

Synthesis of nanoparticles by laser pyrolysis: from research to applications

Nanoparticles (NPs) are the building blocks for realizing a wide range of nanostructured materials and devices, hence their synthesis plays a key role in the development of nanosciences and nanotechnologies. The technique of laser pyrolysis of gas- or vapour-phase precursors appears as a very flexible tool for the synthesis of a variety of NPs that can be used for promising structural and functional applications. An overview of the ENEA activity in this field is given

■ *Elisabetta Borsella, Rosaria D'Amato, Fabio Fabbri, Mauro Falconieri, Gaetano Terranova*

Sintesi di nanoparticelle mediante pirolisi laser: dalla ricerca alle applicazioni

Le nanoparticelle (NP) sono il punto di partenza per numerosi processi di fabbricazione di materiali e dispositivi su scala nanometrica, per cui la loro sintesi è un elemento critico nello sviluppo delle nanoscienze e delle nanotecnologie. La tecnica di pirolisi laser di reagenti in fase gassosa o vapore, sviluppata all'ENEA, è un metodo estremamente versatile per la sintesi di un ampio spettro di NP utilizzabili in promettenti applicazioni strutturali e funzionali, che verranno qui passate in rassegna

- **Elisabetta Borsella, Rosaria D'Amato, Gaetano Terranova**
ENEA, Unità Tecnica Sviluppo di Applicazioni delle Radiazioni
- **Fabio Fabbri**
ENEA, Unità Tecnica Fusione
- **Mauro Falconieri**
ENEA, Unità Tecnica Tecnologie dei Materiali

Introduction

Nanoparticles are particles having one dimension that is less than 100 nanometers in size. To put this size in perspective, a human hair is approximately 80.000 nm wide and a red blood cell is approximately 7.000 nm wide. Atoms are smaller than 1 nm whereas molecules range from sub-nm (water molecule) to a few nm (proteins, hemoglobin) or larger. In the 90's, scientific evidence was found that several conventional materials showed improved mechanical and tribological properties when formed from nanoparticles or when nanoparticles are added as second phase [1]. Later on, it was demonstrated that materials on the nanoscale may possess properties (optical/electronic/magnetic) that are dramatically and even entirely different from the bulk [2]. After this discovery, the development of nanosciences and nanotechnologies has created a whole new "nanoworld". Nanoparticles can be regarded as the fundamental building blocks of nanotechnology since they are the starting point of several "bottom up" approaches for fabricating nanomaterials used, or being evaluated for use, in many fields ranging from catalysis to photonics and optoelectronics, from energy production to thermal management. Moreover, biological systems are considered as the ideal playground for nanoparticle applications. In fact, due to their very small size, nanoparticles are able to gain access and even operate within cells. Promising applications in bio-medicine span from drug delivery to cancer therapy by hyperthermia and to bio-imaging.

Nowadays, nanoparticles of a wide range of chemical compositions and phases can be prepared by a variety of methods; however the production of large amounts of pure, non-agglomerated NPs, with desired size and narrow size distribution, still results to be an extremely difficult task [3].

At the ENEA Research Centre of Frascati a technology has been developed for the CO₂ laser pyrolysis of gas- and vapour-phase reactants, a scalable synthesis route for preparing NPs with controllable morphology and in quantities sufficient to be tested for structural and functional applications. The present review focuses on the properties and applications of the nanoparticles produced by this technique .

Laser Pyrolysis for Nanopowder Production

Process Modelling

The CO₂ laser pyrolysis technique is usually classified as 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 [4]. 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 [4]. 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 CO₂ 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).

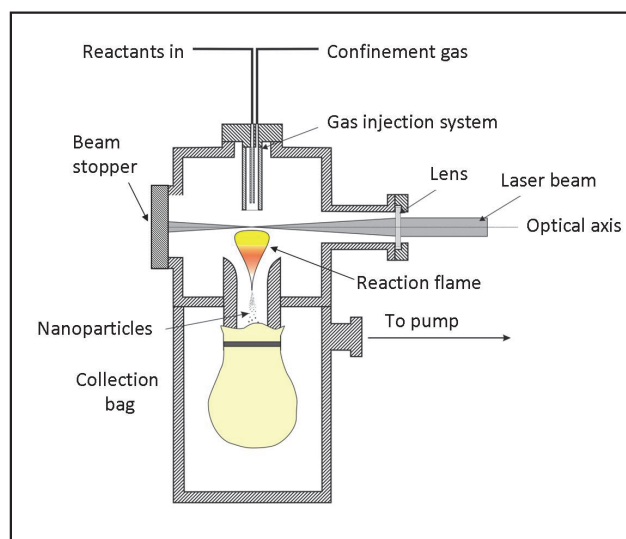


FIGURA 1 Schematic of the set-up for laser synthesis of nanoparticles from gas-phase reactants
Source: ENEA

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) CO₂ laser radiation tuned at about 10 μm [5]. Alternatively, an inert photosensitizer is added to the vapour phase mixture. The high power of the CO₂ 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 in the gas through V-T (vibration-translation) energy transfer processes, often accompanied by the appearance of a flame in the interaction volume [5]. 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 [3, 4], 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 mm³, 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. Unavoidable agglomeration, however, occurs when the nanoparticles leave the high temperature region since coalescence becomes much slower than coagulation.

Experimental Methods

The ENEA set-up for the production of nanopowders by CO₂ laser pyrolysis is shown in Fig. 1 and Fig. 2. The cw CO₂ laser beam ($\lambda=10.6\mu\text{m}$) is focused by a cylindrical 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/cm². 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 300-700 Torr.

In the laser pyrolysis process, the reactants are most often in the gas-phase, however in some cases, liquid

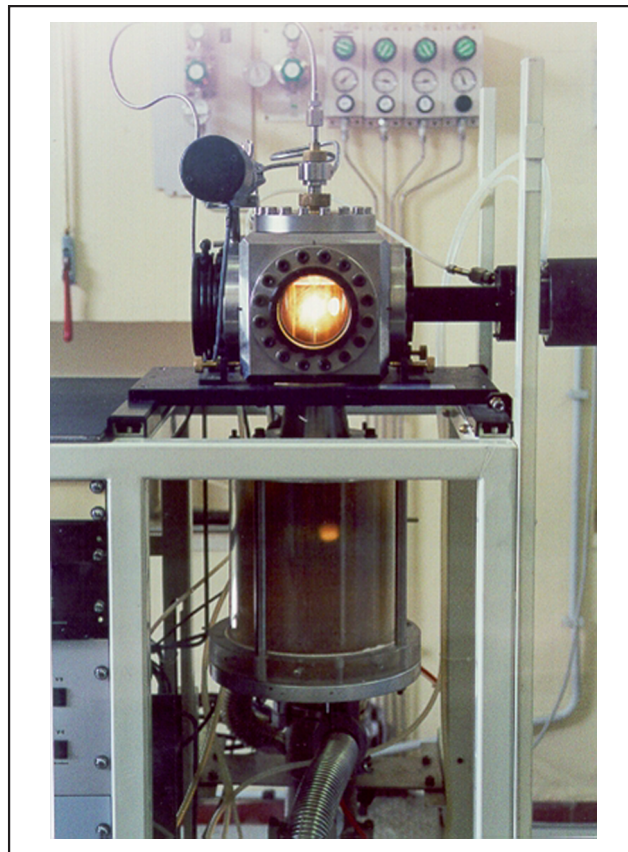


FIGURA 2 Picture of the set-up for laser synthesis of nanoparticles from gas-phase reactants
Source: ENEA

precursors are either the only choice or the most advantageous from an economical point of view. 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.

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.

Nano-powders preparation and properties

The technique of laser pyrolysis of gas-phase reactants has been applied at ENEA to the synthesis of a large variety of oxide (TiO₂, SiO₂, Al₂O₃, Fe₂O₃) and non-oxide (Si, SiC, Si₃N₃, Si/C/N, Si/Ti/C, MoS₂)



nanopowders. Results have been published in a series of papers fully referenced in [6] and more recently in [5].

As reviewed in [5-6], Si and Si-based nanoparticles were the first to be produced by laser pyrolysis and probably the most widely investigated for two main reasons: (i) silane gas, a common precursor for Si radical formation, has a very high absorptivity for the emission line of an untuned, multimodal CO₂ laser (at 10.6 μm); (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 [7].

Silicon carbide (SiC) and silicon nitride (Si₃N₄) are formed by addition to silane of small hydrocarbons or ammonia, respectively [5-6]. 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 100g/hr.

The flexibility of the laser pyrolysis technique has also made possible to synthesize ternary composite nanopowders like Si/C/N and Si/Ti/C with a different, controllable composition, by acting on the ratio between the reactant flows in the gas mixture. 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.

Formation of oxide nanoparticles by laser synthesis requires the addition of an inert photo-sensitizer to the reactants in order to couple the laser energy into the system and reach the activation energy for molecular decomposition. Ethylene gas (C₂H₄) or sulfur hexafluoride (SF₆) are the most widely employed sensitizers due to their resonant absorption at about 10 μm and to the relatively high dissociation energy (7.2 eV for C₂H₄ and 3.95 eV for SF₆). Metallic oxides prepared at ENEA by laser synthesis include Al₂O₃ [6], Fe₂O₃, TiO₂, and SiO₂. Silica formation needs a precursor other than silane, since its reaction with oxygen is spontaneous and explosive. Nano-silica can be prepared either by laser pyrolysis of an aerosol of tetraethoxysilane-TEOS, an IR absorbing liquid precursor, or by a two-step process, i.e., through wet chemical oxidation of Si nanopowders produced by pyrolysis of pure silane.

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 can be used to remove contaminants with volatile oxides (as carbon), trying to keep a moderate heating temperature to avoid grain growth.

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 great 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 nano-aggregate 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. Repulsive inter-particle forces are required to overcome the attractive Van der Waals forces be-

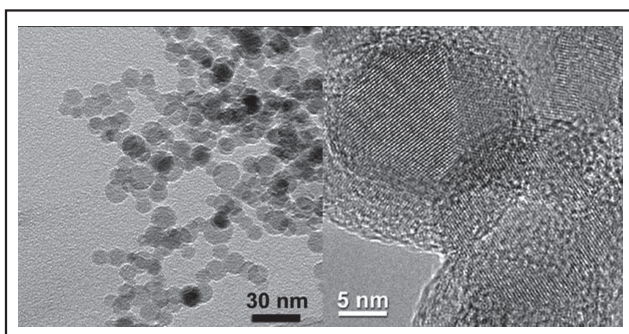


FIGURA 3 TEM image of Si nanoparticles prepared by laser pyrolysis of SiH₄
Source: courtesy of Prof. G. Mattei, Univ. of Padova, Project SINERGIA

tween particles. The two most common methods used are based on either electrostatic repulsion or steric forces [2, 4].

Structural nanomaterials based on nanoparticles prepared by Laser Pyrolysis

The class of nanophase ceramic materials has drawn wide and considerable interest in high-temperature structural applications mainly as a consequence of the impressive mechanical performances reported for these materials by Niihara and his co-workers [1].

It was soon recognized that conventional processing routes are not often efficient to fabricate structural materials from nanophase constituents. It came out that pressureless sintering of nanosized powders results either in nano-grained but partially dense materials at low sintering T or in fully dense materials with micron-sized grains at higher T. In fact, the larger the agglomerate size in the starting nanopowders, the higher the sintering temperature needed to eliminate the large inter-agglomerate pores, with consequent loss of the nanostructure in the sintered material as a result of the unavoidable grain growth [2]. This trend was confirmed for pyrolytic nanopowders [8]. A high degree of densification (up to 98% of the T.D-Theoretical Density) was achieved only at temperatures above 2100 °C by pressureless sintering of laser synthesized SiC nanopowders in a resistively heated graphite furnace [8]. SEM analysis of the specimen sintered at 2150 °C showed the presence of elongated grains (with size in the μm range) embedded into a matrix of nano-sized equiaxed grains.

Fully dense SiC ceramics with sub-micrometric grain size were produced at CNR-ISTEC by hot pressing of ENEA pyrolytic SiC nanopowders through liquid phase sintering [9]. The mechanical properties of these specimen were found to be affected by the scarce homogeneity of the starting powders and by the grain boundary phases [9].

Better results were expected by using pyrolytic nanopowders as second phase in structural ceramic nanocomposites, i.e., in multi-phase materials in which the first phase (called *matrix*) has a micrometric or sub-micrometric grain structure and a second phase (on the nanoscale) is dispersed into the matrix to improve the mechanical (and eventually thermo-

mechanical) properties as compared with the matrix phase alone. The systems most intensively investigated were $\text{Al}_2\text{O}_3/\text{SiC}$ and $\text{Si}_3\text{N}_4/\text{SiC}$ (or Si/C/N), where the particulate reinforcement is the last mentioned phase. In particular, an extensive study on $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites was performed by D. Sciti et al. [10] using both commercial alumina powders and SiC nanopowders prepared by laser pyrolysis as raw materials (either at ENEA or at CEA-Saclay, France). In the hot-pressed specimen, TEM analysis of the microstructure showed the presence of SiC agglomerated nanoparticles predominantly located along the matrix grain boundaries, often in triple junctions, while only very small particles are entrapped inside the alumina grains. As a result, a change in the fracture path from intergranular, as in pure alumina, to transgranular was observed in the nanocomposites (Fig. 4). Concerning the mechanical properties, all nanocomposites showed a slightly increased hardness over monolithic alumina and a lower Young modulus. However, an increase of 49% was observed in the flexural strength and up to 40% in the fracture toughness, over monolithic alumina. This last result is likely related to the change in fracture mode from intergranular to transgranular, which implies a reinforcement of the grain boundaries [10].

In summary, in several studies it was found that the

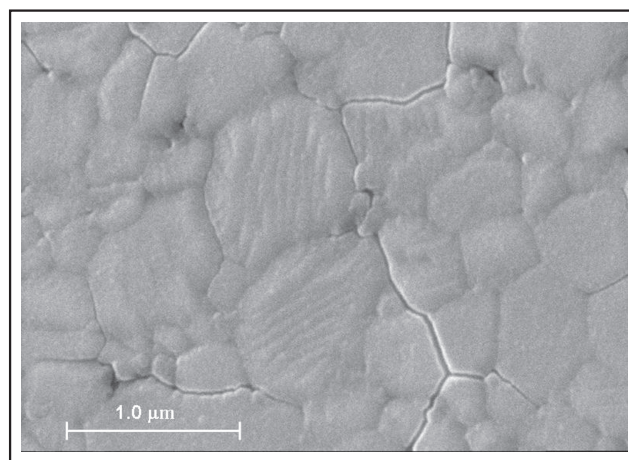


FIGURA 4 Thermal etched surface of $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposite showing microcracking along grain boundaries
Source: courtesy of Dr. A. Bellosi, ISTEC-CNR, Project NANOMAT [10]

predominant effect of adding nanoparticles is the creation of obstacles to the grain boundary movement during sintering and the formation of defects where nanoparticles agglomerate. The size and volume of the flaws was found to be inversely proportional to the particle size. These processing flaws act as critical defects under mechanical stress, thus limiting the positive effects that should derive from the very fine microstructure of nanocomposites. Thus, the manufacturing of nanostructured ceramics with improved mechanical properties demands for a complete revision of the processing procedures concerning both powder treatments and sintering, in order to fully exploit the potentialities of these materials [10]. These conclusions are valid for all nanopowders tending to agglomerate, like those prepared from vapour-phase synthesis [4].

Inherent brittleness of the ceramics has prevented their widespread use in several applications. Consequently, significant scientific effort has been targeted to make ceramics more flaw-tolerant through design of their microstructures. An advanced class of materials designed to improve toughness of conventional ceramics are the Ceramic Matrix Composites (CMC), that is a class of materials consisting of a ceramic matrix reinforced by either continuous (long) fibers or discontinuous (short) fibers. Matrix material for long-fiber (continuous fiber) composites may be silicon carbide, alumina (alumina-silica) or carbon. Most CMC are reinforced by silicon carbide fibers due to their high strength and elasticity or by carbon fibers. Silicon carbide matrix composites are fabricated by chemical vapor infiltration or liquid phase infiltration of a matrix material into a preform prepared from silicon carbide fibers. The infiltration-pyrolysis cycle needs to be repeated several times until the desired density is achieved. It was found that a significant reduction in the number of cycles needed for densification can be obtained by using pyrolytic SiC nanopowders as filler of the polycarbosilane precursor [11]. A refinement of the microstructure was also observed as well as an improvement of the mechanical properties: flexural strength increased from 150 MPa (without SiC nanopowders) to 370 MPa (with SiC nanopowders as filler) [6, 11].

Pyrolytic SiC nanopowders were also used for prepar-

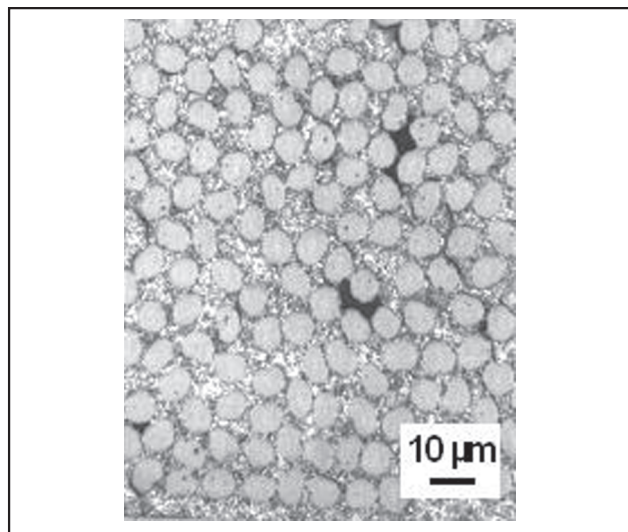


FIGURA 5 Optical micrographs showing the electrophoretic infiltration of carbon fibre mats with SiC powders
Source: courtesy of Dr. R. Dittrich, TU Bergakademie Freiberg, Project NANOMAT [12]

ing fiber reinforced CMC by electrophoretic infiltration of two-dimensional woven carbon fiber fabrics [12]. To produce the composites, the infiltrated fabrics were sintered by hot pressing (Fig.5). After sintering, the composite filled with laser synthesized SiC nanopowders showed lower density than the fiber fabric infiltrated with commercial SiC powders, but better mechanical properties. A further improvement is expected at higher densification.

Functional Nanomaterials based on nanoparticles prepared by Laser Pyrolysis

The results obtained so far in the fabrication of structural nanocomposites from laser synthesized nanopowders urged the scientific community to develop new processing and forming techniques on the one hand, and to address more attention to the development of nanocomposites for applications where the sensitivity to defect population is not so critical (abrasion resistance, polymer reinforcement by addition of nanoparticles, etc.) or specific functions are required (optical, magnetic, electrical, thermal, etc..) on the other.

In the following paragraphs, we will review the main results obtained in recent years in the development of

nanocomposites from ENEA laser synthesized nanopowders for applications in several fields ranging from manufacturing protective layers to optoelectronics & photonics, bioimaging and heat management.

Protective layers containing laser synthesized nanoparticles.

There is a considerable demand for protective coatings with improved resistance to highly aggressive environments in order to drastically extend 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 [13]. Two different types of coatings were prepared: nickel-SiC and bronze-SiC nanocomposites. The mean size of SiC nanoparticles was of about 20 nm. The result of co-deposition of nickel with SiC nanoparticles was the formation of a more uniform deposit with smaller, rounder nickel grains conferring better mechanical and anticorrosive properties to the coating.

The promising results achieved on lab scale led to 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]. An image of the profile coated with the Ni/SiC nanocomposite is shown in Fig. 6. The prototype parts were tested under working conditions. An increased microhardness and comparable erosion-corrosion re-



FIGURA 6 Real-scale propeller profile coated with nanocomposite Ni deposit containing SiC NPs prepared at ENEA by laser pyrolysis
Source: results of PROCOMP-RINNOVA Project at the Univ. of Trento, Italy [13]

sistance were found with respect to the small scale specimens [13]. It was found that the ship propeller and profile coatings withstood the severe erosion-corrosion attack without worsening the cavitation [13]. These activities were performed at the Univ. of Trento, in the framework of the Italian RINNOVA Project led by PROCOMP consortium .

Applications of Si and Si-based nanoparticles in photonics and opto-electronics

Research on nanomaterials was further 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 was drawn by the new optical and electronic properties which appear on the nanoscale. For example, in semiconductor nanoparticles, when the size is comparable to the Bohr exciton radius, the energies of bulk electron states are shifted and transition selection rules change. This “quantum confinement” effect results in the possibility to tune the optoelectronic properties of the semiconductors by changing the particle size [2] as described by the quantum mechanical model of the “particle in a box”. Therefore, great effort was devoted to the development of semiconductor “quantum dots” (QD) for applications in optoelectronic devices [2]. In this framework, the discovery of room temperature visible photoluminescence emission from nanostructured, porous Si (p-Si) [14], raised great scientific and technological interest. As a matter of fact, bulk silicon is a most successful electronic material, but its application in optoelectronics is strongly limited by its lack of photoluminescence (PL) emission, which is due to the combination of indirect bandgap optical properties and long carriers diffusion length. Therefore, a luminescent emitter based on silicon was expected to pave the way for all-silicon optoelectronics and photonics due to its intrinsic compatibility with existing silicon based electronic technologies [15].

One of the first attempts to merge the world of optoelectronics and photonics with silicon technologies was related to doping Si with Er atoms. In this way the Er emission at the 1.54 μm telecommunication wavelength could be attained in a silicon-based material.

However, realization of this scheme with bulk Si suffered from limited performances, because of intrinsic loss mechanisms due to the electronic properties of Si. On the other hand, replacement of bulk material with nanostructured Si was expected to overcome many of these drawbacks, producing 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 (Fig. 7). Silicon nanocrystals (Si-nc) produced by bottom-up methods gradually emerged in this landscape and were shown to efficiently sensitize Er ions, as the effective excitation cross section of Er in presence of Si-nc in a silica matrix is more than two orders of magnitude higher than direct excitation by resonant photon absorption [15-16]. Moreover, exploiting this mechanism, the very expensive pump sources for excitation of Er ions at about 980 nm could be replaced by low-cost broad band lamps for excitation of Si-nc.

Si-nc and Er co-doped glasses were intensively investigated in the course of the FP5 EC Project SINERGIA with the aim to produce broadly pumpable waveguide amplifiers for the 1.54 μm telecommunication wavelength [16]. In this project a sol-gel waveguide formulation was also experimented, based on the synthesis of Si nanopowders by laser pyrolysis of SiH_4 followed by the sol gel synthesis of a Si-nc and Er co-doped nanocomposite glass material [16]. A preliminary formulation of the sol-gel glass using pure Si-nc nanopowders showed the necessity of a high temperature (1400 $^\circ\text{C}$) thermal treatment to produce a fully densified material. This treatment caused the com-

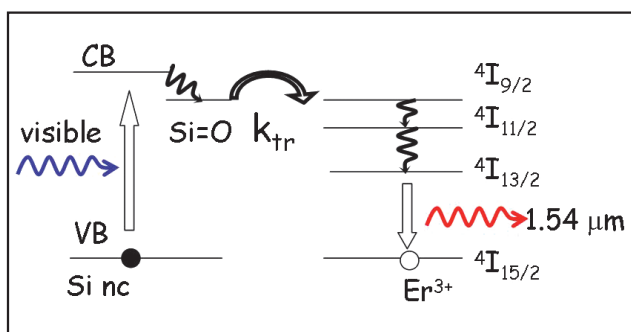


FIGURA 7 Schematic of the Si-nc sensitization of Er emission at 1.54 μm

plete oxidation of the Si-nc which disappeared nullifying the possibility of a sensitization action. Therefore, a solution based on the incorporation of compound nanopowders that can withstand high temperature processing was conceived. To this purpose, Si-based nanopowders were synthesized [17] and integrated into an Er doped silica glass by standard dispersion procedure and sol-gel processing. Photoluminescence (PL) measurements on a glass sample containing 5at.% of Si-based nanopowders and 0,5 at.% of Er revealed that Er ions emit at 1.54 μm not only by direct pumping, but also under out-of-resonance excitation. It was also observed that the PL intensity ratio between out-of-resonance and in-resonance excitation conditions increases with the Si-based nanopowders content, confirming the activation of the energy transfer mechanism [16-17]. Thus, the functionality of silicon and silicon-based nanoparticles as antennas or sensitizers of otherwise poorly addressable luminescent centres was clearly assessed.

Another option for a new generation of optoelectronic devices that could be fabricated with minimal disturbance to conventional silicon technology is represented by exploitation of luminescent Si nanocrystals. However, the basic mechanisms of the luminescence emission process are still unclear and the experimentally determined optical properties of Si-nc depend on the synthesis techniques and are strongly influenced by surface effects due to the presence of atoms and/or radicals at or near the surface [15]. 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.

In the debate on the Si-nc PL emission mechanism, consensus was reached by the scientific community that both localized defects at the Si/SiO₂ interface, and the quantum confinement of photogenerated carriers play a major role. Experimental assessment of the role of interfacial oxide-related defects has long been based on the comparison of PL emission from strongly different systems containing nanostructured oxidised silicon [2,15], and consequently published results were not free from ambiguities. On the other hand, in a recent paper [18] we have reported on the spectroscopic properties of the same sample as-prepared by

laser synthesis (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 states, likely non-bridging oxygen centres (NBO).

Development of Si and Si-based nanoparticles for bio-imaging

Although strongly influenced by material properties and surface effects, Si-nc luminescence has some interesting characteristics for application in the field of fluorescence bio-imaging which were investigated in the framework of the EC FP6 Project BONSAI [19-20]. As a matter of fact, the rapid progress of bio-medical sciences has stimulated the development of new advanced imaging techniques, which are traditionally based on organic fluorophores. Recently, semiconductor quantum dot (QD) fluorophores have become of interest for this application because of their narrow and tuneable emission, wide band excitation capability, and resistance to photo-bleaching. Emission tunability allows for multicolour detection of different entities in cells, as QDs can be surface functionalised to link with selected receptors. However, commonly investigated QDs contain cadmium, which is toxic and harmful for biological entities. On the other hand, luminescent Si-nc are based on Si which is an intrinsically inert, non-toxic material, and is, in principle, more suitable for in-vivo studies. Other appealing characteristics of Si-nc photoluminescence are its long decay time (of the order of several tens of microseconds) which provides the possibility of using gating techniques for rejection of the short-lived biological background fluorescence, and the red-near infrared band falling in the transparency window of living tissues [19]. Moreover, we demonstrated [21] the possibility of two-photon luminescence excitation which is very interesting for advanced imaging techniques.

In order to exploit their potential for bio-medical applications, Si-NPs 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 in physi-

ological fluids is high enough to decrease the electrostatic repulsion between NPs, which normally prevents aggregation. Therefore a great effort was spent on this issue in the BONSAI project [19]. Disaggregation of dried powders to well-dispersed Si nanoparticles in water using both acid etching and alkali etching procedures resulted problematic. Yet, successful results were achieved by a combined alkali-etching procedure terminated by addition of H₂O₂. It was also found that the use of HF/HNO₃ mixture as etching agent can make the Si NPs photoluminescent with various emission colors depending on the etching time (Fig. 8), however, the stability of the emission needs to be enhanced [19]. To prevent the formation of large aggregates, NPs can be coated with a biocompatible polymer in order to improve biodistribution. Consequently, the second step was the fabrication of colloiddally stable and biocompatible Si NPs by grafting hydrophilic polymer chains, such as poly(ethylene glycol) PEG, on the Si NPs. First, disaggregated Si NPs were coated with functional silanes terminated with amine or epoxy groups, and then conjugated with PEG. It was found that the PEGylated Si NPs remained stable in water for weeks.

Negligible cytotoxicity of PEGylated Si-NPs 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].

Although promising results were obtained in the functionalization of Si pyrolytic NPs and first in-vivo bio-imaging tests were done on guinea pigs, preparation of Si-NPs to be routinely used as bio-markers is still a challenging task. Recent reviews on the state of the art and perspectives in this field can be found in [19-20]. In particular, it comes out that the main advantage ex-



FIGURA 8 Functionalised Si-nc suspensions emitting at different colours

Source: results of the BONSAI Project [19]

pected by replacing conventional organic fluorophores with Si-NPs, i.e., the tuneability of the PL emission wavelength by pumping at one selected wavelength, appears far to be reached. The PL emission spectrum of Si nanoparticles is, in fact, very broad and seems to be determined more by the surface termination and/or the presence of defects at the surface [7,15,18-20] than by quantum effects, i.e., by the crystalline size of the nanoparticles.

Therefore, using the past experience on Er sensitization by Si-nc, a different approach was experimented to get tuneable and stable photoluminescence from Si-based NPs, that is, binding a rare-earth ion to the NP surface. 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 NPs 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, to exploit the aptitude of this ion to form complexes with amino groups which are easily linked to the surface of pyrolytic Si-nc [22]. 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 NPs [22]. 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 NPs emitting at different wavelengths in a rainbow of colours.

Development of nanofluids for enhanced heat exchange

Nanofluids are a new class of high performance nanotechnology-based coolants engineered by dispersing and stably suspending in base fluids a limited amount of nanoparticles (metallic or nonmetallic) with typical size of the order of 10-250 nm. A firm assessment of the enhancement in nano-fluid heat transfer with respect to conventional coolants and a deep com-

prehension of the mechanisms behind it would pave the way to industrial development of nanofluids for a variety of applications ranging from cooling of electronic components, transformer oil and heat-exchange devices to improving heat transfer efficiency of chillers, domestic refrigerators-freezers and more [23]. To this respect, nanopowders for the preparation of selected nanofluids are produced at ENEA by CO₂ laser pyrolysis in the framework of the EC FP7 Project NanoHex, having the objective of developing high performance nanofluid coolants for Data Centres and Power Electronic Components. An enhancement in the thermal conductivity (with respect to distilled water) was observed in all the nanofluids based on ENEA pyrolytic NPs (TiO₂, SiO₂ and SiC) in water. 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 which provides the possibility for *in situ* monitoring of coolant performances [24]. Measurements of the heat transfer coefficient of water-based nanofluids containing pyrolytic nanoparticles are currently in progress in the course of the EC FP7 NanoHex Project [25]. Starting from the obtained results, perspectives for exploitation of nanofluids based on pyrolytic NPs will be evaluated.

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. Applications in the field of structural nanoceramics, wear resistant coatings and functional nanomaterials for optoelectronics, photonics and bio-imaging were reviewed. Actual plans include feasibility studies for new, challenging applications such as the development of doped and pure TiO₂ nanoparticles for photovoltaics and photo-catalysis, of nanoparticles containing zero-valent iron for contaminated soil and groundwater remediation and the realization of protective nanocomposite coatings for cultural heritage preservation. Increasing attention will be paid to initiatives aimed at assessing the risk to human or ecological health in the widespread use of nanoparticles.

Acknowledgments

We wish to thank all the ENEA scientists who have contributed in the course of the last years to the development of the research activities here reviewed. We thank Dr. R. Fantoni for her valuable contribution to the understanding of the process of infrared multiple-photon excitation of polyatomic molecules and the following formation of gas-phase intermediates; Dr. S. Botti, Dr. L. Caneve, Dr. M. Carpanese, and Dr. S. Martelli (now at CSM-Pomezia) for their fruitful contribution in different phases of the experimental activity for laser synthesis of nanoparticles; Dr. R. Giorgi, Dr. T. Dikonimos-Makris, and Dr. G. Zappa for cooperation in the investigation of microstructural properties of composite nanopowders; Dr. C. Alvani, Dr. C. A. Nannetti, and Dr. A. Donato for having developed processes for the fabrication of nanocomposite materials starting from pyrolytic nanopowders; Dr. R. Pilloni, and Dr. E. Serra for characterization of nanopowders with electron microscopy; Dr. F. D'Annibale, and Dr. A. Mariani for the determination of the heat transfer coefficient in nanofluids containing laser synthesized nanoparticles; Dr. S. Gagliardi for recent results on the possibility to exploit nano-titania for photovoltaic cells. The past technical support of R. Belardinelli, P. Cardoni, R. Ciardi, M. Di Fino, and R. Giovagnoli is also gratefully acknowledged.

We wish to mention the valuable long lasting cooperation with N. Herlin (CEA-Saclay, France) and with the researchers of INFLPR-Bucharest : R. Alexandrescu, I. Mojan, L. Gavrilă-Florescu, and E. Popovici (in the framework of a bilateral Italy-Romania agreement promoted by the Ministry of Foreign Affairs).

Funding for our research in this field came from EC funded Projects: BRITE-EURAM Project "Development of nanocomposite materials for cutting tool applications", FP4-NANOMAT Network, BRITE Project CERA-POL-NANO, FP5-IST-SINERGIA Project, FP6-Life-Science-BONSAI Project 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. Financial support from Italian Industrial Research Projects (RINNOVA and TECVIM) is also acknowledged.

References

- [1] K. Niihara (1991), *New Design concept of Structural Ceramics*, J. Ceram. Soc. Jpn, Vol. 99, 945-952.
- [2] Edelstein A.S. and Cammarata R.C. eds., (1996) *Nanomaterials: Synthesis, Properties and Applications*, IOP publishing Ltd., (Bristol and Philadelphia).
- [3] O. Masala and R. Seshadri (2004), *Synthesis Routes for Large Volume of Nanoparticles*, Annu. Rev. Mater. Res. Vol. 34 pp. 41-81.
- [4] M. T. Swihart (2003), *Vapor-phase synthesis of nanoparticles*, Current Opinion in Colloid & Interface Science, Vol. 8, 127-133.
- [5] E. Borsella, S. Botti, L. Caneve, L. De Dominicis, R. Fantoni (2008), *IR multiple-photon excitation of polyatomic molecules: a route towards nanostructures*, Phys. Scr., Vol. 78, 058112 (9pp.).
- [6] E. Borsella, S. Botti, S. Martelli (1997), *Nanopowders from gas-phase laser driven reactions: characteristics and applications*, Mat. Sci. Forum Vols. 235-238, Trans. Tech. Publications (Switzerland), pp. 261-266.
- [7] R. D'Amato, M. Falconieri, F. Fabbri, V. Bello, E. Borsella (2010), *Preparation of luminescent Si nanoparticles by tailoring the size, crystallinity and surface composition*, J. Nanopart. Res., 12, 1845-1858.
- [8] A. Donato, E. Borsella, S. Botti, S. Martelli, C.A. Nannetti, M.R. Mancini, I. Morjan (1996), *Thermal shock tests of -SiC pellets prepared from laser synthesized nanoscale SiC powders*, J. Nucl. Mat., Vol.233-237, 814-817.
- [9] D. Sciti and A. Bellosi (2000), *Effects of additives on the densification, microstructure and properties of liquid-phase sintered silicon carbide*, J. Mater. Sci. 35, 3849-3855
- [10] D. Sciti, J. Vicens, and A. Bellosi (2002), *Microstructure and properties of alumina-SiC nanocomposites prepared from ultrafine powders*, J. Mater. Sci. Vol. 37, 3747-3758.
- [11] A. Donato, C.A. Nannetti, A. Ortona, E. Borsella, S. Botti, S. Casadio, G. D'Alessandro, A. Licciulli, S. Martelli, A. Masci (1996) *Compositi a Matrice Ceramica e Processo di Produzione degli Stessi Mediante Infiltrazione Liquida con Precursori Ceramici Polimerici e l'Uso di Nanopolveri*, Patent RM96A000220.
- [12] E. Müller, R. Dittrich, E. Borsella (2005), "A new possibility for preparing C/SiC" in: *Verbundwerkstoffe und Werkstoffverbunde*, pp.121-126, Ed.:M.Schlimmer, Werkstoff-Informationsgesellschaft mbH Frankfurt/M (Germany).
- [13] M. Lekka, C. Zanella, A. Klorikovska, P.L. Bonora (2010), *Scaling-up of the electrodeposition process of nano-composite coating for corrosion and wear protection*, Electrochimica Acta 55, 7876-7883.
- [14] L.T. Canham (1990), *Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers*, Vol. 57, Appl. Phys. Lett., 1046-1048.
- [15] L. Pavesi and R. Turan eds. (2010), *Silicon Nanocrystals: Fundamentals, Synthesis and Applications*, Wiley-VCH Verlag GmbH & co. KgaA, Weinheim-Germany.
- [16] E. Borsella (2004), *Si nanocrystals and erbium co-doped glasses for optical amplifiers*, Solid State Phenomena, Vol.99-100, 3-11.
- [17] F. Costa, L. Gini, E. Borsella, M. Falconieri, G. Mattei, E. Trave (2006), *Materiale Composito Trasparente Fotoluminescente e Metodi per la Sua Produzione*, Patent N° NO2006A000002.
- [18] E. Borsella, R. D'Amato, F. Fabbri, M. Falconieri, E. Trave, V. Bello, G. Mattei, Y. Nie, and D. Wang (2011), *On the role of non-bridging oxygen centres in the red luminescence emission from silicon nanocrystals*, Phys. Status Solidi C, 1–5/ DOI 10.1002/pssc.201000553.
- [19] E. Borsella, M. Falconieri, N. Herlin, V.Loschenov, G. Miserocchi, Y. Nie, I. Rivolta, A. Ryabova, D. Wang in [15], *Biomedical and sensor applications of silicon nanoparticles*, pp. 507-536.
- [20] E. Borsella ed. (2010), *Breakthrough in nanoparticles for bio-imaging*, AIP Conference Proceedings, Vol. 1275, American Institute of Physics, Melville, NewYork (USA).
- [21] M. Falconieri, R. D'Amato; F. Fabbri, M. Carpanese and E. Borsella (2009); *Two-photon excitation of luminescence in pyrolytic silicon nanocrystals*, Physica E, Vol.41, 951-954.
- [22] R. D'Amato, M. Falconieri, E. Borsella in [21], *Synthesis and photoluminescence of Ytterbium doped silicon nanocrystals*, 75-79.
- [23] R. Saidur, K.Y. Leong, H.A. Mohammed (2011), *A review on applications and challenges of nanofluids*, Renew. Sust. Energy. Rev., Vol. 15, 1646-1648.
- [24] F. Rondino, M. Falconieri, E. Borsella, R. D'Amato, (2011), *Measurements of thermal diffusivity by Forced Rayleigh Light Scattering*, Proc. ECONOS 2011, May, 23-25, Twente, The Netherlands.
- [25] D'Annibale F., Ghidini L., Mariani A., Saraceno L., Borsella E., D'Amato R., Cao J., Schoolderman C. (2011), *Heat Transfer Coefficient of Water-based SiC and TiO₂ Nanofluids*, Proceed. Conference NanotechItaly 2011, Venice Nov. 23-25, 2011.