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I. Murataj,[1-2] A. Angelini,[1-2] F. Frascella,[2]

N. De Leo,[1] M. Laus, [3] L. Boarino,[1] F. Pirri,[2] F. Ferrarese Lupi,[1]*

[1] Nanoscience and Materials Division, Istituto Nazionale Ricerca Metrologica, Strada delle Cacce 91, 10135 Torino, Italy

[2] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi, 24, Torino, Italy

[3]Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale ''A. Avogadro'', Viale T. Michel 11, 15121 Alessandria, Italy

Corresponding author e-mail: irdi.murataj@polito.it

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ABSTRACT

Hyperbolic materials are high uniaxial anisotropic materials that display hyperbolic dispersion with distinctive properties including negative refraction index, control over light propagation and enhanced Purcell factor that can be exploited for metrological applications such as in guiding and increasing the single photon sources (SPS) performances and in sensing, by reducing the detection limit in surface-enhanced Raman spectroscopy (SERS). Since naturally-occurring hyperbolic materials exhibit hyperbolic dispersion in fixed wavelength ranges, artificial structures *i.e.* hyperbolic metamaterials (HMMs), are therefore required for a greater flexibility and broader hyperbolic dispersion bandwidths. So far, the realization of metamaterials that work in the visible and near-infrared wavelength regions has been prevented by the fabrication of features at sub-wavelength dimensions which require the use of advanced nanofabrication techniques. Here we exploit the ability of block copolymers (BCPs) to self-assemble into highly ordered arrays of nanostructures, used as templates for the subsequent fabrication of hybrid metal-dielectric HMMs.

Hyperbolic materials

Hyperbolic materials are a particular class of optical materials in which one of the diagonal components of either the permittivity (ε) or permeability (μ) tensors hold an opposite sign with respect to the other two. The presence of positive and negative signs of the tensors' components leads to distinct behaviour of the material, as a metal or a dielectric, depending on certain directions [optic]. In contrary to isotropic dielectric that show a spherical iso-frequency surface (fig. 1a), these materials possess uniaxial anisotropy in which the dispersion relation (eq. (1)) describes one- or two-sheeted hyperbolic iso-frequency surfaces (fig. 1b,c). The hyperbolic iso-frequency contour is responsible for unique optical properties of such materials. First of all, the large anisotropy directs the wave propagation in the bulk as well as in the surface, leading to a directional emission of light. Secondly, the infinitely large volumes of the hyperboloidal shells allow the propagation of high-*k* wavevectors, resulting in a larger local density of states (LDOS) [5]. The significant increase in additional LDOS provides a higher light-matter interaction [6] (higher Purcell factor) thanks to numerous extra decay channels, consequently enhancing the spontaneous emission rate of a single-photon source (SPS) placed in proximity of the hyperbolic material. Although there is a number of natural 2D materials with hyperbolic dispertion, such as graphene and transition metal dichalcogenides (TMDs) [1,2], they exhibit hyperbolic dispersion only at certain wavelength ranges. In order to tailor the hyperbolic dispersion of optical materials over a broad wavelength range, a lot of attention has been dedicated to the development of an artificial subclass of hyperbolic materials with properties unavailable in nature, namely the hyperbolic metamaterials (HMMs). Hyperbolic metamaterials are nanostructured materials composed of alternated metal-dielectric features at sub-wavelength dimensions that show hyperbolic dispersion across UV-visible and IR spectrum enabling different applications such as high-resolution imaging [3], negative refraction index for planar lenses [2,4], waveguiding [1] and lifetime engineering [8]. So far in literature, the typical configurations of HHMs are multilayer stacks of thin films of sub-wavelength thicknesses [book HMM] that act in the out-of-plane direction ($\varepsilon_x > 0$, $\varepsilon_z = \varepsilon_y < 0$). Their fabrication relies on sequential growth or deposition of metal-dielectric multilayers [single photon]. However, for the implementation of HMMs in metrology, the design of more complex systems, such as waveguides (WGs), with a great control over dimensions and position is a fundamental requirement for the emission rate enhancement of SPS in a well-determined direction as well as for significant signal enhancement in SERS analysis for the detection of biomolecules (fig. 2). The realization of HMM-WGs with the optical axis in the plane of the metal-dielectric interface ($\varepsilon_y = \varepsilon_z > 0$, $\varepsilon_x < 0$), is still challenging, prevented by several physical and technological limitations of conventional fabrication techniques. The fabrication requires a perfect control of the deposition process of periodic dielectric/metal features perpendicularly oriented to the substrate at sub-20 nm level with minimum feature sizes well below the wavelength of the light propagating inside the HMM-WG.

Nanofabrication

For the realization of novel and more complex HMM structures we exploit the ability of block copolymers (BCPs) the self-assemble into vertically oriented features at the nanoscale [9] that show to be ideal platforms for the fabrication of HMM-WGs. The self-assembly (SA) of BCPs is a non-optical bottom-up lithographic approach that in the last years become subject of an intense research activity in a

vast number of advanced applications due to their ability to build up periodic sub-20 nm structures with a high degree of reproducibility and regularity [10]. The BCPs consist of two or more distinct homopolymers, usually immiscible to each other, joined by a covalent bond [BCP book]. The chemical incompatibilities among the polymer chains are responsible for the microphase separation in different periodic structures such as spheres, cylinders, lamellae and gyroids with nanometric feature sizes in which the dimensions and shapes can be modulated by opportunely varying the degree of polymerization of each polymer block. The phase separation strongly depends on the molecular weights and on a thermodynamic parameter, χ, that measures the enthalpy of interactions between the two blocks [11]. Among all the block copolymers, polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) has been the most widely investigated system in the field of microelectronic [science], nanolithography [grapho] and in the design of novel functional materials thanks to the easy fabrication even on a large scale [12]. For the realization of HHM-WGs, a key requirement is the perfect nanostructures registration. However, BCPs self-assembled over a flat, unpatterned substrate are characterized by a fingerprint like morphology caused by the presence of many defects such as dislocations, disclinations and grain boundaries, that prevent their effective implementation in the realization of such materials. So, in order to achieve the defect-free alignment of BCPs on wide areas, we combine the self-assembly process of BCPs into prepatterned substrates obtained by conventional lithographic techniques *i.e.* EBL, UVL in a so-called directed self-assembly (DSA) process (fig. 3) [14,15]. Since the correct outcome of the DSA is strictly related to long-range ordering of the nanostructures over an unpatterned surface, it is necessary to increase the grain sizes of lamellar or cylindrical systems. Mixing BCPs with low molecular weight homopolymers of their constituent blocks significantly increases the grain sizes up to one order of magnitude higher compared to the neat BCP thanks to the solvent-like effect of the homopolymers that act as plasticizer thus, enhancing the coarsening kinetics [13, doerk]. For the final realization of HHMs, the BCPs highly ordered nanostructures are used as a template for subsequent incorporation of the metal/dielectric species inside each block respectively. The dielectric constituent of the metamaterial is fabricated by sequential infiltration synthesis (SIS) which enables hybrid organic/inorganic materials to be obtained from nanostructured block copolymer templates [16]. The SIS consist in the selective synthesis of various robust metal-oxides (Al_2O_3, ZnO, TiO_2) based on the cyclic exposure of the BCP to organometallic precursors of such metal-oxides and water. The selective association of the gaseous precursors with the Lewis basic functional groups of the polar polymer block leads to the formation of metal-oxides replicating the exact same morphology of the selected nanodomain [17]. For the incorporation of the metallic phase, the conventional top-down techniques such as evaporation or sputtering [18] suffer from strong limitations in the possibility of creating epitaxial structures. A promising pathway for the inclusion of metals at the nanoscale dimensions is represented by a template-assisted nanopatterning approach [Steiner] *via* electro- or electroless-deposition [19,20] after the selective degradation of one of the copolymer block nanodomains and backfilling of BCP's scaffold with a variety of metals *i.e.* Au, Ni, Pt.

In conclusion, highly anisotropic materials show distinctive optical properties suitable for metrological applications as the promotion of spontaneous emission and the increasing of SERS signal. Naturally available 2D materials (graphene and TMDs) demonstrated hyperbolic dispersion, however only in certain fixed wavelength ranges. This rise the necessity to realize artificial materials with tailored optical responses in the visible and near-infrared wavelength spectrum, such as HMMs. In order to overcome the technological limitation imposed in the fabrication of HMMs at the nanometric scale we propose the use of the directed self-assembly (DSA) of block copolymers (BCPs) as templates for the subsequent

fabrication of hybrid metal-dielectric hyperbolic metamaterials (HMMs) by sequential infiltration synthesis (SIS) and electrochemical deposition.

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