thank all the partners involved in these Projects for their precious contribution to the development of our activities.

REFERENCES

- [1] EDELSTEIN A. S. and CAMMARATA R. C. (Editors), *Nanomaterials: Synthesis, Properties and Applications* (IOP publishing Ltd., Bristol and Philadelphia) 1996; CAO G. and WANG Y. (Editors), *Nanostructures and Nanomaterials*, 2nd edition: *Synthesis, Properties, and Applications*, *World Scientific Ser. Nanosci. Nanotechnol.*, Vol. **2** (World Scientific Publishing Co. Pte. Ltd., Singapore) 2011.
- [2] SWIHART M. T., *Current Opinion Colloid Interface Sci.*, **8** (2003) 127.
- [3] KRUIS F. E., FISSAN H. and PELED A., *J. Aerosol Sci.*, **29** (1998) 551.
- [4] BORSELLA E., BOTTI S., CANEVE L., DE DOMINICIS L. and FANTONI R., *Phys. Scr.*, **78** (2008) 058112.
- [5] HERLIN BOIME N., MAYNE-L'HERMITE M. and REYNAUD C., in *Encyclopedia of Nanoscience and Nanotechnology*, edited by NALWA H. S., Vol. **10** (ASP, Valencia) 2004, p. 165.
- [6] REAU A., BENOIT G., CANEL J., GALY J. and TENEGAL F., *J. Am. Chem. Soc.*, **95** (2012) 153.
- [7] BORSELLA E., BOTTI S. and MARTELLI S., *Mat. Sci. Forum*, **235** (1997) 261.
- [8] TRAVE E., BELLO V., MATTEI G., MATTIAZZI M., BORSELLA E., CARPANESE M., FABBRI F., FALCONIERI M., D'AMATO R. and HERLIN-BOIME N., *Appl. Surf. Sci.*, **252** (2006) 4467; D'AMATO R., FALCONIERI M., FABBRI F., BELLO V. and BORSELLA E., *J. Nanopart. Res.*, **12** (2010) 1845.
- [9] BORSELLA E., BOTTI S., FANTONI R., ALEXANDRESCU R., MORJAN I., POPESCU C., DIKONIMOS-MAKRIS T., GIORGI R. and ENZO S., *J. Mater. Res.*, **7** (1992) 2257.
- [10] ALEXANDRESCU R., BORSELLA E., BOTTI S., CESILE M. C., MARTELLI S., GIORGI R., TURTU' S. and ZAPPA G., *J. Mater. Sci.*, **32** (1997) 5629.
- [11] NIIHARA K., *J. Ceram. Soc. Jpn*, **99** (1991) 945; SCITI D., VICENS J. and BELLOSI A., *J. Mater. Sci.*, **37** (2002) 3747.
- [12] BORSELLA E., D'AMATO R., FABBRI F., FALCONIERI M. and TERRANOVA G., *EAI Energia, Ambiente e Innovazione*, **4-5** (2011) 54.

- [13] LEKKA M., KOULOUMBI N., GAJO M. and BONORA P. L., *Electrochimica Acta*, **50** (2005) 4551; LEKKA M., ZANELLA C., KLORIKOVSKA A. and BONORA P. L., *Electrochim. Acta*, **55** (2010) 7876.
- [14] CANHAM L. T., *Appl. Phys. Lett.*, **57** (1990) 1046.
- [15] PAVESI L. and TURAN R. (Editors), *Silicon Nanocrystals: Fundamentals, Synthesis and Applications* (Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim-Germany) 2010.
- [16] IACONA F. F., FRANZÒ G., IRRERA A., BONINELLI S. and PRIOLO F., in *Silicon Nanocrystals: Fundamentals, Synthesis and Applications*, edited by PAVESI L. and TURAN R. (Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim-Germany) 2010, p. 247.
- [17] BORSELLA E., *Solid State Phenom.*, **99-100** (2004) 3.
- [18] BORSELLA E., D'AMATO R., FABBRI F., FALCONIERI M., TRAVE E., BELLO V., MATTEI G., NIE Y. and WANG D., *Phys. Status Solidi C*, **8** (2011) 974.
- [19] BORSELLA E., FALCONIERI M., HERLIN N., LOSCHENOV M., MISEROCCHI G., NIE M., RIVOLTA M., RYABOVA M. and WANG M., in *Silicon Nanocrystals: Fundamentals, Synthesis and Applications*, edited by PAVESI L. and TURAN R. (Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim-Germany) 2010, p. 507.
- [20] BORSELLA E. (Editor), *Breakthrough in nanoparticles for bio-imaging*, *AIP Conf. Proc.*, **1275** (2010).
- [21] FALCONIERI M., D'AMATO R., FABBRI F., CARPANESE M. and BORSELLA E., *Physica E*, **41** (2009) 951.
- [22] SUDEEP P. K., PAGE Z. and EMRICK T., *Chem. Commun.*, (2008) 974.
- [23] BORSELLA E., D'AMATO R., FALCONIERI M., TRAVE E., PANARITI A. and RIVOLTA I., *J. Mater Res.*, **28** (2013) 193.
- [24] SAIDUR R., LEONG K. Y. and MOHAMMED H. A., *Renew. Sust. Energ. Rev.*, **15** (2011) 1646.
- [25] RONDINO F. and FALCONIERI M., private communication.
- [26] CELATA G. P., D'ANNIBALE F., MARIANI A., SARACENO L., D'AMATO R. and BUBBICO R., *Heat Transfer Engin.*, **34** (2013) 1060.
- [27] PERSIA F., CANEVE L., COLAO F., D'AMATO R., GIANCRISTOFARO C., RICCI G., PILLONI L. and RINALDI A., submitted to *J. Nanoengin. Nanosyst.*; PERSIA F., D'AMATO R., PADELLA F., PILLONI L., RINALDI A. and TATÌ A., *EAI Energia, Ambiente e Innovazione*, **Special II/2012** (2012) 77.
- [28] LOFFREDO F., GRIMALDI I. A., DEL MAURO A. D., VILLANI F., BIZZARRO V., NENNA G., D'AMATO R. and MINARINI C., *J. Appl. Polym. Sci.*, **122** (2011) 3630.