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RELAZIONE ATTIVITA' ANNUALE DEI PERFEZIONANDI/DOTTORANDI – SECONDO ANNO
REPORT ON THE PHD ACTIVITY – SECOND YEAR

NAME AND SURNAME	Francesca D'Elia
PHD COURSE	Nanoscienze (progetto ERC-CoG "xPRINT")

ATTENDED COURSES (WITH FINAL EXAM)	MARK	HOURS
Seminar Cycle in Biophysical Sciences		45

OTHER PHD ORIENTED ACTIVITIES (SEMINARS, WORKSHOPS, SUMMER SCHOOLS, ETC) – DESCRIPTION	HOURS
02/10/2018 – Seminar – Alfonso Pedone: Modelling molecolare di Vetri Bioattivi	2
19/10/2018 – Nano colloquia – Simone Zanotto: Chiral metasurface optomechanics	1
21/02/2019 – Nano colloquia – Francesco Cardarelli: Capturing dynamic molecular processes in a trafficking organelle: the lysosome case	1
21/03/2019 – Nano colloquia – Gina Greco: Surface acoustic wave (SAW) technology: towards miniaturized and high-performance biosensors	1
16/05/2019 – Nano colloquia – Filippo Fabbri: Nanoscale Optical Spectroscopy of Two-dimensional MoS2 Grown by Chemical Vapor Deposition	1
23/05/2019 – SEMINARI SULLE FRONTIERE DELLA CHIMICA - Benedetta Mennucci: Which modeling for investigating photoresponsive proteins?	2
23/05/2019 – SEMINARI SULLE FRONTIERE DELLA CHIMICA - Marco Pagliai: Molecular dynamics simulations of condensed phase systems	2
10-11/06/2019 – Workshop – HIGHLIGHTS IN NANOSCIENCE: NEST annual meeting	16
20/06/2019 – Nano colloquia – Adam Szukalski: Hybrid and bio-materials for all-optical switching and light	1
Ore totali	**27**

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RESEARCH ACTIVITY (MAX. 8000 CHARACTERS)

The research activity of the second year was focused on the development of 3D printing methodologies for photoluminescent and photoresponsive materials.

Additive manufacturing processes include a variety of technologies that have been classified into seven macro areas, taking into account their basic operating principles [1]. The first step in all additive manufacturing technologies is a digital model of the object to be realized, which is sliced in various layers. The object is then realized by fabricating consecutively the layers, in the so-called layer-by-layer fashion. The fabrication of individual layers can be carried out by curing liquid pre-polymers, by extrusion of melted polymers and viscous solutions, by sintering fine powders, and by delaminating solid layers [1,2].

In the present PhD project, Direct Light Processing (DLP) and Stereolithography (SLA) are selected as the 3D printing methods. Both these technologies are based on the photo-polymerization of a liquid pre-polymer (i.e. a mixture of monomers/oligomers and a photo-initiator). While SLA uses a scanned UV laser (wavelength 405 nm) beam to solidify the individual layers, DLP exploits a 405 nm light from a UV light emitting diode (LED) for projecting in the object plane the pattern of individual layers by a digital micro-mirror array device [3]. DLP and SLA have been used to successfully print various optical components, such as aspherical lenses, mirrors and optical guides operating in the visible range [4-6]. However, current 3D printing methods are still limited to passive materials, which allow the propagation of light to be controlled, but do not feature specific optical functionalities such as the emission of light and the possibility to vary the optical properties by external light signals. The latter property is particularly relevant in view of manufacturing reconfigurable systems, with properties that can be varied in real-time by suitable external signals [8]. This requires the development of 3D printing techniques capable of preserving the optical properties of the active compounds incorporated into the starting materials used for the additive manufacturing process.

In this framework, the research activities of the second year focusses on:

1. The development of 3D printing processes for transparent photo-curable materials using SLA and DLP. To this aim, two transparent pre-polymers were used:
    1.1. A commercially available resin (E-Shell 600, ENVISIONTEC). SLA and DLP process parameters (thickness of individual layers, laser power, laser scanning speed and exposure time) were varied with the aim of obtaining transparent layers and object well-reproducing the original design of the objects. Moreover, in order to improve the optical properties of the printing structures, and particularly, the intensity of light transmitted by

the printed structures, a post-processing finishing approach was implemented. Indeed, the intensity of the light transmitted by as-printed samples is found to be in the range 40-50 % in the visible and NIR spectral range. However, post-printing surface finishing through the deposition of a thin resin film on printed samples, is highly effective in improving the transmittance of these samples, leading to T values larger than 80%, due to the decrease of the surface roughness, and the associated diffusion of incident light. In this context, in collaboration with researchers @NEST, I am developing printing processes for the additive manufacturing of complex optical windows (the so-called "Magic Windows" [9,10,]), which are able to focus a specific pattern when illuminated by a light beam.

1.2. A pre-polymer mixture made of the oligomer Bisphenol A ethoxylate dimethacrylate (BPA) (Sigma-Aldrich), and the photoinitiator Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) (Sigma-Aldrich) with weight:weight ratios between the photoiniziator and the oligomer varying from 1 to 5 %. SLA process parameters (thickness of individual layers, laser power, laser scanning speed) were specifically optimized for obtaining objects with geometrical features matching the original digital model. This pre-polymer was developed for the incorporation of photo-active molecules (see point 2 below).

2. The study of the optical properties of photo-responsive molecules embedded in photo-curable pre-polymers. This activity includes (i) the investigation of the solubility of the photo-active molecules in the pre-polymers and (ii) the study of the optical properties of the embedded materials before and after the printing process. In fact, the exposure time to the UV light during the additive manufacturing process must be determined in order to provide sufficient polymerization of the matrix, while preventing the occurrence of photo-bleaching phenomena for the active components.
   In particular, the photo-curable layers with the following active molecules were investigated:
   2.1. Three photoluminescent chromophores (Stilbene-420, Coumarine-500 and Rhodamine-590), which emit light in the visible range (400-650 nm) by optical pumping with UV light.
   2.2. A photochromic molecule (pseudogem-Bis(diphenylimidazole)[2.2] paracyclophane), able to switch from a colorless state to a colored one under UV illumination, with an associated back-conversion to a colorless state in absence of light, on timescales of seconds [11].

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REFERENCES

1. ISO/ASTM Standard 52900. Standard terminology for additive manufacturing-general principles. Part 1: Terminology. ISO/ASTM International, Switzerland, (2015).
2. Bourell, D. L., “Perspectives on additive manufacturing,” Annu. Rev. Mater. Res. 46, 1–18 (2016).
3. Hull, C. W., (UVP, Inc.), U. S. patent 4,575,330, (1986).
4. Chen, X., Liu, W., Dong, B., Lee, J., Ware, H. O. T., Zhang, H. F. and Sun, C., “High-Speed 3D printing of millimeter-sizee customized aspheric imaging lenses with sub 7 nm surface roughness,” Adv. Mater. 30, 1705683 (2018).
5. Vaidya, N. and Solgaard, O., “3D printed optics with nanometer scale surface roughness,” Microsyst. Nanoeng. 4, 18 (2018).
6. Heinrich, A., Rank, M., Maillard, P., Suckow, A., Bauckhage, Y., Rößler, P., Lang, J., Shariff, F. and Pekrul, S. “Additive manufacturing of optical components,” Adv. Opt. Technol. 54, 293–301 (2016).
7. Camposeo, A., Persano, L., Farsari, M. and Pisignano, D., “Additive manufacturing: applications and directions in photonics and optoelectronics,” Adv. Optical Mater. 7, 1800419 (2019).
8. Bertrand, O. and Gohy, J.-F., “Photo-responsive polymers: synthesis and applications,” Polym. Chem. 8, 52–73 (2017).
9. Berry, M. V., ‘’Laplacian magic windows’’, J. Opt. 19, 6 (2017).
10. Ries, H., and Muschaweck, J., ‘’ Tailored freeform optical surfaces’’, J. Opt. Soc. Am. A. 19, 3 (2002).
11. Kishimoto, Y., and Abe J., ‘’A fast photochromic molecule that colors only under UV light’’, JACS. 131, 4227–4229 (2009).

*se si intende sottoporre una relazione di ricerca più estesa, utilizzare il campo per una descrizione sintetica e allegare il documento in formato .pdf

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PUBLICATIONS (IF AVAILABLE)
Szukalski, A., Uttiya, S., D'Elia, F., Portone, A., Pisignano, D., Persano, L., and Camposeo, A. "3D photo-responsive optical devices manufactured by advanced printing technologies", Proc. SPIE 10915, Organic Photonic Materials and Devices XXI, 1091503 (2019).
Portone, A., D’Elia, F., Romano, L., Szukalski, A., Matino, F., Fabbri, F., Persano L, Pisignano D, Camposeo A., “Shaping of photo-active materials by 3D printing”, NOMA. NoM2B.3 (2019).

THESIS ADVISOR
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DATE	06/10/2019	SIGNATURE	