

OPTICAL AND STRUCTURAL CHARACTERIZATION OF PERIODIC SILVER-POLYSTYRENE NANOCOMPOSITES

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Ordered arrays of polystyrene nanospheres were self-assembled on glass substrate and subsequently used as templates for thin silver film deposition. Silver-polystyrene nanocomposites with periodicity given by the polystyrene spheres diameter (400 nm) were obtained and investigated by optical measurements and electron microscopy. The resonant interaction of light with surface plasmons supported by periodically structured silver-polystyrene nanocomposite leads to important spectroscopic applications like molecular sensing and enhanced Raman scattering.

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1. Introduction

Nanostructured materials are of increasing scientific interest due to their optical, electrical, magnetic, thermal properties, which are not present in the bulk phase. The main parameters which determine their properties are divided in two categories: (1) structural parameters (nanometric size, periodicity, ordering, and interparticle distances) and (2) compositional parameters (chemical or biological functions attached to the surface of nanostructures). In order to implement novel applications in the field of nanotechnology is of paramount importance to control as much as possible the above parameters [1].

There are two possible approaches to fabricate nanostructures in a controllable manner: the so called top-down and bottom-up methods. The first category includes photolithography, holographic interferometry, electron beam lithography, X-ray lithography. Recent developments of scanning tunneling microscopy, atomic force microscopy and scanning probe lithographic techniques show great promise. However, during the past decades, various nanoparticles of polystyrene, silica, noble-metal and semiconductor, nearly monodisperse in terms of their size, shape, internal structure, and surface chemistry, are being produced through a reliable manufacturing process. Building complex nano-architectures from self-assemblies of such stable building blocks has also become an increasingly popular topic in nanofabrication. As for example polystyrene (PS) nanospheres can self-organize on a solid substrate in two-dimensional compact hexagonal arrays and, then, can serve as template for (nano)structuring other materials. This method known as nanosphere lithography (NSL) has been used recently to fabricate regular arrays of noble metal nanoparticles and metallic holes with controlled size, shape and spacing [2,3].

Here, we report new optical properties of periodically arrayed silver nanostructures fabricated through a variant of NSL technique. The optical properties of noble-metal nanostructures result from the interaction of light with confined conduction electrons. For instance, when visible light impinges a noble-metal nanoparticle, excitation of localized surface plasmons occurs. The surface plasmons are electromagnetic waves coupled to the oscillations of conduction electrons at

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the metal-dielectric interface. A few of the consequences of the surface plasmons excitation are strong selective photon absorption, scattering and local electromagnetic field enhancement. The strongly enhanced fields (10^3 - 10^5 times) decay exponentially with the distance (on the order of 10 nm in the metal and ~ 100 nm in the dielectric) [4].

Noble-metal nanostructures are highly desirable in several technological applications including optical energy and information transport, photonic crystals, near-field scanning optical microscopy, surface-enhanced spectroscopy, chemical and biological sensors [5,6].

2. Sample preparation

As solid substrates we used glass microslides of 24×24 mm size. The slides were sonicated in isopropyl alcohol for degreasing, then treated in piranha solution (mixture of 95% H_2SO_4 30% H_2O_2) and sonicated again in a mixture of $\text{H}_2\text{O}/\text{NH}_4\text{OH}/\text{H}_2\text{O}_2$ for at least 30 min. The substrates were stored in deionized water until nanospheres deposition. A water suspension of polystyrene nanospheres of 400 nm diameter was dropped onto the cleaned substrate (Fig. 1A). We deposited the right volume of suspension to cover the substrate taking in account the substrate area, diameter of the spheres and concentration of the PS spheres in solution.

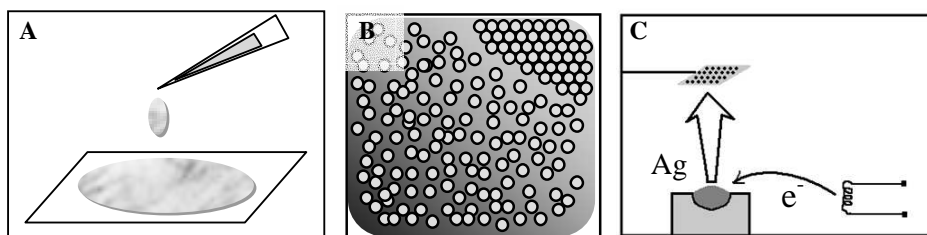


Fig. 1. Schematic representations of (A) drop-coating of glass slide with nanosphere solution, (B) self-organization of the nanospheres and (C) the vacuum deposition chamber.

The wet substrate was placed in an oven at constant temperature between $40 - 80$ °C in order to evaporate the water and get self-assembled nanoparticles (Fig. 1B). In the next step of sample preparation, a silver film of 40 nm thickness was deposited over the PS nanospheres layer by means of an electron-beam evaporator. A schematic representation of the evaporation system is shown in Fig. 1C. The accelerated electron beam from a wolfram filament is directed onto a solid piece of silver, the metal heats up and silver atoms arrive on the PS array substrate mounted above.

3. Results and discussion

The microstructure of the prepared sample was mapped by scanning electron microscopy using a JEOL JSM 5510 LV electronic microscope. Fig. 2A is a representative SEM picture of regular hexagonal close packed nanospheres on the substrate. Most of sample surface exhibits a single layer ‘polycrystalline’ structure with ordered domains ranging from 10 to 50 μm lateral size. Typically the crystallization process leads to the formation of two-dimensional (2D) colloidal crystals along with multilayered structures and randomly self-assembled nanospheres. Small domains where the spheres form a rectangular lattice can also be observed (not shown here). In the literature it is generally accepted that the mechanism and the driving forces of assembling process involve: (1) formation of a nucleus, under the action of attractive capillary immersion forces, and (2) crystal growth, through convective particle flux caused by the water evaporation from the already ordered array [7]. This implies that the 2D crystal nuclei are formed under the capillary attraction arising when the tops of the spheres protrude from the water layer. In the schematic representation of figure 1B the spheres from the darker region of the picture move towards the ordered array by passing through the brighter region. The origin of the lateral capillary forces is the overlap of

perturbations in the shape of the liquid surface surrounding the PS nanospheres. The dynamics of ordering is strongly dependent on the evaporation rate. A spring-block stick-slip model was recently introduced for simulating the phenomenon of nanosphere self-assembling and to study the influence of several controllable parameters on the sample polycrystallinity [8].

Many different silver-polystyrene nanocomposites can be easily fabricated by depositing silver on top of ‘‘polycrystalline’’ structure. As for example, Fig. 2B shows ordered array of triangular silver particles left on glass substrate after removing the spheres mask, and figure 2C shows randomly distributed nanocavities made in metal film. PS spheres can be removed from the substrate by dissolution in toluene (Fig. 2B) or happens that the spheres fall down accidentally (Fig. 2C). A periodic array of smaller metallic particles than those shown in Fig. 2B can be obtained by depositing metal through a mask consisting of two layers of PS spheres [2]. On the substrate, along with crystalline domains, there are various types of defects of crystallization too. The so-called ‘‘line defects’’ (gaps between domains) and ‘‘point defects’’ (missing spheres) can serve as optical (nano)microcavities to control the fluorescence rate of emitters *via* density of localized optical modes [9]. The metallic nano-apertures as those fabricated in this work (see Fig. 2C) were recently employed as nanocavities for studying the luminescence of single quantum dots [10].

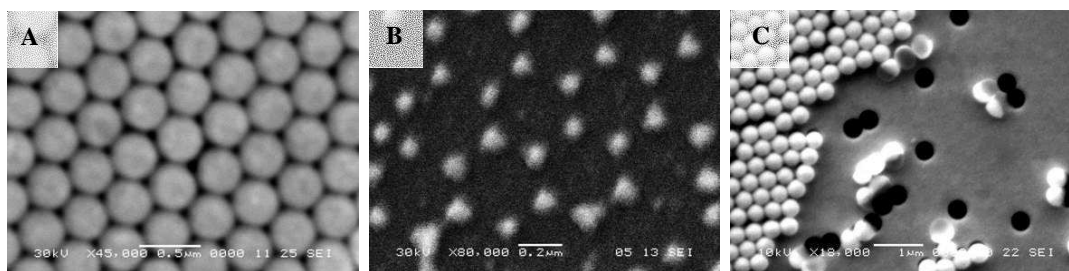


Fig. 2. SEM images of: (A) PS spheres array (scale bar: 500 nm); (B) array of triangular silver nanoparticles (scale bar: 200 nm), (C) perforated silver film area (scale bar: 1000 nm).

The first proof of interesting optical properties of fabricated nanostructures is given even by naked eye. If observed in reflection, the substrates show beautifully iridescent green, blue, violet colors, depending on angle of observation. Contrary, the samples appear to be brownish-red colored in transmission. In the first approximation, the colloidal lattice surface can be considered a two-dimensional diffraction grating of close packed spheres and the appearance of such colors can be explained in terms of light diffraction and scattering. The phenomenon is rather complex as many different local 2D gratings (domains) and structural defects (points, lines and gaps) co-exist. In order to characterize the optical properties of as fabricated nanostructures, optical extinction measurements were recorded for three distinct cases: a) bare layer of PS nanospheres (before silver deposition); b) silver-coated polystyrene layer; c) silver nanoparticles on the substrate (after removal of the spheres). The extinction spectra were recorded using a JASCO UV-530 spectrometer with a probe beam of approximately 9 mm^2 size and unpolarized light.

Fig. 3A shows the grating extinction recorded at 0° , 20° and 40° angles of incidence. Resonant phenomenon between the incident light and the eigenmodes of the regular array of nanospheres [11] are responsible for the peak (transmission dip) observed in the normal incidence spectrum around 480nm, bulk polystyrene film not being an absorber at these wavelengths. The peak is a specific optical response of ordered arrays of nanospheres and its existence demonstrates the degree of ordering on the substrate. It is conceivable that the individual responses of different single domains are very locally sensitive. However, the probe light beam of about 9 mm^2 cross-section integrates many domains and the measured optical spectra give finally only an area-averaging extinction behavior.

The peak moves towards longer wavelengths as the incidence angle is increased as a result of crossover phenomenon due to the interaction between eigenstates of the monolayer and those of the substrate. Light interacts not only with surrounding spheres but also with the substrate and the

optical interaction between spheres as well as interaction between spheres and substrates changes as function of the incidence angle [12]. This grating resonance at wavelength comparable with the size of the spheres is likely associated with Mie resonances and cannot be explained by Bragg diffraction as in the case of colloidal photonic crystals. The diameter of nanospheres and refractive indices of polystyrene and substrate determine the position of the peak, while the degree of polycrystallinity (defects) determine its width.

The spectra in Fig. 3B look drastically different as compared with spectra in Fig. 3A. On the contrary to eigenmode resonances observed in the grating of dielectric spheres, the main features of optical spectra in Fig. 3B are connected with surface plasmons resonances. Both propagative plasmons supported by corrugated silver film on polystyrene hemispheres (interconnected caps) and localized plasmons supported by quasi-isolated caps and nanoparticles on glass have to be involved.

In order to get insight into the origin of spectra shown in Fig. 3B we subsequently measured the extinction spectra of the sample after removing the silver coated spheres from the substrate. We assign the recorded band situated at around 450 nm (Fig. 3C) to localized surface plasmons on silver triangular nanoparticles which were left on the substrate. Indeed, the band is still visible in spectra of silver-polystyrene nanocomposite in Fig. 3B.

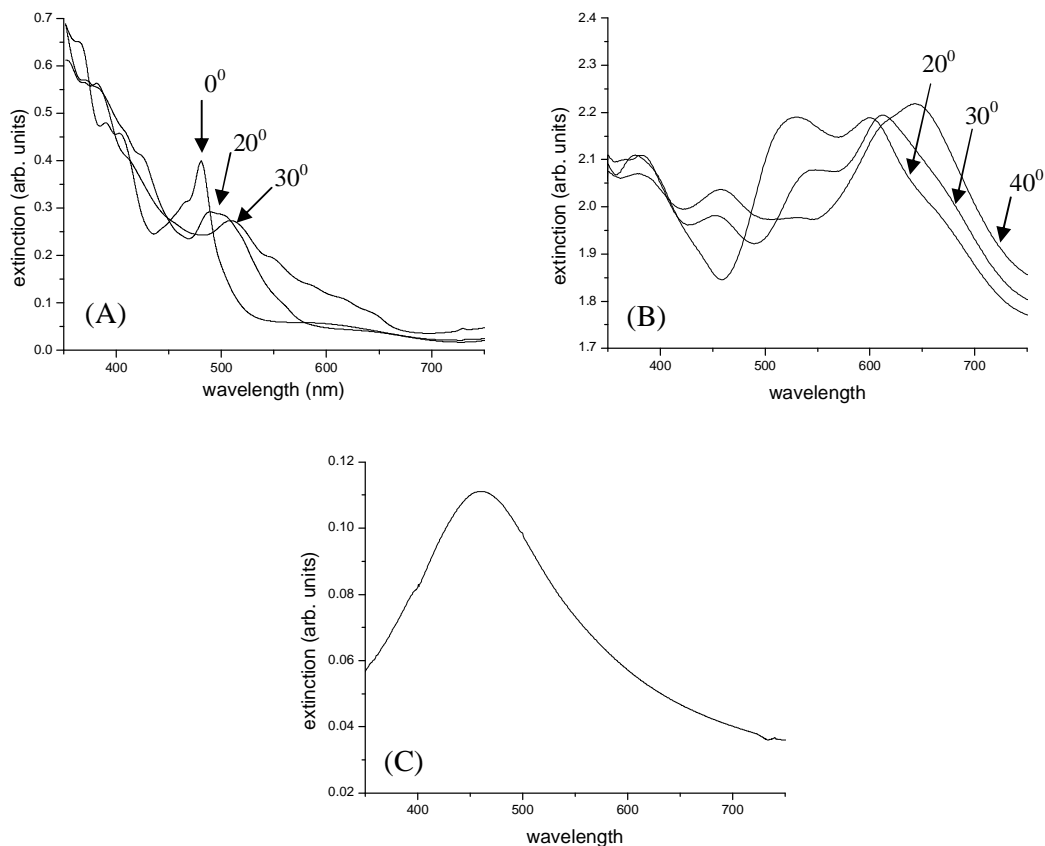


Fig. 3. Extinction spectra of: (A) array of PS spheres; (B) composite silver/PS nanostructure; (C) array of silver nanoparticles.

Consequently, the strong bands above 500 nm could be likely associated with interplay between localized surface plasmons on quasi-isolated spherical caps and propagative plasmon-polaritons bound to corrugated silver film of interconnected caps. The bands are broad and red-shifted as a result of the electromagnetic coupling between silver nano-features of different shape and size (caps, triangular island, rods) [13]. Moreover, with increasing the incidence angle of light the coupling between plasmonic modes increases too.

Our spectra are consistent with plasmons resonances and as a result with enhanced electromagnetic fields supported on silver/PS nanocomposites. Previous theoretical studies of the enhancement of local electromagnetic field on noble-metal nanoparticle suggest that the average electromagnetic enhancements can approach 10^{11} for silver nanodisks and 10^9 for silver nanosphere arrays [14]. They established there is a critical relationship between the field enhancement and the size, shape and interparticle spacing. We believe that as fabricated periodic silver-polystyrene nanocomposites can offer enough control in order to optimize such parameters. Therefore further investigation are envisaged to implement periodically structured silver-polystyrene nanocomposites as active substrates for surface-enhanced Raman scattering (SERS) and surface plasmons sensing [15].

5. Conclusions

Regular arrays of 400 nm diameter PS nanospheres on solid substrate were prepared by a self-assembling method. Useful silver-polystyrene nanostructures were fabricated via nanosphere lithography and characterized by optical extinction spectra and scanning electron microscopy. The optical response is dominated by the excitation of surface plasmons which provide potential for using such silver-polystyrene nanostructures as active surfaces in surface-enhanced Raman scattering (SERS), fluorescence control and optical biosensing.

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