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RELAZIONE ATTIVITA' ANNUALE DEI PERFEZIONANDI/DOTTORANDI – TERZO ANNO

REPORT ON THE PHD ACTIVITY – THIRD YEAR

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

OTHER PHD ORIENTED ACTIVITIES (SEMINARS, WORKSHOPS, SUMMER SCHOOLS, ETC) – DESCRIPTION	**HOURS**
15/11/2019 – Webinar – Roboze: Heat Treatment Process	1
15/11/2019 – Webinar – Roboze: High Performing Materials	1
28/11/2019 – Seminar – Paul Dalton: Melt Electrowriting: A Method to Design and 3D Print Microscale Objects	2
10-11/12/2019 – Webinar - Mathematica e le Tecnologie Wolfram	8
13/01/2020 - Photonics Online Meet-up (POM) Conference	5
18/06/2020 – Nano colloquia – Melissa Santi: Targeting strategies to improve cancer treatment	1
13-16/07 2020 - OSA Advanced Photonics Congress	36
20/07/2020 – JBO Webinar - Wearable, Implantable, Mobile, and Remote Biomedical Optics & Photonics	1
23/07/2020 – Seminar – Roberto Cippitani & Valentina Colcelli: Open Science and Open Innovation within the European Research Area	3
23-29/08/2020 - SPIE Optics + Photonics Digital Forum 2020	66
14-17/09/2020 - FiO + LS Conference: Technical Conference & Virtual Exhibits	48
21-25/09/2020 - SPIE Security + Defence Digital Forum 2020	55
Ore totali	**227**

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ATTENDED COURSES (ATTENDANCE ONLY)	HOURS
Ciclo di Seminari “Soft Skills per le imprese di domani”	13

RESEARCH ACTIVITY (MAX. 8000 CHARACTERS)

The objective of the research activity of the third year was the development of (a) a mechanically deformable free-form optics by 3D printing and soft lithography, (b) a 3D printed photo-luminescent system emitting white light and (c) a naturally degradable optical device with transient functionality.

Additive manufacturing (AM) technologies were exploited as the fabrication platform. They are based on the realization of a 3D object starting from a digital model in a layer-by-layer fashion [1]. In the present PhD project, two methods were used, namely the digital light processing (DLP) and the stereolithography (SLA), both based on the UV photo-polymerization of a liquid pre-polymer mixture, made of monomers/oligomers and a photo-initiator (PI) [2].

The first two years’ studies were focused on the development of 3D printing methodologies for transparent photo-curable materials, obtained by utilizing both a commercially available resin (E-Shell-600) and a mixture made of bisphenol A ethoxylate dimethacrylate (BPA) and the PI diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) [3]. In addition, the functionalization of photo-curable layers with luminescent and photo-isomerizable molecules, using as host matrix the transparent resins described above.

Building on these results, during the third year the research activities were focussed on:

1. *The realization of mechanically deformable free-form optics (also known as “magic windows”, MWs)*, in collaboration with researchers @NEST. These optical components are made of transparent materials and are designed to redistribute the intensity profile of incident light into a desired pattern through refraction [4]. To this aim, the following activities were realized:
    1.1. *3D MW design and printing*. First a 3D model of the MW to be realized by 3D printing was designed starting from the target pattern to be projected by the MW. Afterwards, the MW was realized by DLP technique with the thickness of a single printed layer of 15 µm. E-shell600 was chosen as photo-polymer since it is an acrylate-based compound exhibiting good optical transmittance in the visible spectral range.

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1.2. *Characterization of the intensity distribution of the pattern projected by the printed MW*. To this aim, the printed MWs were mounted on a micrometric translation stage and illuminated with either an incandescent light bulb or three light emitting-diodes (LEDs) with emission wavelength peaked at 475, 524 and 633 nm, respectively. The pattern generated by the MWs was projected on a semi-transparent plastic screen and imaged with a CMOS camera (Thorlabs) in transmission mode. Comparison of the measured pattern projected by the MW and the original one was performed by image analysis measuring the size of selected features of the pattern and the intensity contrast between dark and bright areas through analysis of the Weber contrast. Such analysis evidenced a wavelength-independent and faithful generation of the initial pattern at the designed focal distance (3 mm).

1.3. *Realization of a mechanically deformable MW*. Elastomeric MWs were realized by combining 3D printing and soft lithography, namely by using the 3D printed object as the master for a replica molding process. The morphological features of the so-realized elastomeric MW can be varied by uniaxial mechanical elongation, with the possibility of varying the pattern generated by the elastomeric MW through stretching. We exploited this process to fabricate a MW that project the pattern of a microQRCode upon illumination. Such pattern was intentionally deformed in order to be readable by a QRCode scanner only upon deformation of the elastomeric MW. The results of this activity showed that while the pattern generated by the unstretched MW was not readable by the scanner, a 15% of uniaxial strain enabled the correct reading of the information encoded in the QRcode. The developed system can have application as anti-counterfeiting systems and adaptive optics.

2. *The fabrication of white-light-emitting 3D printed system*. White light sources, which plays an important role in many fields such as display, optical wireless communication and diagnostics [5], can be realized by combining multiple components that emit simultaneously different wavelengths in the visible spectral range. In some systems, Forster resonance energy transfer (FRET) can be exploited to tune the relative intensity of the various emitting components [6]. We developed a 3D printed system emitting white light by combination of three luminescent chromophores dispersed in a UV-curable matrix: stilbene-420 (B), coumarine-500 (G) and rhodamine-590 (R). This study involved three phases:

2.1. The chromophore and PI content was initially optimized in order to avoid over-polymerization of the pre-polymer during the printing process and photo-bleaching of photo-sensitive molecules. SLA printing parameters (laser power and laser scanning speed) were concomitantly varied to obtain 3D complex structures with the optimized mixtures.

2.2. The optical properties of the printed luminescent structures were investigated by photoluminescence spectroscopy, measuring the emission spectra of the various mixtures and their photoluminescence quantum yield.

2.3. Finally, the molar ratio between the different dyes was finely tuned in order to achieve printed structures emitting white light. The emission properties of the printed objects were characterized according to the standard of the Commission Internationale de l'Eclairage (CIE). In particular, the printed object with chromophore relative molar content R:G:B=2:2:1 was characterized by CIE coordinates (0.33, 0.34, 0.33) as expected for a white light source. The developed system can find application in optical wireless communication and analytical systems.

3. *Naturally-degradable optical systems.* Combined dry-wet transient materials and devices were realized based on water-dissolvable dye-doped polymers layered onto non-polar cyclic hydrocarbon (cyclododecane, CDD) sublimating substrates (see publication section). To this aim, the following experimental activities were performed:

3.1. First, optically-active heterostructures were realized by solution casting methods. Two polymeric layer (made of poly(vinyl alcohol) (PVA) and polyvinylpyrrolidone (PVP) doped with the red-emitting laser dye [2-[2[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H-pyran-4-ylidene]-propanedinitrile) were casted on a CDD substrates. These substrates had size 2×2 cm2, thickness in the range 1-3 mm and smooth surfaces (root mean square roughness, Rq= 70 nm). The thickness of each layer of the heterostructures was engineered to keep the light-emitting structure mechanically stable and unbent, even upon complete CDD sublimation.

3.2. The samples were characterized by optical and fluorescence microscopy, in order to investigate the layer structures and interfaces. The realized device showed amplified spontaneous emission used as illumination sources for speckle-free, full-field imaging. After device use and complete self-destruction of the CDD layer, the polymer layers can be naturally washed out with water. The developed naturally degradable optical system with transient behaviour might be relevant for environmental sensing, storage conditions monitoring, and organic photonics.

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REFERENCES:

1) ISO/ASTM Standard 52900. Standard terminology for additive manufacturing-general principles. Part 1: Terminology. ISO/ASTM International. PA, 3, 5 (2015).
2) Chen M, Zhong M, & Johnson JA. Light-Controlled Radical Polymerization: Mechanisms, Methods, and Applications. Chem rev. 116, 10167-10211 (2016).
3) Szukalski A. et al. 3D photo-responsive optical devices manufactured by advanced printing technologies. Organic Photonic Materials and Devices XXI. Vol. 10915. International Society for Optics and Photonics (2019).
4) Berry MV. Laplacian magic windows. J Opt. 19, 06LT01 (2017).
5) Adamow A, et al. Electrically controlled white laser emission through liquid crystal/polymer multiphases. Light Sci. Appl. 1-9 (2020).
6) Förster T. Zwischenmolekulare Energiewanderung und Fluoreszenz. Ann Physik. 437, 55 (1948).

PUBLICATIONS

Camposeo, A., D'Elia, F., Portone, A., Matino, F., Archimi, M., Conti, S., Fiori, G., Pisignano, D., Persano, L. "Naturally Degradable Photonic Devices with Transient Function by Heterostructured Waxy-Sublimating and Water-Soluble Materials", Advanced Science, 2001594 (2020).

THESIS ADVISOR

Andrea Camposeo

Francesco Cardarelli (Internal SNS)

DATE	18/10/2020	**SIGNATURE**	