ΠΑΝΕΠΙΣΤΗΜΙΟ ΚΡΗΤΗΣ

ΤΜΗΜΑ ΕΠΙΣΤΗΜΗΣ & ΤΕΧΝΟΛΟΓΙΑΣ ΥΛΙΚΩΝ



UNIVERSITY OF CRETE

DEPARTMENT OF MATERIALS SCIENCE & TECHNOLOGY

ΠΡΟΣ

1) Όλα τα μέλη ΔΕΠ του Τμήματος Επιστήμης και Τεχνολογίας Υλικών

- 2) Την Επταμελή Εξεταστική Επιτροπή
- 3) Όλα τα μέλη της Πανεπιστημιακής Κοινότητας

Πρόσκληση σε Δημόσια Παρουσίαση της Διδακτορικής Διατριβής της

κ. Ασημίνας Ελένης Καμπουράκη

(Σύμφωνα με το άρθρο 41 του Ν. 4485/2017)

Τη **Δευτέρα 8 Ιουλίου 2019** και ώρα **15:00** στην **αίθουσα τηλεεκπαίδευσης Ε130** στο κτήριο **Τμήματος**

Μαθηματικών και Εφαρμοσμένων Μαθηματικών, Πανεπιστημίου Κρήτης, θα γίνει η δημόσια παρουσίαση

και υποστήριξη της Διδακτορικής Διατριβής της υποψήφιας διδάκτωρ του Τμήματος Επιστήμης και

Τεχνολογίας Υλικών κ. Ασημίνας Ελένης Καμπουράκη με θέμα:

«Direct Laser Writing of 3D Photonic Structures with Tunable Optical Properties»

Abstract:

DLW by multiphoton polymerization (MPP) has become a powerful tool for the fabrication of fully threedimensional micro- and nano-structures for microfluidic, biomedical, metamaterial, and photonic applications. In DLW, the beam of an ultrafast laser is tightly focused into the volume of a photosensitive material, initiating multiphoton polymerization within the focused beam volume (namely, voxel). By moving the focus of the beam in the three-dimensions, arbitrary 3D, high-resolution structures can be written into the volume of the material. By simply immersing the sample in an appropriate solvent, the non-polymerized area can be dissolved, revealing the 3D structure.

The materials developed in this work are photostructurable organic-inorganic hybrid materials, prepared using the sol-gel process. This versatile technique has been exploited for the incorporation of inorganic networks into polymer matrices, using as monomers molecules that carry an inorganic part (which serves as the precursor to the inorganic network) and a polymerizable organic group (which acts as the precursor to the organic polymer). For the fabrication of 3D structures by DLW, it is often necessary to add a photoinitiator, that is a molecule which, upon multiphoton absorption, generates the active species which initiate the polymerization process.

In this work, we present for the first time the fabrication of excellent quality 3D structures by photoinitiator-free multiphoton polymerization. The process relies on the synthesis of a novel vanadium-based hybrid material, containing vanadium (V) triisopropoxide oxide, which self-generates radicals via a light-induced redox reaction. In particular, upon multiphoton absorption the composite generate radicals by the photoinduced reduction of vanadium (V) to vanadium (IV). We exploit this material for the fabrication of fully 3D structures by multiphoton polymerization with 200 nm resolution, employing a femtosecond laser operating at 800 nm, in the absence of a photoinitiator. Nonlinear

absorption measurements indicate that the use of an 800 nm laser initiates the photopolymerization due to a three-photon absorption of the vanadium alkoxide. The laser power required to induce this three-photon process is comparable to that required for inducing two-photon polymerization in materials using standard two-photon absorbers, most likely due to the high content of vanadium in the final composite (up to 50% mole).

In the second part of the present study hybrid organic-inorganic materials were modified by the addition of a quantum dot precursor molecule, which becomes chemically attached onto the fabricated 3D structures during the photo-polymerization process. Next, the 3D structures are reacted with sodium sulfide (Na2S) to form CdS quantum dots within the structures. Such semiconductor nanoparticles enrich the fabricated structures with third order non-linear properties. 3D printed active photonic devices, of a woodpile geometry with an inlayer periodicity as low as 500 nm, are successfully fabricated at high resolution and exhibit clear photonic stop bands in the visible spectral region, while for the first time, evidence of ultrafast dynamic tuning of the photonic band gap properties in the visible, is also demonstrated.

In the final part of this thesis, pre-synthesized highly fluorescent CdSe-CdS quantum dots, bearing appropriate functionalities, were permanently bound onto the surface of 3D photonic crystal structures, following chemical functionalization of the surface of the particles or the surface of the 3D structures. Woodpile 3D photonic crystal structures, with an inlayer periodicity of 550 nm, were fabricated, using the Direct Laser Writing technique, exhibiting photonic stopgaps at visible wavelengths. Next, the structures were coated with the synthesized quantum dots that can act as a gain medium. Near the band edge of these gaps, the group velocity, ug, of photons localized in the structure, approaches zero and photons undergoing multiple reflections in the lattice experience longer interaction with the gain material, thus resulting in an enhanced effective gain. By matching the photoluminescence of the nanoparticles with the bandedges of the photonic crystals a functional device that can act as a nanolaser was developed.