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Fabrication and characterization of silver inverse opals

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Abstract

Artificial structures with two- or three-dimensional arrangement of materials (photonic crystals) are being considered in recent days a key structure for the fabrication of advanced optical devices with the potential to substitute present electronics by all-photonic systems in the near future. Special interest has also arisen for their use as chemical sensors and in the fabrication of solar cells. In this work, a fabrication process for silver artificial structures from a colloidal solution of polystyrene spheres is presented. The colloidal spheres are arranged onto a glass substrate to form an artificial opal that is subsequently infiltrated with silver.

Additionally, the structural and optical properties of the fabricated structures are studied. The structural characterization of the opals shows good order in the long scale. Reflectance measurements of these samples present a reflection peak centred around 800 nm. SEM images of the silver infiltrated opals show that the infiltration has been carried out successfully. Even so, the optical characterization of the infiltrated samples shows a big intensification of the original reflectivity with a displacement of only few nanometres from the original peak. After the removal of the spheres, the samples show total inversion.

Keywords: Photonic crystals; Self-assembly; Opals; Polystyrene; Reflectance; Silver

1. Introduction

Periodic three-dimensional structures have gained a great interest in the last decade due to their potential applications in a wide variety of fields, ranging from photonic devices to sensors. The photonic properties of such structures have been widely analyzed [1,2], being this research mainly focused in dielectric systems. Besides, some studies have been carried out showing photonic band-gaps (PBG) in metallic 3D arrangements [3–7]. The large real part of the dielectric constant of metals makes metallic structures very interesting for the fabrication of photonic devices, which may show, apart from photonic behaviour, a plasmonic resonance effect [8]. It has been demonstrated that some metals, when taking into account absorption, loose part of their photonic properties. However, this property does not affect equally to all metals, been silver one of the less affected [9].

Most of the theoretical and practical research performed on metallic photonic structures is focused in the millimetre and microwave frequencies [3,5,10–13], owing to the fact that metals are absorbing at optical and near infrared frequencies. Some studies, anyway, suggest that it is possible to create a metallic structure with interesting optical properties in the visible or near infrared frequencies [14,15].

In a more practical approach, there are many different applications for this kind of devices. In the field of pure optics, metallic structures have been demonstrated to be used as filters [16]. In the field of telecommunications, they are been studied to work as antennas [17], waveguides [18] and as components for microwave integrated circuits [19]. Moreover, the applications of metallic oxides photonic structures in electrochemistry, especially in the fabrication of solar cells [20] and electrochemical capacitors, are also very promising [21]. In addition, the application of this type of structures in sensing, in particular in the construction of chemical sensors mainly based on plasmonics, has been also studied [22].

One of the most challenging issues in order to obtain such metallic structures is the fabrication of the device. Different

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techniques have been used with the aim of achieve well ordered 3D metallic structures and can be divided, basically, into micromachining, lithographic [23] and self-assembling techniques [24–28]. Comparing to the micromachining approach, self-assembling techniques are the most promising method due to its low cost and its relative simplicity.

In this work, we present the fabrication and characterization of a 3D metallic structure. The structure is made via self-assembly techniques, using electrodeposition for the infiltration of the metal.

2. Experimental

2.1. Fabrication process

The fabrication process of the silver nanostructures is divided in three main steps: polystyrene template fabrication, silver infiltration and polystyrene template removal.

The three dimensional polystyrene templates have been fabricated by vertical deposition from a colloidal solution onto a 5 mm × 5 mm glass substrate. In order to carry out the electrodeposition, a conductive layer is needed and, for this reason, the substrate is covered with indium-tin oxide (ITO). A solution of 419 nm polystyrene spheres, 1% in weight, is used for the fabrication of the artificial opals. The substrate is placed into a 500 mm^3 chamber filled with the polystyrene solution and it is positioned with an inclination of 10°. The vessel containing the chamber is then placed into an oven at 40 °C for 5 h. Afterwards, it is cooled at room temperature for several hours and no sintering process is applied to the samples. All the process is carried out in a clean-room atmosphere.

Silver is then infiltrated in the polystyrene opals by electrodeposition from a thiosulfate solution. This method of silver electrodeposition is chosen due to the toxicity of the traditional technique, which employs cyanide-based plating solutions [29]. The aqueous solution is 0.2 M $AgNO_3$/2 M KI/20 mM $Na_2S_2O_3$. The concentration of thiosulfate has been adjusted in order to improve the stability of the solution. The electrodeposition has been carried out at a constant current density of 1500 μA/cm^2, varying the deposition times from 10 to 50 min. A three-electrode configuration has been employed for the electrodeposition, where both the counter and the reference electrodes are Platinum films sputtered onto a Silicon substrate. After the deposition, the samples are rinsed-off with ultra pure water. All the samples are dried at room temperature for several hours prior to their optical characterization.

Finally, in order to remove the polystyrene spheres, two different methods have been tested on the samples after the infiltration, one physical and the other chemical. The physical method consists in a 5.5 h calcination process at 300 °C in air atmosphere (80% N_2/20% O_2). The chemical method comprises the removal of the spheres by soaking the samples in toluene.

2.2. Characterization

All the samples are optically characterized before and after the infiltration. Reflectance measurements at different incident angles, 15°, 30° and 45°, are carried out using a standard white reference. The measurements have been performed with the illumination of a 50 W halogen lamp, using a spectrometer ORIEL MS257 and a CCD camera ANDOR DU401A-BR-DD for the measurements.

The morphological characterization of the samples has been done by SEM techniques before and after the infiltration and after the removal of the spheres. The composition of the deposited silver has been studied by means of EDX.

3. Results and discussion

Polystyrene opals with good quality are obtained as observed in Fig. 1. These samples possess order at long scale, although a number of cracks appear on them. The cracks are thought to be generated during the drying process. The samples are rugged enough to withstand the infiltration process without substantially loosing their morphology.

Electrodeposition is a very convenient process for the infiltration of the opals, because this method produces a down-to-top penetration of the material into the spaces of the polystyrene structure. This allows a complete infiltration of the opal. The electrodeposition has been carried out successfully, as shown in Fig. 2, finding silver on top of the opal. It has also been noticed that the silver does not completely cover the polystyrene spheres around small structural defects, such as vacancies or dislocations. This may be due to the extra volume of silver that must be infiltrated locally around the defects. As electrodeposition is, in principle, a homogeneous process, this extra volume is not available to fill the extra space and therefore these small heterogeneities are generated. This underlines the importance of starting the infiltration process with a highly ordered polystyrene opal.

Several depositions of silver with different lengths: 10, 20, 30, 40 and 50 min have been performed. A dependence on the grain size of the silver with the deposition time in continuous

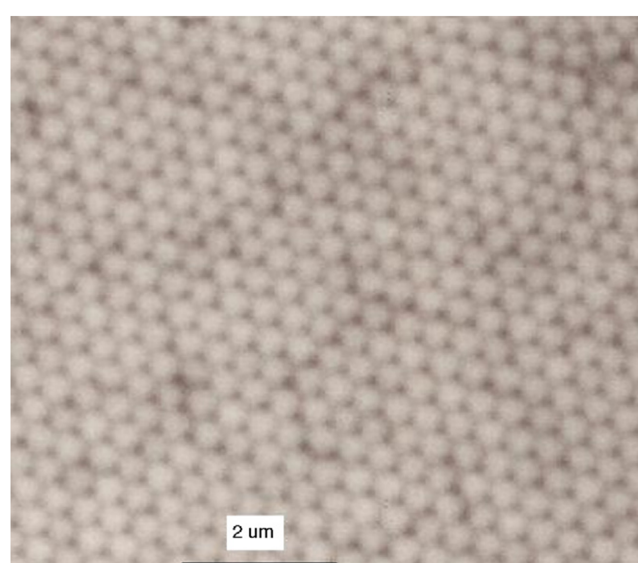

Fig. 1. Polystyrene opal.

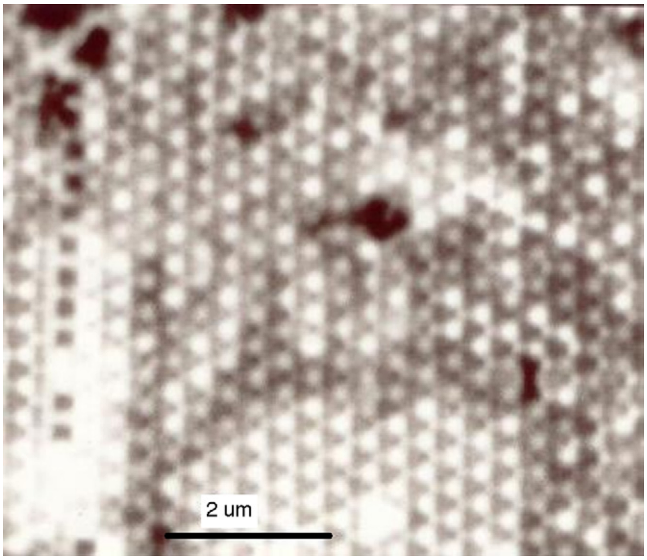

Fig. 2. Silver infiltrated opal.

metallic films deposited on bare ITO is observed. This feature ranges from 500 nm for 10 min deposition time, to 18 μm for 50 min of deposition. Moreover, the external aspect of the silver electrodeposited into the polystyrene opals, does not seem to have a direct dependence on the deposition time. However, the resolution of the electronic microscope is not high enough to measure the grain size of the silver infiltrated into the opals, which means the grain size of these films is much smaller than that of the silver deposited onto bear ITO.

Inversion is one of the most critical parts of the process. Both methods, calcination and chemical removal of polystyrene, are standard techniques for the elimination of the spheres. The calcination seems to be a convenient process due to the low melting point of polystyrene. Although a 5.5 h process at 300 °C has yielded to some good results, it is observed that inversion is not achieved regularly. The resulting silver structures after the calcination process present plenty of damage probably originated by the mechanical stress generated in the calcination process. The chemical removal of the polystyrene using toluene, has led to total inversion of the structures, as can be appreciated in Fig. 3.

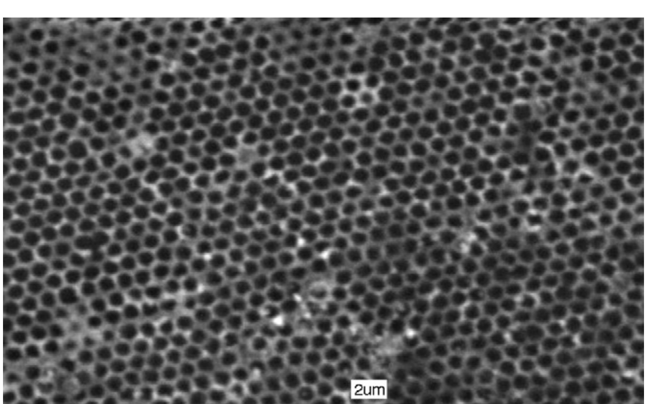

Fig. 3. Nanostructured silver after removal of the polystyrene spheres with toluene.

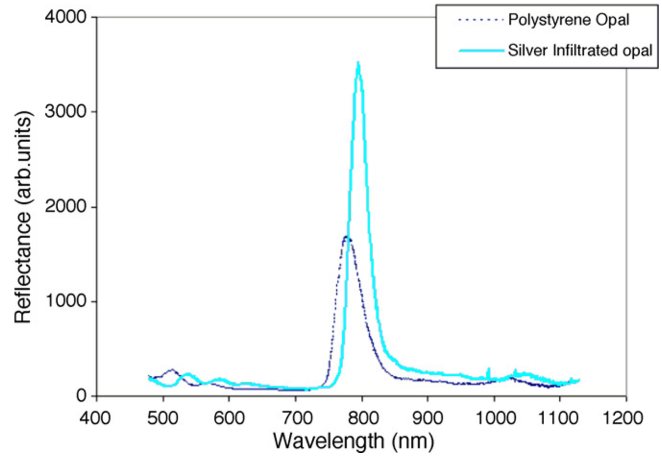

Fig. 4. Reflectance measurement of non-infiltrated and silver-infiltrated opals. Incidence angle is 45°.

The optical characterization of the polystyrene opals shows a reflectance peak at around 780 nm. The maximum of the reflectance is almost doubled when the opal is infiltrated with silver (see Fig. 4). The peak wavelength shifts an average of 16 nm towards longer wavelengths.

Our results suggest that silver introduces a greater dielectric contrast with polystyrene than air, incrementing accordingly the intensity of the reflected peak and introducing a shift to larger wavelengths. Small peaks in the visible appear for wavelengths smaller than 600 nm, but the intensity of these peaks is much smaller than that of the main peak.

The results of the optical characterization of the polystyrene opals at different angles of incidence are shown in Fig. 5. In this case, it has been observed that the main peaks shift towards shorter wavelengths as the angle of incidence increases. In both non-infiltrated and silver-infiltrated opals, the displacement of the peaks is close to 90 nm in total, as can be seen in Fig. 6.

The optical characteristics of the non-infiltrated polystyrene opals have been simulated using the Translight Software [30], available in the public domain. A good agreement between theory and simulations has been shown, as can be observed by

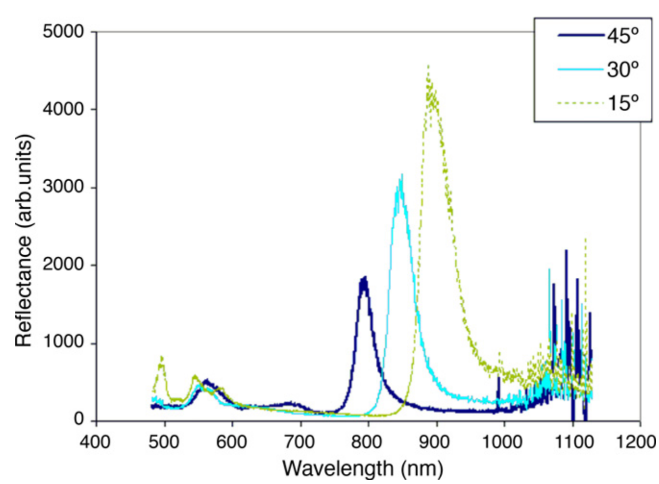

Fig. 5. Reflectance measurements of non-infiltrated polystyrene opals with incident angles of 15°, 30° and 45°.

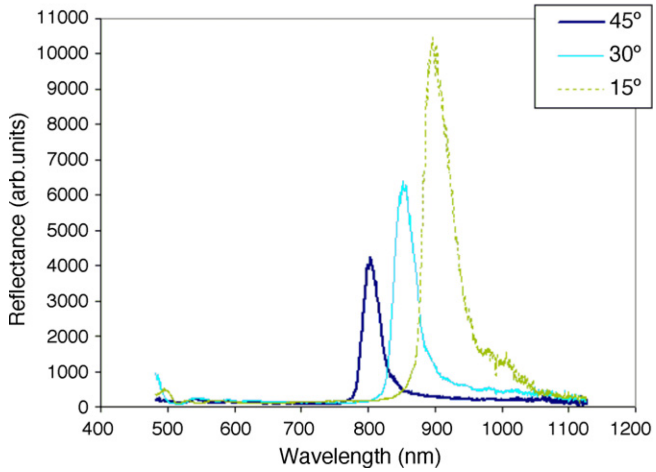

Fig. 6. Reflectance measurements of silver-infiltrated polystyrene opals with incident angles of 15°, 30° and 45°.

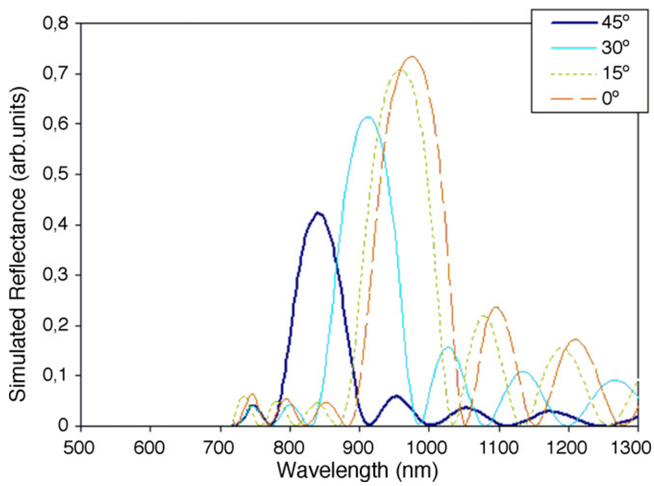

Fig. 7. Theoretical simulations of the reflectance of polystyrene opals with incident angles of 15°, 30° and 45°.

comparing Fig. 5, which shows the reflectance measurements of a polystyrene opal at different angles of incidence, with Fig. 7, which shows the simulated reflectance of the polystyrene structure.

4. Conclusions

We have presented a fabrication process to develop inverse metallic structures based on self-assembled colloidal polystyrene spheres and electrochemical deposition. The optical characterization of the structures shows an intensification of the reflectance when silver is infiltrated. The optical properties of the polystyrene opals are in good agreement with theoretical simulations. These results make this structures promising for photonic applications.

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