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Abstract

Meta-atoms interact with light in interesting ways and offer a large range of exciting properties. They exhibit optical properties inaccessible by natural atoms but their fabrication is notoriously difficult because of the precision required. In this perspective, we present the current research landscape in making meta-atoms, with a focus on the most promising self-assembly approaches and main challenges to overcome, for the development of materials with novel properties at optical frequencies.

Introduction

Meta-atoms are structured artificial composite nanostructures designed to absorb and scatter light in ways not accessible by natural atoms or molecules. These properties result not only from the materials that compose the structure but also from the geometry and positioning of the components of the meta-atom. They are usually optically resonant structures at visible and infra-red frequencies. Similarly, a metamaterial is a structured artificial material composed of large amounts of meta-atoms arranged into two- or three-dimensional structures to provide optical responses that do not naturally occur. They inherit their optical properties from the meta-atoms as well as from their spatial arrangements. The field of metamaterials is now a little over twenty years old and its community has produced many devices and applications, in most cases by top-down fabrication. These top-down approaches usually consist of devices manufactured using lithography, as well other techniques such as electrodeposition into track-etched membranes [1–3] or electrochemical anodization [4]. Lithographic approaches offer precise morphological control, but suffer limited throughput and are not well suited to the manufacture of 3D materials. Some of its most prominent examples include cloaking, hyper-lensing, negative refraction, flat optical devices, and optical magnetism [5–11].

More recently, a complementary bottom-up fabrication approach has emerged (figure 1). Typically, researchers use soft matter techniques, such as colloidal nanochemistry, to synthesize nanoresonators, and then assemble them into metamaterials. These techniques can produce much larger quantities of meta-atoms per synthesis than top-down approaches, and in sufficient volume to fabricate metasurfaces ($\sim 10^8$ meta-atoms mm^{-2}) and bulk metamaterials ($\sim 10^{12}$ meta-atoms mm^{-3}). Bottom-up methods offer a high control over morphology and unrivalled scalability. They allow the synthesis of optical resonators with high precision and can achieve smaller gaps between resonant nanostructures than top-down methods, such as lithography. The meta-atoms can be dispersed in aqueous or organic solvents to produce inks that can coat surfaces or assemble into a 3D material with varying degrees of order and disorder. This ability to separate the design of the meta-atom from that of the metamaterial holds a lot of promise for the development of novel applications.

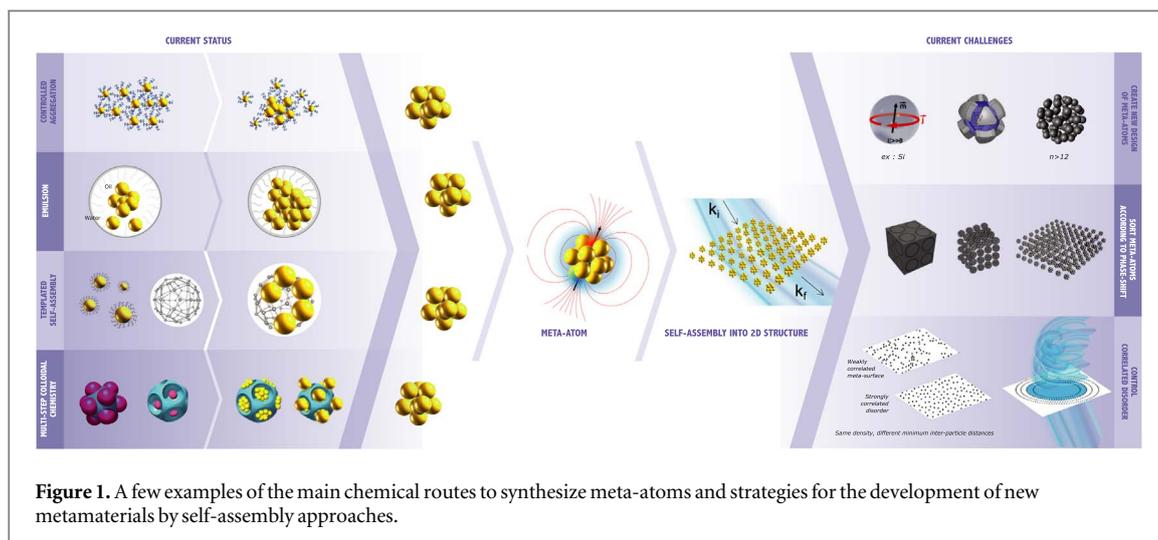


Figure 1. A few examples of the main chemical routes to synthesize meta-atoms and strategies for the development of new metamaterials by self-assembly approaches.

Tailored optical properties

A major focus of this bottom-up approach has been the generation of artificial optical magnetism [12, 13]. Gomez-Graña *et al* produced a bulk self-assembled three-dimensional isotropic material that exhibited a magnetic response at visible frequencies [14]. They realized this metamaterial by carefully engineering meta-atoms to exhibit strong magnetic dipolar resonances. The ability to design meta-atoms with specific electric and magnetic dipoles—and even multipoles—has enabled tailoring the scattering direction of individual nano-objects [15, 16]. In principle, by achieving an adequate distribution of radiating multipoles, it is possible to produce any angular radiation pattern. This means that metasurfaces, or 2D metamaterials, can be designed to totally absorb, reflect or transmit light. To achieve this, Huygens' meta-atoms (dually resonant systems with equal odd and even multipoles) should be precisely designed and positioned so as to create a phase-shift that may be as large as 2π with respect to the incident wave. The resulting interference is what produces the overall response of the metasurface [17–21]. More generally, spatial control of the phase of meta-atoms deposited into an ordered two-dimensional array can be achieved either by varying the geometric parameters of the meta-atom or the separation of neighboring meta-atoms. The excellent geometric control offered by lithography has made it popular as a means to produce such devices. It remains a challenge for bottom-up approaches to surpass lithographic techniques. Arranging meta-atoms into arrays with sub-wavelength periods and sorting them according to the phase-shift they impart is far from trivial on large surfaces. However, achieving this would enable the production of bottom-up flat optical devices that shape optical wave fronts such as flat lenses, prisms, phase plates, or even vortex-beam generators.

Disorder and inaccuracy are inherent to bottom-up methods and are often viewed as a fundamental limitation of these approaches. However, recent trends in the literature have seen the inclusion of a controlled degree of disorder into such systems as potentially advantageous [22–24]. For instance, disordered surfaces can achieve perfect absorption, an application where 100% of the impinging light is resonantly absorbed [21]. Furthermore, the sharp 2π phase-shift across the resonance imparted by Huygens' meta-atoms implies a rapid spectral variation of the phase over the resonance bandwidth. Practically, this means that a disordered surface composed of such structures would potentially exhibit strong group velocity dispersion, a property that is commonly used to chirp or compress ultra-short optical pulses [18]. Without being fully disordered, 2D meta-atom assemblies with correlated disorder, may produce metasurfaces with similar efficiency to ordered lattices [25, 26]. For instance, Akselrod *et al* have demonstrated near-perfect absorbance from metasurfaces of partially disordered self-assembled Ag nanocubes [27]. Further investigations of bottom-up approaches should explore these regimes to see if elegant optical properties are possible, notably because self-assembly often leads to correlated systems.

As meta-atoms are generally optically resonant structures, clusters of plasmonic particles are particularly promising candidates. Therefore, the development of new designs and mathematical models to explore the full potential of the radiation capabilities offered by individual or assembled composite metal/dielectric meta-atoms is required. This includes, for instance, finding homogenized versions of dense plasmonic clusters composed of many nanoparticles, because simulating assemblies of such clusters has a giant computational load.

Synthesis of meta-atoms

The current approaches to the bottom-up synthesis of plasmonic clusters can be grouped into four main strategies: controlled aggregation, emulsion, templated self-assembly, and multi-step colloidal chemistry (figure 1 and table 1) [28]. The first two of these are direct methods to produce batches of clusters via either rapid aggregation or emulsification. These techniques produce broad distributions of cluster valencies, and are controlled using stoichiometry and by stopping the aggregation/emulsification processes at precise times. Templates-assembly approaches and multi-step colloidal syntheses are more complex and selectively target the synthesis of clusters of a single valency.

Templated-assembly exploits the high uniformity of certain biological molecules such as viral capsids or DNA origami to template the self-assembly of nanoparticles. On the other hand, multi-step colloidal syntheses uses fine control over polymerization of latex emulsions onto SiO₂ nanospheres to generate symmetric templates used to direct nanoparticle growth [60, 67, 68]. For example, this was employed to produce precise icosahedral arrangements of twelve Au or Ag nanospheres around a SiO₂ core [16, 69].

In general, the optical properties of meta-atoms become more complicated as the number of constituent resonant nanostructures increases; with higher order resonance modes becoming apparent and lower order resonances becoming redshifted and broader. The field enhancement of such clusters typically scales with the square of the cluster valency [70]. These optical properties are highly sensitive to disorder in the structure of the clusters, such as polydispersity or positional disorder, which induce large shifts in resonances and enhanced electric quadrupolar and magnetic dipolar contributions, resulting in a very broad optical response when measured in bulk [71, 72]. Therefore, bottom-up approaches typically target the production of meta-atoms with a high homogeneity in their size, structure, and valency. In that regard, templated self-assembly and multi-step colloidal chemistry represent the most promising approaches. For example, the optical properties of dodecahedral plasmonic clusters made by multistep colloidal chemistry have been explored in-depth and show already potential for use as Huygens' sources for metasurfaces [16, 69]. However, challenges remain to optimize these protocols for the production of even higher yields and further expand the range of achievable cluster morphologies. Finding metrics to quantitatively compare these approaches is difficult as information on meta-atom yield or their optical properties are often missing from the literature. Reliable protocols capable of producing clusters of single valencies above twelve are currently non-existent. The range of materials used in plasmonic clusters remains relatively modest. Clusters of Si or Ge have been theoretically predicted to behave as Huygens' sources [20, 21], and could be prepared in the near future, as synthetic protocols already exist for Si and Ge nanoparticles [73–75].

Self-assembled metamaterials

A range of methods exist for the self-assembly of meta-atoms into metasurfaces and metamaterials. To prepare monolayers and thin films from colloidal materials, several techniques can be used, such as convective assembly (dip- or doctor-blade coating), interfacial transfer (Langmuir-Blodgett troughs) or spin-coating [61, 76–78]. They offer reliable protocols to produce both disordered sub-monolayers and highly ordered close-packed monolayers (or multilayers) on surfaces. More control of nanoparticle positioning can be achieved by combining convective assembly techniques on patterned substrates produced *via* top-down approaches [79, 80]. Typically, these substrates feature arrays of indentations capable of simultaneously trapping multiple particles forming clusters. Particles are directed over the substrate in high concentration by techniques such as dip-coating. The particles then become trapped by capillary forces when they come into close proximity of an indentation. The size and shape of the traps can be used to control the morphology of the clusters, and the traps distribution can be varied to position and orient the clusters for study, examples of which are discussed in the final row of table 1 [81]. The high degree of spatial control over meta-atom positioning allows regulation of the phase shift across the metasurface and thus control of its optical properties. However, the number of clusters produced by such methods is tiny in comparison to the bulk liquid-phase syntheses mentioned previously. They are realistically only suitable for the on-substrate self-assembly of plasmonic particles into meta-atoms with predetermined spatial configurations relative to one another.

Bulk metamaterials can be assembled through techniques, such as sequential coating with thin films of meta-atoms, or by direct assembly of large numbers of particles into colloidal crystals or disordered solids through microfluidic evaporation [82]. The fabrication of 3D metamaterials by self-assembly of plasmonic meta-atoms has already been successfully demonstrated, opening the expansion on these studies to other candidate meta-atoms [74, 82, 83]. However, there remains considerable scope for further improvement of bottom-up self-assembly techniques. Finer control over meta-atom positioning and orientation will allow for the realization of a greater range of metamaterials. If meta-atoms could be precisely positioned into patterns of different sizes or

Table 1. Summary of the main bottom-up approaches developed to synthesize meta-atoms.

	Method	Pros	Cons
	Control of Aggregation Kinetics		
	<i>Controlled aggregation of NP suspensions through changes in solvent stability [29–31] or salinity [32, 33], or mixing binary populations of NPs functionalized with complementary DNA strands. [34–38]</i>	Facile.	Polydisperse cluster valencies.
	Emulsion-Based Assembly		
	<i>Surfactant stabilized droplets of colloidal suspensions evaporated in situ to produce clusters. [28, 39–42]</i>	Facile.	Polydisperse cluster valencies. Requires chemical modification for long-term stability and assembly (surfactant stabilized).
	Templated Self-Assembly		
(1)	<i><u>DNA origami</u> - specific binding sites on DNA origamis produce clusters of controlled geometry. [43–49]</i>	Control of cluster valency and shape. Many possible cluster geometries.	Requires further chemical modification for long-term stability and assembly.
(2)	<i><u>Molecular Printing</u> - Surface of NPs patterned using DNA origami as a mask with molecular ‘inks’ which bind secondary NPs at specific sites on the NP surface. [50–52]</i>	High control of valency. Reusable DNA mask. Many possible cluster geometries.	Requires further chemical modification for long-term stability and assembly.
(3)	<i><u>Viral Assembly</u> - Use of symmetric viruses modified to present cysteines at specific locations to bind nanoparticles to the surface in a symmetric manner. [53–56]</i>	Uniform cluster sizes	Limited range of cluster geometries (icosahedra/helical filament) Bare particles after synthesis, some modification needed.
	Multi-Step Colloidal Chemistry		
	<i>Formation of a core particle with a known number of PS satellites at controlled positions which can then be replaced with noble metals through a multi-step synthesis. [12, 24–27, 57–59]</i>	Moderate control of valency Many possible cluster shapes	Long synthesis (many steps) Difficult polymerization of styrene onto SiO ₂ core.
	Substrate-Directed Assembly		
	<i>Use of a substrate modified with physical traps into which particles can be directed via convective self-assembly. [60, 61, 62–66]</i>	High control of cluster valency, shape, and positioning.	Low final concentration. Substrates require top-down methods.

type, optical wave front manipulation with such metasurfaces will become a realistic prospect. A potential route to these maybe substrates patterned with multiple DNA sequences complementary to different meta-atoms allowing any arbitrary configuration to be achieved.

Overall, early reports of self-assembled metamaterials have demonstrated the viability and huge potential of this approach. The possibility of building meta-atoms independently of the metamaterial, and in large scale, offers important advantages compared to top-down lithography. Improvements to the fabrication of both meta-atoms and the self-assembled metamaterials will pave the way. For example, plasmonic bottom-up meta-atoms typically possess strong local fields or hot spots, which can be exploited for nonlinear metamaterials. Nonlinear polarization scales as a power expansion of the microscopic electric field, which can be several orders of magnitude larger than the exciting field [84]. Therefore, we should pursue the design of nanoscale materials which produce large nonlinear responses. This would considerably reduce the command power (proportional to the magnitude square of the incident light) required to activate a given nonlinearity in comparison to the bulk material. These considerations are of prime importance in reducing the energy footprint of nonlinear optical systems and their miniaturization. Nonlinear metamaterials already have application in lasers, signal processing and telecommunications.

Conclusion and perspectives

In this article, we have summarized the various chemical routes developed to synthesize highly symmetric meta-atoms and their assembly into ordered nanoarrays. Early applications revolved around the exploitation of the extraordinary optical properties of plasmonic clusters with precisely designed morphologies. The second and current generation of meta-atoms will explore building units made of materials with higher refractive index and low losses, such as Si or Ge, as well as hybrid systems such as Au or Ag/Si. The synthesis of Si or Ge nanoparticles below 100 nm remains challenging, as well as their assembly into precise configurations. Meta-atoms containing these materials would further tailor and optimize performance of myriad applications in the visible and infrared (negative refraction, zero reflection, zero index of refraction, super-lenses). Particle shapes can drastically effect phase behavior and optical properties. For example, clusters with negative magnetic permeabilities may be reached by using plasmonic or dielectric triangular structures assembled onto a spherical core [85]. Furthermore, synthetic methods for clusters comprising more than twelve precisely arranged building units, such as chiral ones, are currently unreported in the literature. Yet, they offer potential to explore various optical applications such as broadband circular polarizers, manipulation of chiral optical forces, chirality switching devices, chiral mirrors, ... etc.

The next generation of functional applications will see clusters immobilized into two- or three-dimensional architectures with highly configurable spacings to create a multitude of superlattices or irregular three-dimensional configurations. Looking even further forward, fabrication of assemblies with controlled disorder are opening novel opportunities to explore unharnessed properties of light/matter interactions. 2D meta-atom assemblies featuring correlated disorder may lead to new optical functionalities that will find use in many applications including optics (for instance, for chirping or compressing ultra-short optical pulses), holography, light emitting devices, optical non linearities. In bulk three-dimensional materials with correlated disorder, the modified light scattering translates into spectral variations of the reflectance and transmittance which may yield structural colors, and also generate wave interference phenomena. These effects are of high interest to the physics community. However, to control experimentally the disorder of self-assembled meta-atoms in 2D or 3D remains particularly challenging. We foresee exciting and ground-breaking opportunities ahead.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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