Introduction. – Metamaterials are artificial composite materials that exhibit extreme physical properties that do not exist in natural materials. The origin of the scientific field is often associated with the theoretical work of Veselago in 1968 who discussed the propagation of light in a hypothetical negative index material (NIM) resulting from simultaneous negative values of the electric permittivity $\varepsilon$ and of the magnetic permeability $\mu$ [1], but the interest for metamaterials really started and grew tremendously at the beginning of the years 2000 when the first realization of a NIM occurred, based on the novel design proposed by Sir John Pendry of a sub-wavelength inductive-capacitive resonant circuit (split ring resonator or SRR) enabling the control of the magnetic response to light [2,3]. Although limited to microwave frequencies in the GHz range, the demonstration of the non-natural NIM property suggested that unprecedented extraordinary optical applications such as perfect lensing [4] or cloaking [5] were achievable, especially since the recipe for the design of metamaterials was given: the functionality is based on resonant inclusions of sub-wavelength size (meta-atoms) distributed in a transparent matrix. The resonant behaviour of the inclusions warrants an intense optical response upon approaching the resonance frequency $\omega_0$ (high $\varepsilon$, high $\mu$) as well as a phase shift leading to the desired sign inversion upon crossing $\omega_0$. The sub-wavelength condition is required to enable homogenization, i.e., a valid description of the optical properties by the usual effective parameters $\varepsilon$ and $\mu$ or equivalently the refractive index $N = (\varepsilon\mu)^{1/2}$ and the optical impedance $Z = (\mu/\varepsilon)^{1/2}$. The concept of metamaterials, which can be summarized as the full control of the reflection, refraction, phase and polarization of light waves at the sub-wavelength scale, hence led to the blossoming of a tremendous set of potential applications that were abundantly discussed in the literature like filters, light couplers, light concentrators, field enhancers for sensing or non-linear optics, miniaturized antennas to name a few [6]. The concept was actually extended to all types of waves with spectacular applications.
in acoustics [7], mechanics [8,9], ocean [10,11] and seismic waves [12].

For electromagnetic waves, the vast majority of the experimental realizations are devices fabricated by lithography techniques. This top-down approach offers a quasi-perfect control of two-dimensional composite structures, sometimes referred to as metasurfaces. It is however hard to extend to 3D materials, because the number of inscribed resonators is generally limited and the lithography techniques reach their limits when nanometre resolution is needed for visible-light applications. In this case, the size of the resonators and the distance between them should not exceed $\sim 100 \text{nm}$ to satisfy the homogeneity condition, which requires $\sim 10^{12}$ resonators per $\text{mm}^3$ to make a bulk metamaterial or $10^8/\text{mm}^2$ for a metasurface. The bottom-up approach that combines nanochemistry for the synthesis of optical resonators and colloidal physics for their self-assembly in 2D or 3D structures appears as an appealing alternative for the fabrication of metamaterials operating in visible light or near IR [13,14]. It can easily produce and handle large volumes of materials at low cost, though at the expense of a lower degree of structural control of the nanostructure. The aim of this paper is to illustrate the bottom-up approach with a selection of recent examples of self-assembled metamaterials.

**Self-assembly of resonators.** – Advanced optical functionalities require resonators of complex morphologies that can be achieved by self-assembly of simpler units. The power of the bottom-up approach lies in its ability to synthesize a huge number of resonators ($\sim 10^{13}$ per batch in the laboratory) which can be subsequently assembled into macroscopic materials. Two examples are given below.

**Magnetic nanoclusters.** The generation of optical magnetism in visible light is a tough challenge: the response time of para- and ferromagnetism is far too slow and natural diamagnetism is notoriously negligible [15]. Nonetheless, the generation of intense magnetic dipoles at the frequency of visible light has been achieved in devices based on pairs of plasmonic elements organized on a surface by the top-down approach [16–19]. However, the optical magnetic response of such metasurfaces is anisotropic and highly non-local. It is depicted by spatial dispersion of the dielectric permittivity rather than by a homogeneous permeability parameter $\mu$ [20,21]. An alternative model of raspberry-like isotropic magnetic nanoclusters (MNC) shown in fig. 1(a) was proposed by Simovski and Tretyakov [22] in which the light wave induces loops of resonant plasmonic currents [23]. Figure 1(b) shows a realization of the MNC by Gomez-Graña et al. [24] formed by silver nanoparticles surrounding a spherical silica core. The spontaneous self-assembly of the raspberry structure results from electrostatic interaction between the positively charged core and the negatively charged silver satellites, the final MNC being encapsulated in a thin silica layer to warrant its structural stability. The magnetic response of the MNCs was demonstrated by analyzing the polarization of the light scattered by a dispersion of MNCs in water. Figure 1(c) shows plots of the electric and magnetic scattering cross-sections, perfectly consistent with numerical simulations [24].

**Plasmonic nanohelices.** Enhancing the chirality of nano-objects or substrates is another important challenge of metamaterials with applications in chiral recognition, sub-wavelength circular polarisers or low-index materials. A natural strategy for the synthesis of super-chiral meta-atoms consists of organizing nanoresonators in a helical fashion [25]. Cheng et al. used chiral colloids as templates for grafting gold nanoparticles (GNPs) [26]. These hybrid nanohelices are synthesized from organic chiral self-assemblies forming very well-defined helices or ribbon structures (fig. 2(a)) [27]. The mineralization of these organic self-assemblies produces silica nanohelices of very well-controlled morphologies in terms of diameter and pitch (typical values are, for the helices diameters of 35 nm and pitches of 65 nm and for twisted ribbons widths of 20 nm and pitches of 95 nm). The handedness of the structures is governed by the constituent molecular chirality [28–30]. These silica nanohelices are then used as chiral templates in order to organize GNP helical superstructures. Varying the GNP size between 4 nm and 10 nm, as well as the surface chemistry of both the GNPs and the silica nanohelices, it is possible to span a large range of grafting densities. When the GNPs are densely
Self-assembled nanostructured metamaterials

Fig. 2: (Colour online) (a) Synthesis of the chiral meta-atoms: from organic self-assembly forming nanohelices used as template for the silica transcription and grafting of 9 nm GNP s on their surfaces. (b) Circular dichroism spectra showing the opposite signals for left- and right-handed GNP s/silica helices [26].

adsorbed on the helices, they follow the helicity of the silica template and a strong resonant chiroptical activity is evidenced by circular dichroism spectroscopy showing opposite CD signal for left- and right-handed helices (fig. 2(b)). The measured anisotropy factor (g-factor) is of the order of $10^{-4}$, i.e., tenfold larger than typical values reported in the literature [31]. The optical activities depend on the size and the organization of the GNP s on the surface of the helical silica template which are closely correlated with the surface chemistry of both the GNP s and the silica helices [26,32].

**Self-assembly of a macroscopic material.** – Once the meta-atoms have been synthesized, the next challenge is to assemble them into a bulk material or into a metasurface while preserving their optical functionality. In contrast with photonic crystals, which operate in the diffractive regime where the structural ordering is critical, metamaterials are not much affected by structural disorder, as long as the response of the meta-atoms is not degraded by their mutual coupling, because they function in the regime of homogeneous optical response. The popular self-assembly routes of colloidal physics hence appear as excellent tools for the macroscopic organisation of large numbers of meta-atoms. Thin films of large area can for example be produced by Langmuir-Blodgett assembly, dip- and spin-coating or meniscus evaporation. 3D materials may result from sedimentation of a suspension of meta-atoms or controlled evaporation of their solvent. Two examples are illustrated below.

Fig. 3: (Colour online) (a), (b): SEM views of the assembled magnetic metamaterial showing flat surfaces in (a) and random packing in (b). (c) Real part of the magnetic permeability extracted from spectroscopic ellipsometry. Red and blue colours correspond to two different samples. Natural materials lie on the black line at $\mu' = 1$.

**Bulk magnetic metamaterial.** The magnetic nanoclusters shown in fig. 1(b) have been assembled in a bulk 3D material in a micro-evaporator made in a microfluidic chip designed so as to enable a slow evaporation of water across a thin polymer (PDMS) membrane [24,33]. After complete evaporation, a dense material made of a random close-packing of MNCs is formed which replicates the shape of the microfluidic canal (fig. 3(a)). The optically flat surface and the large thickness of the metamaterial enables a full determination of the optical parameters $\varepsilon$ and $\mu$ by variable angle spectroscopic ellipsometry. The real part of the magnetic permeability $\mu$ is shown (fig. 3(b)). Two results of this study are remarkable. First, the permeability deviates significantly from 1. Variations from 0.8 to 1.45 correspond to a magnetic susceptibility $\chi = \mu - 1$ ranging from $-0.2$ to 0.45, three to five orders of magnitude higher than natural diamagnetism. Second, the angular study shows that the values of the optical parameters $\varepsilon$ and $\mu$ do not depend on the angle of incidence.

This example illustrates two positive points of the bottom-up approach. The sample thickness larger than the absorption length equivalent to a semi-infinite geometry enables an analytical extraction of the optical parameter without any ad hoc model. Moreover, the random packing of the MNCs implies a continuous rotational symmetry of the nanostructure which minimizes the effects of spatial dispersion as explained in ref. [24]. As a result, this metamaterial is the first bulk material that breaks the Landau-Lifshitz rule stating that the magnetic permeability $\mu$ should always be 1 in visible light [15].
Resonant metasurfaces. The optical properties of 2D arrays of resonators have been widely investigated by theoretical, numerical and experimental studies. Malassis et al. prepared dense arrays of silver nanospheres of large area by transferring Langmuir monolayers on a flat substrate [34,35]. Interestingly, the distance (and hence the electromagnetic coupling) between the silver resonators can be controlled by encapsulating them in a silica layer of controlled thickness. Figure 4(b), (c) shows a film made of 6 layers of core-shell silver@silica on a silicon substrate [34] by 6 successive Langmuir-Schaefer transfers, a variant of the Langmuir-Blodgett technology in which the Langmuir monolayer is transferred to an immersed substrate by lowering the water level of a Langmuir trough. The presence of sharp, blue-shifted optical resonances (with respect to single resonators) was demonstrated in these films which exhibit the interesting property of plasmonic Brewster extinction (topological darkness) whereby the reflection from an absorbing substrate is totally extinguished by optical interferences in the film [35].

Chiral films. Organizing elongated objects like nanorods or nanohelices within a thin film usually requires the control of the orientation as an additional degree of freedom. Several fabrication techniques promote the orientation of anisotropic objects on a surface like dip-coating [36], grazing incidence spraying [37] or surface patterning [38] to name a few recent examples. Another approach is illustrated in fig. 5 in which the silica nanohelices mentioned above are incorporated in a polymer film which is subsequently stretched along one direction. Figure 5(a) shows bare silica ribbons with random orientation after dispersion in a polymer matrix of poly(ethylene-co-vinyl acetate). By stretching 10 times the matrix, the transparent film becomes slightly hazy as the chiral nanoribbons get perfectly oriented along the strain direction (fig. 5(b)).

In situ synthesis within a self-assembled template. Another self-assembly route for the fabrication of metamaterials consists in introducing resonators in selected regions of a pre-existing self-assembled nanostructure, which acts as a template. An example is given below.

Self-assembled hyperbolic metamaterials. Some meta-properties are related to the anisotropy of the materials rather than to the presence of complex resonant objects. This is the case for hyperbolic metamaterials, in which a combination of nanostructuration and anisotropy gives rise to non-natural dispersion relations, and which are now regarded as highly promising metamaterials, because of their ability to provide a multi-functional platform to reach different meta-properties [39].

A hyperbolic metamaterial presents two eigenvalues of the dielectric permittivity tensor \( \epsilon \) with opposite signs, as if it behaves like a metal (\( \epsilon_{ii} < 0 \)) along at least one direction and like a dielectric (\( \epsilon_{jj} > 0 \)) along at least another. Consequently, the isofrequency dispersion relation exhibits a hyperboloid branch, allowing for the propagation of large-magnitude wave vectors. These large wave vectors carry the information of fine details and are usually associated to evanescent waves in natural materials, which make them inaccessible to regular microscopes. Soft-matter self-assembly can provide powerful fabrication routes for such extreme anisotropy. Liquid crystals and block copolymers, in particular exhibit self-assembly properties described theoretically and experimentally to a high degree of detail over the last fifty years [40,41]. They present spontaneous molecular organization, possibly strongly anisotropic, with long-range order and characteristic sizes in the range 2–500 nm. From the optical point of view, the anisotropy of these
organic materials is high enough to generate a strong birefringence, exploited in liquid-crystal displays for instance, but still too low to reach the hyperbolic regime in their native state. In order to enhance the optical anisotropy, block copolymer self-assembled nanostructures can be used to template and order optically resonant nanoparticles [42,43]. Such complex hybrid nanostructures have proven useful to monitor optically probed nanoscale sensing [44] or produce photonic bandgap materials [45].

Lamellar nano-composite thin films have been produced on a silicon substrate via the in situ synthesis of gold nanoparticles, selectively grown in the poly(2-vinylpyrididine) domains of a lamellar phase of poly(styrene)-b-poly(2-vinylpyrididine) block copolymer. The SEM images in fig. 6 show that the films are structurally uniaxial and homogeneous, enabling the definition of the dielectric permittivity tensor with ordinary (parallel to the substrate, \( \varepsilon_{||} \)) and extraordinary (normal to the substrate, \( \varepsilon_{\perp} \)) components. Using variable angle spectroscopic ellipsometry, the existence of the hyperbolic regime with \( \varepsilon_{||} < 0 < \varepsilon_{\perp} \) was demonstrated in a wavelength domain around the plasmon resonance of the gold nanoparticles loaded in the nanocomposite (fig. 6) [46].

In the hyperbolic region, the dispersion relation allows propagative modes for large values of \(|k_z|\), potentially providing super-resolution. These modes are however significantly attenuated due to the resonant—and therefore lossy—nature of the permittivity. These detrimental losses should be minimized by optimizing the quality factor of the resonances, through tuning the nature, size and organization of the nanoparticles.

**Perspectives.** Just like their top-down counterparts, bottom-up metamaterials are severely affected by optical losses which are indeed fundamentally associated with highly dispersive resonances by the causality principle. The compensation of plasmonic losses by an active gain medium has been proposed as a possible solution in which energy is injected at the plasmon frequency by external sources via optically pumped fluorophores or quantum dots [47]. This active technology, still to be developed, is likely to be expensive and limited to high added-value applications.

In passive systems, two options can be explored to reduce the effect of losses in future bottom-up metamaterials. The first one consists in exploring all-dielectric metamaterials which exhibit much lower losses than plasmonic materials [48], the other option consists in producing metasurfaces rather than metamaterials [6].

**All-dielectric metamaterials.** A dielectric nanoparticle with an index of refraction \( n \) exhibits Mie resonances when the typical size of the nanoparticle \( a \) is on the order of the wavelength \( \lambda \) of the impinging radiation. The scattering properties of these nanoparticles are perfectly described by the Mie scattering theory [49] and two strong resonances of interest are the so-called magnetic-dipole resonance, which occurs when \( a \sim \lambda/(2n) \) and the electric-dipole resonance, which occurs when \( a \sim \lambda/n \). The larger the index of refraction of the material, the smaller the nanoparticle can be for a given wavelength of operation, therefore allowing for the homogenization condition \( a \ll \lambda \). Semiconductors such as silicon are good candidates. Indeed, the index of refraction of crystalline silicon (Si-c) is larger than 3 across most of the near-infrared spectrum and even rises above 4 in the visible range. Several commercially available particles of spherical shape that exhibit large values of \( n \), such as amorphous silicon (Si-a) and crystalline TiO\(_2\), can be purchased at low cost and in large quantities in the form of powders, which can subsequently be suspended in a solvent so as to obtain colloidal dispersions of all-dielectric optical resonators.

Figure 7(a) provides the typical spectral variations of the scattering cross-section efficiency of a silicon nanoparticle of 150 nm in diameter. The total scattering (\( \sigma \)) is the sum of the scattering from the magnetic and electric
dipoles. The magnetic-dipole moment is almost one order of magnitude larger than that of raspberry-shaped plasmonic magnetic nanoclusters [24,50], and it is moreover comparable in amplitude to the electric dipole. Following the extended Maxwell-Garnett theory [51] we can infer the effective medium properties of a host medium containing such spherical inclusions. Figure 7(b) shows the electric permittivity ε and magnetic permeability μ computed for a volume fraction of 60% close to that of typical dense metamaterials self-assembled by microfluidic evaporation [24,52].

Both ε and μ show large spectral variations in the visible. Notably for λ ∼ 658 nm, the electric and magnetic dipoles are in phase and have equal amplitudes (fig. 7(a)), so that light is scattered in the forward direction following the well-known Kerker condition [53]. Consequently, ε ∼ μ (fig. 7(b)) and the impedance of the air/metamaterial interface is z = (μ/ε)1/2 ∼ 1 which corresponds to the cancellation of the reflection through a perfect coupling of light to the metamaterial. This condition is of particular interest for the enhancement of the light-matter interaction as well as for perfect absorption.

**Self-assembled metasurfaces.** Another aim in the self-assembly of optical resonators is the production of two-dimensional metamaterials. Since the skin depth rarely exceeds a single-layer of resonators in resonant metamaterials, the functionality can be preserved with a so-called metasurface, defined as a two-dimensional artificial material that provides some optical functionality. Notably, most metasurfaces up to date have been designed with the aim of achieving spatial control of the wavefront. By carefully arranging resonators, each of which will scatter light with a tailored phase shift with respect to the impinging wave, one can design a surface that effectively scatters as a bulk medium shaped so as to imprint a given phase. Using this principle, many flat-optical components have been imagined, such as flat lenses, axicons, beam steerers or diffractive elements [6].

**Conclusion.** – Bottom-up fabrication can certainly play a significant role in the area of metamaterials and metasurfaces for applications where a perfect ordering of the meta-atoms is not necessary. Producing amorphous materials is what comes to mind first, which would enable a cost-effective production of large-area devices. The bottom-up approach is particularly suited to hierarchical self-assembly, which makes it possible to design the nanoresonator independently of the assembled material. Moreover, chemical synthesis is able to produce huge amounts of meta-atoms in a single batch (e.g., > 1013 in refs. [24,34,50]), far beyond the capabilities of the lithography methods. As a result, it should be possible in principle to produce inks containing meta-atoms, which can subsequently be deposited on a surface in a disordered fashion, or else on a pre-patterned template, to make ordered or periodic arrangements, for instance using capillary force assembly [54]. The possibility of dissociating these two scales (resonator and 2D or 3D material) is quite unique to the bottom-up scheme.

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Self-assembled nanostructured metamaterials