Research Article

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High-performance Nanocavities-based Meta-crystals for Enhanced Plasmonic Sensing

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Abstract: We report on a novel procedure of fabrication to easily obtain highly reproducible nanocavities-shaped photonic crystals with strong plasmonic performances. Thus, we also report on the morphological and optical characterization of the obtained structures. They are classifiable as 2-layers (organic and inorganic) photonic crystals based on iso-Y-shaped nano-cavities. Such novel designed structures are compelling candidates for the development of highly sensitive biosensors due to their unique surface plasmon resonances (SPRs) and SPR enabled surface-enhanced Raman spectroscopy (SERS). The planar photonic crystal comprises a polymeric (ZEP520A) layer (thickness ~80 nm) sandwiched between a layer of gold (~50 nm thickness) and a glass substrate. For what concerns the cavities’ shape, iso-Y units are chosen on the basis of their third order nonlinearity and are coupled in hexagonal-based configuration to produce extended meta-structures. The substrates are functionalized with a probe made by a self-assembling monolayer (SAM) of 4-mercaptobenzoic acid (4-MBA). The average SERS Enhancement Factor >10⁶ and SPR sensitivity of ~300 nm/RIU confirm that the proposed 2-layers iso-Y meta-structure is very suitable for high sensitive label-free plasmonic sensing.

Keywords: Photonic Crystals; Plasmonics; Sensors; Nanofabrication; Nanolithography; Raman; Surface Enhanced Raman Scattering (SERS); Localized Surface Plasmonic Resonance (LSPR); Metamaterials

1 Introduction

Photonic crystals [1, 2] and quasi-photonic crystals [3] in one, two and three dimensions are largely used in a wide number of applications fields: optical data storage [4], photonic applications [6–9], sensors [10, 11], metamaterials [12–16], etcetera. In particular, a large body of literature reported on their use as ideal platforms for plasmonic label free sensitive detection [17–21]. Surface Enhanced Raman Scattering (SERS) and Surface Plasmonic Resonance (SPR) are commonly used plasmonic techniques to detect and characterize very small amounts of matter [18, 21, 22]. Both SERS and SPR are based on the typical plasmonic resonance antenna effect of a metal surface on an analyte placed in its proximity [23]. In particular, the plasmonic resonance in SERS technique allows the amplification of the Raman signal of the considered analyte, while in the SPR technique allows to detect very low refractive index changes in proximity of a metal surface. Both SERS and SPR effects could be considered as “two sides of the same coin” since their efficiency is based - as mentioned - on the plasmonic response of the used surface. However, to obtain a same surface suitable for both techniques is - at all intents and purposes - a real challenge. In fact, even if the two phenomena are dependent on the plasmonic characteristics of the substrate, it is not ensured that a high-performance SERS platform can give a good SPR response or viceversa. The design parameters that are important for a SERS substrate are the size, shape, and composition of the nanostructures, which are important for controlling the SPR frequency that needs to be excited to generate the SERS effect. SERS or SPR substrates are nowadays mostly made of nano-pillars [24, 25], fabricated by e-beam lithography by selectively controlling their geometrical characteristics in terms of shape, dimensions and distance between them. By opportunely reconfiguring and choosing those parameters, it is possible to increase...
the sensitivity and the efficiency of SERS or SPR structures. Also the plasmonic coupling between nanocavities is already well known [26, 27]. In particular, attempts to make nanocavities-based photonic crystals based on a two layer configuration, by using a dielectric waveguide with high refractive index, sandwiched between silica glass and cladding - all grown on silicon wafers- [22] are reported.

The dual goal of our activity was to adopt a novel fabrication technique easy and fast, and to propose uniform highly sensitive plasmonic substrates with homogeneous density profiles for simultaneous sensing with SERS and SPR for use in biological detection, medical diagnoses, food safety and environmental monitoring. The plasmonic resonance is simply obtained by a deep in the gold layer that was created by deposition of the gold on a hole resist layer. In order to accomplish our last goal, we focused on structures based on iso-Y nano-cavities. Iso-Y shaped cavity is a single plasmonic unit. It is called "iso-Y" since it is made by a "Y" shape, where each one of the three arms of the Y is equal one to the other, and are disposed 120° one from the other (see scheme in Figure 4B). Iso-Y is known for its third order nonlinear response when designed as a pillar. The plasmonic response for iso-Y is high and mainly localized at the pillar boarders [28]. Then, we have decided to study the plasmonic response relatively to the coupling between iso-Y units when inserted a photonic crystal configuration to obtain homogenous, uniform, high sensitive and efficient SERS and SPR nano-structures.

2 Experimental

2.1 Materials

ITO glasses (BK7), 4-mercaptobenzoic acid and Glycerin are purchased from SIGMA ALDRICH. ZEP520A is purchased from ZEONREX® Electronic Chemicals. ZEP520A is a solution of 11% a copolymer (composed of methyl-styrene and chloro-methyl acrilate) and 89% anisole (solvent). The solution used in this work is obtained by a further dilution of ~47% (w/w) of ZEP520A in anisole, so that the final concentration of the copolymer in anisole is ~5.17% (w/w).

2.2 Sample cleaning and preparation

ITO glasses are washed by 2h sonication in a solution of a surfactant and H2O dd (1:1); then, they are rinsed with H2O dd and washed many times with Acetone and Isopropanol before to be dried under N2 flux. 300 µl of a solution of ~47% (w/w) ZEP520A in Anisole are deposited on a previously washed 1 cm2 ITO glass. The sample is then placed on the spin coater (Karl Suss CT62 V08) and spun for 60 seconds at 7000 rpm to obtain a final ZEP520A coating thickness of ~80 nm. At this stage the sample is ready to be patterned via Electron Beam Lithography (EBL).

2.3 Electron Beam lithography

The EBL instrument used is a Raith 150. The samples are exposed to 12.8 pA electron beam with an area dose of 22 μC/cm². Iso-Y nano-cavities are generated in the ZEP520A. For the layer development the sample is immersed for 90 s in MIBK (Methylisobutylketone), then 60 s in a solution (1:3) of MIBK: Isopropyl alcohol and, finally, is washed for 30 s in Isopropyl alcohol (IPA).

2.4 Gold deposition and characterization

Gold deposition on the copolymer (methyl-styrene and chloro-methyl acrilate) derived from ZEP520A deposition after the evaporation of Anisole is made by using a SISTEC CL-400C e-beam evaporator. A scheme showing the whole fabrication process is reported in Figure 2a. After gold evaporation (50 nm thick) the sample is ready to be used (see Figure 2b). Morphological characterization of the plasmonic nanostructures was performed by Scanning...

Figure 2: (a) Schematic diagram-process for the 2-layers iso-Y meta-structure realization; (b) Scheme showing the cross section of the sample.

2.5 Substrate functionalization with 4-mercaptobenzoic acid (4-MBA)

A SAM of 4-MBA on the gold substrate is simply obtained by depositing a solution of 4-MBA (100 µM in Ethanol) for 12 hours (overnight). In these experimental conditions the adsorption of the molecule on the gold surface is guaranteed, due to the presence of -SH group attached to an aromatic ring. After 12 h, the sample is washed many times with H₂O dd and EtOH and is dried under N₂ flux.

2.6 Optical set-up for SERS

SERS measurements are realized by using the QE Pro-Raman system (Ocean Optics), configured for λ = 785 nm. Laser power = 12 mW, with a grating of 1200 lines/mm and an input slit of 50 µm. The spectra are collected in the range between 200 - 2200 cm⁻¹, by using 10 s of acquisition time and a 50X (N.A. = 0.75) microscope objective (the Raman system is fully integrated into an upright microscope Olympus BX51). A Scheme for the Optical Set-up for SERS is reported in Figure 1. Mapping experiments were run by a confocal Raman spectrometer (Horiba-Jobin Yvon Mod. Labspec Aramis) operating with a diode laser excitation source emitting at 785 nm. The 180° back-scattered radiation was collected by an Olympus metallurgical objective (MPlan 50, NA = 0.75) with an exposure time of 0.7 s; a grating with 600 grooves/mm was used throughout. The radiation was focused onto a CCD detector (Synapse Mod. 354308) cooled at ~70 °C by a Peltier module. The SERS substrate was placed on a piezo-electrically driven microscope-stage and scanned at a constant stage speed in the x–y plane with a 2 µm step size. The SERS spectra were collected in the Raman-shift range 800–1800 cm⁻¹.

2.7 Optical set-up for SPR

SPR measurements are realized in transmission by using an Ocean Optics halogen white Lamp, an objective 40X, N. A. 0.65, and an Ocean Optics Spectrophotometer coupled to an optical fiber with core of 50 µm diameter to detect the signal. For details see Figure 3.

Figure 3: Optical LSPR set-up.

3 Results and Discussion

We report on the fabrication process, functionalization, morphological and plasmonic characterization of iso-Y shaped nanocavities-based photonic crystals. The iso-Y shaped unit was chosen since already well known and described in literature - even if in form of nanopillars - since it is used to enhance the third order nonlinearity in plasmonics [28]. The nano-cavity configuration allows a large distribution of the analytes on a surface, while
the nanopillars can be considered very confined regions. Usually, the process to produce nanocavities-based photonic crystal for plasmonic purposes is complex involving many steps, time consuming procedures and/or the use of EBL and Ion-beam, etching, et cetera. Firstly, we report an easy way to obtain nano-cavities of metal surface on a co-polymer methyl styrene and chloro-methyl-acrylate (the solid part of the ZEP520A solution). It is extrapolated by the method to produce high-sensitive plasmonic substrates made on an array of nanopillars attached to a conductive glass. The nano-lithographic process is mainly made by the following series of steps: 1) a positive resist is spin-coated on a conductive glass; 2) the Electron Beam exposes the resist in correspondence of the designed patterns (proper nanolithography); 3) the developers series are used to remove the exposed holes; 4) gold is deposited on the sample. Finally, in order to obtain a substrate made of gold nano-pillars is sufficient to operate with a 5) lift-off procedure, by dissolving the co-polymer on which the gold is deposited and leaving the nano-pillars attached on the substrate. At this stage, we noted that a two layers nanocavities-based plasmonic sample is easily obtainable by just omitting the last fifth lift-off step from the mentioned procedure. In spite of the number of works on the argument and on the very large use of ZEP520A, there is no evidence in literature, as far as we know, on the feasibility of nanocavities-based plasmonic substrates in this simple manner. The morphological goodness of the obtained structure is assessed by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy measurements of an extended patterned area (as reported in Figures 4 and 5). The pattern is constituted by the periodic repetition of iso-Y unit whose meaning will be reported below in the text. The multiplicity of nanocavities constitutes a photonic crystal of which the unit is designed on the basis of a hexagonal cell (see picture in Figure 4). The photonic crystal has two different periodicities: 1) a first periodicity, the pitch of which is $\Lambda = 346$ nm, due to the minimum distance between two neighbor iso-Y units; 2) the periodicity with longer pitch $\Lambda = 600$ nm (see Figure 4). The very high quality of the entire meta-structure is evident from the SEM measurements, since the cavities are well fabricated and uniformly repeated on x, y directions of the plane (Figure 4). The iso-Y unit is also reported in the inset of Figure 4 and the values for the expected dimensions for each single iso-Y (reported in the scheme of Figure 4b) are very accurately respected, and transferred with high precision on the meta-structure. However, to further confirm the goodness of the fabrication process that we propose, Atomic Force Microscopy and topographic profile measurements were performed on our 2-L meta-structure, in order to explore even the z dimension (the measurements are reported in the graphs of the Figure 5). In this case it is appreciable the good quality of the iso-Y cavities. In fact, the deepness of each cavity is in the range of $\approx 65$ nm, that is close to the expected thickness for ZEP520A, deposited on the 2-layer meta-surface. Even in this case, it is confirmed the good quality of the entire structure in terms of homogeneity, uniformity and units repeatability in x, y, z.
Figure 6) [29, 30]. Furthermore, our structure can be considered as a plasmonic crystal combining properties of both photonic crystals and plasmons, and exhibits a rich variety of different interactions with incident light [31–34]. The resonant peaks in Figure 6 can be attributable to the excitation of plasmonic and photonic modes where surface plasmon polaritons form standing waves and create band edge resonances. These band edge resonances can also couple with photonic crystal modes from the dielectric layer and Localized SPR modes. In the complex hybrid structure considered here, the patterned dielectric layer might play a two-fold role, acting both as a diffraction grating for the excitation of surface plasmon polaritons and, at the same time, as a guiding layer supporting photonic modes. For a proper resonance classification we are going to numerically compute extinction spectra and electric field intensity maps at the extinction maxima. Furthermore, to identify the different photonic and plasmonic resonances as well as surface plasmonic bandgaps we shall perform broadband reflectance spectroscopy in order to compare spectra on uncoated and Au-coated samples [23]. This work is in progress and will be fully discussed in another paper.

Figure 6: LSPR sensitivity for iso-Y-based meta-structures. (a) Extinction is calculated vs wavelength in presence of Air (black line), H2O dd (red), Glycerin (green), Anisole (blue). (b) Linear plot of the LSPR resonances of the sensor as the refractive index of the embedding medium varies.

In order to assess the SPR sensitivity of the system, we have chosen the maximum extinction peak (650 nm). The extinction is measured in four different conditions in order to calculate the sensitivity of the meta-structure for SPR: a) versus air (n = 1); in this case the peak recorded is specific for the considered plasmonic structure and for the iso-Y based metacrystal is at wavelength \( \lambda \approx 690 \text{ nm} \); b) versus water of which the refractive index is \( n \approx 1.33 \): in this case the peak shifts to 741 nm; c) versus glycerin, of which the refractive index is \( n \approx 1.475 \), and the peak further red shifts reaching a maximum extinction at \( \lambda = 788 \text{ nm} \); d) versus anisole, of which the refractive index is \( n \approx 1.516 \), and the peak further red shifts reaching a maximum extinction at \( \lambda = 803 \text{ nm} \). At a first glance, the differences between the peak positions are very clear, being in the order of many nanometers even for small \( \Delta n \). By monitoring the peak shift, it is possible to produce a linear fit, of which the slope’s degree provides the sensitivity degree (S) of the considered plasmonic meta-structure. In our case, by fitting the obtained curve the sensitivity value is very high \( S = 299 \pm 14 \text{ nm/RIU} \) (correlation factor for the fit \( \sim 0.99 \)), showing that the proposed meta-structures are a good platform for LSPR measurements. The observed sensitivity of 299 nm/RIU is favorably compared to other Localized SPR-based sensors. It ranks this interface among the highly sensitive LSPR sensors with plasmon band in the visible at 650 nm [35–37].

A second evaluation on the fabricated meta-structure was made by measuring the SERS response of the system (Figure 7). In order to perform SERS measurements, we have used a self-assembling monolayer (SAM) of 4-mercapto-benzoic acid. Such a molecule is easily adsorbed on the gold surface to form a SAM, due to the presence of sulphidric group (-SH) in its structure. Furthermore, the sulphidric group is linked to an aromatic group, in para position with respect to the acid, making this molecule a good reference for SERS measurements [25]. The SAM of 4-MBA is easily obtained by depositing overnight 300 \( \mu \text{l} \) of a solution of 4-MBA in Ethanol on the metasurface. The SERS spectrum was obtained as a mean of 20 measurements realized in different areas of the nanopattern. A first evidence of the huge plasmonic response in terms of SERS is shown by the signal intensity of all the peaks in the SERS spectrum that is in the order of \( \sim 10^6 \) counts. Particularly intense is the peak at \( \sim 1074 \text{ cm}^{-1} \) - typical of the vibrational modes of the aromatic groups of the mercapto-benzoic acid - that reaches \( \sim 100k \) counts. Furthermore, the comparison of SERS signal with the spontaneous bulk Raman signal offers the enhancement factor (EF) for the structure. The EF was calculated by taking into account the area of higher intensity peak \( I_{\text{SERS}} \) in the SERS spectrum (at 1074 cm\(^{-1} \), see Figure 7) and comparing it with the area of the peak at 1096 cm\(^{-1} \) of the bulk in the Raman spectrum \( I_{\text{NR}} \), see inset of Figure 7), as indicated in the following formula (both the peaks represent the vibrational modes (stretching) of the aromatic group in the 4-MBA molecule):

\[
EF = \frac{I_{\text{SERS}}}{I_{\text{NR}}} \frac{N_{\text{SERS}}}{N_{\text{NR}}}
\]

where \( N_{\text{SERS}} \) and \( N_{\text{NR}} \) are the number of molecules that contribute to the SERS signal and to the Raman signal, respectively.
The number of molecules that contribute to the SERS signal is dependent on the area of the laser spot ($A_{\text{laser}}$), on the filling factor (FF) and on the cross section for 4-MBA ($\sigma$), as indicated in the following equation 2:

$$N_{\text{SERS}} = A_{\text{laser}} \times \text{FF} / \sigma$$

(2)

in our case, $A_{\text{laser}} = 1.28 \text{ µm}^2$ [31], the filling factor for gold in our structure is FF = 1, and the cross section $\sigma = 0.33 \text{ nm}^2$. So that the $N_{\text{SERS}} = 3.14 \times 10^6$.

The number of molecules that contribute to the Raman bulk signal is given by the following equation 3:

$$N_{\text{NR}} = V_{\text{exc}} \times N_{\text{Av}} \times D_{\text{AMBA}} / W_{\text{AMBA}}$$

(3)

where the excitation volume $V_{\text{exc}} = A_{\text{laser}} \times D_{\text{depth}}$, the focus depth $D_{\text{depth}} = 2\lambda/(NA)^2$, the Avogadro’s number is $N_{\text{Av}} = 6.022 \times 10^{23} \text{ mol}^{-1}$, the density of 4-MBA is $D_{\text{AMBA}} = 1.5 \text{ g cm}^{-3}$, the molecular weight for 4-MBA is $W_{\text{AMBA}} = 154.19 \text{ g mol}^{-1}$, the used excitation wavelength $\lambda = 785 \text{ nm}$ and the numerical aperture of the objective is N. A = 0.75. So that, $N_{\text{NR}} = 21 \times 10^9$.

Finally, the calculated value for the SERS enhancement is: EF $\sim 1.3 \times 10^6$. Such a value makes our structure suitable for high performances label-free SERS.

Figure 7: Comparison between intensities (Raman intensity (counts) vs wavenumbers (cm$^{-1}$)) of a SERS signal (black line) for 4-MBA obtained by depositing overnight a solution of 100 µM of 4-MBA in EIOH on the iso-Y metacystal and the spontaneous Raman from the bulk obtained depositing a solution of 0.1 M of 4-MBA in EIOH deposited on a glass surface (red line). Raman spectrum of 4-MBA, recorded after deposition of 0.1 M of 4-MBA, is also reported in the inset. For these measurements we used the QE Pro-Raman system.

Furthermore, by considering that iso-Y based meta-structures have an area of 200 $\times$ 200 µm$^2$ and that the plasmonic response was examined in each part of this area with negligible differences on the SERS signal, the obtained results suggest a uniform plasmonic near field distribution on our sample. Thus, the characterization of the SERS substrate was completed by mapping experiments whereby the Raman images were reconstructed by considering the space-distribution of the peak intensity at 1073 cm$^{-1}$ over 45 $\times$ 45 µm surfaces. The spectra collected across the whole sensing area (a typical map is displayed in Figure 8A) are very consistent in terms of overall pattern and absolute intensity. The average EF value ($5.3 \times 10^9$) was close to that obtained by Raman macrosampling and, more importantly, remarkably uniform. This is demonstrated by the homogenous color of the Raman image (see Figure 8A) and the closeness of the average spectrum with those relative to the average spectrum ± standard deviation (see Figure 8B).

Figure 8: A) Typical Raman image (intensity-color map) reconstructed by considering the intensity of the 1073 cm$^{-1}$ peak as a function of the position in a 45 $\times$ 45 µm area of the SERS substrate. B) Average SERS spectrum of 4-MBA (red trace) and average SERS spectrum ± standard deviation (black and blue traces, respectively). For these measurements we used a confocal Raman spectrometer (Horiba-Jobin Yvon Mod. Labspec Aramis).

The near field distribution is dependent on the arrangement and on the shape of the units of a plasmonic structure, and on the intensity, wavelength and polarization state of the incident light (along $\chi$, double arrow in Figure 4). Moreover, the generation of a large plasmonic field is the resultant of the single moments induced by light - with a specific polarization - related to each cavity. In our case, it is to be admitted that the proposed hexagonal configuration for the photonic crystal based on iso-Y-shaped cavities ensures a strong plasmonic signal intensity and contemporary ensures a homogenous near-field distribution, reasonably due to a large plasmonic coupling between nano-cavities. It’s also worthwhile to notice that, there are sharp tips inside the nanoholes, which produce additional field enhancement for SERS.

Finally, due to the versatility of the system, that is contemporary usable in SERS and in SPR contexts, the iso-Y based photonic crystal here described is really suitable for high-performance label-free sensing and bio-sensing,
by opportunistically modifying and functionalizing the SAMs of the molecule probes.

4 Conclusions

A plasmonic crystal for simultaneous sensing with dual-resonance cavity SERS and SPR is fabricated. Such a high quality nanocavity-based 2-layers 2D photonic crystal is realized in a relatively easy manner, by simply modifying a pre-existing nanolithography procedure. The proposed fabrication technique may bring significant progress to the field thanks to its low cost and relatively fast processing time. Such a plasmonic crystal is based on a largely used copolymer (ZEP520A) and gold thin layers. The morphology of the meta-structure based on nano-cavities, from a side ensures that large areas between units can be coated with the chosen analytes while, from the other side allows to obtain strong intensity plasmonic signals and remarkably homogeneous near field distributions. Thus, we envisage that this dual SERS-SPR sensing structure with powerful local refractive index detection and Raman enhancement offering high-performances in SERS (EF >10^6) and high sensitiveness in SPR (~300 nm/RIU) regimes can find many future applications for high-performance plasmonic sensing and bio-sensing.

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References

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[38] The SERS laser spot effective area (A_laser) is dependent on the laser density (D_laser) as in the following equation: A_laser = π(D_laser/2)^2 = 1.28 μm^2 = 1.28 * 10^6 nm^2, being D_laser = λ * 1.22 / N.A. = 1.276 μm.