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Metamaterial 3D Gain Nanostructures Fabricated Using Direct Laser Writing

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14. ABSTRACT

The objective of this grant was to attempt to develop materials and processes for the fabrication of Gain 3D metallic Metamaterials (MM) via Diffusion-Assisted Direct Laser Writing (DLW) and multiphoton polymerization (MPP). The research's particular goal was to fabricate a fully three-dimensional metallic MM using a novel technique which employs quencher diffusion to fabricate structures with resolution beyond the diffraction limit. The grantees were successful in making dielectric 3D nanostructures by MPP using a metal-binding organic-inorganic hybrid material covered with silver or gold via selective electroless plating. This produced spirals and woodpiles with 600 nm intralayer periodicity below the diffraction limit. The resulting photonic nanostructures have a smooth metallic surface and exhibit well-defined diffraction spectra, indicating good fabrication quality and internal periodicity. These results show that DLW and selective electroless plating combine for a viable route for the fabrication of 3D dielectric and metallic photonic nanostructures.

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Summary

We present our research into Metamaterial 3D Gain Nanostructures fabricated using Direct Laser Writing. More specifically, we present the synthesis and characterization of highly fluorescent quantum dots emitting at infrared wavelengths, and their incorporation into 3D photonic nanostructures fabricated using direct laser writing. In addition, we show the synthesis and characterization of core-shell highly fluorescent quantum dots, for incorporating into 3D nanostructures emitting at visible wavelengths. Finally, we discuss our current and future work.

Introduction

Photonic crystal lasers are lasers at the micrometer scale and the device consists of a photonic crystal in which a gain medium is embedded. In order for the device to act as a photonic crystal laser the emission of the gain medium must fall at the bandedges, (edges of the bandgap of the structure), of the photonic crystal. There the group velocity of photons approaches zero and this "forces" light to travel slower, thus, the interaction time with the gain medium is longer, resulting in an effective gain. Lastly, it is worth mentioning that the wavelengths where the bandgaps and thus the bandedges will arise, depends on the geometry of the structure.

IR quantum dot Synthesis

The photonic crystal structure that we are working on is shown in the following Figure 1 (in collaboration with Prof. Kostas Soukoulis, Prof. Maria Kafesaki and Dr. Sotiris Droulias, who performed the theoretical calculations):

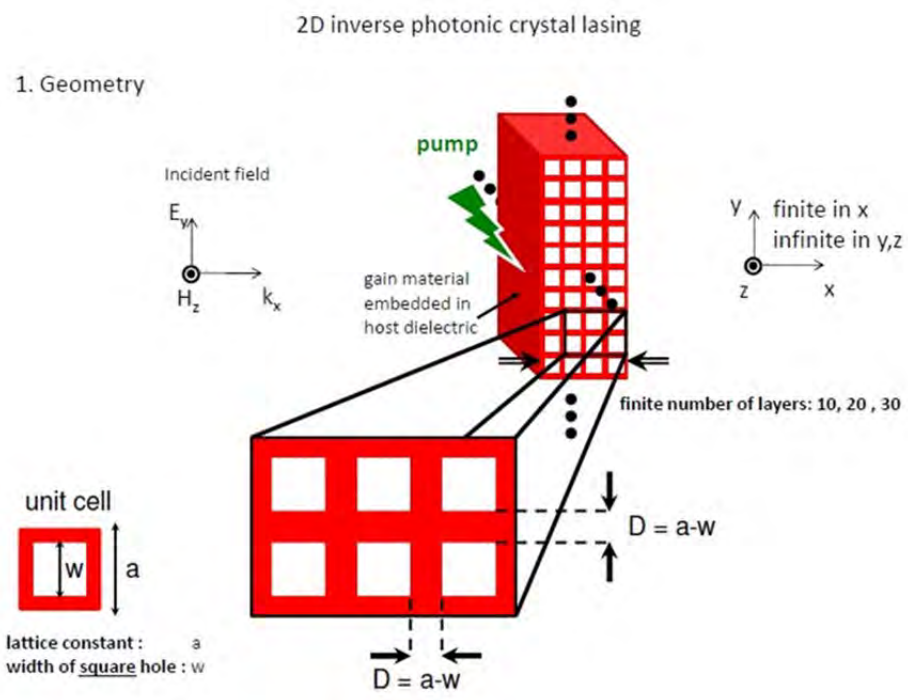

Figure 1: Photonic Crystal Structure

The gain medium that was found more appropriate was Lead Selenide (PbSe) quantum dots, which emit at the IR region. These were synthesized using a hot solution chemical method. The precursors used were cadmium oxide (PdO) and selenium powder. To avoid aggregation of the nanoparticles oleic acid and trioctylphosphine were used as stabilizing agents. The reaction was quenched at different time intervals in order to obtain different sized nanoparticles. The synthesized quantum dots were characterized using UV-Visible and photoluminescence spectroscopy as well as Transmission Electron Microscopy (TEM).

The Absorbance spectra of the synthesized quantum dots are shown in Figure 2. The different colors represent the different time in minutes that the reaction was terminated. As the reaction proceeds the particles grow bigger, thus, higher reaction times correspond to higher nanoparticle sizes.

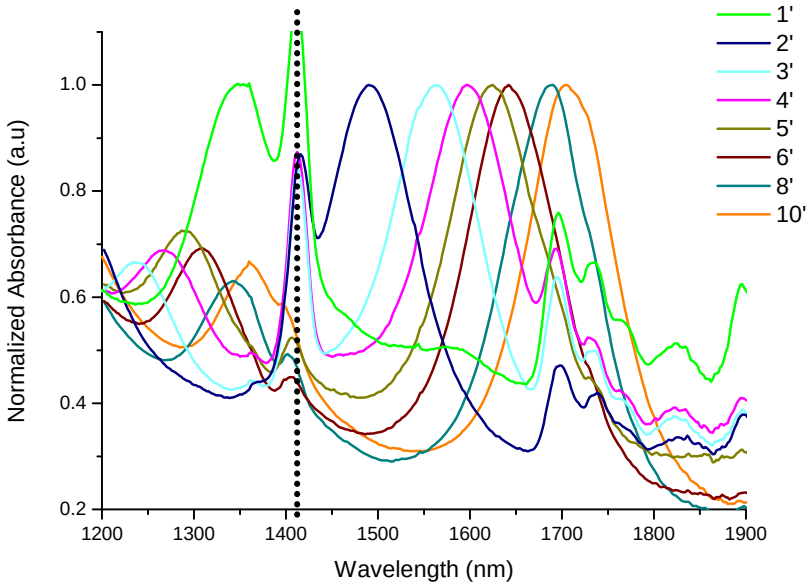

Figure 2: Absorbance spectra of the PbSe quantum dots

It is apparent from the absorption spectra that as the particles grow bigger in size their absorbance shifts towards larger wavelengths. This is in good agreement with the theory of semiconducting nanoparticles. As they increase in size their energy gap decreases and this leads the first absorption peak to arise at larger wavelengths.

IR Quantum Dot Characterization

Next, the nanoparticles where characterized by photoluminescence spectroscopy. Figure 3 depicts the measured spectra. Once more, the different colored spectra represent the different time intervals that the reaction was terminated. So, larger reaction times correspond to larger particles.

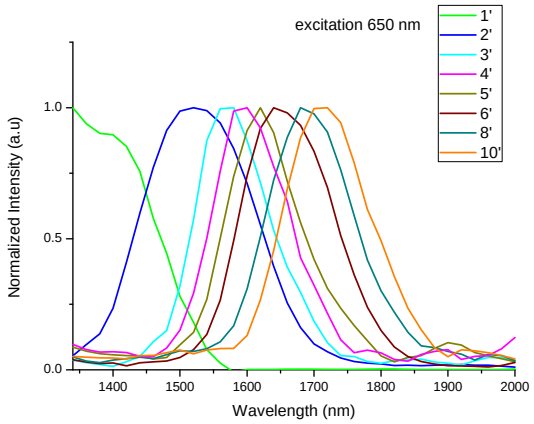

Figure 3: Photoluminescence spectra of the synthesized quantum dots

It can be seen that as the particles grow bigger their emission is red shifted. Such a response is expected since larger particles exhibit smaller energy gaps between the valence and the conduction band, resulting in smaller frequency emissions.

Next, the particle diameter was calculated using the effective mass model and the following equation:

$$Eg\ (QD) = Eg\ (bulk) + (\frac{h^2}{8R^2})(\frac{1}{m_e} + \frac{1}{m_h}) - \frac{1{,}8\ e^2}{4\pi\varepsilon_o \varepsilon \mathrm{R}}$$

Where ε is dielectric constant of the bulk PbSe, m_e and m_h are the effective masses of the electron and hole of PbSe respectively, ε_0 is the vacuum permittivity and e is the electron's charge. The results can be seen in the following table 1.

The nanoparticles were also characterized using Transmission Electron Microscopy (TEM). Representing results are shown in Figure 4. As depicted in the pictures the particles size distribution seems quite narrow.

Reaction time (min.)	Diameter (nm)
1	7,62
2	8,2
3	8,46
4	8,62
5	8,72
6	8,8
8	9
10	9,1

Table 1. Calculated diameter of the PbSe nanoparticles

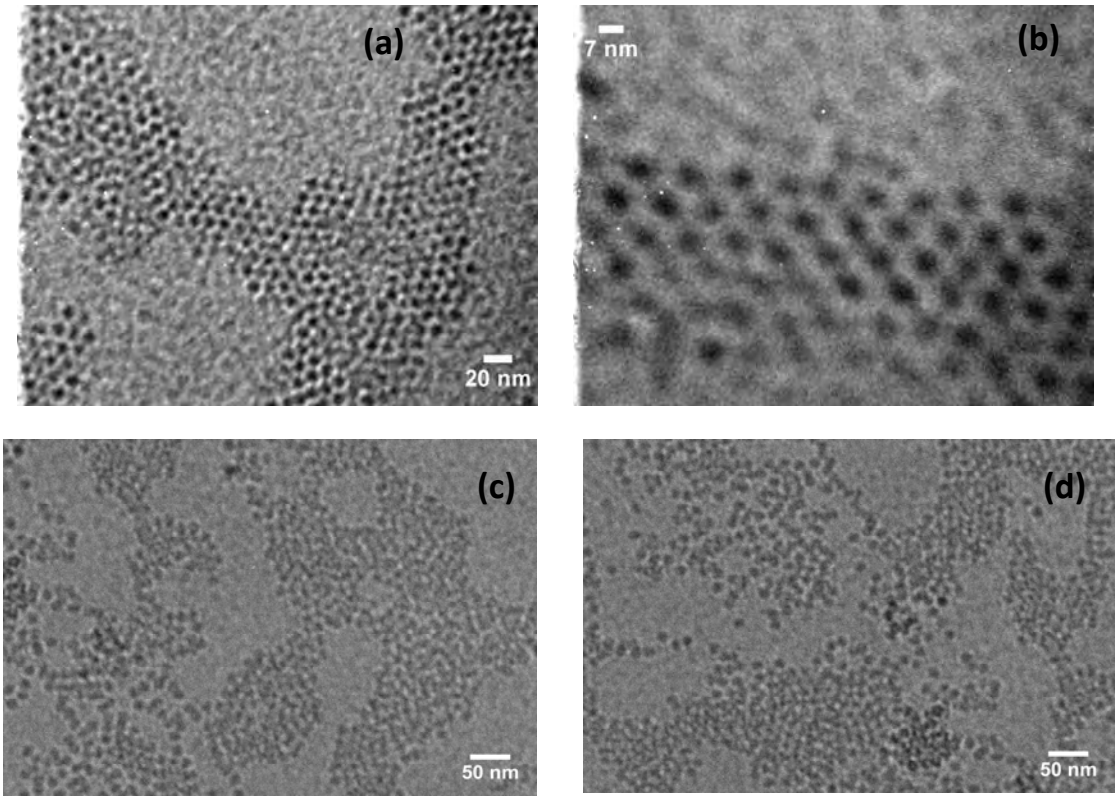

Figure 4: TEM images of the PbSe quantum dots. a-b) **sample of the 1' reaction** c-d) **sample of the 2' reaction.**

After the synthesis and characterization of the gain material, the theoretical calculations showed that the most feasible lattice for the photonic structure is 700 nm period with 240 nm resolution, in order for the bandedges to be at the same frequency as the emission of the nanoparticles (Figure 5).

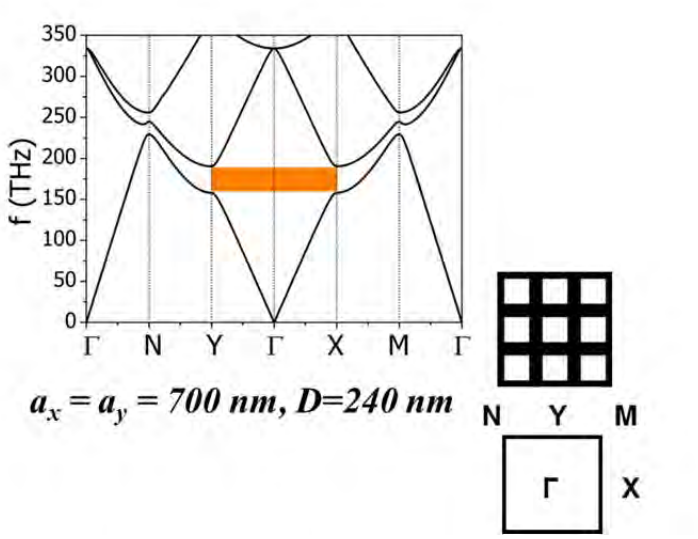

Figure 5: The theoretically calculated bandgap graph of a photonic crystal structure of 700 nm period and 240 nm feature size.

Structure Fabrication

Using Direct Laser Writing (DLW) via the Two-Photon Polymerization (TPP) technique the fabrication of the structures was tested. In order to achieve such relatively large feature size (240 nm) the fabrication energies used were quite above the polymerization threshold. Some representative results are shown in figure 6.

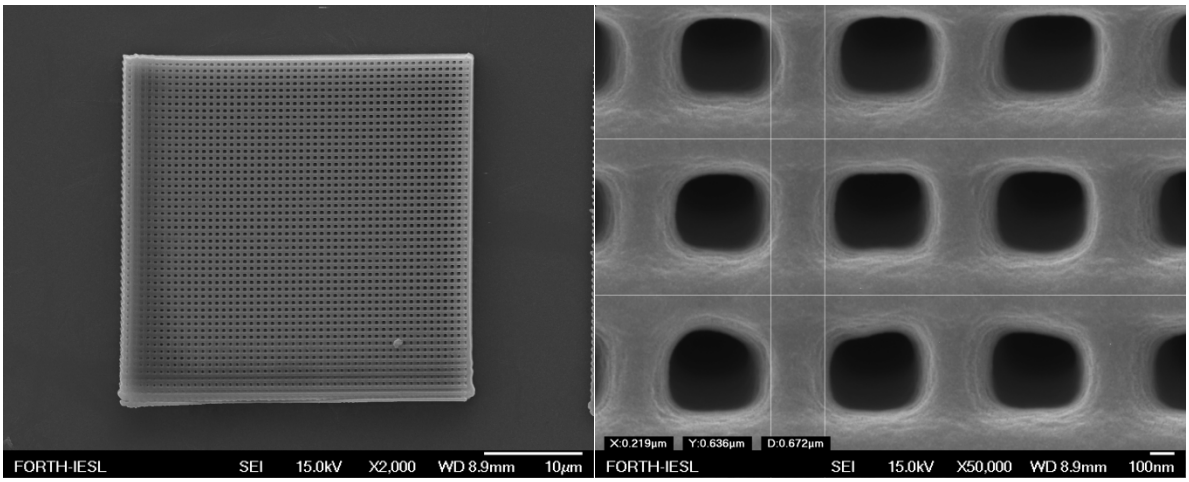

Figure 6:SEM images of the fabricated photonic structures

As we can see, we can achieve structures very close to the needed values.

Visible Wavelength Quantum Dot Synthesis and Chatacterization

Another research activity that is under investigation is the synthesis of quantum dots that exhibit emission at visible wavelengths. This specific gain medium is going to be combined with photonic crystal structures of appropriate geometry in order to examine the lasing activity at visible wavelengths. For this purpose CdSe (Cadmium Selenide) quantum dots were synthesized. The synthesis once more involves a chemical hot solution method, which in general principles is the same as the synthesis of the PbSe quantum dots. The precursors used are CdO (Cadmium oxide) and Selenium powder and as stabilizing agent oleic acid was used. The nanoparticles were characterized using UV-Visible and photoluminescence spectroscopy. Figure 7 and 8 show the collected spectra.

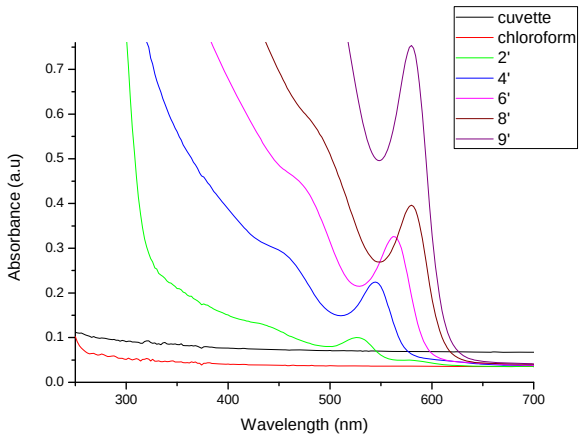

Figure 7UV-Visible spectra of the synthesized CdSe quantum dots. The different colored spectra represent different reaction times (in minutes) and thus nanoparticles of different size.

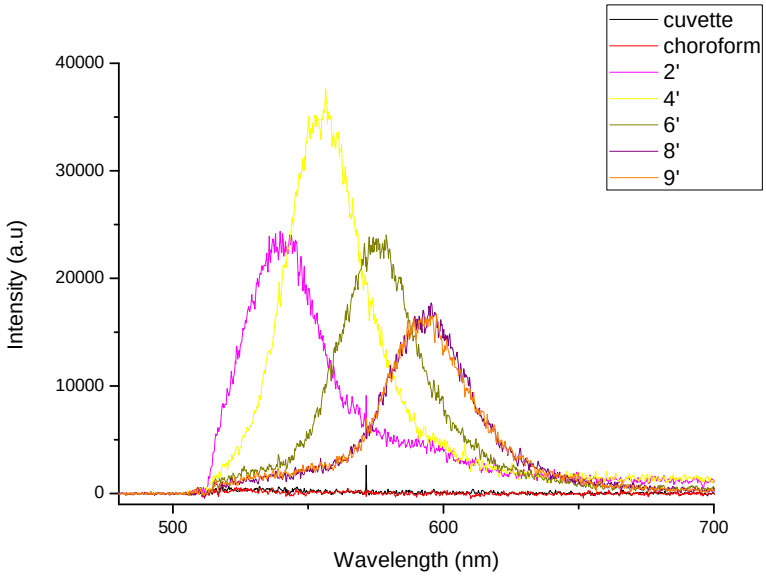

Figure 8Photoluminescence spectra of the synthesized quantum dots.

As it is observed for different reaction times we can achieve the synthesis of different sized nanoparticles which accordingly, emit at different visible wavelengths. In order to enhance the emission intensities of the nanoparticles a thin CdS (Cadmium sulfide) shell was grown on the surface of the CdSe cores. The growth of a few monolayers of a higher bandgap semiconductor helps the passivation of the surface of the quantum dot cores resulting in an enhanced gain. Below in figure 8 the emission of CdSe/CdS core/shell particles is depicted.

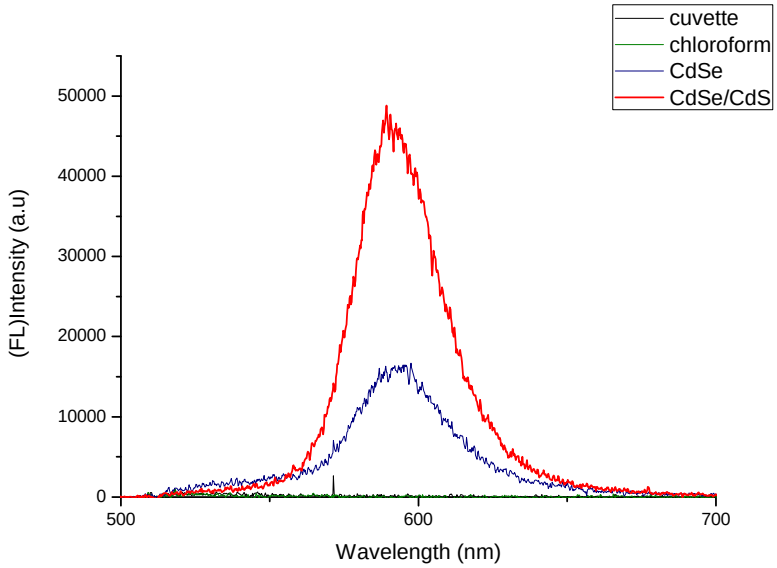

Figure 9:The emission of CdSe/CdS quantum dots

As we can see, by adding the CdS shell we have managed to achieve a three times higher emission in comparison to the bare CdSe nanoparticles.

Current and Future Work

At the present time, we are working on the incorporation of the quantum dots in the photosensitive materials that are used for the fabrication of the structures. For this purpose different strategies are followed. These involve the diffusion of the quantum dots at the fabricated structures as well as the dispersion of the nanoparticles in the photosensitive materials prior to structuring. The later strategy also involves the ligand exchange of the particles with methacrylate moieties that will result to nanoparticles that are chemically attached in the laser fabricated photonic crystals.