

Block-copolymer-based plasmonic metamaterials

Antonio Capretti^{a,b}, Finizia Auriemma^c, Claudio De Rosa^c, Rocco Di Girolamo^c, Carlo Forestiere^b, Giovanni Miano^b, Giovanni P. Pepe^a

^aDepartment of Physics & CNR-SPIN, ^bDepartment of Electrical Engineering and Information Technology, ^cDepartment of Chemistry, Università degli Studi di Napoli Federico II, Italy

ABSTRACT

Block-copolymer (BCP) self-assembling provides a unique tool for realizing large-area ordered metamaterials, with desired optical properties. The benefits of using BCPs as templates for metamaterials come from two main aspects: first, BCPs show a rich range of available nano-morphologies, whose domains can be conveniently tuned in size, shape and periodicity, by changing molecular parameters; second, the chemical properties of the block polymers can lead to the selective inclusion of functionalized nanoparticles (NPs) of different materials in specific nanodomains, generating periodic arrays of NPs according to the geometry of the BCP acting as template. This approach allows finely modulating the optical properties of NPs and can be used as an intriguing and versatile tool to build useful devices for Optics & Photonics applications, with significant benefits for both fundamental and applied investigations. In this work, we investigate nanostructured thin films of polystyrene-block-poly(methyl methacrylate) BCP (PS-PMMA), characterized by an hexagonal array of PS cylinders in the PMMA matrix. The PS cylindrical domain are selectively filled by functionalized metallic (Au, Ag) NPs. The optical properties of such nano-structures are strongly affected by localized surface plasmons (LSPs) in the NPs, arising from the collective resonances of conduction electrons in the metal at a characteristic spectral range, usually in the visible range. LSPs induce high field enhancement (FE), with respect to an incident light, in proximity of the NP surface, and in particular in the gap between two close NPs (hot-spot). Moreover, LSPs increase the intensity of absorption and scattering of light by the NPs in their range of resonance.

Keywords: Metamaterials, Block-copolymers, Self-assembly, Plasmonics

1. INTRODUCTION

Metamaterials are re-defining the use of naturally-occurring materials for technological applications. In particular, electromagnetic metamaterials allow for unexpected effects of light ranging from the optical to the microwave spectra. They consist of regular structures made of common media, such as dielectrics and conductors, with geometrical features much smaller than the wavelength of the light interacting with them. As a result, it is possible to control to electromagnetic response of these novel materials by accurately designing their geometries and by selecting the composition of their constitutive bricks.

The fabrication of metamaterials is typically achieved by nano-patterning thin films with physical or chemical methods, such as lithography or self-assembly. In particular, nano-scale geometrical features are needed for applications in the optical spectrum of light. Moreover, the use of different materials is necessary to obtain the desired optical response. As a matter of fact, these heterostructures are often characterized by several nano-scale objects of different materials, at very small separations. The effective operation of nano-structured thin films as metamaterials requires that the nano-patterns are regularly repeated on the surface and that the wavelength of the interacting electromagnetic field is much larger than the pattern features. As a consequence, the incident light 'sees' an effective medium with unexpected optical properties, different from those of the starting materials, and strictly depending on their patterning.

It is clear that the establishment of metamaterials in technological applications strictly depends on the ability to fabricate large-area cost-effective films with nanostructured features and selected composite materials. In the present work, we illustrate the use of a self-assembly method based on block-copolymers (BCPs), for

Further author information: (Send correspondence to Giovanni P. Pepe)
Giovanni P. Pepe: E-mail: gpepe@na.infn.it, Telephone: +39 081 768 2584

the fabrication of metamaterials. The use of such polymeric materials is a promising route to realize ultrahigh density devices, though maintaining low cost processing.

Block copolymers represent a class of materials that exhibit unparalleled versatility in the creation of nanostructures. BCPs consist of two or more chemically distinct polymer fragments, or blocks, covalently bonded together. If the constituent blocks are immiscible, the chemical incompatibility induces microphase separation with formation of periodic nanostructures having chemically distinct domains with size and periodicity that depend on the relative lengths of the blocks.^{1,2} Thus, depending on the molecular architecture of BCPs and relative molecular masses of the polymeric blocks, different nanostructures can be produced, such as alternating lamellae or spherical and cylindrical microdomains packed in cubic or hexagonal ordered lattices respectively,³ as shown in Figure 1.

The different microdomains of BCP nanostructures (spheres, cylinders or lamellae) can act as hosts for sequestering metal nanoparticles of appropriate chemical affinity and geometry.³ In this approach, the nanostructured block-copolymer matrix act as a structure-guiding matrix, where the nanoparticles are sequestered into target microdomains of the BCP structure, resulting in an ordered spatial positioning of the guest particles guided by the ordering of the host matrix and a hierarchical assembly of organic-inorganic (polymer-metal) nanostructures, in which one level of self-assembly guides the next. This ability makes BCPs ideal as scaffolds for the engineering of new materials characterized by patterned surfaces, and controlled and ordered assembly of metal nanoparticles.

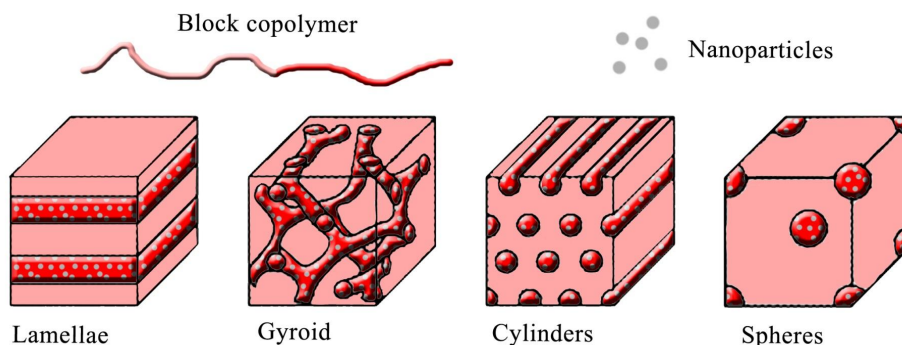


Figure 1. Nanostructures generated from a di-block copolymer. The chemical incompatibility between the two different linked polymeric blocks induces microphase separation and formation of periodic nanodomains (lamellae, gyroid, cylinders or spheres) that may act as hosts for sequestering guest nanoparticles.

In this work, we present a theoretical and experimental study of the collective plasmonic oscillations observed in a BCP-based periodic nanostructure of nanocylinders filled with surface coated gold nanoparticles, whose topological characteristics allow both important LSPs and strong collective effects due to the near field coupling. The ability to tune the collective resonances in plasmonic nanostructures allows for the creation of a new rich set of engineering materials with a wide range of controlled optical properties.

2. NUMERICAL RESULTS

In this Section, we numerically investigate a polystyrene-block-poly(methyl methacrylate) (PS-PMMA) thin film with hexagonal geometry as a plasmonic metamaterial. We first consider the optical response of gold nanoparticles confined in a single PS cylindrical domain, at different loading concentration, by using a coupled-dipole numerical method.^{4,5} Then, we consider array effects arising from the regular distribution of the PS cylinders into an hexagonal lattice by using the TMatrix method.⁶

2.1 Single domain

By using functionalized gold nanoparticles it is possible to introduce gold into the PS domain, if their diameter is smaller than the cylinder size. The extinction spectra of the PS cylindrical domain, with sequestered gold NPs, are shown in Figure 2. The cylinder diameter is 40 nm and its height is 65 nm , in agreement with the geometrical features of the fabricated BCP films discussed in Section 3. The nanoparticles diameter is $r = 5\text{ nm}$, and their volume filling fraction inside the cylinders is varied in the range $0\% - 40\%$. It results that, for a filling fraction lower than $\sim 20\%$, the nanoparticles do not interact, and the extinction spectrum is similar to that of isolated particles. As the filling fraction increases, the particles begin interacting, and the cylindrical domain shows extinction peaks in the red and near-IR part of the electromagnetic spectrum.

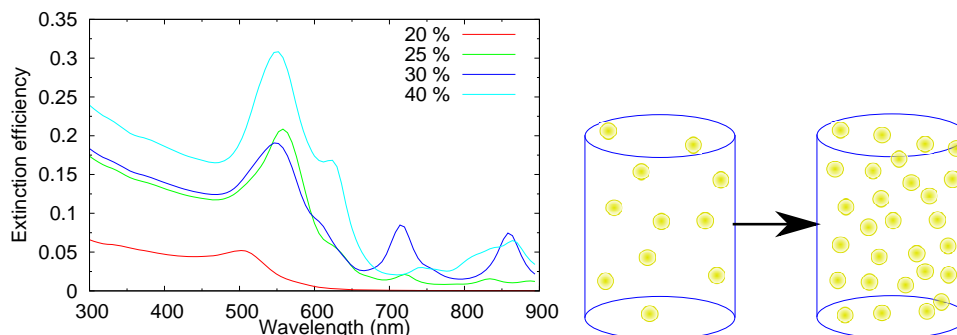


Figure 2. Extinction spectra of cylindrical PS domains filled by gold NPs with radius $r = 5\text{ nm}$, at different filling fraction.

A similar analysis is conducted by keeping fixed the number of particles inside the cylindrical PS domain, and by increasing the particle size. Figure 3 shows the extinction efficiency of a cylindrical domain filled with ~ 90 particles. It is clearly shown that there is no particle interaction for shorter radii than 3 nm . For larger size ($r = 5\text{ nm}$ and blue line in Figure 3), the particles interact and a second extinction peak arise at a wavelength $\approx 800\text{ nm}$. It is worth to notice that fabrication issues arise when trying to insert particles of diameter comparable with the size of the hosting cylindrical domains. In conclusion the previous analysis reveals that, in order to achieve a cylindrical domain with tunable optical properties by including nanoparticles, the best strategy is to use medium-sized particles with high filling fraction.

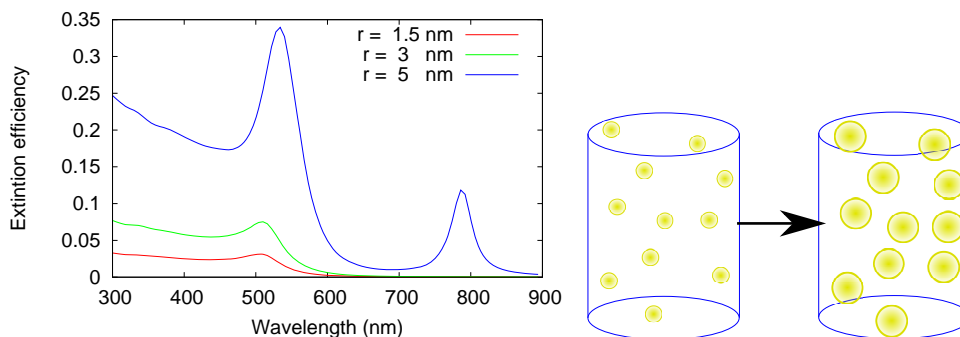


Figure 3. Extinction spectra of cylindrical PS domains filled by ~ 90 gold NPs, with varying radii.

2.2 Array effects

In the following, we investigate the effects of the hexagonal geometry on a PS-PMMA plasmonic array composed by completely filled gold cylinders. We have performed an accurate numerical analysis to investigate the role of the particle arrangement with the TMatrix method, also known as Null Field or Extended Boundary Condition

method.⁶ To this aim, a set of monolithic nano-cylinders arranged in an ideal hexagonal lattices with axes oriented along the wave vector of an incident plane wave has been considered. The diameter and height of cylinders have been set equal to the case described in the previous analysis on a single PS domain. The calculated extinction spectra for a relatively large hexagonal array of $N = 37$ cylinders are shown in Figure 4. Calculations are shown for arrays characterized by inter-particle center-to-center distances D ranging from 65 nm to 48 nm .

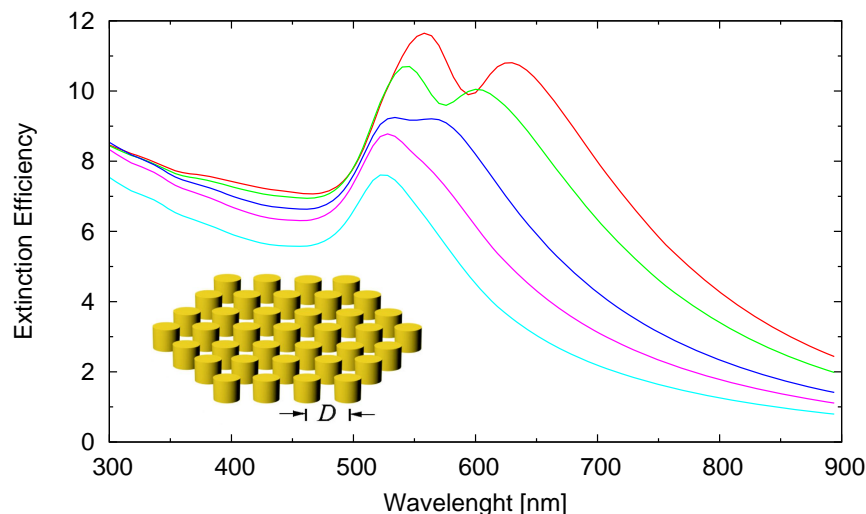


Figure 4. Extinction spectra for hexagonal arrays of $N = 37$ gold cylinders for different values of center-to-center inter-particle distance D of 65 nm (cyan), 60 nm (magenta), 55 nm (blue), 50 nm (green), 48 nm (red).

The calculated spectra of Figure 4 indicate the occurrence of an asymmetric broadening toward the red electromagnetic region of the extinction peak for low inter-cylinder distances, indicating that with decreasing the lattice spacing the extinction contributions at wavelengths higher than 520 nm increase. In particular, for center-to-center distances smaller than the cylinder diameter ($D < 60\text{ nm}$), a second extinction peak is observed. Numerical simulations of Figure 4 are a clear indication that the distance between first-neighboring cylinders is the major leading parameter driving the occurrence of near-field interactions.

3. EXPERIMENTS

3.1 Fabrication

We fabricated thin films with regular patterns of hexagonal array of cylinders, by employing a PS-PMMA copolymer.⁷ The volume fraction of the PS block has been chosen in order to select the desired cylindrical microphase-separated morphology. The cylinder domains inside the film consist of PS, while the surrounding matrix is made by PMMA. Gold nanoparticles bearing on the surface 2-naphthylthiolate (NT) units (NT-AuNPs) have been synthesized using the method of Brust *et al.*, featuring an average diameter of $\sim 3\text{ nm}$.⁸ The presence of NT units on the surface of nanoparticles favors the chemical affinity of the nanoparticles with the PS domains. Thin films consisting of PS-PMMA and gold NPs have been prepared by spin coating a toluene solution containing 2 wt% PS-b-PMMA and 0.1wt% functionalized gold NPs. We obtained a configuration characterized by PS domains with their axes parallel to the film surface, as shown by the TEM image in Figure 5a, and schematically represented in Figure 5a'.

By employing a simple method of annealing of the BCP film in a solvent atmosphere, starting from the disordered configuration, we obtained a partial alignment of PS cylinders, as shown by TEM image of Figure 5b. In this way a short range lateral order in the hexagonal packing of PS cylinders has been obtained. It is clear that the fabricated films can be schematically represented as in Figure 5b', where the PS cylinders are mainly oriented with the axes parallel to the film surface, and the mean inter-domain spacing is 60 nm .

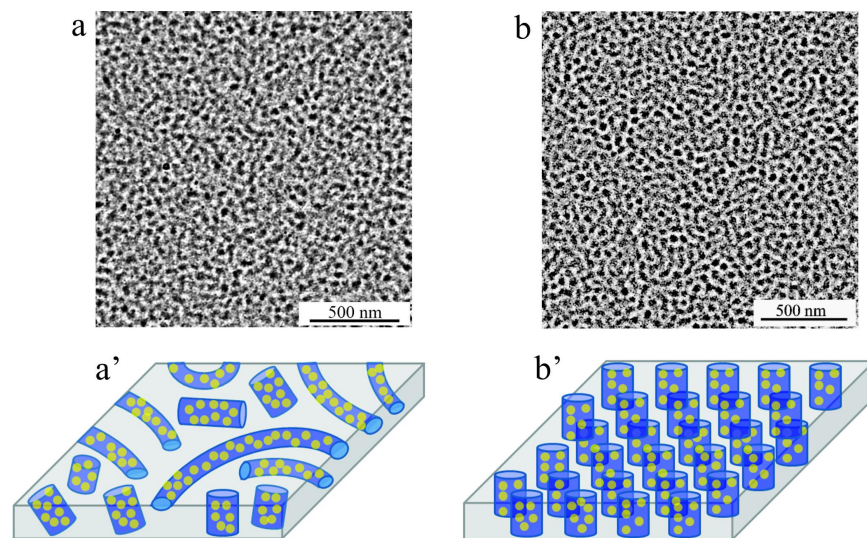


Figure 5. (a, b) TEM images of thin films of PS-*b*-PMMA based nanocomposite obtained by spin coating a slight excess of a toluene solution containing 2wt% BCP and 0.1wt% gold NPs, after drying at room temperature (a) and successive exposition at room temperature to dichloromethane vapors (b). (a',b') Schematics of the cylindrical morphology obtained in a and b.

3.2 Measurements

The optical properties of the fabricated BCP films with sequestered gold nanoparticles were studied by measuring the extinction spectra using an UV-Visible spectrophotometer. Spectra were recorded by measuring the ratio of transmitted to the incident radiant power and subtracting the spectrum of a thin film of the sole PS-*b*-PMMA film as background. The extinction spectra of the BCP thin films in the two configurations, *i.e.* the random orientation (Figure 5a') and the vertical orientation (Figure 5b'), are shown in Figure 6. We used an unpolarized light beam perpendicular to the film surfaces, in the wavelength range 500 nm – 800 nm. Therefore, in the case of oriented films (Figure 5b'), the incident beam wave vector is parallel to the axes of PS cylinders, whereas for the unoriented film (Figure 5a'), there is no definite relationship between the direction of wave vector of incident beam and the local axes of PS domains.

The spectrum of the unoriented film (Figure 5a') is characterized by the typical plasmonic resonance of AuNPs centered at 520 nm (curve a of Figure 6). On the contrary, the extinction spectrum for the thin films with vertically aligned cylinders (Figure 5b') differs considerably from that of the unoriented film, since it shows enhanced contributes at wavelengths higher than 520 nm, and consequently a broadening of the resonance peak centered at 550 nm (red shift) (curve b of Figure 6). These data clearly suggests that the vertical orientation of PS cylinders and their pseudo-hexagonal bidimensional arrangement at distance of few nanometer (average center-to-center distance $D \approx 62$ nm) should be responsible for the variation of the extinction spectrum. We argue, indeed, that since the gold NPs are selectively included in the PS domains, the nearly periodic array is able to generate collective plasmon resonances which play a key role in the broadening of the extinction peak toward the red spectral region, *i.e.* at wavelengths > 550 nm.

4. CONCLUSIONS

In conclusion, we investigated the optical response of plasmonic metamaterials based on self-assembled PS-PMMA block-copolymer with sequestered gold nanoparticles. We showed that the nanoparticles inside a single PS cylindrical domain interact if the particle size is sufficiently large and the particle concentration is sufficiently high. Moreover we investigated the effects of the hexagonal lattice of the PS domains inside the PMMA matrix. Eventually, we experimentally observed the effects of the array order in PS-PMMA thin films with small gold nanoparticles sequestered in the PS domain. These results confirm the importance of block-copolymers as a technological platform for fabricating large-scale metamaterials with tunable optical properties.

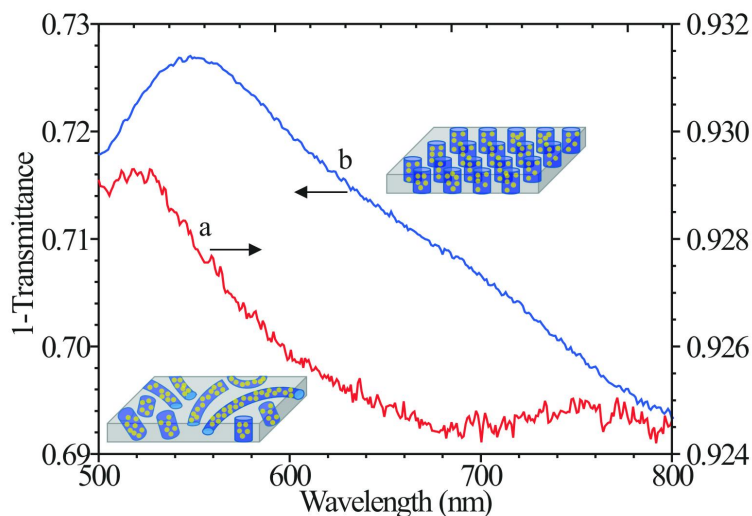


Figure 6. Extinction spectra of PS-b-PMMA thin films (measured by the absorption factor = 1-Transmittance) presenting random orientation (a), and vertical orientation of PS cylindrical domains (b). PS cylinders in b form an hexagonal array with short range order and average periodicity of $\approx 62 \text{ nm}$. In both cases AuNPs are selectively included in the PS domains.

REFERENCES

1. G. H. F. Bates and G. H. Fredrickson, "Block copolymer thermodynamics: Theory and experiment," *Annual Review of Physical Chemistry* **41**, pp. 525,557, 1990.
2. M. J. Fasolka and A. M. Mayes, "Block copolymer thin films: Physics and applications," *Annual Review of Materials Research* **31**, pp. 323,355, 2001.
3. M. Bockstaller, R. Mickiewicz, and E. Thomas, "Block copolymer nanocomposites: Perspectives for tailored functional materials," *Advanced Materials* **17**(11), pp. 1331–1349, 2005.
4. E. M. Purcell and C. R. Pennypacker, "Scattering and absorption of light by nonspherical dielectric grains," *The Astrophysical Journal* **186**, pp. 705–714, 1973.
5. B. T. Draine, "The discrete-dipole approximation and its application to interstellar graphite grains," *The Astrophysical Journal* **333**, pp. 848–872, 1988.
6. A. Doicu, T. Wriedt, and Y. Eremin, *Light Scattering by Systems of Particles: Null-Field Method with Discrete Sources: Theory and Programs*, Springer Series in Optical Sciences, Springer, 2006.
7. C. D. Rosa, F. Auriemma, R. D. Girolamo, G. P. Pepe, T. Napolitano, and R. Scaldaferri, "Enabling strategies in organic electronics using ordered block copolymer nanostructures," *Advanced Materials* **22**(47), pp. 5414–5419, 2010.
8. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, "Synthesis of thiol-derivatised gold nanoparticles in a two-phase liquid-liquid system," *J. Chem. Soc., Chem. Commun.* (7), pp. 801–802, 1994.