Physics of Matter: From the Nanoscale Structure to the Macroscopic Properties of Materials

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Abstract The physicists of the Polytechnic University of Marche (UNIVPM) have been conducting research in the physics of matter since the early seventies. Here we report a number of topics of the research activities carried out by the physicists working at the Department of Materials, Environmental Sciences and Urban Planning (SIMAU) of the Engineering Faculty, limiting our review to arguments and methods that are currently subject of investigation. The main scientific achievements and the most promising future developments are highlighted. The main purpose of this activity is the study of the macroscopic properties of matter in connection with its atomic structure for a variety of materials of technological interest in physics, chemistry, engineering, biology and medicine. These investigations require experimental tools capable of accessing the materials structure at the nanoscale. X-ray

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diffraction (XRD) and scattering techniques have represented the primary tool used to probe the structure of matter with atomic resolution, whereas electron microscopy techniques have provided complementary information on the structure and morphology of materials from the microscale down to the nanoscale. XRD studies have been performed using the X-ray instrumentation available at the departmental laboratories and, more recently, with the high-performance machines of the European synchrotron radiation facilities. Electron microscopy techniques have been implemented in an inter-departmental laboratory aimed at the structural and morphological characterization of soft and hard materials. The more recent set-up of laser optics laboratories has allowed an extended investigation of the properties of soft materials with focus on nonlinear optics of liquid crystalline and polymeric compounds.

1 Introduction

All the macroscopic properties of materials, such as mechanical, electrical and optical properties, are inherently connected with their atomic structure. Therefore, probing the structure of matter at the nanoscale is the best way to find the relationships between nanostructure and macroscopic behavior of the materials. X-ray diffraction (XRD) is one of the most powerful tools to study the structure of materials and living matter with atomic resolution. On the other hand, electron microscopy techniques provide complementary information on the structure and morphology of materials from the microscale down to the nanoscale. The physicists of the Polytechnic University of Marche (UNIVPM) have been involved in structural studies of materials by means of XRD since the early seventies. XRD studies have been traditionally performed using the conventional X-ray diffractometers of the departmental laboratories and, more recently, with the high-performance machines of the European synchrotron radiation facilities. Electron microscopy techniques have been implemented in an inter-departmental laboratory starting from the early eighties, aimed at the structural and morphological characterization of soft and hard materials. The more recent set-up of laser optics laboratories, started in mid-nineties, has allowed an extended investigation of the properties of soft materials with focus on nonlinear optics of liquid crystalline and polymeric compounds, holographic materials for optical processing and storage, optical manipulation and development of novel optofluidic devices. The above techniques have been applied to investigate a variety of materials for innovative applications in the fields of engineering, life and environmental sciences and medicine. In the following sections we report a number of results of the research activity carried out over the past fifty years in the laboratories of XRD, electron microscopy and optics of the UNIVPM.

2 X-Ray Diffraction Studies of Soft Materials

The interest in the structure of matter at the nanoscale in the Polytechnic University of Marche dates back to the mid-seventies, when a small group of physicists started pioneering studies of the structure of liquid crystals (LCs) by means of XRD, neutron diffraction and calorimetry. At that time, the novelty of the LC science and the discovery of a variety of new LC phases motivated scientists worldwide to investigate their nanoscale structure and its link with the macroscopic properties. XRD [1] was the primary experimental technique used in these studies, performed with the conventional diffractometers originally installed at the UNIVPM laboratories. LC molecules with a variety of chemical structures were investigated in those years, not only for fundamental reasons but also for the potential technological applications spanning from physics and engineering to biology and medicine: among these, rod-like mesogens based on a rigid aromatic core linked with fluid aliphatic tails of various chemical structure and length [2], metallo-mesogens consisting of LCs incorporating metal atoms in various molecular architectures [3, 4], thermotropic main-chain and side-chain LC polymers [5–10] and polymeric composites [11]. In those years, interest was mainly addressed to the identification of new mesophases [2], the study of pre-transitional critical effects [1], the mesogenic behavior of the recently discovered polymeric and organometallic LCs [3–10].

A turning point in this research field occurred with the advent of the large-scale facilities for synchrotron light, in particular the European Synchrotron Radiation Facility (ESRF, Grenoble) in 1994 and ELETTRA (Trieste) in 1995. The extremely high brilliance and coherence of these powerful X-ray radiation sources has made it possible to access the structure and dynamics of matter on increasingly smaller space and time scales with very high resolution. Since then, the scientists of the UNIVPM soft matter group have become regular users of these facilities, performing challenging experiments not achievable in a home XRD laboratory. The variety of materials investigated is quite large but essentially belongs to the category of soft materials, in particular LCs, polymers and polymeric composites for applications in photonics, opto-electronics, information and communications technology, renewable energies, biosensors and biomedicine. To summarize the most recent activity of the group, here we focus on a few representative examples of this research, which stand out for the international resonance of the obtained results and the future perspectives.

At the beginning of 2000s, a series of pioneering studies were conducted on the physical properties of LCs in confined geometries. Interest was focused on polymer-dispersed LCs (PDLCs), a family of composite materials consisting of spherical droplets of LCs randomly dispersed in a polymeric matrix [12]. Because of the composite nature and the large surface-to-volume ratio, these materials exhibit unique optical properties for practical applications and a variety of unusual physical effects that are strictly connected with the space configuration of the average orientational order of the LC molecules within the droplets. Whereas conventional experimental techniques allow to access only areas involving a large number of droplets, for the first time we used a micron(μ)-sized synchrotron X-ray beam to probe the nematic ordering in a single droplet of LC [13]. We thus demonstrated the effectiveness of μ-XRD as a unique tool to characterize LC ordering in single droplets, opening the way to the possibility of studying LC ordering in dispersed mesophases with space resolution of 1 μm [13].

A few years later, we started an extensive investigation of the structure and function of self-assembled liposome-DNA complexes for gene-therapy applications. Liposomes are self-closed structures composed of curved lipid bilayers that form the basic matrix of the cellular membranes. Recent completion of the working draft of the human genome has convinced scientists about the reliable possibility of using gene medicines to combat genetic diseases. The goal is to achieve the transfer of extracellular genetic material into somatic cells (transfection) and thereby provide therapeutic effects. Realization of the full potential of gene therapy depends in a major way on the development of safe and efficient nonviral gene delivery agents. Complexes composed of neutral lipids and DNA offer a promising alternative to conventional viral delivery agents with much lower inherent cytotoxicity. Within a large collaboration including physicists, chemists and biologists we have studied the nanostructure of a variety of liposome-DNA complexes, discovered new supramolecular architectures and found correlation with their biological function and transfection efficiency [14, 15]. In particular, we have demonstrated the self-assembled formation of the lamellar L_α phase in dioleoylphosphatetidylcholine (DOPC)-DNA(plasmid)-Metal^{2+} complexes (Fig. 1a). In vivo transfection tests on mouse fibroblast cell lines (NIH 3T3), using DOPC-DNA(pGreenLantern1plasmid)-Metal^{2+} as DNA vectors,

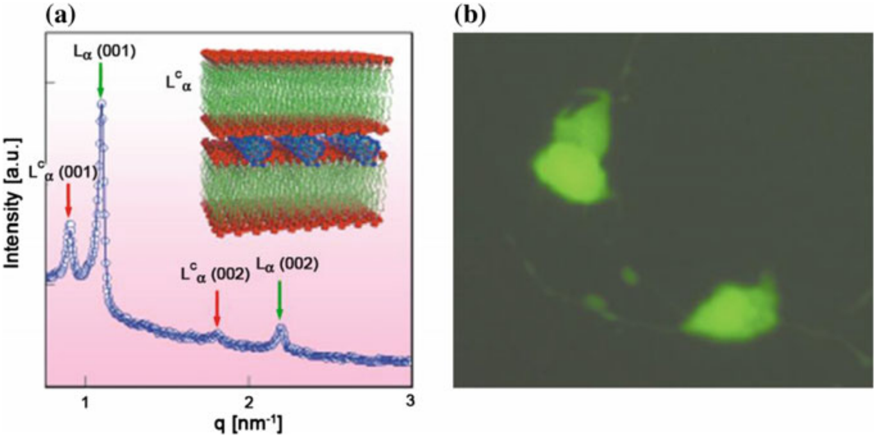

Fig. 1 **a** The XRD pattern of the DOPC-DNA-Mn^{2+} (4:3:12) solution mixture. L_α^c and L_α refer to the lamellar structure of the ternary complex and of the coexisting unbound liposome, respectively. The structure of the L_α^c phase consists of smectic-like arrays of stacked lipid bilayers with monolayers of DNA molecules intercalated within the water gaps (inset of figure); the metal cations bind the polar headgroups of DOPC with the negatively charged phosphate groups of DNA. The lamellar repeat distance is $d = 7$ nm. **b** Fluorescence micrograph of mouse fibroblast NIH 3T3 cell lines transfected with pGreenLantern1 DNA. The DNA was complexed to DOPC liposomes in presence of Ca^{2+}

demonstrated the transfection capacity of these systems (Fig. 1b). Our results have represented a first but fundamental step in the development of new biological materials and in the refinement of procedures to achieve efficient and tissue-specific transfection for gene therapy applications [16], a research area still very active in the group with great future perspectives [17].

A final example, probably the most representative for importance of the topic, experimental effort and international resonance of the results, concerns the extensive study of the nematic (N) phase of a new class of LCs, the bent-core mesogens, featuring a nonlinear molecular structure [18, 19]. The N phase of conventional LCs is characterized by the uniaxial nonpolar orientational order of the molecules, which in principle makes inherently impossible the existence of biaxial or polar/ferroelectric fluid N mesophases. On the other hand, starting from the seventies a number of theoretical studies and molecular simulations have predicted the existence of the biaxial N phase and, in parallel, the possibility of a polar N order, although their experimental demonstration in thermotropic LCs has proved quite challenging and elusive. For this reason, biaxiality and polar order in nematics have long been considered as the *Holy Grail* of the LC science. Our group has greatly contributed to this hot and widely debated issue, starting from the beginning of the 2000s with the discovery of the cybotactic N mesophase of bent-core nematics (BCNs). With a series of fundamental XRD experiments covering a fifteen years period [18–25], we have demonstrated the ferroelectric N switching in bent-core nematics (BCNs) and their potential to exhibit macroscopic biaxial N ordering. Both properties are due to the peculiar nanostructure of the cybotactic phase, which is constituted of biaxial and polar clusters of smectic-like ordered molecules (Fig. 2). These results represent an outstanding step in the LC science for both fundamental reasons, as they unveil the existence of a new state of matter, and from the technological point of view,

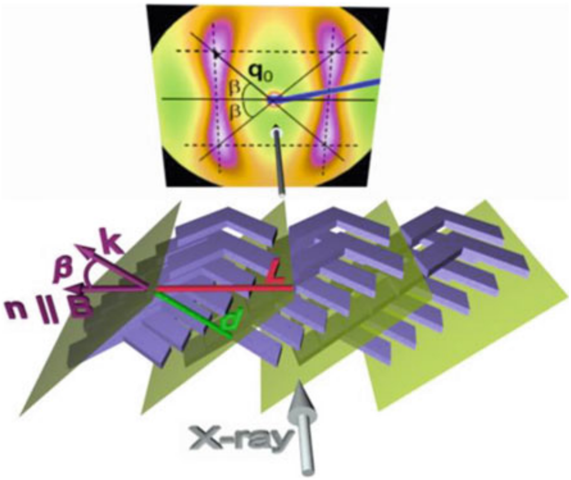

Fig. 2 Schematic drawing of the molecular arrangement of bent-core molecules within a skewed cybotactic cluster (aligned under a horizontal magnetic field **B)** together with the corresponding small-angle XRD pattern (After ref. [23] Reproduced by permission of The Royal Society of Chemistry)

because these materials have great potential in the development of a new generation of electro-optical devices for a variety of applications in different fields.

In parallel with the above mentioned studies, the current scientific activity of the soft matter group is focused on a new long-term research project, in collaboration with scientists of the ESRF, aimed at studying the mechanisms of anchoring, self-assembling, space arrangement and molecular orientation of ultra-thin films of LCs deposited on solid substrates with different techniques. This represents a research field with great potential and still essentially unexplored.

3 Electron Microscopy and Microanalysis of Materials

Electron microscopy and X-ray analysis are perhaps the two most frequently used modern tools for studying the materials structure down to the nanoscale. They each have many variants for addressing many materials types and properties and very often, they are used concurrently due to complementary information.

Modern electron microscopy techniques play essential roles in the characterization of material structures and properties. Electron microscopes utilize electrons of a pre-set energy, usually from tens of electronvolts to 200 keV. The electron beam is used to generate secondary signals from interaction with the investigated specimen. The signals arising from the beam–specimen interaction include secondary electrons (SE), backscattered electrons (BSE), transmitted electrons elastically and inelastically scattered, characteristic X-rays, Auger electrons, cathodoluminescence (CL), and electron-beam-induced current (EBIC). Each type or combination of signals can provide imaging or mapping contrast at its corresponding resolution. The wide variety of signals/information available in the electron microscope contributed to the widespread of the technique in almost all scientific field.

Electron microscopy characterization at the Faculty of Engineering of the Polytechnic University of Marche have initiated in the early eighties when the first scanning electron microscope (SEM) was installed for studies on materials for engineering applications. From those years the increasing demand of materials characterization at the micro- and nano-scale was the driving force for the implementation of laboratory equipment. A new laboratory for sample preparation was established. In the middle nineties an analytical transmission electron microscope (TEM) equipped with diffraction facilities and energy dispersive X-ray (EDX) microanalysis was acquired. Consequently, the laboratory for sample preparation was further implemented with the most advanced techniques, including electrochemical and ion beam thinning. Since then, every specimen from hard and soft materials can be successfully prepared for SEM and TEM observations. Recently, a field emission high resolution SEM, capable of investigating materials at the nanoscale even at low voltage operation, was added as a new facility available to researchers. Since 2006 all electron microscopy facilities at the Faculty of Engineering are organized in a Centre for electron microscopy (CISMIN), which administrates instrumentation and offers scientific and technical support on issues concerning electron microscopy techniques and sample preparation.

Over the years, electron microscopy techniques have been used in the characterization of a wide variety of materials and devices such as p-n junctions and semiconductor devices [26], thin films and multilayers [27–31], light metal alloys (based on Al, Mg and Ti) [32–35], nanostructured materials for magnetic and energetic applications [36–41], scintillating crystals [42, 43], biomaterials and materials for additive manufacturing [44–46].

At the end of eighties strong collaborations with national and international research groups involved in production and characterization of thin films and multilayers by unconventional deposition techniques have been established. Pulsed laser deposition (PLD), pulsed laser reactive deposition (PLRD) and electron beam deposition (EBD) techniques have been used to produce thin films and multilayers or induce surface modifications of bulk materials. In particular, attention was focused on nitrides, silicides and carbides for applications in electronics or as hard material coatings [27–29]. Furthermore, the potentialities of laser and electron beam energy pulses in the production of metastable and non-stoichiometric compounds as well as in the modification of surfaces or in the interfaces intermixing have been also investigated [30, 31].

One of the most promising topic developed over the years have pertained the structural characterization of light metal alloys (Al, Mg, Ti). Outstanding results have been obtained by using electron microscopy in conjunction with positron annihilation techniques, small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC). Attention was focused on the atomic mechanisms in the early precipitation stage that lead to the formation of atomic clusters and ordered crystalline zones. The results obtained on different materials have clarified the nature and the extent of the physical processes active in the early stage of precipitation and the role of interaction between lattice vacancies and precipitates in the formation of the hardening nanophases (Fig. 3). Based on the results obtained, new material treat-

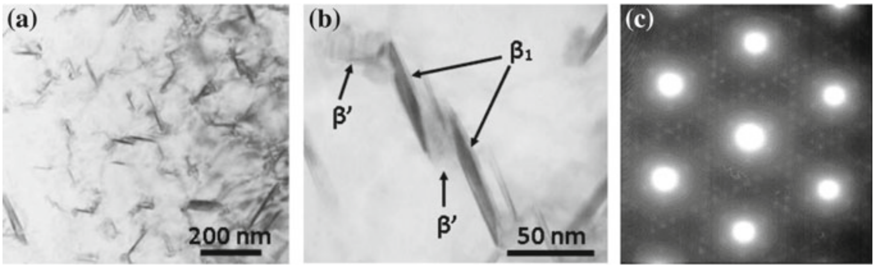

Fig. 3 TEM micrographs of the WE 43 Mg alloy in the T6 state: **a** bright field general view, **b** details of the phases present, the globular precipitate is β' while platelets are β_1, **c** selected area diffraction pattern showing the extra spots due to the secondary phases. Zone axis <0001> $_{\mathrm{Mg}}$ (Copyright (2008), with permission from Elsevier, ref. [34])

ments capable of improving the mechanical properties of alloys used in aerospace, automotive and biomedical fields have been proposed [32–35].

Mg-based alloys other than structural applications have been also investigated as solid-state hydrogen storage material for energy production in fuel cells. The mechanisms of formation and decomposition of hydrides in systems based on Mg and the catalytic properties of Nb have been deeply studied. The results obtained allowed clarifying the mechanisms responsible of the hydride (MgH_2) decomposition, the role of the lattice vacancies in such mechanisms and the processes of hydrogen diffusion and release out of the material [36–39].

Currently, the ongoing activity concerns the characterization of nanostructures responsible of the mechanical properties of materials produced by additive manufacturing (AM). The most investigated materials for structural mechanical applications are Ti6Al4 V, maraging steels and Al10SiMg. Outstanding results have been obtained in the characterization of pure and contaminated metal powders used in the AM process. Furthermore, in Co–Cr biomedical alloys produced by AM, for the first time, alternated lamellar nanostructures of the ε-Co (hcp) and γ-Co (fcc) phases have been identified in the as sintered condition as well as after thermal treatments (Fig. 4).

This peculiar microstructure developed in the layer-by-layer production process is responsible of the improved mechanical properties of the material [44–46].

All the results reported here have clearly evidenced how the macroscopic properties of materials depend on the nanostructure. Therefore, to understand and improve the macroscopic performances of materials, it is essential to investigate and control the material structure down to the nano-scale.

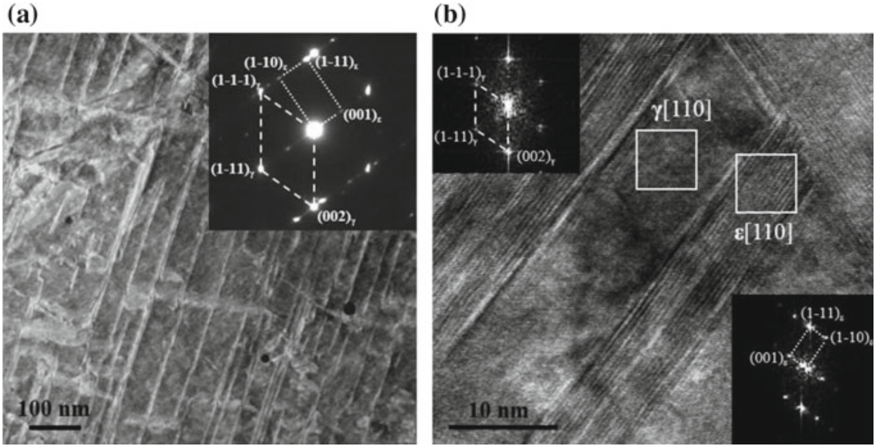

Fig. 4 High resolution TEM images taken in $\langle 110\rangle_\gamma$ zone axis orientation showing the lamellar structure of the Co-Cr biomedical alloy: **a** as sintered condition—inset: SAED pattern, **b** heat treated condition—insets: Fourier analysis of the squared regions (Copyright (2016), with permission from Elsevier, ref. [45])

4 Photonic Materials and Devices

Starting from the year 1995 new laser optic laboratories have been equipped to be devoted to the investigation of liquid crystalline and polymeric materials and to the development of demonstrators of novel optical devices. The main stream of researches has been the one concerned with photo-induced effects in these materials leading either to transient nonlinear phenomena or to permanent modification of the structures. In this context many original results have been obtained and several scientific collaborations at international level have been established.

Concerning nonlinear optics of liquid crystals, the most important achievement has been the discovery of the "Colossal Optical Nonlinearity" [47], still subject of several investigations around the world, concerning both fundamental aspects and possible applications. It has been observed that nematic liquid crystals doped by a specific dye known as Methyl Red at low concentration (0.1% in weight), under proper conditions, exhibit a nonlinear refractive index n_2 up to 10^3 cm^2/W, that is 8 order of magnitude higher than the conventional value characterizing the optical nonlinear response of liquid crystals, the well-known Giant Optical Nonlinearity observed for the first time in 1980.

This effect consists in the onset of a Kerr-type intensity dependent refractive index in the material that can be written as: $n = n_0 + n_2 I$, being n_0 the low intensity value. Such colossal response allows realizing a strong coupling between light beams at the same frequency and different wavevector leading to the generation of nonlinear phase grating producing beam diffraction with efficiency close to the theoretical limit in thin liquid crystal samples. This effect is shown in Fig. 5 that reports the pattern of the light induced diffraction of a probing He–Ne laser beam. The high number of diffracted beams originated by the nonlinear effect is a visual evidence of the high nonlinear response given the small sample thickness (1 μm) and the low power density of the interacting beams (100 μW/mm^2) [48].

The origin of this phenomenon has been explained as a light-induced modification of the surface conditions at the substrate-liquid crystal interface that in turn gives rise to bulk reorientation [49]. The basic role of space charge in this process has been

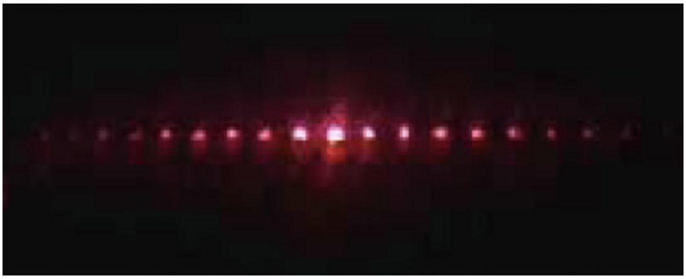

Fig. 5 Transient grating diffraction pattern due to colossal nonlinearity of dye-doped nematic liquid crystals (Reprinted with permission from ref. [48], Optical Society of America)

recently demonstrated [50]. This strong nonlinearity has been exploited to get wave front correction of aberrated beams at low power level (microwatts range) using a standard wave conjugation geometry and for the all-optical control of the trajectory of solitons created in liquid crystal cells.

The same compound when irradiated at higher intensities or using higher dye concentration (1%) shows permanent reorientation of the liquid crystal molecules, leading to permanent modifications of the optical properties that allow recording high resolution holograms [51] using both c.w. and pulsed [52] laser beams.

Driven by these results, investigation on holographic recording was extended to other polymeric and composite materials, with the aim of finding materials suitable for high resolution holographic storage. In the frame of a large European Network and an European project focused on optical holographic disks, technologies for 1D and 2D holographic lithography were built and high sensitivity polymeric materials suitable for micro-holography were developed [53].

This optical patterning approach allowed demonstrations of a number of optical devices. Among them it is worth to recall the achievement of phase-only modulation in a Polymer Dispersed Liquid Crystal were nano-size liquid crystal droplets are obtained by UV photo-polymerizzation leading to samples transparent to visible light but exhibiting a change of the refractive index when submitted to electric field [54]. Besides that, the technology of holographic lithography allowed to develop plastic microlaser using different designs to fabricate DBR (Distributed Bragg Reflector) [55] and DFB (Distributed Feed-Back) optical resonators [56].

Based on the mentioned activity the group achieved international leadership in:

(i) study of nonlinear optical properties of liquid crystalline materials;
(ii) holographic optical patterning of soft matter;
(iii) demonstration of optical active and passive devices based on the above phenomena and methods.

The applications driven activity led to getting 3 patents and the establishment of a spin-off company for development of optical sensors.

Starting from the described expertise new research directions have been undertaken to be further developed in the future.

Nonlinear optical reorientation of liquid crystals has been demonstrated to be the basic mechanism to get optical trapping of microsize beads dispersed in a nematic liquid crystal. This phenomenon leads to an optical tweezing effect with peculiar features with respect to the conventional one based on high intensity gradient. In this case the trapping range can be a few orders of magnitude larger, easily overcoming the distance of 100 μm distance between optical trap and the particle. Moreover, such trapping range and the associated force can be tuned by an applied electric field enhancing or quenching the effect in dependence on the dielectric anisotropy of the liquid crystal [57–59]. These studies have to be considered as preliminary ones to the further development of the optical tweezers apparatus to investigate DNA exhibiting liquid crystalline order and other biosystems of interest for biomedical application.

Active and passive optical devices are currently developed in the frame of Optofluidics in view of possible development of novel platforms for the Lab-on-Chip (LOC)

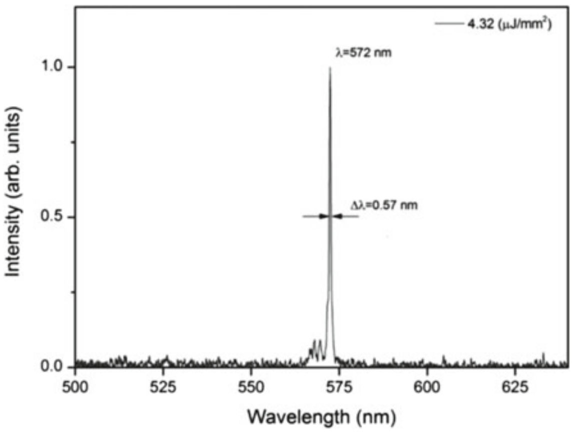

Fig. 6 Laser spectral output of a glass embedded optofluidic laser based on Fabry-Perot cavity (Reprinted with permission from ref. [60], Optical Society of America)

technology. In collaboration with the Italian Institute of Technology (IIT), a new optofluidic laser based on a Fabry-Perot cavity fully embedded in a glass chip has been realized and optically tested. It represents a record result for what concerns low threshold (2 μJ/mm^2) and high-quality factor Q (~10^3) for optofluidic lasers based on Fabry-Perot cavity [60] (Fig. 6).

Further investigations are under way testing different configurations of the optical cavity for a further reduction of the pumping threshold in view of development of portable biosensors. Under a wider international collaboration, the investigation of photo-induced phenomena in liquid crystal cells based on substrates made by iron-doped Lithium Niobate (LN) crystals allowed realizing all-optical phase modulators [61] and getting LC reorientation in microfluidic channels [62].

Another research direction is the light-induced actuation of object at a macro scale. Along this research direction one recent achievement was the realization of a novel photo-mobile polymeric compound based on composite structure allowing photo-induced caterpillar-miming robot [63]. At the same time the Marangoni effect was exploited to get translational [64] and rotational [65] motion of objects floating on common liquids. All these results go towards the direction of light-controlled robotics.

5 Conclusions

We have reported a number of topics of the research activity carried out by the physicists working at the SIMAU Department of the UNIVPM. We have highlighted relevant scientific achievements and most promising future developments in the study of the relationships between structure of matter at the nanoscale and macroscopic properties of materials. Regarding the future perspectives of this research, a great boost is expected from the upgrade of the scientific instrumentation currently underway at the XRD and electron microscopy laboratories, as a part of a strategic project aimed at the creation of a large inter-departmental facility to support innovative research in the fields on nano-science and nano-technology. The scientific results obtained so far, together with the excellent growth prospects, are expected to open new avenues for the next fifty years of the physics and materials science research at the UNIVPM.

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