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Chirality of plasmonic structures and materials

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Chirality refers to a fundamental property of certain structures that lack mirror symmetry. This asymmetry is common in nature at all scales, from galaxies to molecules, and is a property of particular interest in biology and life sciences, because many chiral biomolecules are found to be homochiral, i.e., appear only in one of its possible mirrored configurations or enantiomers. Biological systems thus set expectations for the particular stereochemistry of their constituents, making the study of chirality critically important to understand the building blocks of life. This is manifested in different ways and at different scales, such as in the characterization of the folding of large proteins and its related functionality,[1] or ensuring that we only use the desired enantiomer of chiral drugs, such as ibuprofen.[2] Both these examples highlight the interest and importance of accurately measuring the chirality of microscopic compounds, while the latter also makes clear that we need to either synthesize certain molecules enantioselectively or filter out the undesired enantiomer in racemic mixtures. Interaction of light with molecular media offers opportunities to measure, and in some cases to control,[3] their chirality, by virtue of the differential response of each enantiomer to circularly polarized light with opposite handedness.

Plasmonic materials are crucial tools for studying and controlling chiroptical activity at the nanoscale, extending and complementing research in molecular chiral media. The spectral tunability of plasmonic nanostructures hinges on the constraints over the spatial displacement of their charge, which also dictates the resonant modes they can support.[4] This characteristic makes plasmonic nanostructures ideal for generating robust chiroptical responses through geometry engineering. Plasmonic nanostructures can also create strong optical near fields that amplify the dichroic signals of chiral molecules, enabling precise analysis of chiral asymmetry even at the single-molecule level.[5,6] The field of chiral plasmonics has been rapidly evolving in various aspects, ranging from simulation, synthesis, and fabrication to characterization and practical applications.

This Special Topic issue collects notable contributions to different aspects of the study of chirality by leveraging plasmonic structures and materials at the nanoscale. Some of the selected manuscripts focus on the analysis of fundamental aspects behind chiroptical signals. Chiral planar metamaterials, made of an array of plasmonic chiral nanostructures, are excellent platforms for analyzing the critical connection between the geometry of plasmonic systems and their chiral responses, as demonstrated by several papers highlighted in this Special Topic issue. One paper reports the detailed analysis of the pseudochirality of plasmonic nanoresonators in terms of their rotational symmetry, both as independent units and in square arrays.[7] Another paper numerically studies the collective chiroptical response arising from the coupling of small planar resonators, both chiral and achiral, in terms of varying coupling strength, as modified by resonator handedness and interparticle distance. The authors show that the g-factor of the system can be enhanced by the coupling.[8] On a more general approach, Cheng and Sun present a theoretical study of interacting nanoparticles modeled as non-aligned harmonic oscillators. With it, the authors explore fundamental properties of systems whose chirality arises, not only in absorption and scattering but also in photoluminescence, from the coupling of achiral nanoparticles.[9]

When discussing chirality at the nanoscale, we are dependent on characterization methods that allow us to investigate and quantify the broken symmetry in molecules or nanostructures. Several articles in this Special Topic issue explore this aspect of the field. The readers will encounter a proposal to measure the inhomogeneous near-field around chiral planar nanoresonators by using an AFM-based technique, supported by theoretical modeling and computational simulations of the fields and optical forces responsible for generating the signal.[10] On the other hand, readers interested in the measurement of chirality in molecular samples will encounter a review discussing light–matter coupling in chiral media, as well as different paths to influence and exploit this phenomenon in the optical detection of molecular chirality with high sensitivity based on plasmonic confinement of chiral optical fields.[11] Another study on the topic presents computational work involving the atomistic modeling of chiral molecules, at different levels of description, to obtain detailed spectral responses and the circular dichroism resulting from their interaction with circularly polarized light with and without the enhancement of surface plasmon modes.[12]

Among the many quotes that Feynman left echoing in his wake, "what I cannot create, I do not understand" seems to guide much research effort in the study of chirality, as this is a field in which scientists have developed sophisticated techniques for making a diversity of systems with specific chiroptical properties. One of such approaches exploits molecular chirality as the origin of the asymmetry, as demonstrated by the fabrication of bimetallic Au@Ag structures built from concave Au nanocuboid seeds, in which chirality is introduced in the structure via L-glutathione as the Ag layer is grown.[13] By combining experimental and computational methods, this study shows the enhancement of the UV circular dichroism of glutathione, as well as its induced chiroptical signal in the visible spectrum. Another approach is the use of DNA strands to engineer chiral superstructures out of achiral elements, as shown in a study exploring reconfigurable chiral assemblies of Au nanorods. More specifically, the authors use DNA origami to create complex arrangements of the minimal nanorod dimer that exhibit a chiral response, studying systems with up to four of these dimers in different combinations of their handedness.[14] Another paper in this collection exploits two phases of a liquid crystal, which serves as a substrate for the deposition of Au nanostructures, with the latter developing spiral-like patterns and chiroptical behavior with minimal linear dichroic/birefringent effects.[15] We also highlight work demonstrating enantioselective control over the nucleation and growth of ethylenediamine sulfate crystals in an optical trapping setup, through the helical fluid motion induced by the optical forces created by a laser beam.[16]

Finally, the collection of works in this Special Topic issue also addresses specific applications of chirality, either intrinsic or extrinsic, to develop our capabilities in both the lab and society at large. One such example is the documented creation of photoelectrochemical systems sensitive to the handedness of circularly polarized light, by combining cysteine-grown chiral Au nanostructures with TiO_2 electrodes, so that the photoelectrochemical process can be controlled through the handedness of the incoming circularly polarized light.[17] The readers will also find a proposal, alongside its computational analysis, of a molecular sensor implemented by a multilayer hyperbolic metamaterial with periodic nanocavities in the plane, a system supporting magnetic modes dependent on the handedness of the circularly polarized light inducing them. The chiroptical signal arising from the excitation of these magnetic modes is shown to be very sensitive to local changes in the refractive index of the surrounding medium.[18]

In summary, this Special Topic issue presents some exciting advancements of chiral plasmonics, which have a significant impact on molecular science, photochemistry, physics, and biosensing. Progress in this field is cementing new ways of investigating chiral light–matter interaction at the nanoscale and is providing new avenues for technological development, especially at the intersection of materials science, biology, and medicine. This field is being advanced by a very active scientific community, so novel research developments in the aforementioned areas are expected in the near future. Moreover, the study of the interaction between light carrying spin or orbital angular momentum and plasmons is anticipated to contribute not only to the creation and study of chiral substances but also to significantly impact the field of magneto-optics. This is an area that can be deeply involved in the creation, detection, control, and exploration of new functionalities of chiral materials. Last but not least, chiral plasmonic nanostructures could be used to manipulate quantum states of matter, leading to advancements in areas such as quantum computing, quantum communication, and quantum sensing. As a whole, research in chiral plasmonics has the potential to establish new research directions with implications to the entire field of optical-materials science.

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