Self-assembly of plasmonic chiral superstructures with intense chiroptical activity

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Abstract

Chiral nanostructures are asymmetric nanoarchitectures that cannot be superimposed with their mirrored-symmetric counterparts, which have attracted considerable attention due to their special photophysical properties and potential applications in plasmonics, spectroscopy and nanosensors. In particular, Self-Assembly of chiral nanostructures with symmetric or asymmetric objects might exhibit exceptional optical activity because those chiral superstructures can manipulate chiral states of light that leads to circular dichroism (CD) effect. This review highlights recent advances on the self-assembly of plasmonic chiral superstructures from simpler dimeric, and trimeric chiral nanoassemblies to complicated chiral nanoarchitectures, especially emphasizes the resulted superior optical activity and the corresponding principles.

1. Introduction

Chirality is one of the general features existing in the universe, covering from galaxies [1] and hurricane [2], to trumpet shell [3], and biomolecules such as DNA [4] and proteins [5], which have a preference for one handedness over the other, which exhibits a particular principle of nature. Although the theory of chirality for organic molecules have been well-established, such theory for many typical inorganic nanoparticles, including metal plasmonic nanoparticles (NPs) [6–15], quantum dots (QDs) [16–21], metal nanoclusters [22–32] or carbon nanomaterials [33–35] have been incrementally studied, because those chiral nanoarchitectures can be a bridge between the chirality of building blocks and macroscopic functional entities with promising potentials in applications such as chiral sensing [36–39], or negative index materials [40–42], polarization control [43–45], catalysis [46, 47], chiral electronics, and photonics [48–50].

In general, the chemically synthesized nanocrystals producing equal portions of the possible enantiomers are chiral-random that show no optical activity on the as a whole. The macroscopic asymmetric electron density of the inorganic core of the chiral nanoparticles due to its high polarizability. Wei Ma et al [51] involved in the chiroptical activity of chiral NPs with symmetry breaking geometry and the mechanical strain in crystal lattices, and the researchers found that chiral NPs should be considered as complex chiral systems with several types of chiral geometries presenting at the same time. However, what is the true origin of chirality in NPs still remains challenging, because the chiral arrangements of the stabilizer shell often interacts with each other. Another kind of chiral nanostructures refers to NP assemblies that constructed from two or more individual NPs, whose chiral principle is easier than that of individual NPs. Some chiral nanostructures have been previously reviewed by researchers on synthesis of chiral nanostructure [52, 53], nanoclusters [54, 55], and plasmonic effect in nanoscale metals and semiconductors [36, 57]. This review is followed by preparation of NP assemblies with different chiral geometries. To facilitate reveal the hierarchical chirality when NPs assemblies at smaller, details of the dimeric chiral nanostructures are emphatically discussed section 2. Then, the bigger scale trimeric, tetrameric or more complicated chiral nanoassemblies relevant research will be sequentially summarized in the following sections. By experimentally and theoretically analyzing of these chiral nanoarchitectures with different...
sizes, numbers and arrangements, the principles and applications of assemble-dependent chirality of nanostructures could be systemically investigated.

2. Chiral assemblies

2.1. Dimeric nanoassemblies

It is well known that dimeric nanospheres (NSs) can’t exhibit any chirality because it wouldn’t satisfy the essential principle of chiral structures that objects cannot coincide with its mirror image, which always requires at least four groups or objects to form spatial structures. In contrast, two nanorods can be arranged in different planes to form spatial asymmetrical structures with potential chiral signals. Anisotropic gold nanorods (AuNRs) dimers are the easiest chiral dimeric assemblies benefiting from the boom of DNA origami technology in the past ten years. Although Yan et al. [58] successfully achieved AuNRs dimer nanostructure on the triangular origami in 2011, their potential plasmonic chirality had not been studied until 2013, Lan et al. [59] experimentally observed the chiral optical responses of the discrete dimeric nanoassemblies by designing two batches of capturing strands on the opposite sides of the DNA origami templates which direct the assembly of 3D plasmonic AuNR nanoarchitectures (figure 1(A)). Theoretical calculations (discrete dipole approximation) were also performed to reveal that the pure metallic 3D AuNR dimer nanoarchitectures could generate intrinsic plasmonic characteristics. Another similar work was almost simultaneously finished by Ding’s group [60] who demonstrated that the anisotropic nature of the AuNRs enables the high orientation dependence of the chiral molecule-induced CD, which means the DNA molecule together plays a role in the plasmonic chirality. To obtain a deeper understanding of the plasmonic chirality, Ding’s group [61] further fabricated a series of parallel AuNRs dimers on DNA origami templates, and they found that Plasmonic CD is highly dependent on both the orientation of the dimers relative to the DNA axis and the dipole–dipole distances (figure 1(B)). Chen et al. [62] also reported a strong plasmonic chirality observed in quasi 2D AuNR dimer nanoarchitectures assembled on one side of DNA origami templated as a ‘L’ shape or a linear shape. Those results to prove that the plasmonic CD originates not only from the metallic nanostructures but also from the induction of DNA molecules. Moreover, Wang et al. [63] complemented the comprehensive account of CD effects consistent with another plasmonic phenomena, circular differential scattering (CDS). A simple twisted side-by-side AuNR homo- and hetero-dimer using a citrate linker molecule were used to investigate the CDS and the authors found that CDS exhibits only on one band of a certain sign, which is different from the bisignate response of the corresponding conventional extinction-based CD spectrum. It also accounts for the two major components of the CD spectra of chiroplasmonic systems, the absorption and scattering contributions (figure 1(C)).

For the structures of plasmonic nano-dimers that have been widely investigated and are easily assembled from DNA templates, researchers gradually exploit its promising applications in photonics and sensing. Huang et al. [64] developed a nanoscale biosensing device combining the accuracy and precision of the DNA origami nanofabrication technique, chiral plasmonic assemblies, and high affinity and selectivity of aptamer, which enables selective and sensitive detection of targets even in strongly absorbing fluids (figure 1(D)). Very recently, Dong et al. [65] reported another interesting application of chiral plasmonic assemblies, in which DNA-based AuNRs dimeric nanostructures were designed as plasmonic logic gates that return chiroptical signals as outputs by inputs of DNA strands. A complete set of Boolean logical operations (AND, OR, NAND, NOR, XOR and XNOR) could then be performed with such programmable plasmonic logic gates. This work significantly uncovers the potential applications of plasmonic nanoassemblies on more complex tasks giving these unique characteristics.

2.2. Trimeric nanoassemblies

Similar as the dimeric structures, three isotropic nanosphere based nanoassembly in planar configurations cannot show any chiral effects. So anisotropic nanorods still play a vital role in trimeric nanostructures showing chiral effects. Generally, one AuNR plus two AuNSs triplet structures are liable to be controlled and assembled. However, this kind of spatial conformations haven’t been systemically studied because such structures include two possible configurations, the coplanar ones and the non-planar ones. Obviously, three objects placed on one plane is still planar structure, which exhibits no chiroptical activity. The other case is that the two AuNSs stereoscopically cover above the AuNR, which approximatively equal to the crossover or the parallel structures of AuNRs dimer broadly investigated before.

However, tri-AuNRs assemblies haven’t been studied systemically which may be suitable to explain the more complicated chiral assemblies. Early in 2015, Shen et al. [66] successfully fabricated a series of chiral AuNR trimers under the guidance of DNA origami, and those assembled trimeric structures were tuned by modifying the AuNR size, number, and location. The result indicates that mesomeric trimer with symmetric structure is supposed to exhibit no chiral signals, generating an expected weaker CD signal because of slight curvature of
Strikingly, asymmetric multi-component trimer even displays a lower CD signal compared to their daughter dimer components. The authors explain that this asymmetric trimer can be separated into left-handed dimer and right-handed dimer with different CD intensity, which offset the CD signal by the reversed structures. In order to understand the origin of the plasmonic chirality of AuNR trimers, Chen et al. [67] elaborately designed and fabricated three groups of AuNR trimers and their nine daughter AuNR dimers. Researchers corroborated by CD spectroscopy that the plasmonic chirality of asymmetrical AuNR trimers is essentially the summation of the chiroptical response of all its daughter AuNR dimers, regardless of the handedness and amplitude of the CD signal, which experimentally reveals the predictable nature of the chiroptical activity of geometrically complex metallic nanostructures (figure 2(B)).
2.3. Tetrameric nanoassemblies

Inspired from organic chemistry that chiral carbon atoms are covalently bonded to four different functional groups exhibiting chiroptical activity, tetrahedral nanoassembly, one of the configurations most easily associated with conventional chiral features, is artificial plasmonic chiral nanostructures composed of the minimum number of objects required for three-dimensional chirality. Since the invention of gold nanocrystal engineering with DNA by Mirkin \[68\] and Alivisatos \[69\] in 1996, DNA-functionalized nanoreagents have served as an essential tool in the field of detection and controllable preparation of nanoassemblies. This technique enables 3D plasmonic chiral models translated from chemistry to nanophotonics. More than a decade ago, Kotov group \[70\] utilized Polymerase chain reaction (PCR) method to generate a linear DNA dependence of AuNSs dimers, trimers, tetramers, leading to a circular dichroism band of the superstructures coincides with the plasmon oscillations from the three-dimensional positioning of Au colloids (figure 3(A)). Alivisatos group

![Figure 2. Trimeric nanoassemblies and chiral principle. (A) Circular dichroism spectra and anisotropy factors of the AuNR dimers and trimers, reproduced from [66] after permission; (B) The plasmonic chirality of trimer nanostructures origin from the superposition of their daughter AuNR dimers, reproduced from [67] after permission.](image)
constructed discrete pyramids of DNA scaffolds with gold nanocrystals at the tips and confirmed that
tetrameric structures are more rigid in solution than linear DNA, which improved assembly efficiency and
facilitate to the organization of chiral nanostructures (figure 3(B)). Besides those experimentally achieved
nanoassemblies, this group also systematically explored the effects of symmetry breaking on the chiroptical
response of an assembly of plasmonic nanoparticles using simulation so as to design a chiral pyramid using a
mixture of different nanoparticles. Supported from theoretical calculation and accumulation of previous work,
Kotov group further optimized this strategy to successfully prepare a variety of high yield hetero-particle
pyramids comprised of different kinds of metal and/or semiconductor building blocks including small AuNPs
(10 nm, Au1), medium AuNPs (15 nm, Au2), large AuNPs (25 nm, Au3), CdSe@ZnS quantum dots (5 nm,
QDs), and silver NPs (10 nm, Ag). They observed the R- and S-enantiomers of chiral pyramids have opposite
directions of polarization rotation, and the inclusion of QDs to the pyramid produces an additional weaker peak
corresponding to the chiroptical activity of the bandgap transition of QDs that was quite difficult to obtain
before (figure 3(C)).

After 2006, by means of DNA origami technology, the design of DNA sequences has been greatly simplified
and the yield of tetrameric nanoassemblies has been extremely improved due to the stable and rigid DNA frame.
Shen et al utilized this structural DNA technology to precisely organize four nominally identical gold
nanoparticles into a three-dimensional asymmetric tetramer. Supported by theoretical calculations, the authors
also confirmed that both chiral structural symmetry and plasmonic resonant coupling are essential ingredients
for attaining strong chiroptical activity in artificial plasmonic chiral molecules. Dai et al [73] expanded the AuNSs tetrahedron nanoarchitectures by modifying the structural parameters including the AuNS size and the interparticle distance. The latter has potential application as a chiral plasmonic ruler, where shifting the distance between of AuNPs in tetrahedron nanoarchitectures at nanometer scale leads to strong perturbation in plasmonic CD (figure 3(D)). In addition to chiral nanoarchitectures composed of pure nanospheres, anisotropic AuNRs have also been used as building blocks of tetrahedron assemblies. An interesting propeller-Like nanorod-upconversion nanoparticle assemblies [74] was designed and fabricated by adopting the DNA-driven self-assembly strategy (figure 3(E)). These propeller-like nanoscale tetramers not only possess strong and tailorable chiral activity in the visible region and enhance upconversion luminescence with a 21.3-fold by tuning the distance between the UCNP and NRs, but also enable attomolar DNA detection with two-model capabilities, showing potential application in efficient bioimaging and light-guided therapy in vitro and in vivo.

2.4. Helix nanoassemblies
Since the discovery of the DNA double helix, helices and chirality have been closely related. Many organic molecule, polymers or biomolecule exhibit chiral features due to their intrinsic helical arrangement of atoms or groups. Motivated from those natural helical structures with strong optical activity, perfect artificial NP's helices have been finely designed and successfully constructed by virtue of self-assembly technology. Sharma et al [76] used self-association of multi-helix DNA bundle structures and closing up of 2D DNA tile lattices to construct helical geometries of gold nanoparticles, forming tubes that display patterns of AuNPs from stacked rings, single spirals, double spirals, to nested spirals. As described above, DNA origami also extremely simplify the DNA design rules and thus there is no need for stoichiometric mixture of sequences. Shen et al [77] demonstrated a construction of helical geometry of plasmonic nanostructures through rolling up two AuNSs linear chains on a 2D rectangular DNA origami sheet with well-defined positions and spacing that achieves CD effect in the visible range (figure 4(A)). Tim Liedl group directly [7] enables the high-yield production of plasmonic structures that contain AuNSs arranged in helices by 3D DNA origami tube. The consistence of the experimental spectra with classical electrodynamics model confirmed that the circular dichroism and optical rotatory dispersion effects originate from the collective plasmon–plasmon interactions of the AuNSs being rationally designed and tunable in handedness, colour and intensity. In another case, researchers from the same group [78] showed that the optical responses of two distinct circular dichroism spectra of plasmonic helix can be reversibly switched by perpendicular or parallel helix orientation with respect to the light beam, in good agreement with predictions based on dipole approximation theory.

All of those cases above only show the AuNSs spiral along a single origami template, which limits their potential applications such as chiral sensing using chemically based assembly systems. Maximilian et al [79] provided a new scheme to create Plasmonic Toroidal Metamolecules consisting of four identical origami-templated helical building blocks, showing a stronger chiroptical response than their daughter plasmonic chiral building blocks such as helical monomers and dimers and the CD intensity depends on the structure density, which offers a new pathway to create plasmonic platforms with tunable CD for development of polarization conversion devices(figure 4(B)).

Besides DNA nanotechnology, other supramolecular such as peptide and nanofiber assembled into chiral architectures are attractive molecular building blocks that can contribute to the direct arrangement of chiral helices. Merg et al [80] reported the peptide (C18-(PEPAuM-ox)2) directed assembly of unique gold nanoparticle single helices that exhibit exceptionally strong plasmonic chiroptical activity (figure 4(C)). The authors also presented a molecular assembly model based on several characterization techniques to understand how peptide conjugate molecules constructed from inorganic-binding peptides can self-assemble nanoparticles into single-helical nanoarchitecture. Jung et al [81] reported a customizable strategy making use of modular gelator components for controlled growth of well-defined helical gold nanoparticles with tunable diameters ranging from 2 nm up to 200 nm along the nanofiber by UV reduction of Au(I) ions on the supramolecular templates, offering high yield, ‘bottom-up’ assembly to allow rapid advancement of customizable chiroptical properties (figure 4(D)).

Unlike isotropic spherical nanoparticles, rod-shaped nanoparticles are very difficult to precisely direction-controlled self-assemble due to their anisotropy. With the aid of DNA nanotechnology, dimeric and trimeric AuNR nanoassemblies have been successfully located on single layer DNA origami aforementioned before, however, this classic rectangular origami with intrinsic twist are not able to hold anisotropic nanomaterials into well-defined three-dimensional superstructures. To improve the stabilization of single layer DNA origami, Lan et al [82] created a double layer DNA origami with much less structural distortion to successfully construct anisotropic AuNR helical superstructures with tailored chirality in a programmable manner. By tuning the molar ratio of AuNR/origami from 2.5 to 1.7 and 1.1, the average number of AuNR in the helices increased from 2 to 4 and 9 respectively, and the CD intensity is according to the number of AuNR in the assembly system.
Soon, the authors presented another work with a versatile DNA surface adapter that programmably self-assemble novel stair-like and coil-like AuNRs chiral metastructures, and they found that distinct optical chirality is strongly affected by the spatial arrangement of neighboring nanorod pair. Based on this approach, a reconfigurable chiral nanoparticle helical superstructure with fully switchable chirality was also achieved following the dynamical control of the underlying DNA template, where the chiral AuNRs helix was controllably reconfigured between a tightly folded state and an extended state of the same handedness, or between two mirror-image-like structures of opposite handedness.

3. Conclusion

In the past few years, nanomaterials with different sizes, dimensions, chemical components, morphologies, and functions can be designed and synthesized as required. A series of fundamental results have been obtained, and some preliminary attempts have been made in practical applications. Nanoassemblies with more flexibility and
programmability have greater potential around functional nanomaterial, nano characterization, nanosensor and nanomanufacture, nanocalytical, and nano biological, to strengthen the research direction of the advantage and leading role to support and solve several major general and fundamental problems in nanomaterials. In this review, we can witness the fast-growing development of a series of plasmonic chiral superstructures from simpler dimer to, trimer, tetramer and sophisticated helical nanoassemblies over the past few years. Many systematic experimental and theoretical studies for the understanding of the properties and behaviors of these new chiral nanostructures were broadly carried out in above articles. It is interesting to note that most reports of the chiral arrangements rely on DNA technology, especially DNA origami flexibly used to tune the species, size, distance of nanostructures and even directly to switch conformation into enantiomers, which opens up new approaches in the assembly of chiral nanomaterials.  

To date, gold nanoparticle is still the best candidate used in the chiral nanostructure since it is easy to covalently modify with thiol group. Simpler AuNRs dimer have been successfully applied in logic gate, while other multiple-particles based nanoarchitectures could be potentially developed as chiral fluids for future sensing or negative index materials because of their larger plasmonic chirality. However, other nanoparticles are not stable as AuNPs and harder to modify with DNA strands or linked with proteins, so they are seldom used as components for assembling chiral arrangements with high yield and high stabilization, which largely limit their applications in the current cutting-edge fields, such as biological medicine and nano-fabrication. It is expected that DNA origami, peptide or other polymers could be extensively used for the preparation of chiral semiconductive NPs and potentially other luminescent chiral materials. Once successfully arranging a variety of luminescent QDs materials with high efficiency, it will extend the chiral nanostructures not only in CD spectrum analysis where electrons are the in ground state, but also provides the opportunity for studying excited states chiral effects by circular polarized light emission spectrum, which might have greater potential applications in various optical devices, components of chiroptical detectors, polarimeters, even in 3D displays.

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Conflict of interest

The authors declare no conflict of interest.

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