Metamaterials are artificial electromagnetic media structured on the subwavelength scale for controlling the propagation of waves by means of transformation optics. The research activity is now focusing on attaining active metamaterial functionalities, including tunability, and the shaping and modulation of electromagnetic waves. Among all the different architectures, soft-matter-based active metamaterials, or hybrid composites, have gained special importance as they allow a variety of tuning strategies to be used, including those based on temperature, application of external electric or magnetic fields, and all-optical methods that benefit of the strongly nonlinear responses of materials. This review aims to summarize recent and ongoing progress on active metamaterials exploiting resonances in plasmonic and dielectric materials hybridized with soft-matter assemblies including liquid crystals, colloids, polymers, and granular matter. The theoretical background of these hybrid systems is outlined, experimental realizations are overviewed, and state-of-the-art applications in multifunctional platforms for light–matter interactions are presented. Finally, up to date challenges in the field that still remain open for further research are discussed.

1. Introduction

In the last 20 years, since the pioneering work of Pendry and Smith,[1] the compelling evolution of metamaterials (MMs) developed these systems as a standard in fundamental and applied research and a reference point in innovative devices. Indeed, MM as a term is now universally recognized as synonym of disruptive and futuristic: something that goes beyond, as from the Greek root “meta.” In spite of the remarkable achievements we have witnessed, these systems, traditionally realized with “hard matter,” were destined to run into “soft matter” to perform the next exploit and settle on a higher level of maturity. Several reasons lead to this expectation but before considering them in detail, it is timely to realize what is exactly meant by soft matter. The scenario is quite generous because under the hat of soft matter, we actually find pure liquids, mesophases like liquid crystals (LCs), colloids, polymers, granular matter, and bio materials in general. Such a variety of materials corresponds to countless opportunities for MMs including: i) enabling of functionalities tunability; ii) easiness/versatility of fabrication including upscale (large area) or additive manufacturing; iii) moldability, in case of flexible substrates and; iv) finally extremely relevant bio compatibility. Moreover, soft matter can hybridize existing MMs by functioning as substrate, host medium, and surrounding medium. It can be considered as a constituent part of a MM or even as its integral part. Recently, the main trend is to realize hybrid soft-matter based MMs with functionalities at visible/near-infrared range. By considering that MMs functionalities are generally enabled by systems whose sub-wavelength is about two-order of magnitude lower than the probe wavelength, this is quite challenging in terms of fabrication procedures.

Entering more in detail of the present work, a general categorization of hybrid soft-matter MMs is made based on the fabrication approach. This is generally distinguished between top-down and bottom-up. For this reason, Section 2 explores the most relevant recent results of soft-matter MMs obtained by a top-down approach. The particular case of metasurfaces (MSs), i.e. 2D MM, is considered with a convenient distinction between plasmonic MS (PMS), typically based on metal constituents, and dielectric MS (DMS). The discussion within each subsection is organized from the point of view of the employed soft-matter platform, providing key examples of the enabled applications for each case examined. Section 3 takes into account the enabling of MMs tunability by means of soft-matter
and related tuning mechanisms. Much attention is devoted in this section to the use of LCs, whose extraordinary properties upgrade MM devices to active functionalities. In Section 4, those MM systems are considered whose structure is induced by self-assembling procedures and a bottom up fabrication is thus more suitable. In this section, colloidal meta-fluids, liquid-crystalline colloidal MM, 2D and 3D hybrid MMs are particularly mentioned. Finally, the section of conclusions and future perspectives resumes the reviewed arguments and discusses what could be in the next years the most attractive trends in research and technology for the proposed systems.

2. Soft-Matter-Enabled Top-Down Periodic Metastructures

2.1. Metamaterials

The field of MMs revolutionized the understanding of light-matter interaction at the nano/microscale and offered unprecedented potential for the engineering of novel devices in numerous applications. By exploiting resonances in periodic structures with subwavelength elements, MMs expand the portfolio of the optical properties of standard materials toward phenomena, which cannot be manifested in natural materials. One such property that was extensively researched is the negative index of refraction, which can be observed in MMs with simultaneously negative effective permittivity and permeability, the so-called negative-index MMs (NIMs). In the VIS/NIR spectrum, NIMs are based on the archetypal fishnet structure, where two metallic layers with patterned cross-shaped holes account for negative permittivity, whereas the artificial optical magnetism stems from strong magnetic resonances when the two layers are separated by a deeply subwavelength dielectric spacer.

A fishnet multilayer can provide the bulk volume for a truly 3D-NIM, as demonstrated experimentally for the first time in a structure composed of alternating layers of Ag and MgF$_2$, on a rigid quartz substrate. Soft matter, polymers in this context, can expand the practical applications of 3D fishnet MMs. In particular, polydimethylsiloxane (PDMS) is an excellent polymeric material for large-scale transfer of NIR flexible MMs, thanks to its low refractive index, transparency, and low Young’s modulus ($7.5 \times 10^{-4}$ GPa), which permits large and reversible mechanical deformations (up to $\sim 120\%$ reversible stretchability). Combined with large-area fabrication techniques, such as nano-imprint lithography, PDMS provides excellent support, as shown in Figure 1a, which presents both a scanning electron microscope (SEM) microscopic and a macroscopic image of a large-area 3D-NIM printed on a flexible PDMS substrate. PDMS can also be used as a mediating platform to transfer the NIM to a different rigid substrate, should that be the target.

Generally, the fabrication of 3D MMs with arbitrary shapes requires sophisticated stereolithographic techniques, such as direct laser writing based on, for example, two-photon polymerization. Soft-matter can provide solutions for simpler 3D fabrication in self-assembly procedures based on the origami or paper-folding technique. In this approach, the MM features are patterned first in a flat layer of some suitable material, such as swellable polymers, LC elastomers, or shape memory polymers (SMPs). Then, these active materials are triggered to undergo shape transformations, which result in a variety of 3D structures, as broadly demonstrated in the synthesis of origami-based mechanical MMs. NIR optical MMs can be fabricated using the same technique, as demonstrated in Figure 1b, which shows self-folded cubic elements with patterned Au split-ring resonators (SRRs) of various configurations at the nanoscale.

In order to unleash the full potential of MMs, it is highly desirable to boost them with tunable properties in view of active devices. Soft matter plays a crucial role in this respect. In this section we provide a general overview of the soft-matter-enabled tunable functionalities and their physical foundations. A thorough consideration of soft-matter tunable MMs and their achievable performance will be outlined in detail in Section 3.

Key enabling materials for tunable MMs are nematic LCs, organic molecules with inherent large optical uniaxial anisotropy whose local orientation, and hence optical axis, can be externally controlled via a variety of stimuli: electric or magnetic fields, temperature, illumination with optical beams and photoswitchable alignment layers. The advantage in terms of tunability offered by LCs is twofold: control of the polarization of the light beam interacting with the MM and/or broad tuning of the LC effective refractive index. Two of the first examples of LC-tunable NIR MM are shown in Figure 1c,d. In the first case, the LC occupies the volume around a Au/MgF$_2$/Au fishnet MM, whose gap plasmon resonance at 1.55 μm is tuned by optically reorienting the LC molecules thus modulating the transmittance in a non-linear fashion. In the second, the LC occupies the overlayer of a Ag/Al$_2$O$_3$ MM, whose magnetic resonance and effective negative permeability are tuned by thermally modulating the LC refractive index.

In order to enhance the tunability, the active soft-matter medium has to be placed optimally at the electromagnetic hot spots where light–matter interaction is maximized. LC-tunable VIS/NIR metalodielectric multi-layer MMs, such as those of Figure 1c,d, require a thickness of the resonant cavities, namely the volume of the dielectric spacer between the metallic layers, in the range of tens of nanometers in order to induce strongly resonant phenomena. This condition makes LC infiltration impractical in terms of both alignment control, application of the bias signal, and device assembly. In fact, LCs are excellent candidates as tuning media in far-IR or terahertz MMs, where said thickness is micrometric, and thus compatible with LC device fabrication processes, as these have developed in the sector of LC displays.

The same is also true for the case of tunable metal–insulator–metal (MIM) MM resonant cavities, which are under intensive research as perfect absorbers, phase modulators, sensors, and beam steering applications among others. These are composed by a dielectric spacer placed between a metallic mirror and a patterned layer of metallic patch resonators, as in the schematic of Figure 1e. The resonant properties of such structures can be broadly controlled by changing the spacer refractive index, which directly affects the resonant frequency, and its thickness, which controls the coupling strength with an impinging light beam. Both mechanisms are simultaneously exploited in the MIM absorber sensor of Figure 1e, where the spacer is made of a special type of soft matter, a biodegradable
silk fibroin hydrogel. When in contact with water or common organic solvents, it absorbs them such that its volume expands and its refractive index is modulated, thus providing an excellent platform for sensing, for example, glucose with very high sensitivity values.[9] In a similar approach, silk fibroin has been used in MIM chiral MM composed of nanohole-patterned Au layers, which are rotated one respect to the other as in Figure 1f. By exploiting the tunable properties of the soft-matter dielectric spacer, both tunable control of the MM chiroptical response, that is, circular dichroism (CD), and ultrasensitive sensing of trace amounts of solvent impurities were demonstrated.[10]

As a final example of soft-matter-enabled chiral MM, we report a recently demonstrated so-called 2.5D-MM composed of Au elements that undergo out-of-plane twisting thanks to the applied nano-kirigami fabrication method, as depicted in Figure 1g. The twist breaks the in-plane mirror symmetry of the structure and induces it with strong chiral response.[11] PDMS plays successfully the role of the soft-matter host for the transfer of the Au MM but, most importantly, also for its tunability. By externally compressing the polymer using a fiber tip, the Au nanoelements undergo a transition toward a flat, achiral MS. The process is reversible, thus enabling the mechanical tuning of the CD. Having established the multi-faceted utility of soft matter in the design of 3D, as well as 2.5D, MMs, the following of this section aims to highlight their role in MSs, namely flat MMs which are being ever more researched thanks to their compact transverse dimensions, simpler fabrication and, in general, lower losses with respect to their bulk counterparts.

2.2. Plasmonic Metasurfaces

MSs are composed of resonant scatterers, metallic or dielectric, which are typically arranged in bidimensional periodic arrays. By controlling the resonant behavior of the scatterers, along with their collective oscillations in the periodic lattice, MSs can provide extensive control of light transmission, absorption, sensing, optical activity, lensing and steering, to name but a few functionalities. Light–matter interaction is achieved in a non-diffractive regime, thanks to the MS subwavelength pitch, and at a single, deeply subwavelength layer, which minimizes losses and transverse dimensions in view of a new generation of compact, flat optics devices.

In the case of PMSs, their response typically relies on the excitation of surface plasmon resonances (SPRs), stemming from the coupling of the impinging light beam with free electron oscillations in metallic particles or, in a complementary approach, metallic films with a perforated array of holes. SPRs can localize light at a deeply subwavelength scale and they are characterized by strong near-field enhancement, which rapidly decays as the distance from the metallic resonators in the surrounding dielectric increases. This aspect is of
paramount importance when it comes to the functionalization of PMSs with soft-matter materials, such as LCs. In the standard approach, the MS is patterned on a rigid surface and the LC cell is formed between the MS and a top substrate. The use of an alignment layer spin-coated on the MS generally reduces the overlap between the resonating near-field and the LC, thus reducing the overall tunability, although in some cases this issue can be alleviated by judicious MS design and material selection, as in the case of a gold-nanorod PMS studied in ref. [20].

Figure 2a shows the layout and a SEM image of the fabricated prototype of an LC-tunable PMS that circumvents these issues. The MS is made of an array of suspended zig–zag Au nanowires fully embedded in a LC material. Each oblique segment of the nanowires provides a strong SPR, which leads to high field confinement in the air gaps and large variation in the MS transmittance. The conducting wires are used also for the application of the low-frequency voltage bias that switches the LC molecules in the plane of the MS. In this configuration, the strongly polarized plasmonic resonant field interacts with the maximum variation of the LC refractive index between the rest and switched-on cases, leading to high spectral tunability approaching the theoretical limit.[21] Another promising way to boost the performance of LC-tunable PMSs is operation with lattice surface plasmon resonances (LSPRs), which provide more delocalized field profiles, thus relaxing the constraints on both near-field light–matter interaction and high ohmic losses from strong field confinement at the lossy metallic surfaces. Record-high quality factors were recently experimentally demonstrated in PMS based on LSPR,[22] while this approach has also been applied to increase the tunability of LC-boosted PMS of Al nanoparticle (NP) arrays.[23]

Instead of being used as a refractive-index tunable medium, LCs can also be integrated in PMSs as polarization-control elements, by exploiting their optical anisotropy. A straightforward way to this goal is to form a twisted-nematic (TN) LC cell with the MS being one of the two cell surfaces.[24–26] The LC alignment direction is perpendicular between the top and bottom substrates. By properly selecting the cell thickness, light propagating in a TN cell undergoes polarization rotation between the two orthogonal linear polarization states. When a voltage bias is applied, the LC molecules align perpendicularly to the substrates in the LC cell volume, thus canceling the rotation effect. In this manner, the LC can dynamically control the polarization interacting with the MS and thus tune its response. Figure 2b shows a PMS made of a periodic array of rectangular holes etched in an Al layer, coupled with a TN-LC cell backed by an output analyzer. The PMS supports SPR stemming from the collective coupling of the localized resonances in its nanoholes, which results in a profound dip of the PMS transmittance at the resonant wavelength in the visible spectrum. The TN-LC cell induces polarization-dependent response and by controlling the applied bias voltage the PMS transmittance is modulated, acting as a functional plasmonic color filter.[26]

As in the case of their bulk counterparts, soft-matter can provide a powerful platform for the transfer of PMS to transparent, flexible, light-weight, and biocompatible substrates. Figure 2c shows the layout of a PMS of elongated Au NPs embedded in a transparent cyclo-olefin-polymer. The anisotropic shape of the NPs leads to strong polarization-dependent transmission in the visible spectrum and hence color filtering, such that information can be encoded in the nanorod orientation and retrieved by simple polarized illumination of the PMS.[27] PDMS is also in this case an excellent host medium for flexible MS, as demonstrated in ref. [31], where a periodic array of gold SRRs was transferred on a PDMS substrate. The PMS retains its resonant properties and it was used as a biocompatible substrate for surface enhanced Raman spectroscopy (SERS) of organic molecules, such as 2-naphthaleniol, thanks to the strong localized SPR and resulting near-field enhancement.

Apart from providing flexibility, such transfer methods based on nanoimprint lithography allow also for cheap, large-scale fabrication, since just a single rigid mold has to be fabricated. Significantly expanding the applicability of structural plasmonic coloring is a clear example of their utility.[32] Furthermore, by proper design of the rigid mold, exotic plasmonic nanostructures can be transferred, such as the example of an Au nanoprocessed PMS shown in Figure 2d, based on anisotropic etching of a Si3N4 mask,[28] large-area, user-designed iridescent patterns for cryptography at extremely low fabrication cost,[33] and full-color electronic paper based on electrically addressable conjugated polymers coupled with Au nanohole PMS.[34] Finally, the use of reversibly stretchable substrates as PDMS opens extensive opportunities in mechanical tuning of the PMS response, by dynamically changing the PMS pitch through elastic deformations,[35,36] as it will be thoroughly discussed in Section 3.

The same molding technique has recently been extended to organic materials, such as thin films of cellulose or agro-waste, which, contrary to standard polymers and plastics, are biodegradable and eco-friendly, while also being highly transparent and with glass-matching refractive index. Both micro- and nanometric patterns of periodic nanoholes were transferred on such films with very high quality. When coated with metals such as Au or Ag, the resulting PMS shows distinct reflection and transmission spectra stemming from the excited plasmonic modes, leading to angle-dependent plasmonic color filtering as shown in Figure 2e. In addition to color adjustment, the resonant modes also provide strong near-field enhancement, which can be exploited in SERS, such as the detection of 1,4-benzene-dithiol.[29]

Finally, Figure 2f shows a further step toward the development of soft-matter based, biocompatible chemical sensors for real-time, SERS drug monitoring.[30] The sensor integrates a sweat extraction component consisting in a hydrogel film doped with a sweat-inducing drug (acetylcholine chloride) with a PMS composed of a superlattice of Ag nanocubes. The structure is accommodated on a breathable polymer film, such that the induced skin sweating leads to the extraction of the target drug molecules that interact with the PMS and are sensed through the SERS effect. The sensor features excellent mechanical characteristics, it is wearable and allows for the real-time monitoring of numerous human body analytes, as they can be identified by their particular Raman spectral fingerprints. This example clearly demonstrates the potential of soft-matter PMS for the realization of novel functional devices for healthcare and chemical/biosensing.
2.3. Dielectric Metasurfaces

DMSs are typically composed of bidimensional arrays of transparent, high-index dielectric nanoelements (disks, cuboids, posts) patterned on a low-index substrate. The need for high-index particles is crucial, in order to provide strong light–matter interaction at the MS plane, via the excitation of strong resonances, such as electric, magnetic, and toroidal Mie resonances.[37] Proper engineering of the scattering dielectric particles and their inter-particle coupling provides extensive degrees of freedom in terms of modifying the amplitude, phase, polarization, wavefront, and direction of the propagating light beam that interacts with the DMS. As a result, DMS constitute a versatile, compact, flat-optics platform for numerous applications including lensing, holography, sharp filtering, nonlinear process enhancement, polarimetry, beam shaping and steering, and light-emission manipulation.[38–42]

As in case of their plasmonic counterparts, soft-matter can significantly expand the functionalities achievable by DMSs. Again, LCs play in this respect a fundamental role. Figure 3a shows the layout and SEM image of an LC-coupled DMS composed of Si nanodisks patterned on a silicon-on-insulator (SOI) wafer, which supports dipole electric and magnetic resonances in the NIR. By heating the structure the LC overlayer undergoes an anisotropic to isotropic transition with subsequent modulation of its refractive index, which results in the spectral tuning of the NIR resonant wavelengths by 40 nm and large amplitude modulation.[43] Important from the technological point of view, it was demonstrated that a single alignment layer on the superior, flat surface of the LC cell is sufficient to align the LC also at the MS plane, which simplifies fabrication and ensures strong interaction with the active LC molecules with the DMS resonant near-field. Using conceptually the same structure, electrical tuning was also demonstrated for both transmission and phase modulation by applying a voltage between the bottom Si layer of the SOI wafer and a standard ITO electrode on top of the LC cell.[44] Operation in the visible spectrum has been demonstrated by employing...
highly transparent TiO₂ nanodisks.[45] Finally, LC-tuning is also possible in sharper resonances with lower radiative losses, albeit generally at the expense of reduced tunability due to the stronger field confinement in the high-index nanoantennas.[46] The exploitation of delocalized quasi-dark modes, which provides both vanishingly small nonradiative losses and large light–matter interaction with the DMS can provide an approach to highly tunable sharp resonances.[47]

More advanced functionalities in LC-DMSs based on Si nanodisks can be achieved by exploiting operation at the Huygens regime. Under such conditions, the dipole electric and magnetic resonances overlap, which leads to high MS transparency, as shown in the example of Figure 3b[48] with 2π phase control around the resonance.[33] By modulating the nanodisk diameter, gradient-phase DMS can be designed in a straightforward manner. When coupled with LC, such Huygens DMS can provide dynamic light beam steering by means of thermal LC tuning.[54] In a roadmap toward integrated functional devices, these DMSs are being investigated as more performing alternatives to two classical LC-technology applications, displays and spatial light modulators (SLMs). Regarding the first, display functionality was demonstrated in the red part of the visible spectrum.[55] Thanks to the near-field effect, boosted by the use of extremely thin LC photoaligning materials, LC-DMSs need sub-micrometric LC cells, which increases response speed and reduces inter-pixel fringe-field effects and diffuse scattering compared to traditional cells in the LC displays. Moreover, by operating a TiO₂ LC-DMS in the visible as a three-level phase modulator, an SLM has been demonstrated with a field of view of 22° and much smaller pixel size (around 1 μm) with respect to state-of-the-art classical LC-based SLMs, thanks to the near-field resonant effect and the individual electrical addressing of few nanoantenna rows as depicted in Figure 3b.[48]

Other LC-DMS-enabled applications include the tuning of the focal length of DMS lenses. The electrical control of the LC alignment and hence refractive index in the overlayer of a DMS composed of amorphous Si (α-Si) nanopillars allows for the continuous shift of the lens focal length.[56] In a roadmap toward integrated functional devices, these DMSs are being investigated as more performing alternatives to two classical LC-technology applications, displays and spatial light modulators (SLMs). Regarding the first, display functionality was demonstrated in the red part of the visible spectrum.[53] Thanks to the near-field effect, boosted by the use of extremely thin LC photoaligning materials, LC-DMSs need sub-micrometric LC cells, which increases response speed and reduces inter-pixel fringe-field effects and diffuse scattering compared to traditional cells in the LC displays. Moreover, by operating a TiO₂ LC-DMS in the visible as a three-level phase modulator, an SLM has been demonstrated with a field of view of 22° and much smaller pixel size (around 1 μm) with respect to state-of-the-art classical LC-based SLMs, thanks to the near-field resonant effect and the individual electrical addressing of few nanoantenna rows as depicted in Figure 3b.[48]

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nanopillars, properly arranged to induce the necessary geometrical phase. The LC cell provided the dynamic control of the handedness of circularly polarized light impinging on the metaholographic DMS using a variety of external stimuli (electrical, thermal, or pressure), thus producing interactive, spin-dependent images, as shown in Figure 3e.[51]

As in the case of PMS, PDMS is an excellent material for the large-scale transfer of DMS. This is demonstrated, for instance, in the case of a DMS composed of aSi nanodisk arrays fabricated by colloidal lithography and transferred to a flexible PDMS substrate.[57] In addition, the application of strain to the elastic PDMS substrate can change the MS pitch and hence near-field interaction between the dielectric nanoantennas, thus modulating their optical response, as in the case of the TiO$_2$ nanodisk DMS of Figure 3e.[52] Interestingly, by using the same stack and transfer method, PDMS can serve as the host medium not only for periodic DMSs, but also for colloidal suspensions of dielectric nanostructures of various shapes, such as the asymmetric Si NPs with strong chiroptical properties demonstrated in ref. [58].

Colloidal soft-matter has also been successfully coupled with DMSs in light emission devices, where the DMS plays the role of a deflector array in order to increase the directionality of light emitted from a colloidal quantum dot layer placed between distributed Bragg reflectors and integrated with the DMS. Apart from controlling the emission angle of such emitters, DMSs can also play the role of the resonant cavity, by exploiting strongly resonant bound states in the continuum (BIC). This approach was investigated in a recent experimental work, where a film of colloidal CdSe/CdZnS nanoplatelets was integrated with a TiO$_2$ nanodisk DMS supporting BIC resonances. By adjusting the nanodisk diameter the BIC resonant/lasing wavelength was tuned inside the gain bandwidth of the nanoplatelets, demonstrating compact, low-threshold lasing with significant degrees of freedom in terms of the selection of the lasing frequency.

In the thus far outlined paradigms, soft-matter plays the role of an enabling material that induces optomechanical properties to periodically patterned DMSs composed of high-index nanostructures, typically Si in the NIR and TiO$_2$ in the VIS spectrum. Nevertheless, it has been recently shown that soft-matter composite materials, such as a ultraviolet-curable resin doped with TiO$_2$ NPs can serve as the building material of the DMS itself. In particular, such matrix-inclusion composite films satisfy the requirement for high refractive index and pattern-transfer capability, thus rendering them compatible with single-step NIL processes. As such, they significantly reduce the fabrication cost by increasing its throughput and allow for the rapid prototyping of large-area DMSs. Using this approach, DMS metalenses were demonstrated by spatial modulation of the geometric phase resulting from rectangular nanocuboids.[99]

3. Tuning Strategies for Active Metamaterials and Metasurfaces

MMs and MSs outstand as key elements for breakthrough applications spanning from life science, optics and photonics, to telecommunications. These exotic elements, however, possess properties that can be typically reconfigured only by design. In fact, there is a growing interest in the research community toward the development of tuning strategies for enabling an active reconfiguration of their features and thus new functionalities.[60–62] In the context of soft matter, various methods have been proposed including tunable surrounding media (e.g., LCs), mechanical and all-optical stimuli that will be investigated in the following paragraphs. In this section, we report on tuning strategies implemented in systems mainly realized by top-down approaches.

3.1. Tuning by Liquid Crystals

LCs are very well known to the general public for their application in display technology. Their refractive index value can be easily modified by applying external stimuli as thermal, electric or magnetic fields thus representing a very good candidate to reconfigure functionalities of MMs and MSs. For this reason, there is an increasing interest in LC technology not only in the visible/infrared spectral range but also in others like terahertz or microwave ones.[63–67] LCs constitute a mesophase which spreads as a liquid, but maintains a certain orientational order, which corresponds to the optical axis of the system, and sometimes also a positional order.[68] Being made of elongated molecules, the properties of LCs are highly anisotropic and depend on the direction along which they are investigated. There are several types of LCs. One of the most important is the thermotropic one, in which the appearance of a given phase is controlled by temperature. Above a certain temperature specific of each substance, the material appears in visible light as a clear isotropic liquid. Thermotropic nematic LC (NLC) molecules, show in general a random arrangement of their centers of gravity and do not then present a positional order but only a long-range orientational one, indicated by a unit vector $\hat{n}$ called director. From the point of view of the interaction with electromagnetic (EM) field, LCs are described by a dielectric tensor $\bar{\varepsilon}$

$$\bar{\varepsilon} = \begin{pmatrix} \varepsilon_{||} & 0 & 0 \\ 0 & \varepsilon_{\perp} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix}$$

(1)

where $\varepsilon_{||}$ and $\varepsilon_{\perp}$ represent the dielectric constant perpendicular and parallel to the molecular long axis respectively. They can be referred, also, as ordinary $\varepsilon_{o}$ and extraordinary $\varepsilon_{e}$ dielectric constants. It is possible to retrieve the dielectric anisotropy as $\Delta \varepsilon = \varepsilon_{e} - \varepsilon_{o}$ representing the maximum LC tuning capability. In the visible spectral range, it is preferable to deal with the refractive index ($n = \sqrt{\varepsilon}$) and hence the possible tunability is usually referred in terms of birefringence defined as $\Delta n = n_{o} - n_{e}$. The most common LCs possess a birefringence among 0.1 and 0.2. However, there exist some with $\Delta n$ that can reach 0.4 or even higher values.[69] When an external stimulus is applied, for example, electric voltage, the LC molecules reorient along the field thus leading a switch of the average refractive index from the ordinary to the extraordinary value. In the last years, there is an increasing demand of ultra-compact devices and in this scenario flat optics, with extremely reduced size and thickness, emerge as a key technology. A great opportunity arises from the breakthrough properties of planar MSs, artificial media...
with sub-wavelength thickness. All-dielectric arrays designed to work as metalenses for visible wavelengths have been recently demonstrated and fabricated by diverse techniques. However, even showing remarkable optical features like achromatic behavior, suitable depth of focus (DOF) and numerical aperture (NA), these systems have a common drawback in their static nature: once the metalens is fabricated, its optical features are fixed by the actual design. Indeed, this condition severely hinders the possible functionalities of an eventual device embedding the metalens. A step toward the introduction of a dynamic control of the metalens optical properties has been recently made by the group of Prof. Shvets and Prof. Duan who have independently demonstrated the possibility of using the E7 NLC as a medium enabling an active control of the focusing properties of the metalens. In the first case, aSi meta-atoms displacement is optimized to provide a phase difference ($\Delta \phi$) between 0 and $2\pi$ for both LC states still maintaining a satisfactory transmittance at the focal point. The switching of LCs is guaranteed by two transparent thin layers of conductive indium tin oxide (ITO), see Figure 4a. When an external AC voltage, of only $9 \text{ V}_p$, is applied, the focus length is reduced from almost 16 to 12.5 mm. This is due to the refractive index increase of the LCs which represent the surrounding medium of the meta-atoms.

In the same year, another LC metalens based on aSi meta-atoms is proposed in ref. [74]. However, in this case, the LC constitutes a separate layer with respect to the aSi meta-atoms that modulates the incident beam from left (LCP) to right (RCP) circular polarization. In fact, the proposed metalens is designed to determine two different focal lengths, depending on the polarization state, thus allowing an experimentally proven zooming effect on a 1951 USAF resolution target.

The metalens proposed by Prof. Duan is instead based on a geometric phase MS composed from TiO$_2$ nanofins. The innovative characteristic of this metalens is that the electron beam lithography (EBL) resist is not removed after the TiO$_2$ deposition leaving a uniform layer of TiO$_2$. In this way, the alignment layer can be applied on both bottom and upper surface without damaging the MS and resulting into a better LC infiltration and alignment. In fact, when the nanostructures are very closely packaged, the LCs experience diffuseness in uniformly filling the gap among meta-atoms that leads to a reduced performance of the final device. The metalens is designed for switching the focal length from 200 to 400 $\mu$m at 532 nm but it preserves good performance in the whole visible range, as illustrated in Figure 4b. In the same contribution, the realized tunable metalens is also exploited for an imaging application where the 1951 United States Air Force resolution chart is observed with a voltage driven adjustable zoom factor of 1:5 and 1:2 at different wavelengths. Moreover, the focus switch is very fast and can be thus easily implemented in systems already on the market, such as photo-cameras for smartphone, innovative microscopes and so on with the advantage of lightweight compact systems realization.

The possibility offered by LCs to reconfigure the MS properties is of paramount importance in novel emerging beam steering applications which will bring to a breakthrough in several fields like surveillance, automotive, LIDAR, and telecommunication sectors, to name a few. Figure 5 illustrates two MS designs, one based on a) silicon nanodisk and b) one on grating. They exploit in common the LC birefringence to switch the beam diffraction among different orders, however, the involved LC tuning strategy is different. In fact, as observed in Figure 5a, the E7 LC is tuned by a temperature increase that corresponds to the transition from the nematic (anisotropic) state to the isotropic one. At room temperature, the impinging beam is normally transmitted while, by heating the MS, the beam is gradually diffracted to the first order leading to a beam deflection of 12° with efficiency of 50% centered at a wavelength of 780 nm. Instead, in the numerical work of ref. [77], see Figure 5b, a classical electrical tuning strategy is considered. In this case, a triple dielectric grating is optimized to realize a beam steering of about 140° at a wavelength of 1500 nm enabled by the reorientation of LC molecules allowing to change from the +1 to the −1 diffraction order.

MMs and MSs for producing structural colors gained a lot of attention in recent years due to the long term durability and high resolution these systems offer with respect to classical
techniques like dye coloring, absorbing materials or multiple interference. Moreover, possible applications span from display to filtering and anti-counterfeiting.\cite{32,78,79}

In this context, LCs again offer an easy way to actively reconfigure the resulting colors and images as illustrated in Figure 6. In ref. [80], see Figure 6a, Franklin et al. proposed a shallow array of nanowells imprinted on glass and flexible PET substrates covered by a thin layer of aluminum acting as an electrode. The alignment layer is deposited only on the opposite ITO electrode substrate. An 0.42 birefringence LC (LCM1107, LC Matter Corp.) allows a dynamic shift of the plasmonic resonance up to 95 nm which depends on the surrounding dielectric constant. The impinging light reflected by the LC cell is recognized as a color. As an example, the authors converted the image of a girl to a different set of surface periodicity through a mapping process. The color of each period saturates at different applied external voltage thus reproducing the final image. Thanks to the fast switching, in the order of tens of milliseconds, the proposed device can display a video if an appropriate single pixel addressing scheme is employed. Another advantage of the proposed approach is its capability to work with unpolarized light, then reducing the complexity of the final device.

In ref. [81], an externally applied voltage of about 5 V allows varying the perceived color of plasmonic arrays made of Al nanorods layered with twisted-nematic (TN) LC, see Figure 6b. The TN-LC layer on top of the MS enables the control of the polarization state of light impinging on the plasmonic nanostructures that in turn modulates the colors transmitted, reflected or scattered by the system. In presence of standard LCs (5CB), an electrically-driven wavelength shift of about 100 nm is obtained for this system which can be increased by considering LCs with larger birefringence.

In the work of Prof. Duan’s group regarding metalenses\cite{73} reported in Figure 4, their approach has been employed to demonstrate electrically switchable holograms as well. They designed a MS working as variable wave plate for circular polarization (CP) where the phase retardation depends on the applied voltage which in turn enables the switch of two orthogonal helicity channels (left CP or right CP). By using a vector decomposition scheme, the authors encode holograms for both polarization channels during the MS design. The LC dynamic tuning permits the observation of each holograms by using only 5 V, as illustrated in Figure 6c.

A breakthrough application of the dynamic tuning of structural colors is also reported in Figure 6d where an hybrid polymer-dispersed liquid crystal (PDLC) MS is explored for optical encryption.\cite{82} Here it is proposed the combination of aluminum squares and rectangular nano apertures enabling a polarization sensitive behavior in conjunction with the reconfiguration of LCs by external voltage. At 0 V, due to the LC thickness, the image appears dark while by 20 V two different symbols are clearly distinguishable. By rotating the incident polarization from 0° to 90°, the “X” becomes a “V”.

### 3.2. Mechanical Tuning

The properties of soft-matter-based MMs can be actively modified using mechanical deformation, hence their softness can be turned into an advantage. Among various polymer material to be used as a substrate, PDMS represents the most preferred choice due to its extremely interesting properties as high elasticity, transparency, non-toxicity, and low cost. Since PDMS is an elastomeric material, on applying a mechanical strain it will be elongated along the strain direction and restored to the original dimension when the strain is released. This process is completely reversible under hundreds of cycles thus allowing a high reproducibility of the tuning mechanism. Usually, the applied strain is up to 40% with respect to the original dimension. Above this strain percentage, the common PDMS starts to be irreversibly modified until a final fracture occurs.

The previous paragraph has dealt with the dynamic LC-tuning of structural colors (see Figure 6); however, mechanical tuning represents a fascinating alternative way to achieve the same aim.

In fact, in ref. [83] a new MS design is described that produces the same color change with x and y polarization if a strain is applied along the x direction. The proposed MS is constituted by TiO$_2$ inverse trapezoids embedded in PDMS with 2D square arrangement which support, at the same time, electric (ED) and
magnetic dipole (MD) resonances. The latter arise from periodic effect and near-field mutual interaction, respectively. As an example, Figure 7a reports the active color tuning from blue to red passing from 0% to 40% of applied strain for both x and y polarization. This is a particular feature with respect to conventional design where the MS response, under stretching condition, is polarization sensitive.

Figure 7b shows, instead, aluminum mushroom-like nanostructures realized on a PDMS substrate and the corresponding reflectance at different stretching conditions resulting into an increase of period and diameter. The surface plasmon resonance shifts in this case from 530 to 620 nm thus producing a perceived color tuning from green to fuchsia. [84]

Moving from cylindrical to rectangular nanostructures, the optical properties depend on stretching direction as reported in Figure 7c. [85] The authors designed an aluminum MS exhibiting green color at the rest state. A blue shift is obtained when stretching along y-axis due to reduction of the period along x-axis while a red-shift takes place in the opposite case. Based on this concept, they realized a dynamic image switching by fabricating a MS with different arrays periodicity resembling the letters O, W, and L. When illuminated by white light, due to different scattering properties, they appear green, cyan, and purple respectively. If the device is illuminated with a wavelength window of 465−505 nm, only the letter W can be observed at rest. By applying a vertical stretching the letter O appears while the letter W in case of the horizontal one, see Figure 7c.

In the previous paragraph we discussed about metalens reconfiguration by means of LCs. Here, a mechanical approach is proposed based on elastic substrate stretching. Figure 8a reports a metalens made of square nano-posts of high refractive index aSi embedded into a PDMS matrix working at a wavelength of 915 nm. [86] The high difference in refractive index allows a weak coupling between close nano-posts and in this condition the phase shift is predominantly affected by their width. Hence, the substrate stretching does not influence the
local phase shift and the MS still works as a lens. The fabricated nano-posts are shown in Figure 8a before and after PDMS embedding. Two teflon rings are used for clamping the metalens in order to apply radial strain during measurements. At relaxed state, the focal distance is 600 µm reaching a value of 1400 µm with 50% stretch ratio still maintaining nearly diffraction limited focus. In the meantime, the focusing efficiency decreases from 75% to 50%.

In the same year, another work appeared demonstrating the mechanical tuning of the focal length of a metalens working in the visible range, namely at 633 nm. [87] With respect to the previous case, the meta-atoms are in this case made of Au nanorods patterned on top of PDMS, see Figure 8b. In the proposed design, the optical phase profile is more sensitive to relative position of each Au nanorods which can be easily varied applying a strain to the elastic substrate. When the realized metalens is stretched isotropically by a factor s, the resulting focal length is increased by a factor s^2. In fact, as reported in Figure 8b, with a stretching ratio of 130% the authors demonstrate a zooming effect of 1.7x with the focal plane varied from 150 to 250 µm. In the unstretched condition, a pentagon is displayed at 340 µm, then a square at 270 µm with stretching of 12% and finally a triangle at 200 µm with 30% stretching. In both design, the hologram reconfiguration is due to the moving of the image plane with a factor s^2, as discussed earlier for metalenses.

An innovative approach for tuning MS features and, in particular, hologram was reported in ref. [88] and is illustrated in Figure 9b. In fact, the tuning mechanism is not represented by the application of a strain to an elastic material but by its shape/configuration as well as by the polarization of the impinging wave. The holograms were generated using a Gerchberg–Saxton algorithm (GSA) and then, the position of nanorods was determined by means of the P-B notion. In the flat configuration, the obtained features depend on the handedness of circularly polarized light while a conformal substrate allows to add another degree of freedom. The authors combined these principles to design reconfigurable holograms with a perfect fabricated on PDMS, as shown in Figure 9a. The phase distribution, giving rise to the hologram, is calculated using a computer generated hologram (CGH) technique. Then, using a Pancharatnam– Berry (P-B) phase approach, the position and orientation of anisotropic nanorods is determined for imparting the designed phase distribution. In a first approach, the authors realized a MS made of silicon nanorods showing at rest an unhappy face located at the image plane on a distance of 60 µm. By applying a 30% strain, the image changes to a smiling face. A more complex device is demonstrated using gold nanorods generating at three planes different reconfigurable holograms. In the unstretched condition, a pentagon is displayed at 340 µm, then a square at 270 µm with stretching of 12% and finally a triangle at 200 µm with 30% stretching. In both design, the hologram reconfiguration is due to the moving of the image plane with a factor s^2, as discussed earlier for metalenses.

Figure 7. a) Polarization insensitive MS color tuning under stretching condition. b) Structural color variation of periodic array of Al NPs with different stretched length. c) Image variation under vertical and horizontal switching. a) Adapted with permission. [83] Copyright 2019, American Chemical Society. b) Adapted with permission [84] Copyright 2017, Wiley-VCH. c) Adapted with permission. [85] Copyright 2017, American Chemical Society.
agreement between simulation and experimental results. For a concave substrate and right circularly polarized light a distorted image is obtained that changes to game dice with polarization switching. Interestingly, the opposite behavior was obtained for the convex substrate with a rotation of the dice game of 180°.

It is worth noting that the gold MS was fabricated on a flexible membrane of only 2 µm thickness.

Importantly, the ability to easily reconfigure the hologram is an extremely interesting approach to counterfeiting applications.

3.3. Other Tuning Approaches

LCs and elastomers represent the most used soft-matter-based reconfigurable mechanisms. This paragraph presents, instead, other tuning strategies based on optical, liquid, or chemical approaches which are illustrated in Figure 10.

Burch et al., successfully demonstrated holograms generation on conformal epoxy membranes that can be placed on any substrate therefore opening the gateway for new and interesting applications. In particular, they fabricated a reflective MS composed of gold nanorods defining a P-B phase profile. The projected hologram can be easily tuned by passing from a left to a right circular impinging wave, as reported in Figure 10a.

Another optical tuning mechanism for controlling the polarization of light into the 700 – 950 nm wavelength range was presented in ref. [90] and shown in Figure 10b. The hybrid MS was composed of gold L shaped slits covered by a thin layer of polymethylmethacrylate mixed with azodye ethyl red. The latter switches from trans to cis state when excited with green light and turns back in the original state after stopping the exciting light. The proposed MS geometry converts a linearly polarized light into an elliptic one described by azimuth rotation φ and ellipticity angle χ. During the excitation, the refractive index of ethyl red decreases leading a blue shift of polarization parameters which depends on the amount of molecules that undergo the modification. Light intensity controls this mechanism and a maximum variation of 16.7° and 20°, respectively, is obtained using only 4 mW power.

Shape memory polymer (SMP) represents an attractive and extremely intriguing method for active reconfiguration of MS properties. In fact, as the name suggests, SMPs are a class of intelligent material that restore their original shape from a programmed temporary one under external stimuli such as temperature, light, and electric field. The authors first developed a novel SMP photosensitive to be used in a two-photon direct laser writing technique then realized submicron scale grids generating structural colors. The latter depend mainly on grating height and linewidth which can be easily modified during printing. This represents the original shape. For programming the temporary state, the fabricated sample is deformed using a metal load at temperature higher than the polymer glass transition, that is, 80°C in the
reported case. Now, the grids are compressed and no structural colors can be observed. Successively, for restoring the original shape and hence the color, the structures are once more heated at 80~°C. This process is reversible without grids degradation even after several cycles. Finally, an octopus color image is printed and programmed to be transparent in the compressed state. After heating, the colored image is fully recovered. This novel approach can find application in sectors where it is of paramount importance to monitor the local temperature, as in drug and food transport.

An alternative approach for tuning the properties of a MS is based on the injection and ejection of liquids as described in ref. [92]. The presented design is constituted by an array of TiO2 nano trapezoids producing structural colors. A PDMS microfluidic channel allows to inject solvents having different refractive index leading to a modification of the surrounding medium and hence of the generated color. In particular, Figure 10d shows the experimental results of a single device composed of two MS with period of 400 and 380 nm. This small variation leads to a contrast in displayed colors. When water, DMSO, or CS2 is injected into the channel, the surrounding refractive index changes from 1 (air) to 1.333, 1.4795, and 1.6276, respectively, reducing progressively the contrast until the word “HIT” is indistinguishable with respect to the background. The presented device can be used to encode information in security and anticounterfeiting applications.

In 2016, Wang et al., demonstrated a real-time dynamic tuning of MS properties by using electrochemical processes.[93] In particular, the plasmonic cell is made of an Au nanodomes array and filled with an electrolyte gel containing Ag⁺ ions, as illustrated in Figure 10e. The MS reflection depends on the thickness of Ag⁺ ions which can be controlled by applying an external voltage. The resulting color passes from red to blue in a reversible process. The proposed plasmonic cells, thanks to the possibility to be realized on flexible substrate, are integrated on top of a mechanical chameleon equipped with color sensors. The information of detected color is analyzed by a microcontrol system which applies the necessary signal to individual cells as shown in Figure 10e. The developed device provides a new approach for real-time biomimetic active camouflage.

4. Self-Assembled and Bottom-Up Metamaterials

As outlined in the previous section, there is growing interest in achieving tunability and advanced functionalities in hybrid optical MMs through the use of soft-matter platforms. Indeed, soft-matter represents a promising pathway to tailor the optical properties of metadevices, enabling further control of peculiar and intriguing photonic properties. The rich combination of a wide range of material species and structural variations offers new fundamental insights into light–matter interactions. Importantly, such MMs constitute a highly multidisciplinary field that covers the study of a wide range of active hybrids, which nevertheless share some commonalities. The origin of the active response in such MM hybrids generally emerges from soft-matter internal specific energies, which are commensurate with room-temperature thermal energy, $k_B T$, and internal unique structures, which naturally have distinctive length scales, $l$, in the mesoscopic scale. Thus, soft optical hybrid MMs are characterized by low elastic moduli and are easy to control. Indeed, a first approximation states that the scale of the
modulus of elasticity is $G \approx \frac{k_B T}{l}$, which, for typical values of $l$, is between six and nine orders of magnitude smaller than the modulus of atomic or molecular solids.\textsuperscript{[95]} With the development of bottom-up nanofabrication technologies, new avenues have opened for creation of various soft-matter-based MMs, and the field has become intensely studied for the prospect of implementing nanostructured materials that can control light.\textsuperscript{[96–105]} Nanostructured hybrids exhibit fascinating physical properties at visible frequencies and self-assembly methods, derived from advanced nanochemistry, reveal particularly convenient for simple and cost-effective fabrication. Hence, metaphotonics have recently witnessed an explosion of interest and progress in the actual design and study of soft plasmonic hybrids with subwavelength dimensions.\textsuperscript{[98,102,103]} The ability for unlocking advanced optical functions and interplay between multifarious nanoscale building blocks has sparked a variety of plasmonic architectures for soft-matter hybrid MMs. These plasmonic architectures utilize soft-matter as an active spatial linker, which serves to steer the assembly process and control the MM resonance. This section reports an extensive survey of the current state of the art accomplished in photonics and plasmonics by implementing soft-matter-based MMs. In more detail, we discuss a selected set of hybrid and active MMs with bulk soft-matter assemblies, including colloidal, polymeric, and granular matter.

### 4.1. Self-Assembled Optical Metafluids

Colloidal self-assembled optical metafluids play a vitally important function in comprehending the intrinsic peculiarities of
soft-matter in plasmonic hybrids. For the sake of simplicity, let us consider here a colloidal metafluid as a hybrid system consisting of "particles" immersed in a fluid in a certain periodic manner. Obviously, the size of such particles should be much larger than the solvent molecules but small enough to remain dispersed in solution. The etymology of the term "metafluid" has its roots in the theoretical work by Urzhumov et al.,[106] who introduced liquid MMs based on clusters of metallic NPs, and proved that colloidal plasmonic nanomaterials can serve as a medium with variable effective permittivity, $\varepsilon_{\text{eff}}$, and a variable effective magnetic susceptibility, $\chi_{\text{eff}} = \mu_{\text{eff}} - 1$, in the optical and near infrared range. Importantly, colloidal self-assembled hybrids can address numerous crucial points related to the realization of advanced metafluids, such as attaining nanometer spacing over vast domains, improving true 3D configurational complexities, and profitable processing, which all are extremely challenging to achieve via top-down approaches. This serves as the rationale for adopting colloidal hybrid systems as a versatile platform for the realization of nanostructured MMs.[107]

Most plasmonic hybrids contain different colloidal species, with peculiar interparticle interplay. This interplay depends not only on the nature of the colloidal building blocks but also on the solvent properties. The solvent may have various traits, that is, can be complex, including diverse molecular species and various dielectric, conductivity, and viscosity properties.[95,96] Thus, the advanced functions of colloidal metafluids can be customized by adjusting their fusion, configuration, concentration, and environment.[108–111] These special features combined with the versatile functionality of the colloidal building blocks and efficient mechanisms for regulating their self-organization stimulated tremendous interest in a wide range of applications, including low-cost, high-resolution solution-phase spectroscopy of electromagnetic or chiral transitions,[112,113] highly efficient, robust, tunable, and reusable SERS substrates for the detection of trace amounts of organic vapors,[114] convertible optofluidic waveguide systems for lasing,[115] electric dipole (ED), which when coupled to adjoining particles play via soft-matter platform. Nevertheless, full unlocking of such functionality results in numerous all-dielectric hybrids including: i) metafluids enabling directional scattering; ii) metamolecules with nanogap-dielectric responses; and iii) metacrystals with magnetodielectric bandgaps. Soft fluidity of c-Se hybrids can accelerate the immediate utilization of all-dielectric metafluids such as virtually lossless antennas.[116] Another important phenomenon resulting from structuring properties of all-dielectric metafluids is strong electric and magnetic dipole resonances across the optical to near-IR spectrum, which was recently discovered by a group at Kobe.[117] They demonstrated that a solution of size-purified silicon nanoarchitectures manifests strong electric and magnetic dipolar resonances, as displayed in Figure 11b. Importantly, the measured MD/ED intensity ratio is increased than those documented for colloidal metafluids in the optical regime[118] and similar to that in the near-IR range.[119] Thus, such architecture enables efficient and quenching-free Mie responses which are challenging to attain by exploiting plasmonic counterparts. All-dielectric metafluids shown in Figure 11a,b have many uses including fluidic lenses and liquid light-guides and can break the stagnation of the study on plasmonic metafluids arising from the structural entanglement and open up new paths to achieve active index fluids for optofluidic systems.[119,120] Other uses for self-assembled optical metafluids shown in Figure 11c,d include water-based colloidal metamaterials with enhanced broadband absorption and confined active transparency peaks,[121] and polyhedral Au metafluids for low-cost soft moldings of hybrid MMs showing limpidity, nondispersivity, and ultra high indices of refraction.[122]

4.2. LC-Based Colloidal Metamaterials

Within the framework of this section, hybrid MM architectures take advantage of SPR of separate NPs and their interplay via soft-matter platform. Nevertheless, full unlocking of the application potential needs fabrication techniques yielding architectures with high NP filling factors, precisely regulated interparticle spacing, convertible tuning and improved switching kinetics.[123] Fulfillment of this concept is possible by using LCs which belong to a special class of anisotropic fluids that self-assemble into vector fields supervised by spatial and topological guidelines.[66,136] In these conditions, convertible reconfiguration of LC-based hybrid MMs arises from switchable contour of the organic coating of NPs.[137] Thereby, structural arrangement of NPs is modified without affecting...
the form of the nanocluster. Importantly, the LC-based scheme has already proven to enable construction of reversibly tunable metaplasmonics\cite{66,135–138} with electro-,\cite{139–141} magneto-,\cite{142} photo-,\cite{143,144} and thermo-responsiveness.\cite{64,137} Motivated by the great likelihood of implementing tunable ultracompact on-chip devices, the development of LC-based hybrid colloidal MMs has thus become a crucial research area over the last few years.\cite{64,137,143,145–155} This section introduces and discusses LC-based self-assembling phenomena for active colloidal MMs, with particular emphasis on recent advances in the field. It then briefly considers a broad spectrum of properties and capabilities of self-organized plasmonic hybrids loaded with LCs and provide examples of active MMs which interact with electromagnetic radiation in the visible and infra-red regions.

4.2.1. Shape Topology and Self-Organizing Behaviors of Liquid-Crystalline Colloidal Metamaterials

Self-assembly of liquid-crystalline colloidal nanocrystals with controlled orientation and spatial distribution allows the design of trailblazing optical MMs with peculiar shapes and orientation-dependent collective attributes. Thus, the self-assembling attribute of the LC coating is the impulsion resulting in the self-organization of the NPs into specific hierarchical architectures,
with particular emphasis on the structured variation of NP dimension, chirality, contour, and usefulness. This bottom-up strategy is extremely efficient as it integrates the extraordinary possibilities offered by LCs in morphology variety with the combination of useful entities, essential for a wide scenario of nanophotonic applications. Moreover, it enables the creation of hybrid well-ordered nanostructures with efficient switching kinetics that can be stimulated to arrange in a regulated manner, that is, by external stimuli. However, in order to obtain an active liquid-crystalline MM with tailored optical properties, it is crucial to understand the processes governing the self-organization and self-assembly of such hybrid colloidal systems. Basically, there are few fundamental types of such mechanisms. They were reported in 2011 by Goodby et al.,\(^{[139]}\) and are schematically illustrated in Figure 12.

First, Au NPs with hierarchical architectures may exhibit topologically miscellaneous contours, despite the fact that the Au cores are truly globular. For instance, for Au NPs shielded with alkyl thiols at possibly limited concentrations of adsorbates at the surface, the covered NPs can indeed assume a rod-like shape owing to the localized van der Waals correlations of the aliphatic chains and the necessity to reduce hollow spaces. Besides, rod-shaped NPs can self-assemble into lamellar architectures, whereas, raising the density would induce the creation of disc-shaped configurations followed by globular contours, which in turn can lead to self-assembly into cylindrical or cubic formations.\(^{[139]}\) In such hybrid systems, the aliphatic chains are usually proportional to the size of the Au NP, that is, 2–3 nm. At low accumulation of the adsorbate, the surface will have an irregular chain decomposition, which results from the system pursuit toward the minimum energy position. Stronger interlinkages form “poles” by extending out of the aliphatic chains (trans conformers), while the “equator” will manifest a higher density of specific conformers. Hence, the NPs will be deformed and possess anisotropic, tactoidal contours, as shown in Figure 12a. The contours of coated NPs can be influenced as well by the surrounding molecules when they are diffused in diverse backgrounds. In the case of NLCs, the rod-shaped molecules will affect the contours of the NPs such that adsorbates will align themselves, via stretching out, to be parallel to the specific direction called director, and the spherical arrangement of the wrapped NPs will substantially become tactoidal, as shown in Figure 12b. Importantly, mesogenic materials can be effectively used instead of aliphatic chains as adsorbate materials on the outsides of the Au NPs. Hereby, the NPs can reveal self-organizing function and possess improved compatibility with host-LC schemes.\(^{[139]}\) Finally, distribution and coating are crucial when the adsorbate architectures are linked to Au NPs, which now possess rather compact curvature in comparison to the aliphatic coatings that are not as thick, compare

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**Figure 12.** Self-organizing effects accompanying phenomena associated with the decoration of the surface of NPs with LC mesogens in hybrid liquid-crystalline gold MMs illustrated by a) contour change in NPs owing to interplay between the specific adsorbate particles in low density overlay, b) distortion of the NPs from spherical to tactoidal resulting from dispersion of coated gold NPs into a host calamitic LC. The enhance of the NP size induces a splaying of the mesogenic adsorbates, which leads to deformational modifications allowing for a higher packing density at the poles; c) NP with aliphatic covering, d) NP with a mixed covering, e) NP with mesogenic covering. Adapted with permission.\(^{[139]}\) Copyright 2011, Wiley-VCH.
Figure 12c,e. The degree of spread of the mesogenic units at the equator, in relation to the tight packing at the poles, will result in highly anisotropic attributes and even various packing configurations of NPs along the equator with respect to the poles. Cutting down the density of the mesogens linked to the surface is expected to result in less-dense packing at the poles and, accordingly, a strong diminution in the anisotropy of the attributes. An identical effect is anticipated to appear from mixed single-layers in which considerable amount of mesogens is limited because of the inclusion of aliphatic adsorbates, as shown Figure 12d.

4.2.2. Stimuli-Responsive Liquid-Crystalline Colloidal Metamaterials

The availability of MMs with functions that can be triggered by a particular stimulus is enticing for the future development of various MM-based technologies. This subsection demonstrates the advantages of the beforehand introduced self-assembling phenomena of LC-based hybrid colloidal MMs to enhance their performance and endow them with new functions through the use of external stimuli allowing for active control of their optical properties. In particular, self-assembly of both non-plasmonic and plasmonic colloidal nanocrystals into liquid crystalline matrices has immense potential to engineer composite nanostructured MMs through a bottom-up approach.[137,139,144,145,153–158] Indeed, self-assembly of colloidal NPs into liquid crystalline architectures is an encouraging direction to adjust the spatial configuration as well as the orientation of nanoscale building blocks over large areas. This was considered in the early work by Smalyukh et al.[145] who reported the aggregation-free elastic self-alignment of Au nanorods dispersed in LCs and their realignment by shearing and magnetic fields, and thus showed the potential for LC-mediated well-controlled self-assembly of bulk optical MMs with reversibly switchable properties. Quite recently, the bridge between NPs and LCs has been expanded with self-assembled hybrid MMs based on high-index dielectrics as well as biocompatible composites.[151–153] For example, Nair et al.[153] fabricated a hybrid MM by immersing TiO$_2$ nanoparticles functionalized with an organic acid containing a carboxyl group in an NLC and used AC bias voltage to switch Mie resonant forward scattering of the NPs in the visible employing Kerker’s postulate. Note that, the unidirectional scattering, forward or backward, was previously formulated by Kerker et al., on a theoretical molecule that reveals magnetic and dielectric dipolar resonances.[159] The proposed mechanism underlying these phenomena is related to the constructive interference of resonances in one direction and destructive interference in the opposite direction. In addition, Madhuri and co-workers[152] reported a voltage-tunable scattering system based on a MM composite made of hollow biocompatible coxleates cylinders and LC, and proved that the haze of the device gets halved and the total transmittance increases to about 66 % with the application of an AC bias voltage. Recently, LC-based strategy has been intensively tested for many types of NPs to form hybrid MMs, in which the location and orientation of NPs can be directed by stimuli-sensitive liquid crystalline superstructure, as shown in Figure 13. Scharf et al.[147] investigated the optical functionalities of slender aligned films of LC-Au NP hybrids and considered the interaction of the configurational and internal anisotropies, as shown in Figure 13a. Besides, a strong dichroism with a large splitting of the plasmonic band of ~50 nm appeared. The authors proved that this behavior was the result of both the birefringence of molecules attached to a metal atom by coordinate bonding and the interplay between asymmetrical positioned NPs. Not long after that, Lewandowski et al.[137] examined a thermally tunable MM including Ag NPs exploiting a thermally responsive organic coating and investigated the active self-assembly arising from temperature-sensitive variations of the coating form, which translates into a convertible spatial arrangement of the Ag NPs, as shown Figure 13b. A tunability of up to 20 nm was evidenced as a consequence of the plasmon band maxima position shift. Epsilon-near-zero (ENZ) functionalities were additionally verified by ellipsometric tests, which enabled to evaluate the effective optical features of the plasmonic arrangement. Furthermore, photo-tunable ENZ mode in a self-organized LC–NP soft MM was experimentally examined by Bhardwaj et al.[144] The behavior of the effective permittivity of this system, made of Au NPs surrounded by a photo-responsive LC ligand, indicates an ENZ mode at optical wavelengths with a bandwidth of 45 nm which increases by a factor of 1.6 on UV illumination, as illustrated in Figure 13c. Another important phenomenon is related to electrically switchable Mie responses in the visible spectrum manifested by a soft MM produced by dispersing high refractive index dielectric scatterers (selenium) in a LC environment, as shown in Figure 13d. Importantly, such hybrid MM exhibited electrically tunable dipolar and quadrupolar Mie resonant responses at various wavelengths as a result of the interplay between the broad electric dipole (ED) and narrow electric quadrupole (EQ) resonances.[151] The mentioned concepts indicate that LCs have been used effectively in the realization of active and hybrid MMs. A list of their properties along with the tunable functions is summarized in Table 1.

4.3. 2D and 3D Hybrid Metamaterials Assembled by DNA Origami

The self-assembly of nanostructured colloids into 2D and 3D formations with specific architectures is essential for the evolution of numerous MM-based instruments. Among a huge range of different substances for self-organization, DNA constitutes one of the most enticing scaffolds preponderantly owing to its remarkable predictability and programmability.[160–164] To date, a plethora of design schemes for assembling DNA molecules into tailored nanostructures and templates have been introduced.[165] In particular, origami approach has become the most favorable and smart method for bottom-up MMs formation with DNA.[166,167] In this procedure, hundreds of rationally designed “staple” oligonucleotides are combined into a long single-stranded DNA system that can be used to force the assembly of nanostructures into specific 2D or 3D shapes. DNA origami structures are usually formed from a long (7–8 kb) scaffolding DNA single strand and roughly 200 short “staple” oligonucleotides.[164] The main advantage of the DNA origami technology is then to provide 2D and 3D configuration of, for example, NPs with nanometer accuracy, enabling the
construction of composite architectures with adjusted optical resonance. These soft hybrids are completely controllable by their DNA sequence thus allowing additional decoration and functionalization in a not reproducible, sequence-specific manner. Spatial and physical functions can be customized by simple adaptation of the configuration and fabrication strategies, which should allow quantitative fine-tuning of the optical activity of aforementioned nanostructures dispersed in solution. In recent years, DNA origami assembly has proven as a viable method toward precisely controlled 2D and 3D hybrid architectures with high spatial addressability. To demonstrate the ability of DNA origami for the programmable 2D and 3D nanoscale hybrid MMs we chose a set of several different concepts that are illustrated in Figure 14.

Early examples date back to the year 2014, when Mirkin’s and Kuzyk’s group independently reported two concepts of 3D hybrid MMs assembled by DNA origami, as reported in Figure 14a,b. In Mirkin and co-workers’ approach, computational simulations were exploited to prove that superlattices of Ag NPs possess the ability to reveal exceptional optoelectronic properties upon the photothermal conversion of organic coating shape, which leads to a convertible structural reorganization of the Ag NPs.
MM function including ENZ band and an “optically metallic” regime that manifests great reflectivity even if the superlattices are made by over 80% of water. They used DNA as a programmable scaffold to arrange Ag NPs into 3D periodic architectures, and proved that the optical properties of the Ag NP superlattices are practically independent of the interparticle distance (and therefore the metal fill fraction) within the superstructures. In addition, DNA-functionalized Au NPs building blocks, allowing for the assembly of binary (Ag NP)–(Au NP) superlattices, were introduced. Interestingly, when solution-phase ensembles were collected for the 3D binary (Ag NP)–(Au NP) superlattices, the LSPR at 410 nm was greatly reduced when compared to a solution of dispersed Ag and Au NPs in the same amount. In addition, the reduction is more noticeable as the interparticle spacing is decreased by taking advantage of reduced DNA linkers. This observation was additionally confirmed by modeling the hybrid utilizing Mie theory (as shown in lower right panel in Figure 14a). Importantly, for a minimum spacing between adjacent surfaces of ≈10 nm, the LSPR peaks of Ag and Au are comparable in amplitude and significantly expanded. On the other hand, Kuzyk et al. fabricated reconfigurable 3D plasmonic metamolecules, which perform DNA-adjusted nanoscale deformational modifications. In this case, DNA served as both a scaffold to arrange metallic NPs in 3D, as well as fuel for bringing the metamolecules to specific deformational conditions. The two crossed Au nanorods constitute a 3D plasmonic chiral scheme, which induces a theme of handedness when staying in tune with left- (LH) and right-handed (RH) circularly polarized light, being the cause of strong circular dichroism (CD). The relative angle between the Au nanorods and hence the handedness of the 3D chiral architecture can be actively regulated employing two DNA locks, which are extended from the sides of the DNA origami template. Furthermore, the plasmonic nanostructure can be brought to either the LH or RH condition by introducing removal strands R1 or R2 and back to its relaxed condition by introducing reverse strands R1' or R2', as shown in Figure 14b. The CD bands of the LH and RH states are depicted by the red and blue curves, respectively. The CD band of the relaxed state in black reveals RH preference, yet with much lower intensity. Thus, CD behavior of the RH state is much more intense than that of the LH state. Shortly after, Urban et al. reported the first experimental realization of metallic toroidal metamolecules via hierarchical gathering of helicoids templated by DNA origami, as shown in Figure 14c. Here, plasmonic helical monomers, dimers, as well as toroidal metamolecules in LH and RH geometries were assembled via attaching Au NPs onto the origami precursors. The helical configuration of the Au NPs induces a “corkscrew” behavior on the collective plasmons, introducing a twist with the appropriate handedness into the propagation direction of light, thus allowing for different absorption in response to LH and RH circularly polarized light, that is, CD. The LH monomers, dimers, and toroidal metamolecules manifest particular peak-to-dip curves with improving intensities, while their RH equivalents demonstrate mirrored spectra correspondingly. Interestingly, the plasmonic toroidal metamolecules are characterized by the most noticeable CD bands, when compared to the component plasmonic helical monomers and dimers. The scheme could be exploited in polarization conversion in case of on-chip devices with controlled incident intensities. To further emphasize the role the scaffolded DNA-origami approach plays in programming self-assembled superlattices and plasmonic MM, the scheme depicted in Figure 14d can be helpful. In their work, Ke and co-workers designed a collection of hexagonal DNA-origami tiles employing computer-assisted scheme and fabricated self-assembled micron-scale 2D honeycomb lattices and tubes. The approach offered a valuable insight into the programmed self-assembly of low-defect supra-molecular DNA-origami 2D lattices and tubes. The results clearly show that Au NP hexamer and lattices exhibit plasmonic response both in simulation and experimental verification, that is, the magnetic dipolar response (scattering mode at 645 nm) together with essential electric response (scattering mode at 587 nm). Also, a 15.5 nm red-shift on the UV–Vis absorption spectra resulting from enhanced inter-particle coupling was observed. Thereby, the authors proved that DNA-origami hexagon tiles and honeycomb lattices blaze a trail toward assembled hybrid MM via programmable spatial configuration of the Au NPs into clusters and superstructures.

4.4. Hybrid Metamaterials Realized via Hierarchical Block Copolymers

In recent years, another method for creating surface patterns with dense and periodic nanoarchitectures has been of

**Table 1. Surface functionalization of NPs with LC/LC ligands toward hybrid stimuli-responsive colloidal MMs.**

| NP | LC/LC ligand | Tunability | Function | Wavelength | Ref. (Year) |
|----|--------------|------------|----------|------------|-------------|
| Au | LC ligand | Polarization | Strong dichroism | Visible | (147) (2013) |
| Ag | LC ligand | Temperature | ENZ | Visible | (137) (2015) |
| SiO₂ | NLC (6CB) | Voltage | Enhanced Mie resonance | Vis–NIR | (155) (2021) |
| Au | Chiral LC ligand | Temperature | Circular dichroism | UV–Vis | (154) (2021) |
| Cochleate | NLC (BL036) | Voltage | Enhanced scattering | Vis–NIR | (152) (2020) |
| Se | NLC (E7) | Voltage | Dipolar and quadrupolar Mie resonances | Vis–NIR | (151) (2020) |
| Au | Chiral LC ligand | Photo | ENZ | UV–Vis–NIR | (144) (2021) |
| Au | LC ligand | Temperature | Structural reconfiguration | Vis–NIR | (135) (2016) |
| Au | NLC | Polarization | Aggregation-free elastic self-alignment | Vis–NIR | (145) (2010) |
| TiO₂ | NLC (E7) | Voltage | Directional scattering | Vis–NIR | (153) (2020) |
particular interest, namely the bottom-up strategy using the self-organization of block copolymers (BCPs).\textsuperscript{[169,170]} BCPs composed of covalently bonded, chemically different macro-molecular blocks spontaneously phase-separated to arrange compact and periodic nanoarchitectures with sub-100 nm dimensions. An important property of BCPs is their ability to self-assemble into periodic nanostructures. Indeed, an adequate adjustment of the BCP chain length and the volume fraction of each building block can generate size-tunable, laterally ordered, dense nanostructures assembled from periodic arrays of lamellae, cylinders, and spheres with nanometer-scale regularity when triggered by an external stimuli such as heat, structural transformation, and pressure.\textsuperscript{[160]} Importantly, being the characteristic dimension of the BCP self-organization in the tens-of-nanometers scale, an optimal resonant behavior is expected that is highly desirable in optical MM-based technologies. Therefore, the field of BCP-based 2D and 3D optical MM\textsuperscript{s} has become an inspiring modus operandi for state-of-the-art optical meta-devices. As illustrated in Figure 15, BCP templating enables the creation of well-defined 2D and 3D nanoarchitectures with the desired periodicity and arrangement in vast areas, and thus blaze a trail toward straightforward,
swift, and cost-effective fabrication of newfangled optical MMs. For instance, the group from Korea and USA[171] proved that MMs composed of periodically arranged and symmetry-adjusted self-organized nanopatterns enable a steerable refractive index medium for a wide bandwidth, including the optical regime, as shown in Figure 15a. Their methodology utilizes the separate manipulation of permeability and permittivity with nanostructured objects less than the skin depth. The careful manipulation of the inner dimension in BCP nanopatterns via pattern shrinkage enhanced the effective refractive index even more than threefold to a peak value of $n_{\text{eff}} = 5.10$ at a wavelength of 709 nm for Au MM. Moreover, the $n_{\text{eff}}$ is greater than 3.0 in the range of 638–1700 nm. Despite the fact that the BCP nanopattern exhibits a multigrain character because of the entropy-induced grain freedom, it has sixfold rotational symmetry within each grain. Hence, the effective optical features are isotropic for the in-plane fields and are not affected by position of the grain in the long wavelength limit. Consequently, the interparticle spacing and the particle contours are the only crucial factors, and the spatially unchanged $n_{\text{eff}}$ could be achieved before and after contraction. Besides, adaptable steerability of pattern shrinkage afford effective tunability of $n_{\text{eff}}$, including spatially graded or anisotropic refractive index MMs.[171] Besides, 3D BCP-based nanoarchitectures have been

Figure 15. Building blocks, design principles, and optical properties of hybrid MMs via hierarchical BCP illustrated by a) highly tunable refractive index visible-light MM constructed via BCP self-assembled nanopatterning on thermal shrinkage films, b) tunable MM-like systems for surface-enhanced Raman scattering via 3D BCP-based nanostructures, c) gyroid-structured optical MM that exhibits the localized surface modes which result in the anisotropic optical effect, producing the linear dichroism, d) hyperbolic MMs via hierarchical BCP nanostructures. a) Adapted under the terms of CC-BY license.[171] Copyright 2016, Springer Nature. b) Adapted with permission.[172] Copyright 2019, American Chemical Society. c) Adapted with permission.[173] Copyright 2019, Wiley-VCH. d) Adapted with permission.[174] Copyright 2021, Wiley-VCH.
also examined as a tuneable MM-like platforms for SERS, as shown in Figure 15b.\textsuperscript{[172]} The concept proposed by Oppenheimer et al.\textsuperscript{[12]} uses self-assembly driven formations based on adaptable BCP nanoarchitectures and demonstrates regenerateable SERS enhancement over a vast area. The produced 3D gold SERS underlayers are made from BCP microdomain formations comprising the double gyroid (DG), free-standing gyroid (FSG), mixed cylinders morphologies, that is, the fusion of parallel and perpendicular to the underlayer, (MCYL), hexagonal cylinders and only perpendicular cylinders (CYL), correspondingly. Selective degradation of the self-organized phase-separated BCP constituents, coated with Au effectively increases the electromagnetic waves, yielding large SERS actions. Finally, the authors show that the largest absolute enhancement factor (EF) for the FSG-based SERS underlayer reached 6.1 \times 10^7 and 6.7 \times 10^7 at 785 and 633 nm, respectively (as depicted in right bottom panel in Figure 15b). Soon after these groundbreaking works, another original concept demonstrated by Wilts et al.\textsuperscript{[173]} appeared, as shown in Figure 15c. The authors studied the interplay between light and Au gyroid optical MMs and found a significant connection between the surface formation and its linear dichroism. To be more precise, four gyroid unit cell with surface terminations of $\tau = 0.08$, 0.16, 0.24, and 0.40, where $\tau$ is the distance of the terminating plane from the crystallographic origin in units of periodicity in the [110] direction (i.e., $\sqrt{2}a$), were examined. The permittivities for the thin anisotropic MS and isotropic bulk gyroid MM prove that parallel to the long axis of the anisotropic surface morphology ($\phi = 55^\circ$), the MS shows a resonant behavior at $\approx 630$ nm. In contrast, perpendicular to this axis ($\phi = 145^\circ$), the MS operates as a low refractive index transparent dielectric. These results imply that the scheme of a “MS atop a MM” fulfills the function of an extremely effective instrument with which the selected features of uniformly terminated gyroid optical MMs can be comprehended. The latest breakthrough phenomenon is associated with a novel mechanism for the construction of hyperbolic MMs (HMMs) based on BCP blend variability.\textsuperscript{[174]} In this approach, the hierarchically structured BCP nanoarchitectures were utilized as patterns for the construction of a Au/air HMM with unique hyperbolic isofrequency, that is, the permittivity tensor components (along the principal axes) are of opposite signs, resulting in a strong anisotropy and hyperbolic dispersion of the HMM in the optical regime. The hybrid device has a broad bandwidth Purcell factor for wavelengths larger than 580 nm, with a 32-fold enhancement at 580 nm, as seen in the right-low panel in Figure 15d. Thus, the hierarchical patterning traces the path toward advanced nanophotonic systems such as photonic hypercrystals and hyperbolic waveguides and unveils an additional range of possibilities for the construction of complex MSs.

5. Conclusions

Soft-matter hybrid and active MMs represent a reliable opportunity for fundamental and application oriented research. However, apart from their purely scientific significance, these MMs are also expected to achieve in the next future a substantial impact at economic and societal level. Indeed, the related innovation potential is extremely high and the intrinsic content is strongly trans-sectorial and multidisciplinary, covering physics, chemistry, materials science, engineering, biology, and precision nano-medicine. Involved subjects span optics and photonics, sensoristics, anti-counterfeiting, and theranostics, to name a few. In this manuscript, a very rich variety of systems has been considered, sometimes very diverse for fabrication, composition, and functionalities. Throughout the paper, soft-matter based MMs have been distinguished in terms of the involved fabrication approach that typically results in ordered or disordered organization of the main constituents, and respectively requires top-down or bottom-up procedures. In Section 2, a first general overview has detailed how soft-matter recently made its debut in the field of 3D MMs as a fabrication facilitator, given the possibility to realize arbitrary shapes with much more ease. Later on, the attention has moved from MMs to MSs, which represent a natural evolution of the bulk counterpart for their compact transverse dimensions, simpler fabrication, and lower losses. In the following part of Section 2, MSs have been categorized in terms of their plasmonic functionalities (PMS) or Huygens full-phase shaping in presence of all-dielectric sub-elements (DMS). In both cases, soft-matter demonstrates its overwhelming role when entering the field as a tunability key-enabler. Ample room has been given in Section 3 to mechanisms of tuning for MS functionalities and related application as active devices. In this regard, the extraordinary role of LCs as electrically, thermally, and optically tunable material has been largely outlined in a multitude of examples. Indeed, the active control of photonic features enabled by soft-matter represents in perspective a extraordinary opportunity to realize a hype in futuristic technologies. This is particularly effective for instance in dynamic holography that finds ideal application in emerging fields like automotive, virtual and augmented reality, or remote medicine fields. Mechanical and other tuning approaches, including shape memory effects, satisfactory complete a wide scenario of possibilities that assures a disruptive approach in the realization of shape changing devices able to adapt and reconfigure depending on the specific need. On this way, self-adapting systems will be involved in smart sensors, neuromorphic chips and soft actuators toward artificial muscle applications. In Section 4, the bottom up approach to the fabrication of auto-organized assemblies is thoroughly explored. These systems typically result in bulk soft-matter hybrid MMs including colloidal, polymeric and granular matter. In this case also, LCs assume a relevant role for their ability to support the organization and high filling clustering of plasmonic nano-particles. Moreover, the presence of intrinsically tunable molecules, well dispersed in the auto-organized plasmonic composites, endows new stimuli-responsive optical functionalities. In perspective, the precise and highly resolute spatial organization of the involved meta-atoms, enabled by the utilized fabrication approach, facilitates the realization of systems whose topological features can be controlled with limited effort, thus opening novel and exciting possibilities. The panorama of bottom-up hybrid MMs fabrication is completed with the description of the exquisitely original DNA origami and block-copolymers approaches. In the depicted framework, the hybridization of MSs by soft-matter emerges as an effective solution of important challenges of common MSs, like losses and, of course, lack of tunability. These novel systems are then
expected to find a significant role in novel research trends like optical computation and quantum photonics. In case of optical computation, pioneering work of the groups of Engheta[175] and Bozhevolnyi[176] have already demonstrated the possibility for MSs to perform simple mathematical operations. Elaborating on this concept, MSs have been later on exploited for the coding of digital signals,[177] thus establishing a concrete bridge between physics and computer science. Considering instead quantum photonics, the higher degree of freedom introduced by MSs in locally controlling phase and shape of the wavefront materializes as extremely convenient to generate and detect non-classical optical states. With control over single photon emission, the generation of a variety of multi-photon entangled states is possible by MSs. Hybridization with soft-matter would enrich the panorama of mentioned cases by ensuring real-time reconfigurability of specific MS sub-elements. Such an approach would thus enable solutions never imagined before.

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Conflict of Interest

The authors declare no conflict of interest.

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