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Hyperbolic-by-design self-assembled metamaterial based on block copolymers lamellar phases

Xuan Wang [a,b], Kevin Ehrhardt [a,b], Clémence Tallet [a,b], Marc Warenghem [c,d], Alexandre Baron [a,b], Ashod Aradian [a,b], Morten Kildemo [e], Virginie Ponsinet [a,b,*]

[a] CNRS, Centre de Recherche Paul Pascal, UPR 8641, 115 Avenue Schweitzer, Pessac, 33600, France
[b] Univ. Bordeaux, Centre de Recherche Paul Pascal, UPR 8641, 115 Avenue Schweitzer, Pessac, 33600, France
[c] Université Lille Nord de France, Lille, 59000, France
[d] Université d'Artois, Unité de Catalyse et de Chimie du Solide, UMR 8181, Lens, 62307, France
[e] Physics Department, NTNU, Høgskoleringen 1, Trondheim, 7491, Norway

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ABSTRACT

Hyperbolic metamaterials use the concept of controlling the propagative modes through the engineering of the dispersion relation, and are considered highly promising to reach different meta-properties. Here we propose a novel bottom-up fabrication technique for uniaxial anisotropic metamaterials presenting a strongly anisotropic dispersion relation in the visible wavelength range, using self-assembled nanostructured block copolymers hybridized with gold nanoparticles. The materials consist in periodic lamellar stacks of period 28 nm, of alternating layers of pure polymer (dielectric) and layers of composite of polymer loaded with a high density of 7 nm gold nanoparticles. The spectral variation of their anisotropic effective dielectric permittivity is determined by variable-angle spectroscopic ellipsometry using appropriate effective medium models, as a function of the density of plasmonic nanoparticles. For large gold loading and close to the plasmon resonance of the nanoparticles, the lamellar stack presents ordinary and extraordinary components of the dielectric function of opposite signs. We therefore demonstrate for the first time the possibility of using a self-assembly methodology for the fabrication of bulk hyperbolic metamaterial.

1. Introduction

The breakthroughs and innovations in the information and communication technologies rely, to a large extent, on improved performances of the devices, and their constitutive materials. Optical metamaterials lie among these envisioned breakthroughs in the near future: they are artificial materials structurally designed with the purpose of producing extraordinary optical properties. Their potential in revolutionizing the optical technologies has been largely recognized [1–3]. While precise control of both the dielectric permittivity $\varepsilon(\lambda)$ and the magnetic permeability $\mu(\lambda)$ of a 3D artificial material, in the visible or infra-red ranges, would open access to transformation optics and negative index materials, leading to the capacity of engineering the propagation of light in devices in an unprecedented manner [2], these goals are still far from reach. On the other hand, by combining nanostructuration and anisotropy, it is possible to engineer novel and non-natural dispersion relations, in order to control original propagation properties. This is why a recent interest has focused on a special case of uniaxial anisotropic metamaterials, called hyperbolic materials [4–7], which exhibit strongly anisotropic dispersion relations in the visible or infra-red wavelength range. These materials are considered amongst the most promising metamaterials, because of their ability to provide a multi-functional platform [4] to reach different meta-properties.

For example, hyperbolic nanowire and lamellar stacked metamaterials have been studied theoretically and experimentally [4,6,8,9]. Such structures have displayed a variety of promising properties, generating a surge in the activity on the topic over the recent years: negative refraction [10], super-resolution [11], subwavelength modes [12], perfect multi-band absorption [13], optical topological transition [14], epsilon-near-zero light propagation [15], spontaneous emission and Purcell effect enhancement [16–20], thermal emission engineering [21] including super-Planckian regimes [22], or biosensing [23,24].

One very attractive property is the so-called "super-resolution"

* Corresponding author at: CNRS, Centre de Recherche Paul Pascal, UPR 8641, 115 Avenue Schweitzer, 33600 Pessac, France.
E-mail address: ponsinet@crpp-bordeaux.cnrs.fr (V. Ponsinet).

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(i.e., sub-diffraction imaging), because the required structures are relatively less demanding than other metamaterials, and because super-resolution could be profitable to several technological fields. Optical microscopy is indeed an essential tool in many fields such as microelectronics, biology and medicine. It is, however, hindered by the intrinsic diffraction limitation as it cannot obtain a better resolution than half the wavelength of light. This is because the finer detail-carrying, high wavevector components of the field emitted from the object are evanescent, decay exponentially in a medium with positive permittivity and permeability, and cannot contribute to the subwavelength image formation. Near-field scanning techniques [25], and fluorescence-based imaging methods [26] have put forward ways to circumvent this limitation and have brought optical microscopy into the nanoworld, with the fascinating and revolutionary goal to visualize the pathways of individual molecules inside living cells [27]. Similar intrinsic resolution limitations also hinder optical lithography, one of the most important tools equipping the semiconductor industry, ubiquitous in our societies.

In hyperbolic materials, two components of the dielectric permittivity tensor ε have opposite signs, as if the material behaved like a metal ($\varepsilon_i < 0$) along at least one direction and like a dielectric ($\varepsilon_j > 0$) along at least another. Let us consider a uniaxial material with principal axes (x,y,z) and permittivity tensor

$$\underline{\underline{\varepsilon}} = \begin{pmatrix} \varepsilon_{//} & 0 & 0 \\ 0 & \varepsilon_{//} & 0 \\ 0 & 0 & \varepsilon_z \end{pmatrix} \text{with } \varepsilon_{//} = \varepsilon_{//}' + i\,\varepsilon_{//}'' \text{ and } \varepsilon_z = \varepsilon_z' + i\,\varepsilon_z'' \tag{1}$$

where the parallel (//) symbol denotes the (x,y)-plane. The iso-frequency dispersion relation in this material is [4,28]

$$\left(k_x^2 + k_y^2 - \varepsilon_{//}\varepsilon_o\mu_o\omega^2\right)\left((k_x^2 + k_y^2)\,\varepsilon_{//} + k_z^2\varepsilon_z - \varepsilon_z\varepsilon_{//}\varepsilon_o\mu_o\omega^2\right) = 0, \tag{2}$$

where the two terms describe the behavior of waves of different polarizations: polarization in the (x,y) plane for the first term and polarization in a plane containing the z direction for the second.

The latter can be written

$$\frac{k_x^2 + k_y^2}{\varepsilon_z} + \frac{k_z^2}{\varepsilon_{//}} = k_o^2, \text{ with } k_o^2 = \varepsilon_o\mu_o\omega^2 \tag{3}$$

It exhibits a hyperboloid branch when the product $\varepsilon_{//}'\varepsilon_z' < 0$, contrary to dielectrics, for which this relation defines a closed ellipsoidal shape (spherical if isotropic). This peculiar shape allows notably for the propagation of large magnitude wavevectors, carrying details finer than half the wavelength, otherwise corresponding to evanescent non-propagative waves in a usual dielectric. Hyperbolic material fabrication usually relies on metal deposition within top-down produced uniaxial nanostructures, either lamellar or cylindrical, and their permittivity tensor is usually inferred from basic effective medium models. The spectral tunability of the effective medium properties of the material is limited by the large spectral dispersion of the optical properties of the metal, which generally follows the Drude model.

One of the main bottlenecks in the research on metamaterials and hyperbolic materials in particular remains the lack of robust, simple and large scale fabrication technologies which permit tailoring final optical properties at chosen frequency ranges (including visible frequencies), and setting the technological basis for the development of devices: the field is open to innovative fabrication proposals. The powerful 'top-down' techniques such as nanolithography have been successful in manufacturing nanostructured surfaces and in evidencing meta-material properties, such as hyperlensing [29] and cloaking [1], at wavelengths larger or close to the visible domain [30] and even at ultraviolet frequencies [31]. The use of chemistry and self-assembly of metallic nanoparticles, acting as plasmonic resonators, into dense ordered structures, was anticipated as a promising 'bottom-up' alternative [32,33], especially in order to produce large-scale, 3D and tunable metamaterials. The versatility of chemical synthesis and the diverse mechanisms of self-assembly can be combined to produce materials with both nanostructuration and anisotropy, presenting novel propagation properties in the visible or infra-red ranges.

In particular, diblock copolymers [34,35] have long been known to self-assemble into nanomaterials with strong structural anisotropy. They are macromolecules made of two molecular chains of distinct chemical nature linked together, called the blocks, and present solid state spontaneous organizations with long-range order and tunable characteristic sizes, ranging typically from a few nanometers to a few hundred nanometers. The morphology is selected mostly in relation with the volume fractions of the blocks f_A and $f_B = 1 - f_A$, due to interfacial curvature effects [35,36], among the choice of body-centered cubic array of spherical cores, bi-continuous gyroid, hexagonally packed cylinders and lamellae. It is thus largely possible to design a desired material by choosing the chemical nature and the length of the blocks in order to obtain a given morphology, a given characteristic size, as well as a given chemical functionality. Using such ordered block copolymer phases for optical applications is limited by the usually low dielectric contrast between the blocks: the refractive index of almost all easily accessible polymers is in the range 1.48–1.61. One way of improving the contrast, among others [37,38], or of conferring specific optical properties, is to disperse adequate nanoparticles within the ordered polymer phase in such a way that the particles get ordered by the matrix. This is what is reported in this work, in which we show that nanocomposites based on metal nanoparticles embedded in a dielectric host, can present a strongly anisotropic structure, as well as spectrally selective optical anisotropy, as a consequence of the spectral tunability of the plasmon resonance.

Indeed, we propose in this article a novel fabrication technique for lamellar metal-dielectric nanocomposites using self-assembled block copolymer nanostructures, and we demonstrate the relevance of such bottom-up methodology for the fabrication of hyperbolic metamaterials. We first describe the preparation and structural study of thin films of self-assembled nanocomposites of block copolymers and gold nanoparticles prepared by wet chemistry. We then present the study of the relation between the structure of the composites, and in particular the density of the gold nanoparticles, and the anisotropy of their effective dielectric permittivity tensor, which is extracted from variable-angle spectroscopic ellipsometry. We finally discuss the hyperbolic nature of the self-assembled material.

2. Nanostructure design and fabrication

As a first requirement, a structural *uniaxial symmetry* appears highly desirable, in order to obtain a hyperbolic regime of optical anisotropy. Diblock copolymer thin film engineering [39,40] offers a genuine technological platform for the generation of nanostructured thin films with different morphologies of the domains. Two specific thin film morphologies are particularly attractive here, which present a high degree of order and a uniaxial symmetry: the lamellar phase in parallel alignment, which we study in the following, and the phase of hexagonally-packed cylinders in perpendicular orientation, which has been considered for applications including lithography masks [41–43] and enhanced patterned LEDs [44]. A second requirement, for the light propagation properties to be described by a homogenized dispersion relation,