JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 3, March 2007, p. 772 - 775

Understanding plasmonic properties and surface-enhanced Raman scattering of silver coated colloidal crystals

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Two-dimensional colloidal crystals were prepared according to the drop-coating technique, and subsequently covered in a silver film by thermal evaporation. Light transmission through the composite metallo-dielectric film was measured at normal and also oblique incidence. We found that silver coated two-dimensional colloidal crystals exhibit unusually high optical transmitivity, which can be related to the extraordinary optical transmission phenomenon. Additional reflectance spectra and surface enhanced Raman scattering are used to understand the optical/plasmonic properties of the prepared nanostructure. Measured reflectivity minimum suggests plasmonic activity at wavelengths different than those of transmission maximum, this giving a preliminary understanding on the transmission mechanism.

(Received November 15, 2006; accepted December 21, 2006)

Keywords: Colloidal crystals, Extraordinary optical transmission, Surface plasmons, Surface enhanced Raman scattering

1. Introduction

Noble-metal nanoparticles and nanostructures support surface plasmons and exhibit interesting optical properties, for example, large scattering cross section, extraordinary light transmission, nonlinear optical response, and highly localized field enhancement [1]. So far the application of choice for surface plasmons has been sensing and in particular Surface Plasmon Resonance (SPR) and Surface Enhanced Raman Scattering (SERS). Understanding how surface plasmons propagate on nanostructured metal surfaces is crucial in developing efficient SPR and SERS substrates. However, although specific localised plasmons are well understood for isolated nanoparticles of different shape, a general understanding of how plasmons localize or propagate on extended deformed metal surfaces is lacking.

Here, we study the optical properties of deformed extended silver surfaces and correlate them with their SERS activity. The nanostructured metals were quite easily and inexpensively produced by the method of NanoSphere Lithography (NSL) [2]. The method consists of assembling a two-dimensional array of submicrometer colloidal particles, followed by metal deposition. We have already investigated several silver and gold nanostructures generated via NSL and demonstrated their high SERS activity [3-5]. Similar structures were recently proposed as candidate for exhibiting the extraordinary optical transmission phenomenon [6], previously reported only for metallic subwavelength holes arrays [7]. Resonant interaction of light with surface plasmon polaritons [8-10] and interference of diffracted evanescent waves more recently [11], are the main mechanisms proposed for the enhanced transmission, and this matter is still under debate in present. In this study optical transmission and reflectance measurements have been employed in combination with SERS measurements as well as with scanning electron microscopy (SEM) to understand the plasmonic properties of silver nanostructured films deposited over two-dimensional colloidal crystals.

2. Experimental

2.1 Sample preparation

As solid substrates we used glass microslides of 24x24mm size. 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 prepared ordered two-dimensional (2D) arrays of colloidal nanospheres by the drop-coating method described in literature [12]. An aqueous suspension of polystyrene (PS) spheres of 400 nm diameter was dropped onto the cleaned substrate. The right volume of suspension was calculated as the entire support to be coated by a layer of nanospheres, taking in account the substrate area, diameter of the spheres and concentration of the PS spheres in solution. The wet support was placed in oven at a temperature of about 60^0C to evaporate water and get self-organization of the polymer nanospheres. Then the support was transferred into a vacuum chamber to deposit a 50 nm thick silver film on the PS spheres 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.

2.2 Sample investigation

Optical transmission spectra were measured with a Jasco V-530 uv-vis spectrometer using unpolarized light. We measured both the transmission of flat silver film and of silver coated colloidal crystal at normal incidence. Then we measured transmission at oblique incidence, between 0 and 30 degrees by increasing the angle in steps of 3 degrees. In adition we measured also reflectivity at normal incidence of the metal-coated spheres array by using an interchangable Jasco SLM-468S reflectivity module.

To study the SERS activity of the prepared samples we used a $3 \cdot 10^{-5}$ M solution of rhodamine (R6G) in methanol. We dropped 5 μl of R6G solution on each sample and allowed them to dry in normal atmosphere. The SERS spectra of R6G were collected in back-scattering geometry on a Dilor Labram system equipped with an Olympus microscope objective with a magnification of 100 and a numerical aperture of 0.8. Two laser wavelengths were used for excitation: 514nm from an Ar ion laser and 633nm from a He-Ne laser. In order to collect spectra from the desired location the samples were moved with nanometric precision by use of a LANG Eco-Step positioning system.

We checked the morphology of the prepared samples with a JEOL JSM 5510 electronic microscope.

3. Results and discussion

Visual investigation of a sample brings the first information on the ordering obtained on the substrate after colloidal self-organization. The prepared probes show in reflection beautifully iridescent colours from green to red depending on angle of observation. This phenomenon is explained in terms of light diffraction on a two-dimensional grating. Sometimes one can see various colors at the same angle of observation and that is due to different domain orientations since the colloidal monolayer is of polycrystalline nature. Contrarily, if observed in transmission the probes appear to be brownish-red colored.

Fig. 1 is a representative SEM picture of regular hexagonal close packed nanospheres on the substrate. Quality of the prepared 2D colloidal crystal, i.e. degree of ordering, defects, is the first parameter that affects the optical response of the sample. Typically the crystallization process leads to the formation of two-dimensional colloidal crystals along with multilayered structures and randomly self-organized nanospheres. Still, the substrate is mostly covered in a single layer, but of polycrystalline nature, with single crystal domains (as seen in Fig. 1) ranging from 10 to 50 μm lateral size.

SEM imaging does not reveal differences between silver coated and uncoated sphere arrays, but one can see in the inset of figure 1 what is left on the substrate after nanospheres removal. We emphasize that silver-coated colloidal monolayers are rather complicated metallo-dielectric nanostructures comprising three superposed lattices: an array of silver triangular nanoparticles at the bottom, an array of polystyrene spheres in the middle and a periodically deformed silver film on top of the structure.

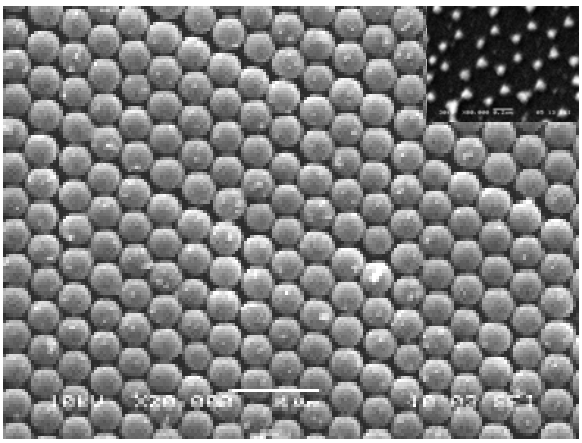

Fig. 1. Scanning electron microscope image of two-dimensional colloidal crystal; inset shows an array of triangular silver nanoparticles formed on the glass substrate.

Fig. 2 shows the transmission spectrum, at normal incidence, of the silver-coated 2D colloidal crystal together with a reference spectrum registered from a flat area of silver film deposited on the same substrate. Transmitivity is strongly increased as compared to that of a flat silver film of the same nominal thickness (dotted spectrum in fig.2). The strong transmission maxima and minima resemble very much with the spectral features previously reported in the case of opaque films perforated with subwavelength holes and associated with the phenomenon of extraordinary optical transmission [8-10]. Another interesting result is that the spectra look identical irrespective of the side of the illumination, and the result is again similar with what was reported in the case of flat perforated films.

To shed some light on the origin of this unusual high transmission we took spectra at different angles (Fig. 3). By increasing the incident angle the main transmission peak deacreses in intensity, but it does not change position considerably. Another non-trivial feature is the emergence of new optical mode at longer wavelengths, which grows in intensity as the angle is increased.

What makes our results distinct when compared to the case of perforated flat films is that the position of the transmission peak does not change very much with the incident angle.

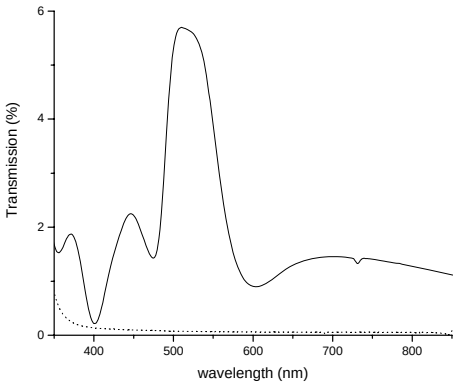

Fig. 2. Transmission spectrum of silver coated 2D colloidal crystal. The dotted spectrum represents transmission of a flat 50 nm silver film.

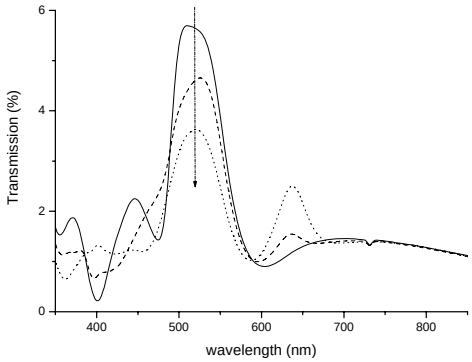

Fig. 3. Transmission spectra of silver coated 2D colloidal crystal recorded at different incident angles. The increase of the incident angle is indicated by the vertical arrow.

The studies on perforated flat films established that the transmission peaks were always highly propagative [7,10] and are usually well described by the following ecuation:

$$k_{SPP} = k\sin\theta \pm iG_x \pm iG_y \qquad (1)$$

where k is the wavevector of the light incident at angle θ, G_x and G_y are the Bragg vectors associated with the two periodicities of the lattice, and i and j are integers. The plasmon wavevector is thus given by the in-plane wavevector of the incident light summed with a vector of the reciprocal lattice. When introducing a periodic pattern on a flat metallic film the momentum-matching conditions can be fullfield, and thus light can couple to surface plasmons, which is not achievable if there is no corrugation. Different authors have proposed coupling of light to surface plasmon polaritons [6-10] on both sides of the metal film as the mechanism of the observed enhanced transmission. Due to the localization of our measured transmission modes we believe this picture does not hold in the case of silver film over nanosphere array, and is more likely that localized surface plasmons are involved. One can also see a propagative mode at lower wavelengths, which corresponds to a peak of much lower intensity. It is conceivable that the overall optical response is a mixture of localized plasmons and propagative plasmons, with an emphasis on the former.

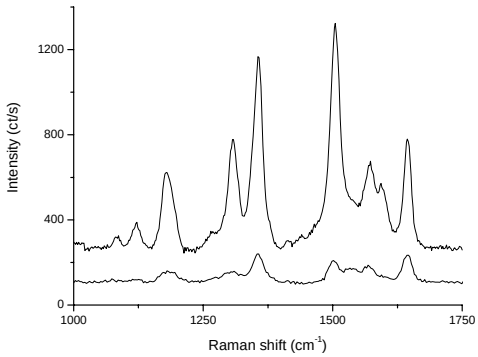

Fig. 4. SERS spectra of rhodamine adsorbed on silver-coated colloidal crystal recorded atr 514 nm (lower) and 633 nm (upper) excitation wavelength.

Previous research in our group demonstrated that noble metal films deposited over colloidal crystals are efficient substrates for surface enhanced Raman scattering (SERS) [3,4]. Since generally the enhancement of Raman signals of molecules adsorbed on metallic surfaces is attributed to surface plasmons excitation [13], this technique could also be a valuable tool for probing the plasmonic properties of those metallic surfaces. Figure 4 shows the Raman spectra of R6G molecule adsorbed at the surface of silver coated colloidal crystal, registered at two excitation wavelengths, which fall in two spectral regions of interest regarding the transmission spectrum. The most intense spectrum (upper) is the one collected under 633 nm laser excitation, which falls out of the transmission peak. Furthermore 514 nm line, which is exactly in the center of the transmission peak, falls also in the electronic absorbtion band of rhodamine. In such case [14] the SERS spectrum of R6G should be already about 1 or 2 orders of magnitude amplified due to resonant Raman condition of excitation or SERRS.

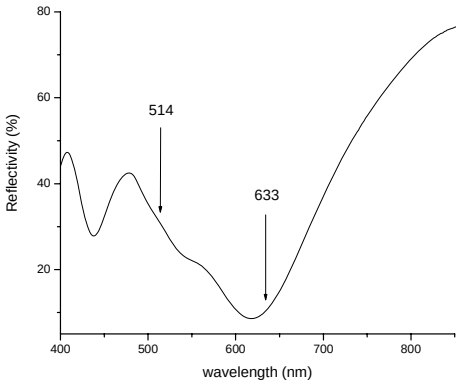

Fig. 5. Reflectivity spectrum of silver-coated colloidal crystal.

In a study on perforated gold films, the role of surface plasmons in the transmission mechanism was probed by surface enhanced Raman scattering [15]. It was shown that the intensity of enhanced-Raman scattering from molecules adsorbed on arrays of nanoholes in gold films is dependent on structural parameters, which determine the wavelengths of enhanced transmission.

In order to better understand the unexpected Raman result, we investigated the reflectivity of the substrate too. A strong and broad dip at about 630 nm dominates the reflectivity spectrum at quasi-normal incidence (see Fig. 5). It was previously shown [16] that such broad reflectivity minima are well corellated to high SERS activity. We therefore believe our measured minimum is indicative of surface plasmon excitation in the silver film covering the colloidal spheres array. This supposition is in good agreement with the maximum of enhancement of Raman spectra at 633 nm excitation line. Since it appears that reflectivity gives a more accurate picture of plasmon activity we are further performing elipsometric measurements in order to elucidate the nature of light-nanostructured silver surface interaction.

5. Conclusions

We have shown that silver coated two-dimensional colloidal crystals exhibit unusual high transmission in the visible range, consistent with extraordinary optical transmission, previously reported for metal films perforated with subwavelength hole arrays. Transmission spectra at different incident angles correlated with SERS and reflectivity measurements suggest different transmission mechanisms in which propagative surface plasmon polaritons might not have the leading role. It is conceivable that localized plasmons could have a role as well as diffraction and interference of evanescent surface waves. Properly understanding and controlling the enhanced transmission mechanism would lead to applications in integrated photonic circuits, near-field optics, nanolithography [17] and also surface enhanced spectroscopies and optical bio-sensing [15].

Acknowledgement

This work was supported by the Romanian National Authority for Research (project Nanobiospec No. 71/ 2006/ Matnatech).

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