Innova Scientific Award 2011

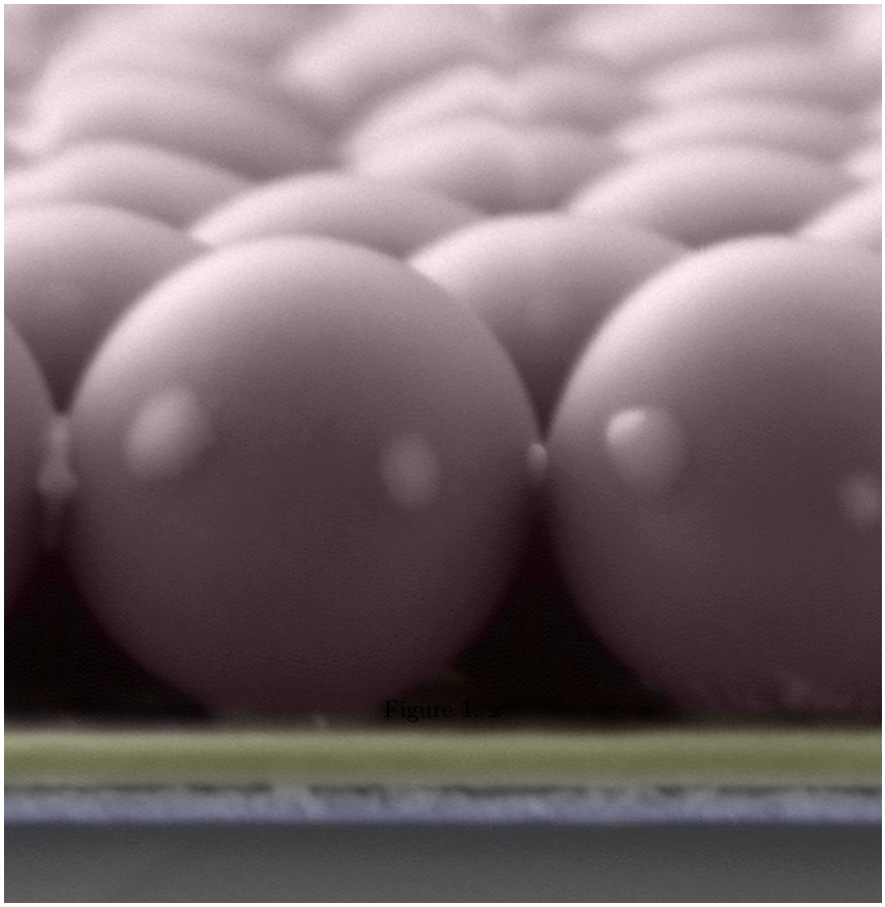

Figure 1. 2

Self Assembled Photonic-Plasmonic Crystals for Light control at the Nanoscale

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I present here the work performed at the Photonic crystals Group of the ICMM-CSIC settled in Madrid under the supervision of Proff. Cefe Lopez and Juan Galisteo. The field of research where the investigaction is framed in has recently shown a high potential for solar cell [1] applications as well as sensing [2] which make as believe that the results we have obtained provides a powerful proof of principle of devices based on self-assembled hybrid structures. This research has been published in two papers in international journals (Small [3] and Advanced Functional Materials [4]) along the period 2010-2011 being the applicant for the prize the first author of both of them.

Introduction

Self assembled photonic crystals have become a widespread approach to produce two dimensional periodic structures. In case of photonic crystals where the aim is to control light propagation 2D periodic systems fabricated from monolayers (ML) of dielectric spheres have been thoroughly investigated over the last few years. They present an easy-implementation at reduced cost method to obtain large area samples of 2D periodic structures. However, some works during the last years have pointed the large reduction on their capability of molding the flux of light when a dielectric substrate is place under this kind of structures [5]. In plasmonics however, self-assembled systems have probed to be a very useful template to obtain 2D periodicities in metallic structures through the so called colloidal lithography [6]. However, in all those cases, the original 2D photonic crystal do not play a role further than as template. Therefore, in the results we have obtained, it is demonstrated that by one side, the photonic "strength" of the monolayer of dielectric spheres on modifying light propagation is enhanced by using a metallic substrate. On the other hand, the dielectric array of spheres acts as an effective structuration of the plasmonic supporting substrate. Due to this two effects this kind of structures are known as self-assembled hybrid photonic-plasmonic structures [7]. In the work presented for this application, we present the in depth study we have performed about this structures. First we have studied its optical properties both, experimentally and numerically. After that we have used that knowledge to obtain large emission enhancements at tho spectral positions were the modes of the systems take place [3]. Finally, we have investigated the effect over the optical response of the reduction of the filling fraction of the close-packed lattice of spheres. We have shown that such reduction provides a tuning effect over the modes of the system. Finally, we have implemented the tuning process to tune not jus the optical response but the emission of a 2D hybrid monolayer of spheres [4].

Self-assembled hybrid structures fabrication

We have used the vertical deposition method to grow high quality samples of organic (polystyrene) spheres. This method has been previously applied with much of success in the Photonic Crystals Group of the ICMM. It was adapted to the growing of one single layer instead of the opal structures more usually describes in photonic crystals literature. After same calibration process, it was found that the best conditions were to introduce a rigid substrate vertically on an aqueous solution of spheres with a sufficiently low concentration (0.08 wt%). The growth process was performed in a furnace with controlled temperature (50^o) and humidity (20%).

We used PS spheres (Duke Scientific) having a diameter of 520 nm and, in the emission measurements case, containing an organic dye (Rhodamine 6G) homogeneously distributed throughout their volume. As substrates, we used 450-μm-thick silicon wafers (ACM) on which a thin gold film (60 nm) was sputtered. The characterization of the growth samples determine that a high quality at short range is obtained regardless of some vacancies and lattice dislocations due to the polidispersity on the size of the spheres (see diagram and SEM microscopy on Fig. 2).

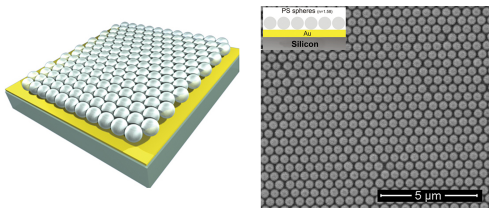

Figure 2: Left: Artistic picture for the kind of photonic structure studied in this work. Right: SEM image of a monolayer made of PS spheres of diameter 520 nm.

Optical properties

In order to study the optical response of the structure, we performed numerical simulation of reflectance spectrum as well as measurements in normal and angular incidence. Fig. 3 shows experimental and calculated reflection spectra for a monolayer of 520 nm spheres grown on gold. Notice that we use the reduced frequency $\omega = \sqrt{(3)}\Phi/(2\lambda)$ in order to compare on a scaled manner the optical response of samples of different diameters. Here, the modes of the system appears at normal incidence as dips in a nearly flat background of high reflectance. The background reproduces the

optical response of the gold film, where the drops in reflectance correspond to those resonances of the leaky modes of the system available to be coupled to due to the periodicity of the system [8].

The spectral position is determined by the dispersion relation of each of that modes which is fundamentally dependent on the kind of lattice considered (hexagonal in this case) and the refractive index contrast between the spheres ($n_{PS} = 1.58$) and the surrounding media (air). As can be observed in Fig. 3b we have also studied by mean of FDTD simulation the toital field intensity profile for the modes shown in the above spectra. WE identified two kind of modes. On the one hand, we have named SPP-like modes those modes showing most of the field concentrated below the sphere and close to the metallic film. As we have recently studied (not published yet) it is possible to excite surface plasmon polaritons if the gold film with this kind of structuration. It is confirmed by the fact that most of the field is concentrated below the spheres for G1 and for G3. On the other hand, we have also obtained another kind of mode that we have named WG-like. It is the case of the G2 mode in Fig. 3. For this kind, field is concentrated mainly within the dielectric part of the structure (the spheres). Moreover, a model based on theory of dielectric waveguides demonstrates that the WG-like modes can present the same properties than those modes of a fully dielectric PC slab [8].

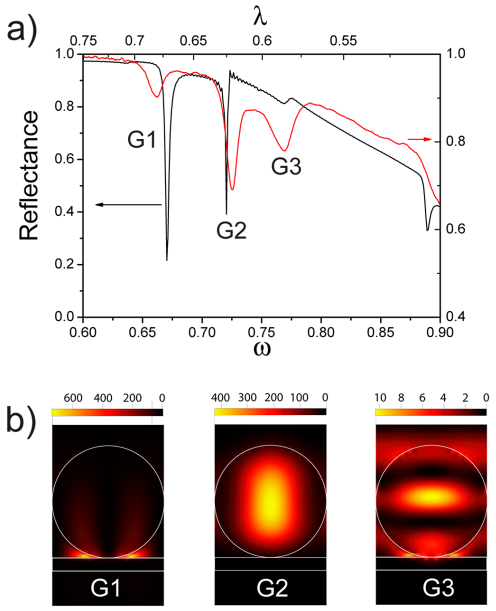

Figure 3: a) Calculated (black curve) and measured (red curve) normal incidence reflection spectra of a monolayer of 520 nm PS spheres grown on a gold substrate. b) Total-field-intensity distribution of selected modes (as indicated in Figure 2a).

It has to be notice that, as we were looking for large field confinements, both type of modes present large values for that property. In case of G3 the total intensity values may not be too high but this fact is related mainly to the gold absorbance. Recent results have shown that for metals with no absorbance at that spectral range the intensity values are comparable to those of the G1 andG2 mode [9].

Enhancement of spontaneous emission

The study of the optical properties of the hybrid mononolayer showed us that a strong field confinement can be obtained at any frequency in the VIS-IR range by tuning the sphere diameter of the spheres. Besides, we can also chose where most of the field is going to be concentrated. Furthermore, as a next step, we thought of using those regions of large field concentration to enhance the emission rate of molecules strategicly placed within the structure. The enhancement in the spontaneous emission was expected by means of the Purcell effect used in other kind of photonic structures to obtain either enhancement or suppresion of emission [10].

In this case, we have fabricated exactly the same sample studied to obtain the spectrum in Fig. 3 but using commercially available PS spheres doped by Rhodamine 6G. Rhodamine present its maximum absorbtion efficiency at 550 nm (aprox.) while for emission the maximum take place at $\lambda = 612$. In order to pump the dye as far as possible from the overlapping between emission and absorbtion, we used a CW (although 12 ps pulsed configuration was also available) diode laser at $\lambda = 485$ nm for the photoluminescence measurements.

If one test the emission of the dye doped spheres in the hybrid monolayer configuration one founds the emission spectra shown in red in Fig. 4. In that figure, black solid line stands for the reflectance spectra of the hybrid monolayer and red dashed line shows the reference for emission which in this case is a monolayer made of the same spheres and grown on silicon instead of gold. As can be observed, the emission of the reference does not show luminescence enhancement at any frequency which agree with the very low field confinement

for the full-dielectric structure (see ref [5]). On the contrary, for the sample grown on the gold substrate, a large enhancement of the emission takes place for the mode located at $\omega = 0.72$, which, as explained before, corresponds to a WG-like mode (G2). For this mode, the electric field is mainly confined in the sphere, where the emitter is homogeneously distributed. A 20X enhancement in emission is observed for this mode when compared with that of the reference sample grown on silicon. Emission is also enhanced over the background for the mode at $\omega = 0.77$ (G3), though much less than for the previous case. This is in agreement with the fact that this corresponds to a mode with some field confined within the spheres (see Fig. 3) although in a much smaller value than for the G2 case.

As next step in the enhancement of emission we performed an angular and polarized resolved spectroscopy of both, reflectance and emission spectra. From the later measurement it is possible to obtain the experimental dispersion relation, that is , the set of pairs (ω,k) available for each mode that we previously shown to be measurable as thin dips in reflectance. As we are studying an hexagonal lattice the angular patter will be dependent on the polarization but also on the direction scanned along the crystal. From the angular emission pattern it can be obtained valuable information about which modes present larger enhancement, but also the angular pattern at a given frequency which is a must for any kind of emissive device based on PC technology.

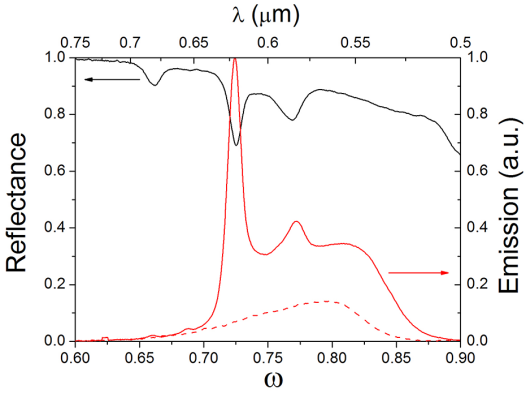

Figure 4: Normal incidence reflection (black curve) and emission (red solid curve) from a ML of 520 nm PS spheres deposited on a gold substrate. The emission from a ML of identical spheres grown on a silicon substrate (red dashed curve) is plotted for comparison.

To optically characterize the samples, angle and polarization resolved reflectance measurements were carried out with a large-numerical-aperture (0.75) 40X objective coupled to a microscope under white light lamp illumination. A 1-cm-large image of the back focal plane of the objective was formed outside the microscope and an optical fiber (100 μm diameter core) was scanned across the image so that different fiber positions provide spectra that can be associated with different angles of incidence/collection. Angle-resolved measurements were collected along different high symmetry directions for which the sample was oriented employing the hexagonal diffraction pattern characteristic of these systems under monochromatic or white-light illumination. Angle and polarization emission measurements were collected using the same experimental setup as reflectance ones only that the sample was illuminated by the pulsed laser described above.

Fig 5 shows the dispersion relation for the same sample grown on gold for which normal incidence measurements were previously presented. Results along the ΓK direction in reciprocal space are presented, although similar results were also obtained along the ΓM direction. It can be observed how emission is channeled only by certain modes, as happened for normal incidence. This fact provides both directionality and polarization selectivity of the dye‘s emission. For p-polarized light, one can observe how most of the dye‘s emission couples to two modes originating from the WG-like mode G2 in normal incidence. For s-polarized light, emission couples mainly to two modes originating from the G2 and G3 modes, respectively, although with different efficiency. As we mentioned above, these two modes have WG-like (G2) and hybrid (G3) nature. No emission couples to the SPP-like modes observed at normal incidence since, as we increase the angle, the energy of these modes decreases and hence we move away from the dye‘s emission spectral range. As for normal incidence, for each pair (ω;k) where a mode of the system is available a large enhancement of the emission takes place when compared with reference of the silicon substrate case. However, the combination of a monolayer of spheres and a metallic substrate is not only advantageous from the point of view of enhanced spontaneous emission or polarization selectivity, as we have just seen. Directionality is also a consequence of the channeling of emission through the modes of the sample and could be easily extended to functional

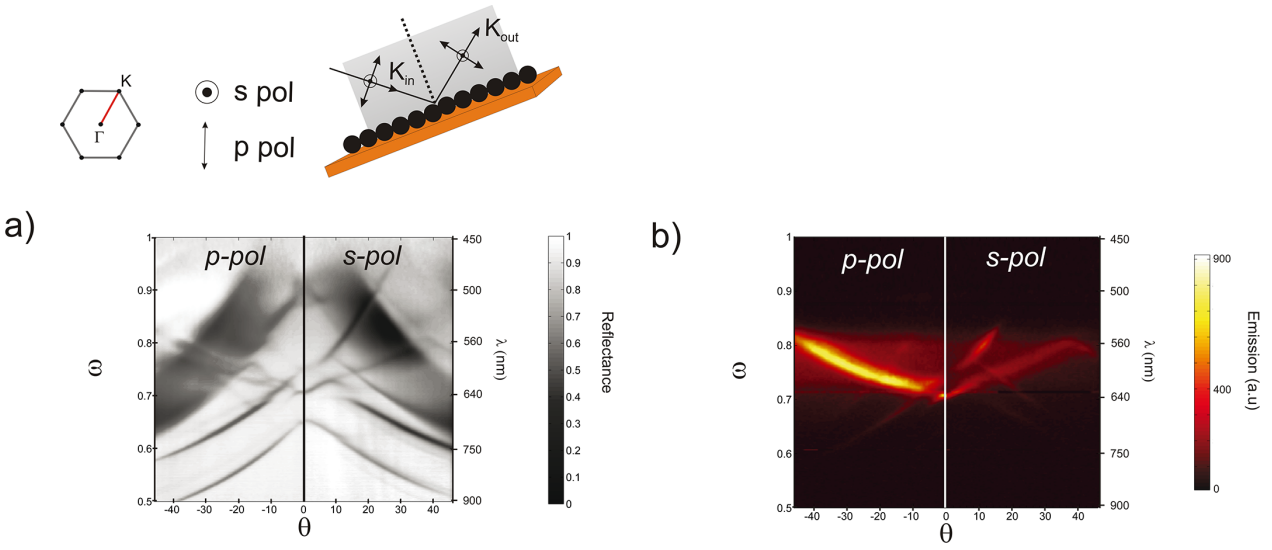

Figure 5: a) Angle-resolved reflectance measurements for a monolayer made of $\Phi = 520nm$ polystyrene spheres along the GK direction for both s (left) and p polarizations (right panel). b) Angle resolved emission in identical conditions to the reflectance ones.

devices in OLED technology.

Tuning the optical response

The functionality of the above-described plasmonic-photonic systems could certainly be enhanced by changing their optical response under an external stimulus, turning them into tunable devices. Counted among the possible strategies already tested in plasmonic systems are optical, electrical or magnetic modifications of the plasmonic modes. Alternatively one can modify the refractive index or lattice constant of the organic lattice to tailor the photonic dispersion and hence the optical response of the system. [23] Certain stimuli could even be employed to simultaneously tune both types of modes and the hybrid modes arising from them.

As a proof of principle of the tuning possibilities of the hybrid monolayer systems, we have obtained an easy-to-implement processing method based on an accurate control of the filling fraction ($ff = \frac{\Phi\pi}{3\sqrt{3}\Phi_0}$) of the lattice. The tuning of their optical response is obtained by homogeneously reducing each sphere of diameter Φ_0 while keeping the lattice parameter constant, i.e. by changing the filling fraction of the hexagonal lattice as studied previously for PCs on dielectric substrates. [24]. As the optical response is dependent on the field distribution within (and under) the spheres, the reduction of the spheres was expected to strongly modify that response, specially concerning the spectral position of each mode. To confirm this fact, we performed FDTD simulations for a monolayer made of PS spheres of 1 μm diameter and it was found that, whether it is SPP-like or WG-like, a blueshift for each mode is obtained in the normal incidence spectrum. A closer look at the calculated total field intensity profiles also shown that the field confinament is not lowered until the reduction of the spheres reach at least a

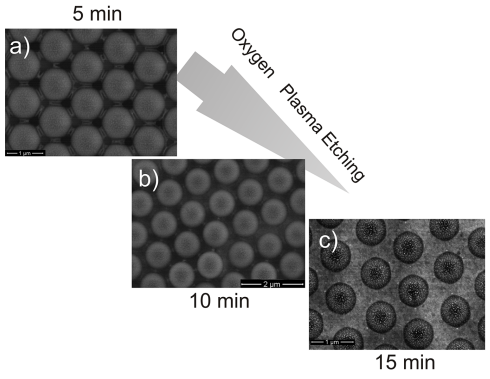

Figure 6: High magnification SEM images for three different stages of sphere reduction by oxigen plasma etching applied on a $\Phi = 1\mu m$ sphere monolayer over a gold substrate.

10% of its original value.

As a next step we perform the experimental demonstration. To do so, we applied an oxygen plasma etching on a monolayer of PS spheres deposited on gold. As well known from colloidal lithography [11], this technique allows a very accurate control on the reduction rate of organic spheres. We calibrate that reduction for two significant diameters (520 nm and 1 μm) for which the two type of modes present in the system fall in the VIS and NIR respectively. Fig 6 shows the evolution of the $\Phi = 1\ \mu m$ PS spheres at three different plasma times. It can be observed that the lattice parameter is kept constant while the diameter reduces. When the optical response of the sample after each reduction was compared with the calculated spectra a very good agreement was obtained. This comparison can be checked in the Figure 2 of our paper [4].

Tailoring of emission

Finally, we applied the tuning process described above to the samples made of dye doped polystyrene spheres and deposited over gold showing previous sections. In particular, we used the same diameter ($\Phi = 520$ nm) previously studied for emission in the close-packed case. Fig 7s shows in a countour map manner the evolution of the reflectance and emission spectra for different sphere diameters ($\gamma = \Phi/\Phi_0$ is a parameter standing for the diameter reduction). When the diameter of the spheres is reduced under plasma etching the blue-shift of the modes in reflectance is now observed in the visible spectral range. Upon comparison of reflectance and emission spectra it is evident that the peaks of enhanced emission (G2 and G3) follow the trend of dips in reflectance, corresponding to the modes of the structure. In this way one can effectively tune the sample‘s emission by controlling the plasma process. Beside the spectral shift, changes in the magnitude of emission enhancement taking place as the etching process advances are a combination of two factors. The first can be associated with the variations in the field confinement taking place as we reduce the sphere diameter and the second to the fact that, as the reduction process takes place, the modes of the system are swiped across the dye‘s broad emission so that enhanced emission should be more probable the closer a mode is to the dye‘s emission maximum.

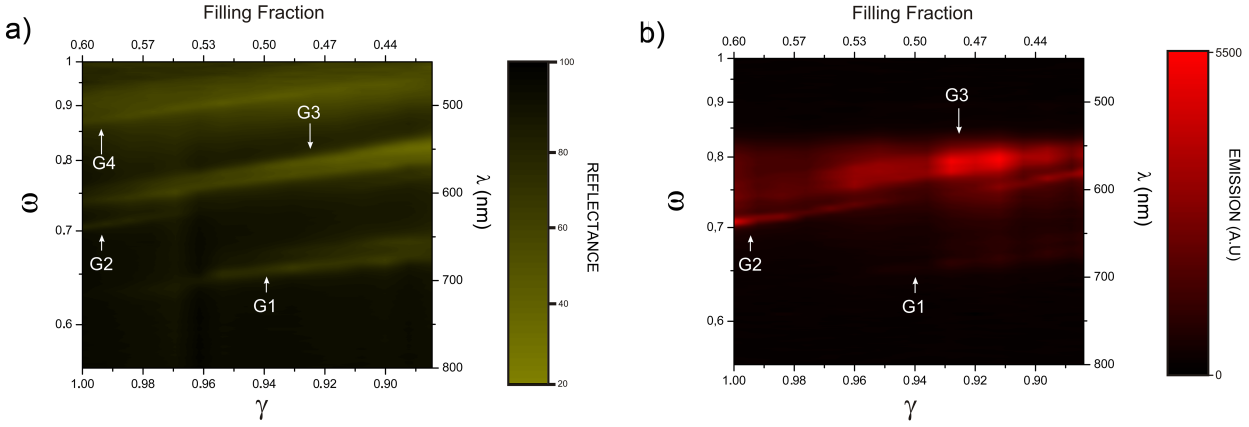

Figure 7: Reflectance (a) and emission (b) as a contour plot for a monolayer of $\Phi = 520$ nm dye-doped PS spheres in a continuous filling fraction reduction process. Oxygen-plasma etching was carried out from the closepacked scenario ($\gamma = 0.60$) to a final filling fraction of $\gamma = 0.41$.

Prospects of the research

As shown above, we have studied the extraordinary properties of a monolayer of dielectric spheres on top of a metallic substrate to obtain a strong control over the flux o flight. Besides, we have presented a proof of principle of different applications for such structures as light emission devices or tunable optical systems. Other groups works have shown proposals that take advantage of similar structures in the field of solar cells [1] and sensing[2]. It demonstrates their usefulness in fields that increase wellnes and sustainability of our society.

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