Self-assembled plasmonic nanostructures

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Self-assembly of plasmonic nanoparticles offers a labour- and cost-efficient strategy for the expansion of the library of plasmonic nanostructures with highly tunable, coupled optical properties. This review covers recent advances in solution-based self-assembly of plasmonic nanoparticles, modelling of the self-assembly process and of the optical properties of the resulting nanostructures, and potential applications of self-assembled plasmonic nanostructures.

Introduction

Metal nanoparticles (NPs) such as gold, silver, or copper can interact with light due to their ability to support surface plasmons.¹ Plasmons are defined as electromagnetic excitations coupled to the free charges of a conductive medium.² In the case of metal NPs, this excitation and associated electromagnetic field are called a localized surface plasmon. Due to confinement in nanoscale, electrons in metal NPs oscillate under external electromagnetic fields, provided the resonance condition between the plasmon and the light is met. The resonant frequency of the

localized surface plasmon is determined by the size of metal NPs, their shape, composition, and local dielectric environment. Nanoplasmonics utilizes this ability of metal nanostructures to interact strongly with light of wavelength significantly exceeding their dimensions. The field of nanoplasmonics is rapidly and successfully developing toward fundamental research and in its numerous applications, such as Surface Enhanced Raman Spectroscopy (SERS),³ plasmon-enhanced fluorescence,⁴ amplification of non-linear optical signals,⁵ nanoscale lasing,⁶ plasmon-assisted photolithography,⁷ light harvesting,⁸ photocatalysis,⁹ and chemical and biological sensing.¹⁰

The field of nanoplasmonics has greatly benefited from advances in colloid chemistry, that is, the synthesis of plasmonic NPs and their deliberate surface characterization. To date, the synthesis of metal NPs has reached the state of art. Numerous synthetic procedures are currently available for the synthesis of NPs with a variety of sizes, shapes and surface chemistries.¹¹ In addition to spheroidal^{12–14} and rod-shaped^{15–18} metal NPs, the

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synthesis has been extended to nanoshells,¹⁹ arrow-headed nanorods (NRs),²⁰ dumbbells,²¹ rice-like NPs,²² triangles,²³ cubes,^{24,25} octahedra,²⁶ cones,²⁷ bipyramids,^{28,29} stars,³⁰ and prisms,³¹ to name just the most representative structures. Comprehensive studies have been performed to establish the relationship between the optical properties of metal NPs and their dimensions, surface chemistry and shapes. For example, it has been shown that for NPs larger than 20 nm, the plasmon absorption red-shifts when NP size increases, due to the inhomogeneous polarization of the NP, thereby leading to excitation of higher order modes.³² Shape also affects plasmonic properties, *e.g.*, anisotropic metal NPs such as NRs display two plasmon resonances and electric field enhancement at the NR tips, in comparison with the single resonance and isotropic electric field surrounding spherical NPs.³³

The organization of plasmonic NPs in small clusters or in lattices comprising thousands of NPs offers another degree of freedom in controlling and tuning their optical properties by coupling surface plasmons of adjacent NPs and enhancing the electric field in interparticle gaps (in the so-called “hot spots”). The enhancement of electric field strongly influences the chemical and optical properties of molecules or other NPs, *e.g.*, quantum dots, placed in the hot spots. Control over plasmonic properties of self-assembled nanostructures can be achieved by changing the number of NPs in the cluster, by varying the directionality of NP organization, and by fine-tuning interparticle distance, in addition to changing the composition, size and shape of individual NPs. Studies of interactions between NPs organized in clusters are of great fundamental and practical importance, as they address the question “*What structural characteristics of NP ensembles yield new and potentially useful plasmonic properties?*”

To address this question, studies of the optical properties of NP ensembles have been performed for clusters fabricated by Electron Beam Lithography, however, this time- and labour-consuming process has a limited resolution of ~10 nm and

Fig. 1 Number of articles published in the Scopus database on nanoparticle assemblies (blue) and plasmonic particles (red).

may lead to the formation of NPs with a rough surface and multiple crystalline domains. Solution-based self-assembly of plasmonic NPs offers the ability to reduce interparticle distance to 1–2 nm with a precision of 0.5 nm. Furthermore, self-assembly enables the fabrication of NP ensembles with a high complexity and can produce nanostructures with hierarchical architectures, which is challenging or not possible for conventional top-bottom technologies. The organization of NPs in plasmonic nanostructures with well-defined geometries (in contrast to massive, uncontrollable NP aggregation) can be achieved in several ways, namely, by carefully tuning nanoscale forces acting between NPs in solution, by using various types of templates and by applying external fields, *e.g.*, a shear field or electric field. The number of publications on plasmonic NPs and NP self-assembly is constantly increasing (Fig. 1), and it may be expected that this trend will continue in the future.³⁴

In the present article, we review recent progress in the self-assembly of plasmonic nanostructures, their established or predicted optical properties, and potential or demonstrated applications of self-assembled nanostructures. This review is based on the reports published in the past six years. It is limited to structures formed in solution. The formation of plasmonic structures in polymer block copolymer hosts is not included.

The review has the following structure. After the brief introduction, in the following section we discuss experimental advances in the self-assembly of plasmonic nanostructures, including direct interactions between NPs, and assisted NP assembly using external fields and templates. The next section describes modelling of the self-assembly process, which is followed with a discussion of plasmonic coupling in ensembles of metal NPs and plasmon–exciton coupling in hybrid metal–semiconductor nanostructures. The review is concluded with a survey of currently demonstrated applications of self-assembled plasmonic nanostructures and an Outlook summarizing future directions of research in the field of self-assembled plasmonic nanostructures.

Self-assembly of plasmonic nanoparticles

Self-assembled plasmonic nanostructures can be grouped in many different ways, namely, based on the shapes of individual NPs or NP ensembles, the methods used for their assembly, the

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type of ligands capping NP surface (*e.g.*, low- and high molecular weight molecules, or ligand mixtures), the nature of nanoscale forces leading to NP self-assembly and based on the dynamic or static nature of NP assemblies. Below we review progress in the formation of plasmonic nanostructures based on the type of the system in which NP self-assembly takes place, namely, direct (non-assisted) NP assembly in solution and assisted NP assembly supported by external fields and template surfaces. For the first category, we reviewed the types of nanoscale forces controlling NP organization. We note that although a particular force may dominate the self-assembly process, in reality, the formation of a particular structure originates from the interplay of several forces. Thus, although in Sections 2.1–2.4 we discuss the examples of NP ensembles according to the major driving force, a balance of attractive and repulsive interactions generally influences the resulting assembly.³⁵

Direct interactions of nanoparticles in solutions

Hydrophobic/poor solvency forces

Attractive interparticle forces acting in poor solvents (solvophobic forces) are typically used for the self-assembly of metal NPs capped with polymer ligands, which contain at least, one functional group strongly binding to the NP.

Polymers are generally attached to the NP surface in the post-synthesis ligand exchange procedure by replacing a low-molecular weight ligand,³⁶ although examples of NP synthesis in the presence of macromolecular ligands have been reported.^{37,38} Prior to self-assembly, NPs are dispersed in a liquid serving as a good solvent for the polymer ligand. Addition of a non-solvent,³⁹ change in temperature⁴⁰ or addition of a salt⁴¹ makes the solvent poor for the polymer. NPs form clusters to minimize the surface energy of the system by screening the unfavourable interactions between the polymer ligands and the solvent *via* NP association.⁴²

This strategy has been used for plasmonic close-to-spherical NPs and NRs, which were stabilized with polystyrene,^{42–44} polyvinyl carbazole⁴⁵ and poly(*N*-isopropyl acrylamide).⁴⁰ Regiospecific attachment of associating polymer ligands to the surface of gold NRs enabled control of directionality of the resulting nanostructures by governing NR assembly in chains⁴⁶ and two-dimensional lattices.⁴⁵ Other structures such as vesicles,⁴⁷ rafts,⁴⁸ dimers of dumbbell NPs,⁴⁹ and networks⁴⁸ were self-assembled.

In the case of gold dumbbell-shaped NPs coated with polystyrene ligands hydrophobic forces led to the formation of dimers in a side-by-side manner and higher order clusters.⁴⁹ When encapsulating the dimers with poly(styrene-*b*-acrylic acid) an interesting temperature-dependent effect was observed: the stress induced within the block copolymer micelle led to a transition between the side-by-side configuration of dumbbells to a cross-like one. Fig. 2a shows a transmission electron microscopy image of the dumbbell dimers in a cross-like configuration with the poly(styrene-*b*-acrylic acid) shell surrounding the cross-like structure.

In addition to homopolymer ligands, copolymers such as poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO)⁵⁰ and poly(styrene-*s*-isoprene)⁵¹

have been utilized to govern NP self-assembly, to stabilize them in water⁵² and to crosslink nanostructures permanently.^{51,53} Similar to NPs stabilized with homopolymer ligands, the self-assembly was triggered by reducing the quality of solvent for one of the components of the copolymer. Exemplary plasmonic nanostructures included clusters and vesicles formed by gold NPs coated with PS-*b*-PEO in tetrahydrofuran–water mixture, or by rehydration of dried films of gold NPs functionalized with PS-*b*-PEO.⁴⁷ With increasing molecular weight of the water-insoluble PS block, the effect of the quality of the solvent became stronger, leading to the formation of NP clusters with a larger aggregation number.

Using mixtures of polymer ligands, *e.g.*, poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) confers the chemical nature of both ligands to the surface of the metal NP without the need to synthesize multi-block polymer ligands.⁵⁴ To functionalize the surface with hydrophobic and hydrophilic polymers, a mixture of preformed thiol-terminated PEO molecules and thiol-terminated atom transfer radical polymerization initiators were grafted to the NP surface, and the polymerization of PMMA was initiated from the surface. The resultant NPs capped with PEG and PMMA formed NP dimers⁵⁵ and vesicles⁵⁶ upon addition of non-solvent.

Electrostatically mediated nanoparticle self-assembly

Self-assembly of plasmonic NPs can also be induced by suppressing their electrostatic stabilization, thereby making attraction forces, *e.g.*, van der Waals or solvophobic forces, dominant. The electrostatic repulsion between NPs can be reduced by changing pH of the system and in this manner, reducing ligand ionization, as has been shown for citrate⁵⁷ or poly([2-(dimethylamino)ethyl] methacrylate)⁵⁸ ligands, by suppressing the double electric layer of the NPs with addition of electrolytes,⁵⁹ or by changing the temperature, as the magnitude of the electrostatic repulsion varies linearly with temperature.⁶⁰ For example, for gold NPs functionalized with poly([2-(dimethylamino)ethyl] methacrylate) ligands,⁶¹ a decrease in pH was used to protonate the polymer and decrease the NP charge. Adjusting the pH of the system allowed for control of the aggregation number of the NP assemblies (Fig. 2b).

Competition of electrostatic repulsion with attraction forces has a profound effect on NP assembly in various types of nanostructures. For example, it is well-established that shape-isotropic spherical gold NPs can form chains, due to the anisotropic electrostatic repulsion.^{57,62} On the other hand, spherical gold NPs stabilized with polystyrene ligands assemble in spherical clusters (globules) in a solvent poor for polystyrene,⁴² while DNA-capped gold NPs form 3D lattices.^{63,64}

Recently, it has been shown how the competition between solvophobic attraction forces and electrostatic repulsion forces leads to transitions between chain-like and globular structures of charged polystyrene-coated gold NPs.⁶⁵ All factors that reduced electrostatic repulsion between NPs, that is, low dielectric constant of the medium, increase in salt concentration or the use of high-molecular weight polystyrene ligands, favoured NP assembly in spherical clusters, while well-defined NP chains formed, when interparticle electrostatic interactions

Fig. 2 Self-assembly of plasmonic nanostructures. (a) Cross-like dimers of gold dumbbells associating due to interactions of PS ligands in a poor solvent. The cross-like structure is induced by internal stress of poly(styrene-*b*-acrylic acid) shell engulfing the dimer. Reproduced from ref. 49 with permission from ACS. (b) Chains of poly((2-(dimethylamino)ethyl) methacrylate)-capped gold NPs, which are formed in response to the change in pH of the solution. pH = 3 yields short chains, whereas pH = 2.5 yields long ones. Reproduced from ref. 58 with permission from Wiley. (c) Chain of gold NPs formed due to hydrogen-bonding of 2-mercaptoethanol ligands. Reproduced from ref. 71 with permission from ACS. (d) Side-by-side self-assembly of gold NRs functionalized with single-stranded DNA molecules. Spacing between NRs increases with increasing spacer length. Reproduced from ref. 86 with permission from ACS. (e) Wells patterned in silicon filled with silver nanocubes, octahedra and etched octahedra. Reproduced from ref. 92 with permission from PNAS. (f) Discrete chiral assemblies of gold NPs assembled on DNA bundles. Scale bar is 100 nm. Reproduced from ref. 97 with permission from Nature publishing group.

were enhanced. Thus, a judicious choice of self-assembly parameters can lead to a variety of structures from the same building block.

Hydrogen bonding and metal chelating

Assembly of metal NPs driven by hydrogen bonding and metal chelation between ligands capping the surface of metal NPs largely resembles approaches used in supramolecular chemistry.⁶⁵ Hydrogen bonding has been used to govern pH-dependent self-assembly of silver and gold NRs^{66,67} and close-to-spherical NPs.^{68,69} For example, self-assembly of gold NRs was mediated by the hydrogen-bonding between mercaptoundecanoic acid (MUA) ligands.⁷⁰ Increase in pH suppressed hydrogen-bonding by deprotonating the acid, making it incapable of forming hydrogen bonds, while subsequent reduction of pH favored NP self-assembly.

Chains of silver NPs capped with cyclodextrin were assembled using hydrogen-bonding between hydroxyl groups of cyclodextrin.⁶⁸ As the silver NPs had a diameter of 5–6 nm, the surface could only be functionalized with a few cyclodextrin molecules. This led to a geometric preference for the assembly of NP chains: the formation of 2-D and 3-D structures was discouraged due to steric repulsion and the geometric position of the few remaining available cyclodextrin ligands.

In another study, formation of chains of gold NPs occurred by hydrogen bonding between surface-bound 2-mercaptoethanol ligands.⁷¹ The choice of solvent was crucial in the formation of NP chains due to the ability of some solvents to hydrogen-bond with the ligands. Chains of NPs assembled in dimethylformamide participating in hydrogen-bonding with the ligands, whereas 2D NP aggregates formed in dimethylsulfoxide, which had significantly weaker H-bond acceptor abilities. The resultant NP chains were used to produce nanofibers of gold after reduction of 1D assemblies of gold NPs with NaBH₄ (Fig. 2c).

Chelation of NP ligands to ions in solution can be used as a driving force for the generation of reversible nanostructures with interesting geometries. Gold and silver NPs functionalized with ligands containing carboxylic or amino groups have been used to coordinate with Hg²⁺ (ref. 72), Cd²⁺ (ref. 73), and Pb²⁺ (ref. 74) ions. Directional, 1D self-assembly was achieved for gold NRs end-functionalized with thiol-terminated terpyridine groups, which coordinated to Fe²⁺ ions.⁷⁵ Linear assembly was also achieved at short self-assembly times for gold NPs bearing peptide ligands binding to Hg²⁺ (ref. 72), while at longer time intervals chain networks and 2D clusters were formed. To disassemble NP clusters, 2,2',2'',2'''-(ethane-1,2-diyl)dinitrilo)tetraacetic acid was introduced into the solution, to preferentially bind

to Hg^{2+} ions and replace gold NP ligands. Superlattice sheets were assembled from palladium NPs capped with rigid tetradentate ligands comprised of four terpyridine groups attached to a central carbon.⁷⁶ Upon addition of Fe^{2+} ions, the interparticle spacing in the sheets increased, because the tetrakis(terpyridine) ligands preferentially bound to the Fe^{2+} ions.

Bio-specific interactions

Functionalization of metal NPs with biological molecules confers their unique hybridization-based possibilities. One example is specific hydrogen bonding between biotin and streptavidin ligands.⁷⁷ Another rapidly developing strategy is the self-assembly of metal NPs stabilized with DNA ligands.^{78,79} The enthalpic gain due to hybridization DNA strands and the ability to synthesize complementary DNA strands with a precisely controlled molecular structure provide a pathway for “programming” the resultant plasmonic nanostructure. Self-assembly driven by DNA hybridisation was used to organize plasmonic NPs into chains,⁸⁰ 3D lattices,⁶³ triangles⁸¹ and Janus nanoclusters.⁸² In some reports, DNA-mediated assembly allowed for switching between self-assembled NP configurations.^{83,84} For example, switching between 3D NP superlattices with different lattice constants was achieved using the addition of simple DNA strands as a trigger.⁸⁵

An unusual mode of self-assembly was observed for gold NRs capped with long, flexible DNA molecules. The NRs underwent side-by-side assembly in 1D ladder-like chains, when complementary DNA strands either directly hybridized, or hybridized to each other *via* a linker⁸⁶ (Fig. 2d). This symmetry-breaking mode of NR self-assembly was attributed to many-body effects, in which the binding free energy of the system decreased with increasing number of hybridized DNA chains. Attractive side-by-side attachment of the NRs led to the minimization of the total DNA binding energy, which included DNA hybridization free energy, the elastic penalty for chain stretching, and excluded volume interactions.

One of the routes to harnessing the functionality of biological macromolecules includes mixing of plasmonic NPs capped with ligands containing a quaternary amine end group with other NPs (such as iron oxide) encapsulated with biological molecules containing nanoscale cavities called “protein cages”. Protein cages offer an effective method to induce directional interactions between plasmonic NPs, due to the presence of electrostatic and hydrophobic domains in protein molecules, which are located at regular intervals on the outside of the cage. For example, spherical superlattices formed from electrostatically directed assembly of gold NPs around iron oxide NPs encapsulated in a ferritin cage.⁸⁷ Mixing NPs with larger and more complex protein molecules such as *cowpea chlorotic mottle* virus yielded an AB_8^{fcc} superlattice, a previously unobserved structure for NPs.

Assisted self-assembly of metal nanoparticles

Assisted self-assembly of plasmonic NPs takes place under the action of magnetic, electric and shear fields or with the use of templates⁸⁵ (patterned surfaces or template objects dispersed in a liquid medium).

Magnetic fields have been used to assemble cobalt,⁸⁸ nickel⁸⁹ and core-shell iron oxide-gold NPs.⁹⁰ The use of applied fields has a limited applicability in NP self-assembly, because control over the resultant structure often decays once the field is removed.⁹¹ A recent attempt to circumvent this shortcoming involved the use of “locking” ligands:⁹¹ after iron oxide NPs functionalized with poly(2-vinylpyridine-*b*-ethylene oxide) (P2VP-*b*-PEO) formed a cluster under a magnetic field at pH 4, the P2VP blocks “locked” the structure, due to hydrophobic interactions. As a result, the nanostructure did not disassemble upon removal of the field. The disassembly was achieved at pH = 2, which ionized the P2VP block, leading to repulsion between the NPs. Although this study focused on non-plasmonic NPs it is conceivable to extend it for heterostructures containing both plasmonic and magnetic components.

In addition to the use of external fields, templates may be used to direct NP self-assembly into desired configurations. For fundamental studies of plasmonic nanostructures this method may be especially beneficial, as the distance and the angle between adjacent NPs strongly affect collective plasmonic properties, yet patterning NP ensembles by nanofabrication techniques offers a limited control over small interparticle spacing.⁹² To achieve well-defined assemblies, pits of discrete sizes were patterned into silicon wafers.⁹³ Evaporative self-assembly brought gold NPs into these wells and yielded oligomer structures for their further studies using spectroscopy techniques.⁹⁴ Fig. 2e shows a scanning electron micrograph of silver polyhedra (cubes, octahedra, and “etched octahedra”) assembled into wells of various shape and size.

The ability to synthesize DNA molecules that undergo folding and assembly into diverse and predictable shapes, known as DNA origami,⁹⁵ is an important innovation whereby structures with a 6 nm spatial resolution may be formed.⁹⁶ To produce a structure with the DNA origami method, a long single-stranded DNA scaffold is synthesized and made to assemble into a desired shape by mixing with short oligonucleotide “staple strands” which bind to specific sites on the scaffold and help it fold. Using this technique, discrete chiral assemblies of gold NPs were formed by hybridizing DNA ligands to a pre-formed DNA scaffold.⁹⁷ Fig. 2f shows a schematic and a transmission electron microscopy image of the chiral assemblies of gold NPs functionalized with single-stranded DNA, which were tethered to single-stranded oligonucleotides placed at discrete intervals along the DNA-bundle scaffold. In another work, the precise control of oligonucleotide placement afforded by the DNA origami method enabled the design of a template with a docking site for a single molecule of a fluorescent dye positioned between two 100 nm-diameter gold NPs.⁹⁸ This well-defined structure provided insight on the effect of plasmonic NPs on the fluorescence of organic dyes. Thus, the ability to organize both NPs and molecules makes DNA an extremely powerful templating entity.

Control of the aggregation number of self-assembled nanostructures

For many applications, the aggregation number of the self-assembled structures of plasmonic NPs has to be controlled.

While for linear self-assembled NP clusters, the average aggregation number can be predicted for a particular self-assembly time, based on the theory of step-growth polymerization,⁴⁴ a number of methods have been developed to quench NP self-assembly on demand. These methods include the encapsulation of the self-assembled structure at a particular stage of self-assembly,⁹⁹ deactivation of the associative ligands⁵¹ and addition of competing ligands.¹⁰⁰

Self-assembled plasmonic nanostructures have been encapsulated within silica,¹⁰¹ block copolymer⁹⁹ and lipid¹⁰² shells after a certain self-assembly time, which suppressed attractive interactions between associating ligands. In addition to quenching NP self-assembly, encapsulation reduced the occurrence of artefacts in imaging and provided stability of the self-assembled structure in water. In particular, encapsulation of NP ensembles within poly(styrene-*b*-acrylic acid) copolymer conducted under mild heating and subsequent slow cooling has become a versatile method.¹⁰³ This process yielded assemblies with controllable average aggregation numbers, which were stable in water for several months and withstood multiple centrifugation cycles.

Another method to arrest the self-assembly of metal NPs and in this manner, control the aggregation number of the NP cluster involves the use of cross-linkable ligands. Photocrosslinking of poly(styrene-*s*-isoprene) ligands after a particular self-assembly time has completely quenched NR self-assembly in linear chains.⁵¹ This effect was attributed to the inability of photocrosslinked polymer ligands to interdigitate and form physical bonds. In addition, photocrosslinking of ligands led to the reduction of interparticle spacings (preferred for enhancement of plasmonic coupling) and increased NR co-linearity in the chains.

Modelling the self-assembly process

Modelling NP self-assembly is beneficial for accounting for multi-body NP interactions, and for systematic exploration of multiple experimental variables, *e.g.*, NP size, ligand type, ligand length and solvent characteristics. Using simulations, NP–NP interactions, ligand–ligand interactions, ligand–solvent and ligand–NP interactions can be accounted for in different combinations, with some simplifications depending on the computational resources available. Molecular dynamics (MD) simulations, density field theory, and Monte Carlo (MC) simulations have been used to predict self-assembly of NPs functionalized with low- and high-molecular weight ligands, including DNA-coated NPs,¹⁰⁴ and patchy NPs.¹⁰⁵ Below, we review important examples of simulations of self-assembly of metal NPs in solution.

Formation of small clusters was modelled by determining NP–NP interaction potential for two gold NPs functionalized with alkanethiol ligands.¹⁰⁶ In a model developed for two NPs, the authors considered van der Waals forces originating from the NP cores, the free energy of mixing of the alkanethiol ligands, and the elasticity of the ligand chains. By using the free energy of mixing, ligand interactions were accounted for without the use of excessive computational resources. The depth of the interaction potential well was also determined for alkanethiol ligands of different length. Greater stabilization

of clusters with shorter ligands was obtained, which was consistent with experimental results.¹⁰⁷ Using the computed interaction potentials, simulations of the kinetics of self-assembly and the critical NP volume fraction for the transition from individual NPs to the NP cluster were determined.

Molecular modelling may also be utilized to systematically compute the free energy of self-assembly of NPs with different surface chemistry. Using this method, useful predictions were made for gold NPs stabilized with alkanethiol ligands of different lengths and varying grafting density, which underwent self-assembly in different solvents under a range of temperatures.¹⁰⁸ The free energy was calculated both by MC and MD simulations, in which the solvent and the atoms along the alkanethiol chain were represented as beads with bond stretching, torsion and rotation accounted for. The nature of the solvent had a strong effect on NP self-assembly: *e.g.*, in good solvent NPs exhibited pure repulsion. Capping NPs with ligands with 2–4 carbon atoms did not significantly shift the equilibrium NP–NP centre-of-mass distance, whereas the potential minimum systematically decreased with increasing carbon chain length (Fig. 3a). Lastly, lower ligand grafting density was found to correlate with a higher propensity for NP “sintering”, the phenomenon in which the crystal lattices of neighbouring NPs merged.

In the case of complex ligands such as polymers, direct modelling of NP self-assembly may be limited due to insufficient computational resources. To simplify the treatment of such systems, a coarse-grained approach is frequently used, which ignores small-scale interactions between the structural components. This computational model considers the dominant interactions, such as van der Waals forces, between NP cores¹⁰⁹ or simplified

Fig. 3 (a) Molecular dynamics representation of interacting gold NPs with octanethiol ligands and plot of variation in potential mean force (free energy) of gold NPs functionalized with butanethiol, octanethiol and dodecanethiol as a function of NP–NP center-of-mass distance in vacuum. Reproduced from ref. 108 with permission from ACS. (b) Schematic of the coarse-grained model used in MD simulations of DNA-functionalized gold NP crystallization. Reproduced from ref. 104 with permission from ACS.

interaction potentials between ligands. The coarse-grained model was used in MD simulations involving DNA-functionalized gold NPs.¹⁰⁴ To model NP crystallization, the system was simplified by combining groups of several nucleotide bases into one “bead”. Interactions of complementary beads were modelled by a modified Lennard-Jones potential, while a Weeks–Chandler–Andersen approximation was used for interactions between non-complementary beads. In addition, although gold NPs are known to have a faceted surface, the NP was approximated as a sphere, since for long nucleic acid ligands the faces tend not to influence the resultant structure. Phase diagrams of the potential structures formed with variations in particle size and stoichiometry were constructed and found to be in good agreement with experimental results. Fig. 3b illustrates the coarse-grained structures used in this theoretical study¹⁰⁴ and a resultant nanostructure formed by two different NP types.

Plasmonic coupling in self-assembled metal nanostructures

The optical properties of metal NPs in the visible and near-infrared regions of the electromagnetic spectrum are governed by the collective oscillation of conduction electrons stimulated by incident light, the effect known as localized surface plasmon resonance (LSPR). The composition, size, and shape of a metal NP, and the refractive index of the dielectric medium surrounding this NP determine the frequency and intensity of LSPR. In assemblies of metal NPs, owing to the transfer and confinement of electromagnetic energy, different plasmon modes can interact with each other by the near-field coupling that occurs when interparticle distance is smaller or on the order of the light wavelength.¹¹⁰ The symmetry, size, and shape of NP assemblies, as well as the interparticle spacing and NP composition determine the spatial distribution of charge polarization and therefore, the splitting and the relative position of the plasmon resonance peaks. For example, the near-field coupling in chains of metal nanospheres results in the splitting of the single plasmon band of a nanosphere into low and high energy coupled modes, which correspond to the longitudinal and transverse plasmon bands of the chain, respectively.⁶² In addition, the near-field coupling leads to the gradual red shift of the longitudinal plasmon band of the chain (as shown in Fig. 4a), until the chain approaches the length of ~ 10 NPs.¹¹¹ Near-field coupling in assemblies of metal NP results in enhancement of electromagnetic field in the nanoscale gaps between NPs, which are referred to as ‘hotspots’. The enhanced electromagnetic field strongly influences optical properties of molecules and non-metal NPs placed in the hotspots. In addition to electric coupling discussed above, plasmonic assemblies can exhibit magnetic and Fano-like resonances, as was demonstrated for types of 2D assemblies of spherical gold NPs and nanoshells.^{112,113} To better understand the effects of plasmonic coupling, the plasmon hybridization model¹¹⁴ was developed, which is discussed below.

Analogously to the hybridization approach in molecular orbital theory, the physical mechanism of the plasmon coupling

between adjacent metal NPs is well-described by the hybridization (mixing) of elementary plasmons (or plasmons supported by the individual NPs), which results in splittings and shifts of plasmon energies.¹¹⁵ Interactions between plasmonic NPs results in the formation of two hybridized plasmons: low-energy symmetric or “bonding” plasmon (with electric field enhanced at the interparticle junction and red-shifted LSPR frequency) and high-energy antisymmetric or “antibonding” plasmon (with the electric field localized on the non-junction ends of the NPs and blue-shifted LSPR frequency), which are called dark (or subradiant) and bright (or superradiant) modes, respectively. Fig. 4b shows an example of hybridization models developed for plasmon NPs with the same and different sizes and corresponding experimental spectra of the system and incident light polarizations along and perpendicular to the interparticle axes (corresponding to σ , σ^* and π , π^* hybridized plasmon modes respectively).¹²¹ Note that in the case of plasmonic dimers formed by identical NPs, the antiphase mode is spectrally dark due to the cancellation of the equal but oppositely oriented dipoles on the two NPs (Fig. 4b, bottom). Bright plasmon modes couple to the incident light directly and are spectrally broadened, due to the radiative damping by the interband transitions in the metal, whereas dark plasmon modes are weakly damped and spectrally narrow. When the bright and dark modes are coupled, Fano resonance (or electromagnetically induced transparency¹²²) appears as a dip in the extinction spectrum.^{123,124} The coupling occurs when the energies of the bright and dark modes overlap, which allows the dark mode to be excited by the bright mode. Because the band corresponding to the dark mode is narrower than the band of the bright mode, their interaction results in the dip in the scattering spectrum at the Fano resonance frequency, due to the cancellation of the induced dipole moments. The plasmon hybridization model was developed in the electrostatic limit (that is, the magnetic field component of Maxwell's equations was neglected) by omitting the electromagnetic retardation effects that become significant on the length scale above a few tens of nanometers.¹²² For metal NPs and their assemblies with dimensions on the order of a few tens of nanometers, the plasmon hybridization theory provided a general principle for the design of complex metal nanostructures and the qualitative and quantitative prediction of their resonance properties. The method allowed for the quantitative description of plasmon resonances in metal nanostructures formed by spheres, ellipsoids, and NRs, whereas for nanostructures formed by NPs with other shapes the use of the hybridization approach was challenging.¹²² In addition, modification of the model was required to allow this approach to correctly account for plasmon coupling in dimers formed by NPs with different compositions, *e.g.*, gold and silver NPs dimers.¹¹⁶ We note that for NPs or their assemblies with dimensions larger than a few tens of nanometers, more rigorous electrodynamic approaches are necessary.¹¹⁰

Scattering of electromagnetic radiation by spherical, homogeneous, isotropic particles in a non-absorbing medium is described by Mie theory.¹²⁵ The extension of Mie theory provides quasi-analytical solutions for metal spheres coated with a dielectric layer, multilayer spheres, and non-spherical NPs such as ellipsoids

Fig. 4 (a) Salt-induced linear self-assembly of gold NPs. Left: schematic of self-assembly process; middle: temporal variation of extinction spectra of NPs chains with different lengths with arrows depicting plasmonic resonance wavelength; right: TEM image of polymer-encapsulated NP chains. Scale bar is 50 nm.⁶² (b) Plasmon coupling of symmetric (left) and size-asymmetric (right) silver NP dimers. Top: hybridisation model. Bottom: the experimental LSPR scattering spectrum of the silver NP dimers at different polarizer angle. Insets: TEM images of analysed dimers, scale bar is 50 nm.⁶² (c) Simulations of electric field enhancements for linear and kinked chains of 20 nm-diameter gold NPs using MMP (the increase of electric field is shown in a gradient color scale from dark to bright).¹¹⁷ (d) FEM-calculated spatial distribution of *E*-field enhancement in 3D self-assembled superstructures comprised of 80 and 20 nm-diameter gold NPs for different excitation wavelengths.¹¹⁸ (e) 3D illustration of electric field behavior surrounding a dimer of gold nanoshells using FEM. Inset is a 2-D slice plot for reference.¹¹⁹ (f) Comparison of the calculated extinction and near-field results of GMM theory and FEM for a dimer of multilayer metal dielectric nanoshells.¹²⁰ Adapted from the data of the cited papers by permission from the Royal Society of Chemistry, Wiley Interscience, and the American Chemical Society.

and cylinders.¹²⁶ For instance, a generalized multiparticle Mie theory was utilized to examine near-field coupling effects in chains of multilayer metal-dielectric nanoshells.¹²⁰ It was predicted that the interactions between these NPs in the chains would lead to Fano resonance, with the strongest field enhancement in the dielectric layer, whereas chains composed of uniform metal NPs would not possess these features. Overall, for studies of light scattering and near-field coupling effects in assemblies of spherical NPs, a generalized Mie theory is a relatively simple and accurate method.

In the case of arbitrarily-shaped NPs or randomly aligned NP assemblies, due to the complexity of the electromagnetic field term, Maxwell's equations have to be solved by using semi-analytical methods or numerical calculations. Two commonly used semi-analytical methods are the multiple-multipole method (MMP) and discrete dipole approximation (DDA).¹²⁷

Fig. 4c illustrates the use of MMP to calculate the electric field enhancement around linear and kinked chains of 20 nm-diameter gold NPs. Examples of numerical methods, include the finite-difference time-domain method (FDTD), the finite element method (FEM), and the boundary element method (BEM).¹²⁸ For example, electric field profile and LSPR of the chains of gold NRs, along with LSPR spectra were calculated using FDTD method.¹²⁹ The theoretical and experimental results enabled the evaluation of the relationship between the dynamic structural characteristics of assemblies of gold NRs and their ensemble-averaged SERS properties. Along with FDTD, an FEM method was used to evaluate the optical properties and the electric field enhancement of various self-assembled plasmonic structures, *e.g.*, 3D self-assembled plasmonic superstructures comprised of gold NPs of different sizes (Fig. 4d), or dimers of gold nanoshells (Fig. 4e). The results of numerical

calculations showed agreement with analytical methods,^{120,130} and could be used for evaluation of optical properties and electric field profiles of interesting plasmonic structures, which were not yet studied experimentally (Fig. 4f).¹²⁰ Examples of commercially available software for electromagnetic simulation are Lumerical FDTD simulations, XFDTD, FEM-based software Comsol Multiphysics (RF module) and HFSS, as well an open-source package such as Meep.

Overall, the theories and the methods discussed above have particular ranges of applicability that depend on the shape and composition of plasmonic nanostructures and the nature and the size of their constituent building blocks. While analytical methods allow a qualitative description of plasmon resonances in metal NPs of simple shapes, for more complicated geometries and self-assembled plasmonic structures accurate simulations must rely on numerical methods. The choice of the theoretical approach depends on the problem of interest, as well as the available computational resources.

Plasmon–exciton coupling in hybrid metal–semiconductor nanostructures

Assembly of hybrid nanostructures paves the way for the development of nanomaterials with multiple functionalities by using individual different types of NPs with plasmonic, electronic or magnetic properties.¹³¹ In addition to straightforward combination of NP properties, new collective properties of the material may be expected due to the interactions of NP building blocks, similarly to the plasmon–plasmon interactions discussed in Section 4.

When plasmonic NPs are co-assembled in hybrid clusters with semiconductor quantum dots (QDs), plasmonic properties of metal NPs and excitonic properties of QDs can be coupled, thereby leading to a change in the optoelectronic properties of the nanostructure, *e.g.*, enhancement or suppression of the fluorescence emission of QDs or to the nonlinear Fano resonance. Plasmon–exciton interactions strongly depend on the interparticle distance in the NP ensemble and the energy overlap between plasmon and exciton bands. Therefore the size and the shape of the constituent NPs and their mutual arrangement to a large extent determine the resulting properties of the hybrid nanostructure.¹³²

The fluorescence of QDs co-assembled with metal NPs can be enhanced in comparison with individual QDs, due to the amplification of the electromagnetic field in the proximity of a metal NP and the increased amount of energy absorbed by the QDs. In addition, electromagnetic coupling between the QD and the plasmonic NP can cause an increase in the radiative decay rate of the emitter, thereby decreasing its excited state lifetime. The shorter the QD–metal NP distance, the greater the effect of the near field on the exciton, however, in the close proximity of the plasmonic NP, the excited electron in QD can rapidly relax by exciting the localized plasmon resonance of the metal NP *via* energy or electron transfer. This effect would result in quenching of fluorescence. In the strong plasmon–exciton coupling limit – when the metal NP and QD are in contact – significant suppression of both plasmon and exciton

Fig. 5 (a) Left: generalized schematic of the self-assembly of hybrid metal–semiconductor nanostructures with the use of the silica spacer (shown with grey color) between metal NPs and QDs. Right: a library of extinction spectra of hybrid metal–semiconductor nanostructures of different composition QDs and metal NPs of different shapes; inserts are examples of TEM images of hybrid structures. Adapted from ref. 134 by permission from the American Chemical Society. (b) Gold NP–QD bar-codes co-assembled using a polyelectrolyte spacer. Adapted from ref. 139 by permission from Wiley Interscience. (c) Left: schematic (top) and a TEM image (bottom) of CdSe/ZnS QD positioned between two gold NPs (scale bar is 100 nm). Intensity of fluorescence emission of the gold NP–QD–gold NP structure (blue line) and individual QDs (red line), plotted as a function of the polarization angle. Adapted from ref. 140 by permission from the American Chemical Society.

excitation takes place.¹³³ To account for this effect, a spacer layer, *e.g.*, made from silica^{134–136} (Fig. 5a) or a polymer^{137–139} (Fig. 5b) with the thickness of 8–21 nm has been introduced between the plasmonic and excitonic NPs to preserve or enhance fluorescence of QDs. Up to twenty-fold increase in fluorescence intensity and up to three orders of magnitude shorter excited-state lifetime have been reported for QDs that were placed in the gap between two gold NPs *via* DNA linkers (Fig. 5c).¹⁴⁰ In addition to the change in fluorescent intensity, a shift in emission wavelength of QDs can be achieved in hybrid metal NP–QD self-assembled structures. For instance, if the exciton lifetime of QDs in the nanostructure decreases, a fraction of excitons can reach the potential minima, which leads to a blue-shift in exciton emission.¹³⁷

Moreover, it has been demonstrated that metal NP–QD self-assembled structures exhibit significantly suppressed blinking than individual QDs,¹³⁹ which is important for the applications of fluorescent QDs as bioprobes and optical devices.

Similarly to QDs adjacent to the metal surface, molecular fluorophores can show fluorescence enhancement when placed in proximity to plasmonic NPs and especially, when placed in the gaps between plasmonic NPs in self-assembled structures. For dyes with low quantum yields fluorescence enhancement factors can reach several orders of magnitude.¹⁴¹

Applications of self-assembled plasmonic nanostructures

The formation of hotspots between adjacent NPs in self-assembled plasmonic nanostructures has a broad range of potential

applications in imaging, sensing, in electronic devices, catalysis, cancer therapeutics and medical diagnostics.¹⁴² The location of hotspots is largely determined by the mutual orientation of plasmonic NPs, interparticle distance and the aggregation number of the self-assembled nanostructures, the characteristics that are controlled during solution-based self-assembly of the NPs.^{129,143,144}

Among various possible applications of assemblies of metal NPs, the most extensively explored and developed is their utilization in chemical and biochemical sensing.^{145,146} Assemblies of plasmonic NPs with controllable architectures are required in quantitative SERS-based sensing.¹⁴² This application requires structural optimization of plasmonic assemblies.^{129,147} Under optimized conditions, up to 10^{12} -fold enhancement of SERS signal can be observed, owing to the enhanced local electromagnetic field coupled with chemical enhancement.¹⁴⁸ The enhancement factor on the order of 10^{11} is the strongest enhancement that can be justified theoretically, based on electromagnetic contribution.¹⁴⁹ Experimentally it has been shown that the enhancement factor value on the order of 10^7 – 10^8 is sufficient for single molecule detection.¹⁵⁰

It has been also shown that strongly enhanced electromagnetic fields in the gaps between plasmonic NPs (as well as in close proximity of individual metal NPs) enhances fluorescence emission and decreases excited-state lifetimes of molecular fluorophores and QDs placed in these gaps. This effect has led to the use of plasmonic NP–QD assemblies in imaging of infectious agents and cancer cells,¹⁵¹ leading to the enhanced fluorescence detection limit and fluorescence images with a high contrast.¹⁵²

The placement of fluorophores close to the surface of plasmonic nanostructures can not only enhance their brightness, but also stabilize them against photobleaching by protecting them from oxidation.¹⁵³ We note that fluorescence intensity of dyes placed in a hotspot showed 2970-fold increase,¹⁵⁴ which was significantly lower than 10^{11} enhancement achieved for SERS. A limited fluorescence enhancement was achieved because in plasmon-enhanced fluorescence the enhancement factor has a square dependence on the incident field, E , whereas SERS enhancement originates from the amplification of both the incident and scattered fields and the enhancement factor scales as $|E|^4$. In addition, in contrast to SERS, plasmon-enhanced fluorescence cannot benefit from the electromagnetic field enhancement at the metal surface, due to the competition of nonradiative energy transfer and fluorescence enhancement. Thus a spacer layer introduced between the surface of metal NP and an emitter can provide the separation between the plasmonic nanostructure and an emitter molecule.^{155,156} Importantly, quenching of fluorescence due to non-radiative energy transfer to metal NPs can have its own applications. Fluorescence resonance energy transfer (FRET) between adjacent molecules has proven to be a powerful tool in biology, *e.g.*, in studies of conformational changes in proteins.¹⁵² Thus, self-assembled structures based on metal NP and QDs can act as efficient sensors. For example, a hybrid self-assembled structure of gold NRs and CdTe/CdS QDs showed efficient turn-on near-IR sensing capability for environmentally harmful compound 2,4,6-trinitrotoluene.¹⁵⁷ As shown on Fig. 6a, with increasing concentration of the analyte

Fig. 6 (a) Turn-on and near-infrared fluorescent sensing for 2,4,6-trinitrotoluene based on hybrid gold NR–QDs assembly. Top: schematic of FRET-based operating principle. Bottom left: structure of the hybrid assembly. Bottom right: fluorescence intensity of hybrid assembly as a function of 2,4,6-trinitrotoluene concentration. Adapted from ref. 157 by permission from the American Chemical Society. (b) Assembly of silver satellite NPs on a large gold NP via Cu^{2+} ion-mediated complex. Top left: schematic of the formation of the self-assembled structure. Bottom left: SEM and dark-field images of the assemblies at increasing concentration of target ions. Right: peak shift and intensity change in scattering spectra of assemblies as a function of silver satellites number. Adapted from ref. 158 by permission from the American Chemical Society. (c) Simulated CD spectra of 4.5×5 nm gold ellipsoids immersed in a homogeneous medium of refractive index 1.33 that are arranged in a helical structure with 12 nm radius and 15 nm pitch. The simulated spectra correspond to different number of particles varying from 2 to 7. Adapted from ref. 154 by permission from Wiley Interscience.

in the solution, the gap between a gold NR and the QDs increases, resulting in linear increase of fluorescence intensity of QDs. Assemblies of plasmonic NPs may be used to improve the detection limit for traces of metal ions. One example involves plasmonic assemblies of large gold NPs and smaller silver “satellite” NPs functionalized with metal-chelating ligands.¹⁵⁸ In the presence of metal ions such as copper ions, plasmonic NPs self-assembled into a core-satellite structure, with copper ions acting as a linker (Fig. 6b). The quantity of metal ions controlled the number of silver satellites surrounding the gold core, which, in turn, determined the intensity and the shift in extinction spectra of the self-assembled structure due to plasmonic coupling.

Photoacoustic imaging, also called optoacoustic or thermoacoustic imaging, can also benefit from contrast agents based on assemblies of plasmonic NPs. Photoacoustic imaging has emerged as a nonionizing and noninvasive imaging modality that combines the advantages of optical and ultrasound imaging.¹⁶⁰ Generation of the photoacoustic signal by metal NPs originates from the conversion of light energy to heat, which is transferred to the surrounding environment to produce pressure transients.¹⁶¹ Recently, it has been shown that self-assembly of gold NPs significantly enhances the photoacoustic signal,¹⁶² which was

attributed to the increase in the rate of heat transfer by assemblies, in comparison with individual NPs. Enhancement of the photoacoustic signal can potentially provide a method for determining whether gold NPs have been endocytosed or remain external to cells when imaged *in vivo*.

Assemblies of metal NPs have also been employed in therapeutic applications, *e.g.*, in photothermal cancer therapy. Metal NPs exhibit light absorption in the visible and near-infrared spectral range, which is several orders of magnitude stronger than that exhibited by conventional laser phototherapy agents.¹⁶³ Laser irradiation of assemblies of metal NPs leads to absorption of light energy and its release as heat energy through non-radiative energy transfer, which is transferred into the surrounding medium.¹⁶⁴ The localized, site-specific heating of the biological tissue is expected to cause cell damage, *e.g.*, by protein denaturation.¹⁵² Thus a combination of bioimaging (SERS or fluorescence) and therapeutic applications of metal NPs assemblies can lead to new strategies in therapeutics and diagnostics (theranostics).¹⁶⁵

Biomedical applications of self-assembled plasmonic nanostructures require detailed studies of their interactions with molecules, cells, and tissues, in order to evaluate their biocompatibility and optimize NP stabilization against aggregation. The effect of the size,¹⁶⁶ shape and surface chemistry¹⁶⁷ of metal NPs and their assemblies¹⁶⁸ on the cellular uptake, intracellular trafficking, toxicity, and gene expression has been investigated in the past few years. A number of studies have been focused on coating NPs with a stabilizing shell of polyethylene glycol, proteins, lipids, or DNA, which render at least, short term stability of NPs *in vivo* and *in vitro*.^{168,169}

Chiral plasmonics is an emerging field, which has received increasing research interest, due to the ability to produce probes for *in situ* determination of the structure and enantioselective separation of amino acids and other chiral organic molecules, as well as optical materials with improved optical circular dichroism.¹⁷⁰ Many types of assemblies of plasmonic NPs have exhibited plasmonic CD features, *e.g.*, gold NPs assembled with amino acids,⁶⁶ single-stranded DNA,¹⁷¹ DNA bundles,¹⁷² and a scaffold of supermolecular fibers,¹⁵⁹ to list a few examples. Based on the directed co-assembly of gold NRs and ds-DNA, temperature-dependent reversible plasmonic CD device was realized, corresponding to the assembly and disassembly transitions.¹⁷³ This reversible change of plasmonic CD responses can be potentially used as a new detection method to produce ultrasensitive sensors. Experiments in the self-assembly of chiral plasmonic nanostructures can benefit from the computational modelling. As an illustration, Fig. 6c shows the calculated CD spectra of chiral self-assembled plasmonic structures formed by different numbers of gold ellipsoids.

Outlook

The organization of metal NPs in plasmonic nanostructures is a delightful concept, yet, a rational and pragmatic approach to NP self-assembly has to be undertaken (i) to generate new knowledge on NP interactions in solution, (ii) to produce materials with new plasmonic properties and (iii) to fabricate

functional nanomaterials and devices beyond the proof of concept stage.

Most of the reports published to date, describe plasmonic properties of gold NPs, with a relatively small number of articles on silver, copper, and palladium NPs. Other materials such as aluminium, titanium, and chromium can also support surface plasmon resonance,¹⁷⁴ and therefore can be used as potential plasmonic nanomaterials. The limitation in the selection of the materials for plasmonic NPs can be partly attributed to relatively low extinction coefficients of alternative metals, as well as the challenges in NP synthesis and/or their poor stability under ambient conditions. Recent publications report promising results on the use of aluminium¹⁷⁵ or even non-metal NPs such as CuTe.¹⁷⁶ For example, aluminium NRs fabricated by lithography have shown tunable plasmon resonance from deep UV to the visible spectral range, in agreement with FDTD simulations. More effort can be focused on the development of efficient and low-cost bottom-up fabrication of a broader range of plasmonic assemblies and fine-tuning of their properties, as well as on the surface passivation of these structures that would enhance their stability.

With regards to the formation of new types of plasmonic structures, a useful approach relies on “molecular thinking”,¹⁷⁷ in which an analogy is drawn between the self-assembling NPs and molecules or atoms undergoing a chemical reaction. This strategy not only enables a qualitative control over NP assembly, but also enables the prediction of the structural characteristics of nanostructures, *e.g.*, their aggregation number and polydispersity and the formation of isomers. The application of this approach has been demonstrated for linear chains made from metal NP repeat units⁴⁴ (so called plasmonic polymers¹⁷⁸). We stress that once the analogy between plasmonic NPs and molecules is established, the self-assembly can be used to study chemical reactions by using the microscopy and plasmonic tools.¹⁷⁹

Among other triggers used for NP self-assembly, light offers a particularly useful tool that may lead to new applications of self-assembled structures. In addition to photothermally triggered self-assembly⁴⁰ and light mediated photocrosslinking of plasmonic polymers,⁵¹ new structures with unusual plasmonic properties can be generated.¹⁸⁰ Furthermore, NP self-assembly induced by irradiating the system with light of a particular wavelength, can potentially lead to nanostructures with narrow distribution of aggregation numbers. Once the self-assembled plasmonic structure is formed, photochemical reactions conducted in hot spots between adjacent NPs show a great application potential, as has been demonstrated by recent work.¹⁸¹

Self-assembly of plasmonic nanostructures paves the door for fundamental studies of the importance of structure–property relationship in SERS, scattering, extinction, Fano resonance, or circular dichroism. These studies can be readily conducted by examining ensemble-averaged properties of NP assemblies in solution or on substrates. Self-assembly of plasmonic nanostructures is particularly useful for single particle spectroscopy experiments.¹⁸² For example, chains of plasmonic polymers with a distribution of aggregation numbers, bond angles, chain conformations or varying compositions give simultaneous access to nanostructures with a variety of structural characteristics.

Currently, chemical and biochemical sensing remains the main application of self-assembled plasmonic nanostructures. Enhancement of electric field in hot spots can control many processes, from precise local delivery of heat and enhanced generation of excited states, to electron- and hole-transfer processes that can contribute to photoredox processes.¹⁸³

Plasmonic–excitonic coupling was demonstrated for fluorescent dyes and individual plasmonic NPs, however, the placement of molecular fluorophores in the gaps between plasmonic NPs in their assemblies potentially offers greater enhancement of fluorescence. For example, simulations predicted an order of magnitude greater enhancement factors for fluorophores placed in the gaps between multilayer gold nanoshells, compared to when those placed in the proximity of individual gold NPs.¹⁸⁴

First applications of self-assembled plasmonic nanostructures in catalysis are emerging. For example, light mediated self-assembly of metal NPs can lead to the formation of dynamic, “switchable” assemblies upon irradiation of the system at a particular wavelength.¹⁸⁵ Since aggregation of NPs capped with catalytic ligands leads to a decrease in surface area and inhibition of catalysis, mixtures of NPs stabilized with different light-responsive catalytic ligands can be used for the selective synthesis of a particular compound.

Finally, chiral plasmonics is a very rapidly developing field of research that utilizes chiral organization of metal NPs and their interactions with light.¹⁸⁶ Self-assembled chiral plasmonic nanostructures offer the ability to achieve strong circular dichroism activity over a broad spectral range. Materials derived from such nanostructures should enrich the field of metamaterials with negative refraction and non-linear optics properties. Promising applications of chiral plasmonic nanostructures include circular polarizers, detectors for circularly polarized light, asymmetric catalysts, and sensors of chiral biomolecules.

With future progress in producing new, dynamic and hierarchical self-assembled plasmonic nanostructures, greater advances can be expected in the field of nanoplasmonics, as well as new applications of such structures in organic synthesis, sensing, solar cells, and detection of analytes.

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