JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 4, April 2008, p. 809 - 812

Periodically nanostructured noble-metal thin films with enhanced optical properties

C. FARCAU*, V. CANPEAN, M. GABOR[a], T. PETRISOR jr.[a], S. ASTILEAN
Nanobiophotonics Laboratory, Institute for Interdisciplinary Experimental Research and Faculty of Physics, Babes-Bolyai University,M Kogalniceanu 1, Cluj-Napoca, Romania
[a]Materials Science and Engineering Faculty, Technical University, C. Daicoviciu 15, Cluj-Napoca, Romania

We present results on fabrication and characterization of a large variety of metallic and metalo-dielectric periodic nanostructures obtained by using a colloidal lithography technique. Their optical properties are dominated by surface plasmons excitation and can be tuned at the desired wavelength. Furthermore we show that the prepared nanostructures can be used to enhance the fluorescence signal of thionine dye molecules placed in their nanoscale vicinity.

(Received February 25, 2008; accepted April 2, 2008)

Keywords: Nanolithography, Noble-metal nanostructures, Surface plasmons, Thin films, Optical properties

1. Introduction

The increased scientific interest in noble metal nanostructures is due to their unique optical properties, which are absent in bulk metals [1]. When light is shined on a metal particle much smaller than the wavelength, collective oscillations of the conduction free electrons, which are generally known as surface plasmons, are excited [2]. Noble metal nanoparticles support localized surface plasmon (LSP) resonances at optical frequencies, while extended nanostructured metal-dielectric interfaces support also delocalized (propagative) surface plasmon polaritons (SPP). Applications of this unique phenomena range from integrated photonic circuits, near-field optics, to nanolithography, surface enhanced spectroscopies and optical (bio)sensing [3,4].

Several lithographic methods like X-ray lithography, electron beam and focused ion beam lithography are currently employed for the production of highly ordered nanoparticle arrays or thin films with periodical features. Although these methods have many advantages, by offering a good control over nanoparticle size, shape and ordering, they require huge and expensive systems.

Here we report on the use of nanosphere lithography [5] to produce a large variety of metallic and metalo-dielectric nanostructures with periodic features: metallic films over polymer nanosphere arrays (FoNA), triangular nanoparticle arrays (TNA), and metallic nanohole arrays (NHA). We show that they exhibit unique size-dependent optical properties, which we can tune by adjusting some experimentally controllable parameters: diameter of the polymer nanospheres, thickness of the deposited metallic films. Finally we show for the first time to our knowledge that silver FoNA can be used as active substrates to enhance the fluorescence emission of thionine dye molecules.

2. Experimental

For all the metallic nanostructures prepared and described here, the fabrication process started with the assembly of regular arrays of polystyrene microspheres (two-dimensional colloidal crystals) on a solid substrate. We used glass microscope slides of 24×24 mm size as solid substrates. The slides were sonicated in isopropylic alcohol for degreasing, then treated in piranha solution (mixture of 95% H_2SO_4 30% H_2O_2) for at least 30 min. We obtained highly ordered colloidal crystals by convective assembly technique. A droplet of water containing polystyrene microspheres (400 nm or 450 nm in diameter) in suspension was injected into the wedge between a substrate slide and a top slide which is positioned in close proximity with the substrate and tilted by an angle of 27°. As the top slide was translated across the substrate, a two-dimensional (2D) array of microspheres self-assembled on the substrate due to water evaporation and particles flow from the solution towards the meniscus. To obtain a highly ordered monolayer, speed of the deposition top slide, diameter of the spheres, concentration of the spheres in solution must be taken into account [6].

After the regular polystyrene sphere (PS) arrays are obtained two different routes can be followed in order to obtain the desired metallic nanostructure, as schematized in Fig. 1. Route A includes the following steps: the glass slide with regular PS arrays was transferred into a vacuum chamber (10^{-6} Torr) to deposit a metallic film (Ag or Au) on the PS by means of an electron-beam evaporator. The thickness of the deposited silver film was monitored with a piezoelectric crystal oscillator. In order to get a reliable internal reference for the optical properties of nanostructured film, we took care to deposit simultaneously a flat film of same thickness onto a small area free of spheres on the glass support. After this step metallic FoNA are obtained. During evaporation silver was deposited on top of the polymer spheres and also directly on the glass substrate through the openings created between each three

spheres in contact. By solvent removal (toluene) of the polymer spheres we obtain metallic TNA directly on the glass substrate.

An alternative approach, route B, which is still under development in our laboratories, comprises the following steps: the ordered PS arrays are etched in a reactive oxygen (plasma) atmosphere, and then the metal film is deposited. By etching the polymer spheres their diameter is reduced, the empty spaces between them become wider and thus the size of the triangular nanoparticles increseas. By controlling the etching time and conditions we control the shape and size of the metallic nanostructure obtained afterwards.

Topography of the obtained metallic nanostructures was studied by scanning electron microscopy (SEM). The optical properties of the fabricated silver and gold nanostructures were investigated by using a Jasco V-530 uv-vis spectrophotometer working with unpolarized light. Reflectivity measurements were performed on the same apparatus by using an interchangable Jasco SLM-468S reflectivity module. For the fluorescence studies we selected thionine molecules, which have a strong absorption band around 600 nm, wavelength which we will further see it is related to the optical properties of the FoNA substrates. A film of thionine molecules in aqueous solution was trapped between the nanostructured Ag substrate (100 nm Ag over 400 nm PS arrays) and a glass slide. The angle between the excitation beam and collection of the emitted fluorescence was 90°. For comparison we measured fluorescence from thionine films of same thickness, in the same experimental setup, by changing the FoNA substrate with i) a flat Ag film (mirror) and ii) a glass substrate. Fluorescence spectra were aquired by using a Jasco FP-6300 spectrofluorimeter.

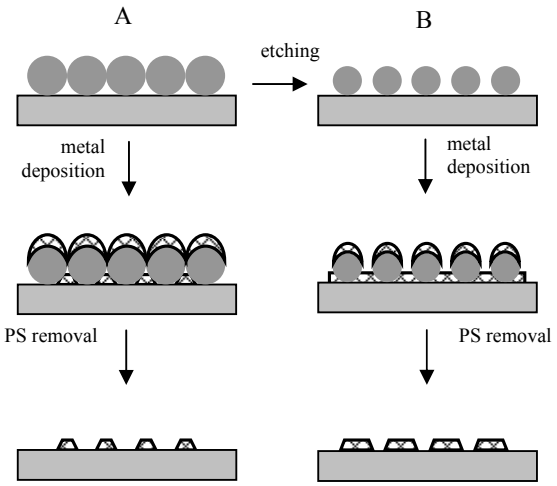

Fig. 1. Schematic representation of nanostructures fabrication process.

3. Results

Fig. 2 shows a collection of representative scanning electron microscopy (SEM) images of the fabricated nanostructures: silver films deposited over polystyrene nanospheres (a), silver triangular nanoparticle arrays (b), etched PS array coated with a gold film (c) and gold nanoholes array (d). The obtained metallic nanostructures always exhibit the defects present in the initial polymer spheres template, which is of polycristalline nature. However the ordered monocrystal domains cover areas of hundreds square micrometers. One can see by comparing Figs. 2a and 2c that the simmetry and period of the array are preserved after PS etching but in 2c the size of the spheres is smaller and they are not close-packed. This readily facilitates the fabrication of a larger variety of metallic nanostructures, as the periodically perforated gold film shown in Fig. 2d.

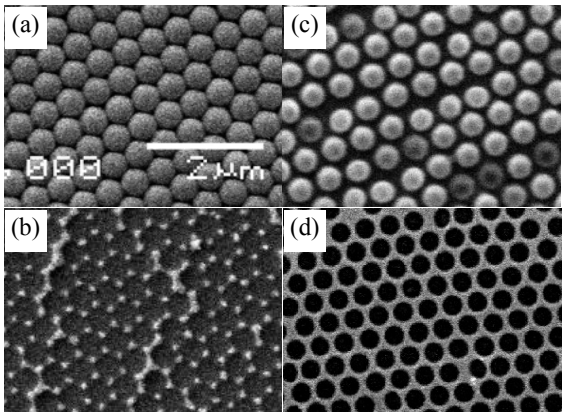

Fig. 2. Scanning electron microscopy images of: polystyrene spheres array (a); triangular nanoparticles array (b); etched polystyrene spheres array (c) and gold nanoholes array (d).

In Fig. 3 we present the optical reflectivity spectra of three specifically prepared FoNA samples: they are obtained by deposition of silver films of different thickness (50 nm, 75 nm and 100 nm) over regular arrays of PS of same diameter (400 nm). The broad reflectivity minimum centered around 600 nm is believed to be due to resonant surface plasmon excitation on the silver film [7].

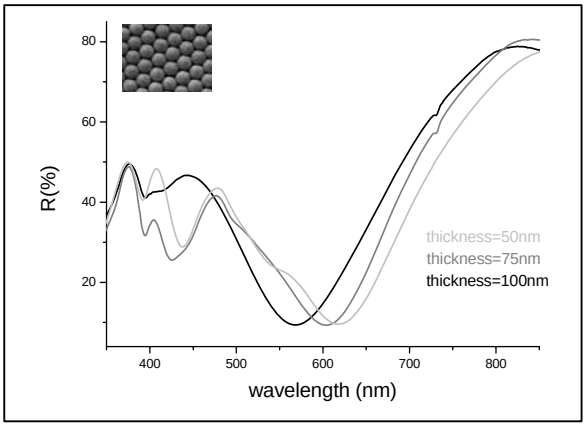

Fig. 3. Reflectivity spectra of Ag films of different thickness (50, 75 and 100nm) deposited over arrays of PS of 400 nm diameter arrays.

As the thickness of the deposited silver film increases the position of the broad minimum shifts to shorter wavelengths. We suggest that this is due to different coupling regimes between surface plasmons excited at the silver-air interface and those excited at the silver-polystyrene interface, or coupling between silver caps on top of the PS and silver nanoparticles on glass.

In order to verify the capability of NSL to tune the optical response of gold TNA (fig.2b) we fabricated a set of samples with different thickness of the deposited gold film. We used for this purpose identical PS arrays, so we obtained arrays of nanoparticles with the same in-plane width but different heights. Extinction spectra of TNA of same lateral dimensions but having different heights are presented in Fig. 4. The nanoparticles were obtained starting from arrays of PS spheres of 450 nm diameter and deposition of gold films of 30 nm, 40 nm and 50 nm thickness. Again one can see that by changing the thickness of the nanoparticles from 30 nm to 50 nm the resonance wavelength shifts from 858 nm to 800 nm. This is in good agreement with theoretical calculations, which shown that the nanoparticle shape determines the position of the resonance wavelength [8].

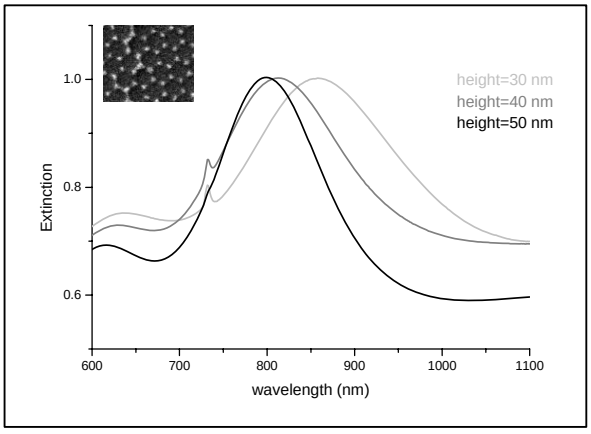

Fig. 4. Extinction spectra of gold triangular nanoparticles of different heights (30, 40 and 50 nm) and same lateral dimesions..

In Fig. 5 we present the fluorescence emission spectrum of an aqueous thionine film sandwhiched between a Ag FoNA substrate and a glass slide. Excitation wavelength was choosed at 590nm, which falls inside the thionine absorption band, but is also close to the surface plasmon resonance of the FoNA substrate. To make sure that the higher emission intensity of thionine film between FoNA and glass slide compared to that of the same film between glass substrate and glass slide is not a result of fluorescence emission reflected from the Ag FoNA substrate we performed the same measurement by sandwhiching the thionine film between a Ag mirror and a glass slide. The results prove that a flat Ag film actually quenches fluorescence, and therefore the higher emission of thionine placed in the vicinity of nanostructured surface must be related to a surface plasmons effect.

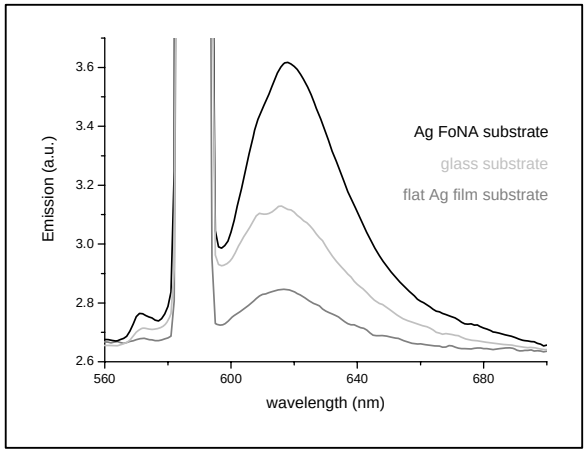

Fig. 5. Fluorescence spectra of thinine molecules sandwhiched between: FoNA substrate and glass slide (black); glass substrate and glass slide (light gray); and Ag mirror and glass slide (gray).

4. Discussion

It is well known that noble metal particles of subwavelength size support localized surface plasmon resonances (LSP) at optical frequencies. The spectral position of the resonance wavelength depends strongly on nanoparticle size, shape and dielectric constant of the environment [9]. It is of high practical importance to be able to tune the plasmon resonances of metal nanoparticle arrays, since they can be very valuable surface enhanced Raman scattering (SERS) active substrates [10]. The nanoparticle arrays we obtained by colloidal lithography can be engineered in such a way that plasmon resonances can be tuned at desired wavelengths, for example the available laser line.

On the other hand, extended metal-dielectric interfaces support delocalized (propagative) surface plasmon polaritons (SPP) and need nanoscale features to relax the momentum matching condition between the incident photon and the electromagnetic surface wave [11]. Therefore we believe the optical properties of FoNA are probably dominated by an interplay of both propagative and localized plasmons.

Metallic FoNA represent a very complex system, comprising three superposed arrays: an array of metallic TNA at the bottom, an array of PS in the middle and an array of metallic caps on top of the polymer spheres. Thus the features from their optical spectra can not be straightforward attributed. However it is very often used in the study of metallic films optical properties to attribute minima in reflectivity spectra to absorption by surface plasmons [12]. The fact that the minimum around 600 nm can be attributed to surface plasmons excitation is sustained by our previous results [13,14] when we established a good correlation between reflectivity minima and high surface enhanced Raman scattering (SERS) efficiency of the fabricated substrates.

As regarding our fluorescence studies, we believe the enhancement occurs due to the presence of surface

plasmons excited on the nanostructured substrates. The enhanced electromagnetic fields at plasmon resonant wavelength lead to an increase in the emitted fluorescence intensity. When the plasmon resonant wavelength coincides with the dye absorption band the excitation rate of the dye increases [15,16]. On the other hand, it was found that when the plasmon resonant wavelength coincides with the dye emission band the enhancement effect involves an increase in the quantum efficiency of the dye [17,18]. In our case the plasmon wavelength is more resonant with the dye absorbtion band so we expect the first effect mentioned above is responsible for the fluorescence enhancement. However due to the large width of the plasmon band, there is overlap also with the emission band of thionine, so it is conceivable that an interplay between the two enhancement effects takes place.

As regarding NHA their optical properties are still under investigation. We expect however that the nanoporous nature of these substrates will make them very efficient in confinement of electromagnetic fields. A very exotic phenomenon observed on metallic films with holes is that they transmit much more light than it is predicted for subwavelength holes, when the holes are placed in a periodic arrangement [19]. Producing inexpensively such structures will allow fundamental studies of the physics underlying enhanced optical transmission. Our further studies will be centered on checking the efficiency of NHA in enhancing the Raman signal of adsorbed molecules and their effect on the lifetime of fluorophors placed inside the nanocavities.

5. Conclusions

We have shown that by using a monolayer colloidal crystal a large variety of metallic or metalo-dielectric nanostructures with periodic features and highly tunable optical properties can be fabricated. We also demonstrated the silver films deposited over PS arrays can enhance by plasmonic mechanism the fluorescence emission of thionine molecules placed in the vicinity. Due to their unique optical properties dominated by surface plasmons excitation, nanostructured materials produced in our laboratories are exploited in applications ranging from controlling the fluorescence or luminescence emission to Raman scattering enhancement and surface plasmon resonance chemo- and biosensing.

Acknowledgments

Financial support from the National Authority for Scientific Research (Matnantech project CEEX No. 71/ 2006) is gratefully acknowledged.

References

[1] M. Hu, J. Chen, Z-Y. Li, L. Au, G. V. Hartland, X. Li, M. Marquez, Y. Xia, Chem. Soc. Rev. **35**, 1084 (2006).
[2] H. Raether, Surface Plasmons, Springer, Berlin (1988).
[3] E. Ozbay, Science **311**, 189 (2006).
[4] J. R. Lakowicz, Plasmonics **1**, 5 (2006).
[5] C. L. Haynes, R. P. Van Duyne, J. Phys. Chem. B **105**, 5599 (2001).
[6] A. Kuttesch, C. Farcau, Z. Neda, S. Astilean, Proc. SPIE 6785, 678500 (2007).
[7] D. A. Stuart, C. R. Yonzon, X. Zhang, O. Lyandres, N. C. Shah, M. R. Glucksberg, J. T. Walsh, R. P. Van Duyne, Anal. Chem. **77**, 4013 (2005).
[8] J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, S. Schultz, J. Chem. Phys. **116**, 6755 (2002).
[9] U. Hohenester, J. Krenn, Phys. Rev. B **72**, 195429 (2005).
[10] M. Baia, L. Baia, S. Astilean, J. Popp, Appl. Phys. Lett. **88**, 143121 (2006).
[11] V. N. Konopsky, E. V. Alieva, Phys. Rev. Lett. **97**, 253904 (2006).
[12] W. Knoll, Annu. Rev. Phys. Chem. **49**, 569 (1998).
[13] L. Baia, M. Baia, J. Popp, S. Astilean, J. Phys. Chem. 3 B **110**, 23982 (2006).
[14] C. Farcau, S. Astilean, J. Opt. A: Pure Appl. Opt. **9**, S345 (2007).
[15] O. Stranik, H.M. McEvoy, C. McDonagh, B. D. MacCraith, Sens. Actuators B, **107**, 148 (2005).
[16] O. Stranik, R. Nooney, C. McDonagh, B. D. MacCraith, Plasmonics, **2**, 15 (2007).
[17] K. Aslan, J.R. Lakowicz, C.D. Geddes, Anal. Bioanal. Chem., **382**, 926 (2005).
[18] J. H. Song, T. Atay, S. Shi, H. Urabe, A. V. Nurmikko, Nano. Lett. **5**, 1557 (2005).
[19] D. E. Grupp, H. J. Lezec, T. W. Ebbesen, K. M. Pellerin, T. Thio, Appl. Phys. Lett. **77**, 1569 (2000).

*Corresponding author: cfarcau@phys.ubbcluj.ro