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Structure-activity collective properties underlying self-assembled superstructures

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ABSTRACT

The structure-activity relationship is a universal principle in nature that relates the structure of a material to its physiochemical properties and behaviors. A classic example of this relationship involves elemental carbon, which exhibits unique properties derived from different atomic arrangements (e.g., diamond, graphite, fullerene, carbon nanotube, and graphene). Nanoparticles also demonstrate this principle because they can effectively serve as artificial atoms that self-assemble into superstructures. These superstructures naturally obey the structure-activity relationship and can be adjusted by regulation of various structural parameters. Additionally, the self-assembled superstructures have collective properties of that significantly differ from the properties of original monodisperse particles and bulk materials. Thus, customized functional materials can be designed according to the structure-activity collective properties. In this review, we discuss the influences of structural parameters, such as particle spacing, size distribution, lattice structure, and order degree, on the properties of various scientific and engineering fields (e.g., optics, electrics, catalysis, and biomedicine), along with future development prospects.

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Review





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Introduction

The end of the 20th century witnessed the prosperity of nanomaterials, a field which has since experienced exponential growth over the past few decades. Notably, the use of nanotechnology can be traced back to ancient Rome to the Lycurgus Cup, in which gold (Au) nanoparticles (NPs) were incorporated to stain the glass [1]. Michael Faraday reportedly brought about the modern era of nanomaterials by determining that the particular optical properties of Au NPs differed from the optical properties of bulk Au [2]. The ability to regulate the size and shape of nanomaterials has been of great interest to the scientific community in its effort to create materials with superior physicochemical properties. Many preparation methods have been proposed in an effort to obtain monodispersed NPs with controlled composition and morphology. These synthetic methods are applicable to a range of metallic, alloyed, semiconductive, magnetic, ferroelectric, thermoelectric, and insulating NPs.

In the 1990 s, the precise synthesis of monodispersed zero-dimensional (0D) quantum dots (QDs) make it possible that man-made components behave like atoms in constructing solids, since they possess unitive size distribution and discrete energy level (Fig. 1). These called "artificial atoms" shed light to the conjecture that we can learn from nature in producing supercrystals with ordered arrangement using functional nanoparticles to assemble crystal equivalents, which may contain stereostructures not present in nature. With the progress of nanomanufacturing technology, precise control over the composition and packing modes of NPs to achieve self-assembled superstructures has gradually matured. Therefore, the supercrystals emerge at the historical moment based on nano self-assembly technology. In view of the current use of attainable instruments, it is still difficult to directly observe the movement of atoms. One of the advantages of the fabrication of supercrystals is that it provides a visual model for the formation and evolution of natural crystals. Inspired by the natural crystalline structure, under the precise control of the composition, size, and interparticle spacing, supercrystals with mono, binary and ternary components have been produced to perfectly duplicate the unit cells existing in nature, like face-centered cubic

(fcc), body-centered cubic (bcc), simple cubic (sc), hexagonal close packed (hcp), AB (isostructural with NaCl, CsCl), AB₂ (isostructural with AlB₂), AB₃ (isostructural with Cr₃Si), AB₆ (isostructural with Cs₆C₆₀), graphite-type, face-perovskite, edge-perovskite; and even structures that have never been found in nature, such as A₂B₃, AB₄, "lattice X" and ABC₁₂ ternary structures [3–6]. On the other hand, selfassembly technique helps the nanocrystals (NCs) to achieve a great leap from microscopic particles to macroscopic devices without changing the unique nano properties of the materials, thereby breaking through its application limitations. It is particularly worth noting that the ability to predictably and periodically place individual NPs into assembled superstructures can endow nanomaterials with renewed properties that cannot be expected since a lack of access to such structures in the past [7]. At present, the self-assembly technology can be used to produce ordered 1D, 2D, and 3D structures [8–11], with collective properties that are distinct from the simple superposition of the characteristics of monodisperse assembly units and the features of the corresponding bulk materials. In addition, as a crystal equivalent solid, the self-assembled supercrystal solid could equivalently achieve the structure-activity collective properties through adjusting the arrangements of nano-building blocks. Therefore, it is possible to construct artificial superlattices through self-assembly of functional nanocomponents to acquire enhanced optical, magnetic, electrical, catalytic and mechanical properties [12-16] (Fig. 2).

The causal relationship between structure and performance has prompted research efforts at the nanoscale, in an attempt to exploit the structure-activity properties of self-assembled superstructures. In this review, we introduce the methodologies used to induce selfassembly, and systematically summarize the structure-activity collective properties from related works, and then analyze the applications of various properties to problems related to self-assembly and future research directions in this area.

Fabrication strategies of self-assemblies

Thus far, many effective preparation methods have been developed to build assembled superstructures (Fig. 3). Self-assembly, as a



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Fig. 2. Scheme of collective properties of superstructures in optical, electrical, magnetic, and mechanical area.

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means of preparing aggregates, is commonly driven by non-covalent forces between nano-building blocks to spontaneously form ordered structures [17–19]. The interparticle forces that participate in the assembly process include spatial repulsion, van der Waals force,

molecular surface force, electrostatic force, and magnetic force [20]. Programmable assembled structures with different shapes, sizes, and dimensions can be obtained by adjusting these non-covalent forces [21–25].



Fig. 3. Self-assembly strategies based on hard templates: (a) patterned silica/glass templates, (b) metal oxide templates, (c) carbon material templates, (d) patterned polymer templates; and soft templates: (e) microemulsion templates; (f) amphiphilic molecule templates, (g) DNA templates, (h) liquid crystal templates. [27] [28] [30] [35] [36] [44] [101] Reproduced with permission.[27] Copyright 2017, Wiley-VCH. Reproduced with permission.[28] Copyright 2019, Elsevier Ltd. Reproduced with permission.[30] Copyright 2018, American Chemical Society. Reproduced with permission.[36] Copyright 2015, Springer Nature. Reproduced with permission.[44] Copyright 2018, Wiley-VCH. Reproduced with permission.[46] Copyright 2020, American Chemical Society. Reproduced with permission.[101] Copyright 2018, Wiley-VCH. Reproduced with permission.[46] Copyright 2020, American Chemical Society. Reproduced with permission.[101] Copyright 2018, Wiley-VCH. Reproduced with permission.[27] Copyright 2018, Marcinan Chemical Society. Reproduced with permission.[101] Copyright 2020, Elsevier Ltd. Reproduced with permission.[27] Copyright 2018, Wiley-VCH. Reproduced with permission.[46] Copyright 2020, American Chemical Society. Reproduced with permission.[101] Copyright 2020, Elsevier Ltd. Reproduced with permission.[27] Copyright 2018, Marcinan Chemical Society.

Self-assembly with a template

The employment of templates is a good strategy when the regulation of interparticle interactions is insufficient for achieving the desired position of the particles in the assembled structure. The limiting effect plays a role in precisely controlling the size and shape of the nanomaterials in the assembly, especially when aligning 1D assemblies such as nanowires and nanotubes [26–29]. According to the characteristics of the templates and their limitations, they can be divided into hard and soft templates, both of which provide a controlled assembly space. Notably, hard templates use a static substrate, whereas soft templates provide a cavity in dynamic equilibrium.

Hard templates

The common hard templates include patterned silica/glass template, anodic aluminum oxide (AAO), carbon nanostructures (nanotubes, graphene) and patterned polymer (such as representative polydimethylsiloxane, PDMS), as shown in Fig. 3a-d [27-30]. The inner or outer surfaces of these materials are used as the nanocomponent filling area. The templates are removed to obtain the desired assembled structures after the nanocomponents complete the process of self-assembly induced by the templates. The hard templates have better stability, and their confinement effects are stronger than the confinement effects of the soft templates. However, removal of the templates usually requires the use of strong acids, strong bases, or organic solvents, which tend to destroy the assembled structure. In addition, it is difficult to precisely control the interparticle spacing of the nanocomponents. Fig. 3a exhibits the use of photolithography and reactive-ion etching to turn the flat substrates into patterned templates for directional assembly of BaTiO₃ NCs [27]. The carved template provided a directional capillary force to induce the long-range-ordered superlattice structures. Topographically patterned elastomeric molds are extensively applied as templates for directing the assembly of AuNPs cluster arrays on a large scale (Fig. 3d), aiming to exploring the tailored optical response [30].

Soft templates

Soft templates are usually ordered aggregates formed by the interaction of hydrophilic and hydrophobic groups of amphiphilic molecules under the action of solvophobic effects, involving surfactants [31], microemulsions [32,33], amphiphilic polymer [34,35], DNA complementary base pairing [26,36–39], DNA-metal coordination chemistry [40–42], gels [43], and liquid crystals [44–46], as shown in Fig. 3e–h.

Notably, surfactant molecules aggregate derived by the hydrophobic interactions to form specific morphologies in solution, which have received the most attention with regard to inducing ordered assemblies [47]. Zhang et al. used self-assembled amphiphilic macromolecules to study sequence isomerization and demonstrated the importance of sequence control in the synthesis of macromolecules [48]; they also showed that different assembled structures could be obtained by changing the hydrophobic position in the macromolecule sequence. The surfactant aggregates have been inherited and developed to a microemulsion method, which can be exploited as water-oil mixtures to create a soft template for spherical confinement of NPs in the emulsion droplets (Fig. 3e) [49,50] or to aggregate NPs at the interface under solvophobic effects when synthesizing superparticles (SPs) [33]. Subsequent heat treatment removes the reagents to obtain size-controllable products with good size uniformity. Li et al. reported the amphiphilic diblock copolymer induced assembly using hydrophobic polystyrene (PS) corona to attach the PS-capped CdSe NPs, as shown in Fig. 3f [35]. Complementary sticky ends in DNA make it a perfect bonding element in assembling superstructures whose interactions are governed by hybridization of base pairs. Mirkin et al. have accomplished a lot work on DNA programmed Au nanoparticle assemblies (Fig. 3g) [36,37,39]. The phosphate domain and nucleobases on the DNA sequence can also be utilized to supply diverse binding sites in building strong coordinating interactions between DNA and metal ions. Li et al. established several self-assembly superstructures driven by the DNA-metal coordination chemistry [40-42]. The mechanism for gel in the self-assembly is it can offer a great deal of functional groups which can be employed to coordinate components. Zang et al. exploited a gelatin-mediated hydrogel decorated

with amide, amino, hydroxyl, carboxyl groups to build weak coordination between transition metal ions and the gelatin strands to assemble a lamellar metal carbide nanostructure [43]. Liquid crystals are recommended as host systems originated with their molecular order and mobility to direct the alignment of nanoparticles (Fig. 3h). Elegant work by Li et al. have expanded topological defects in liquid crystals as templates for directing the periodic assembly of latex nanoparticles by exploiting the anisotropic surface tension and elasticity at the interface [45].

Template-free method for self-assembly

In the absence of templates, the self-assembly process in solutions is always constrained by the balance among various interparticle forces. Pieranski et al. reported the first microscopic observation of an ordered structure assembled with polystyrene spheres through trapping using surface energy wells at the water-air interface [51]; van der Waals force-induced particle aggregation serves to enhance the dipole force between particles, ultimately resulting in an anisotropic structure [52]. The balance of spatial repulsion and van der Waals forces can induce the synthesis of a hexagonal network structure of superlattices [53]. Abelson et al. exploited solvent evaporation in the self-assembly process at a gasliquid interface to acquire a 3D bcc superlattice of quantum dots (QDs), with lattice distortion derived from the crystal plane alignment driven by steric and/or electrostatic forces [54]. Moreover, the directional force can induce self-assembly of particles to create rock salt structures. Murray et al. designed a series of self-assembled structures by balancing the steric force, van der Waals force, electrostatic force, and dipole interactions [55]. At the nanoscale, the electrostatic force is balanced with a short-range van der Waals force; the electromagnetic shielding effect can be varied by modifying the charge of the ligand or the particle concentration. Therefore, the stacking mode of nanocomponents can be adjusted to create AB, AB₂, AB₃, AB₅, AB₆, or AB₁₃ crystal structures. Strategies for self-assembly without templates are discussed in the following sections.

Self-assembly induced by an external field

The ability to control the self-assembly of NPs by varying interparticle interactions through an external field supports numerous possibilities. The external field can be magnetic, light, electric, and force field, as shown in Fig. 4a. In the presence of a magnetic field, the easy magnetization axis of the NC is aligned along the direction of the magnetic field [56]. Ahniyaz et al. studied the assembly behavior of hematite and found that it provided a long-range ordered simple cubic superlattice by creating a weak magnetic field in the initial stage of assembly [57]. Deng et al. used a magnetic field to induce the arrangement of $Fe_3O_4@nSiO_2$ NPs to form a 1D chain structure [58].

The self-assembly of NPs can also be light-induced [59]. Grzybowski et al. demonstrated that light could induce changes in surface molecular dipoles, which could then precisely regulate the dipole-dipole interaction between NPs to achieve self-assembly of robust materials [60]. The participation of photosensitive components can produce substantial changes in the self-assembly process. Yeom and coworkers used circularly polarized light to influence selfassembly, which resulted in nanoribbons with left-handed or righthanded twists, rather than the structures prepared under dark conditions [61]. Yan et al. used the interaction between trapped dipoles and laser irradiation to achieve light-mediated self-organization; the final structure was regulated by changing the intensity and/ or polarization state of the incident light [62]. The external electric field can also trigger NP self-assembly [63]. Using the dielectric anisotropy of liquid crystals, Wang et al. modified the arrangement of Au nanorods by confining them in liquid crystal droplets to realize

an electrically controllable configuration [64]. Boehm et al. used an alternating current electric field to induce the self-assembly of silica-coated Au nanowires to form a 2D nanowire lattice [65].

The ambient force induced self-assembly is an effective approach in eliminating defects, grain boundaries, and vacancies within the close-packed assemblies to facilitate electron or energy transfer. Wu et al. demonstrated the pressure annealing method to transfer amorphous AuNPs film into a quasi-single crystalline superstructure under a continuous hydrostatic pressure up to ~6 GPa inside a diamond anvil cell [66]. The applied pressure induced rearrangements of AuNPs to a lower energy state because the soft ligands provided essential mobility. Schulz et al. further observed the reversible selfassembly and dispersing of AuNPs supercrystal during stressing and releasing process [67]. Time-resolved small-angle X-ray scattering (SAXS) paly essential role in monitoring the structure evolution and kinetics of superlattice formation and dissolution in situ upon the applied pressure [68]. High-pressure processing further produced direct sintering of individual NPs to 1D and 2D nanostructures for external pressure up to > 8 GPa [69,70]. While the preformed superlattices underwent interparticle distance decreasing with the increasing pressure, and further pressure treatment induced NPs fusion and phase transition both in mesoscale and atomic scale [71,72].

Self-assembly driven by interactions between surface ligands

Numerous short-range forces between ligands play a role in the construction of self-assemblies, including van der Waals force [55], hydrogen bonds [73,74], hydrophobic interactions [75–81], π - π interactions [82–84], and covalent cross-links, and electrostatic interactions as shown in Fig. 4b [85,86].

Van der Waals force is a non-directional weak force. The van der Waals force between ligands plays an important role in selfassembly of NPs at the interfaces, including gas-liquid and liquidliquid interface. Interface self-assembly is mainly divided into two categories according to the phase state: gas-liquid and liquid-liquid. Self-assembly at the gas-liquid interface includes Langmuir-Blodgett (LB) technology and evaporation-induced self-assembly (EISA) [10,55,87–89]. Among them, EISA is a mainstream method used to produce self-assemblies with large areas [90]. Murray et al. completed many investigations using the EISA method [55,90]. Evaporation of the solvent drives NP assembly at the gas-liquid interface; the resulting self-assembled structure is affected by ligand factors, NP concentration, assembly substrate, and annealing parameters. EISA can provide various close-packed assemblies, including dual-structure superlattices, binary assemblies, and ternary assemblies [91-93]. With respect to liquid-liquid interface self-assembly, NPs aggregate at the interface between two immiscible solutions [94]. The liquid interface facilitates the movement and rotation of the NCs to achieve conformation adjustment, and finally prepares defect-free 2D/3D assemblies [95,96]. Mao et al. reported on the selfassembly of Au nanorod 2D sheets at the cyclohexane-water interface that exhibited surface-enhanced Raman scattering (SERS) [97].

Hydrogen bonds are one of common interactions in nature and widely exist in DNA double helix, protein, supramolecular polymers. Hydrogen bonds induce self-assembly through interactions between hydrogen donor and acceptor with great difference in electronegativity. Babu et al. utilized the hydrogen bond between pyridine-linked cholesterol and pyrene butyric acid to pre-organize the stacking of 2,4,7-trinitro-9H-fluoren-9-one into a 1D arrangement, thereby obtaining a three-component self-assembled structure [98]. Hydrophobic interactions drive the assembly by stacking nonpolar ligands wrapped on the surface of nanoparticles when they are dispersed in a polar solvent. The extended ligands shrank to reduce the surface tension, while during the process, the wrapped nanoparticles aggregate due to the attractive force between the hydrophobic aliphatic chains. In addition, the polar solvent builds a spatial H–bond network to exclude the solvophobic



Fig. 4. Template-free method for self-assembly, including (a) self-assembly induced by an external field, and (b) self-assembly driven by interactions between surface ligands. Reproduced with permission.[44] Copyright 2018, Wiley-VCH. Reproduced with permission.[48] Copyright 2019, Royal Society of Chemistry. Reproduced with permission.[62] Copyright 2020, American Chemical Society. Reproduced with permission.[69] Copyright 2010, Wiley-VCH. Reproduced with permission.[74] Copyright 2018, Wiley-VCH. Reproduced with permission.[83] Copyright 2017, American Chemical Society. Reproduced with permission.[90] Copyright 2010, Springer-Nature. Reproduced with permission. [105] Copyright 2017, Royal Society of Chemistry. Reproduced with permission.[277] Copyright 2014, American Association for the Advancement of Science.

nanoparticles in. Under these interactions, the nanoparticles self-assembly to minimum total surface area as well as surface energy. Cao and coworkers adopted the hydrophobic and solvophobic interactions to realize the self-assembly of needle-like 1,12-dodecanediamine-functionalized CdSe/CdS nanorods, spherical or cube-shaped oleic acid capped Fe_3O_4 NPs to form superparticles or superlattices [76–81]. The shortrange π - π stacking is one of weak interactions between aromatic nucleus, which can be exploited in the self-assembly of building blocks to construct functional superstructures. Yan et al. fabricated polyaniline (PANI) nanorices via single-handed helical π - π stacking of PANI molecules. The monodispersed PANI nanorices could further self-assemble into hexagonal microplates due to strong π - π stacking interactions [99]. Applying covalent cross-links to induce self-assembly is a strategy in which the covalent bonds between the linking molecules are used to connect the assembly units. Sun and coworkers synthesized core-satellite intermediates through strong covalent bonds and finally realized the preparation of asymmetric nanoassemblies. In particular, the Au NPs initially anchored on the surface of Fe₃O₄/SiO₂ colloidal substrates, and then the second layer of SiO2 was coated on the surface of the coresatellite intermediates, leaving part of the Au NPs exposed. Subsequently, a linker was modified on the surface of the exposed Au NP via strong covalent bond, and the other end of the linker was bound to the second nanocomponent. The asymmetric nanoassemblies were finally acquired after removal of SiO₂ layers [100].

Electrostatic interactions have been extensively applied to drive the self-assembly process [101–103], although the electrostatic force

can be both attractive and repulsive [104-107]. The strength and range of the electrostatic interaction can be adjusted by changing the properties of the solvents. For example, Murray et al. adjusted the ligand charge by changing the solvent to alter the electrostatic interactions; using this approach, they attained various forms of close-packed superlattices [55]. Recently, it was demonstrated that micron-sized colloids can also be used as assembly units to form superlattice structures; this required a balance between the electrostatic attraction and spatial repulsion to regulate interparticle attraction, while preventing particle aggregation. Hueckel et al. adjusted the solution electrolyte concentration to control the Debye length, which played a key role in modifying DLVO theory (proposed by Boris Derjaguin, Lev Landau, Evert Verwey, and Theodoor Overbeek) to describe the particle interactions that occurred during the preparation of ordered superlattices [108]. Wang et al. indicated the effect of graphene in regulating the self-assembly of silica nanoparticles to achieve Janus co-assembly of ordered hcp packed microstructure [109]. According to Le Chatelier's principle, the added graphene oxide adjusted the droplet pH and suppressed the ionization of Si-OH on the surface of silica nanoparticles to reduce electrostatic repulsion and thus benefit assembly.

Collective properties of self-assembled structures

Self-assembled structures exhibit fascinating collective properties in optics and electromagnetic applications that arise from the



Fig. 5. (a) Natural photonic structure in butterfly wings (scale bars: left, 1 cm; right, 100 mm). (b), Artificial SC Janus superparticle assembled with silica nanoparticles, the yellow frame gives an amplifying image of the superparticle surface exhibiting a *hcp* packing mode. Scale bars: top, 100 µm, bottom, 1 µm. (c) Reflection microscope images of three kinds of anisotropic Janus SC particles assembled with increasing diameters of silica nanoparticles; Scale bars, 300 µm. (d) Normalized reflective peaks and reflection images of five different Janus SC superparticles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (a) Reproduced with permission. [110] Copyright 2010, Springer Nature. (d) Reproduced according to the terms of the CC-BY license. [109]

combined responses of electronic coupling, plasmon coupling, exciton coupling, and particle interactions. Because of the influences of particle spacing and disorder degree (i.e, configuration disorders and size inhomogeneity of nanoparticles), assemblies sometimes do not exhibit collective properties. In recent years, self-assembly technology has been widely applied to trigger the outstanding collective properties that originate from controllable spacing and a high-ordered degree of assembly. The following sections will discuss the effects of interparticle spacing and degree of order on the collective properties.

Collective optical properties

Research regarding collective optical properties is a popular field in nanoscience, including studies involving structure color (SC), localized surface plasmon resonance (LSPR), effective refractive index, skin depth, light polarization, and photoluminescence (PL).

Structure color

According to the interaction mechanism between light and periodic or quasiperiodic microstructures, natural colorful materials such as feathers, beetle shell and nacre provide inspiration for the manufacture of artificial SC materials (Fig. 5a) [109,110]. Unlike pigmentary coloration, the SCs are highly durable, characterized with metallic luster and opalescence that are of great aesthetic value. The ordered assembly superstructures with controllable component size, interparticle spacing and packing modes are potent candidate for SC materials with diverse applications. Droplet microfluidic self-assembly method has been extensively exploited to fabricate ordered photonic crystal superparticles that incorporating Fe₃O₄, silica (SiO₂) and polystyrene (PS) nanoparticles [111]. Eq. (1) According to the Bragg-Snell Law, the reflection peak position λ is proportional to the center-to-center distance of adjacent nanoparticles *d* and average refractive index n_{average} . It is feasible to reach desirable SCs (λ) by adjusting diameters of self-assembling nanoparticles (d). Fig. 5b–d exhibit the SCs changed from green to red by employing different diameters of the self-assembled silica nanoparticles in Janus SC superparticles. Zhuo et al. subsequently demonstrated that the assembled microspheres with purple, blue, green and yellow spot colors could be achieved by using the PS nanoparticles with particle size of 120 nm, 200 nm, 220 nm and 280 nm, respectively [106]. Avci et al. designed photonic crystals with SC properties by assembling ZIF-8 particles into millimetresized superstructures [112]. The assembled 3D photonic crystals also exhibited a particle size-related SC behavior, since the Bragg reflection red shifted with larger particle sizes. Fu et al. confirmed that the obtained SC structure could be used as a scaffold to generate a colored hydrogel by infusion gelatin together with subsequent removing of template to facilitate biomedical applications [113]. The varied *d* can be achieved by using building blocks with different sizes and adjusting the interparticle distance between uniform particles. Yin and coworkers produced magnetically tunable photonic crystals by changing the interparticle distance in the alignment of superparamagnetic Fe₃O₄ colloidal particles [114–116]. The SC behavior can be obtained by self-assembly of 1D photonic structures under the external magnetic field, which is driven by the balanced interaction of the induced magnetic attraction and electrostatic/solvation repulsive forces between magnetite particles. Electrical actuation of the lattice spacing has also been extensively studied by exploiting surface charged colloid particles or electrochemical driven swelling of the polymeric matrix, which effectively modulate the interparticle distance and ultimately realize dynamic tunable photonic crystals [117-119].

$$\lambda = 1.633 dn_{\text{average}} \tag{1}$$

Localized surface plasmon resonance

When the frequency of the incident light is equal to the collective oscillation frequency of the metal plasma, LSPR occurs to produce an intense absorption band in the range of the incident light. In general, LSPR is mainly related to particle dimension, size homogeneity, structural order degree, interparticle spacing, superstructure of particle arrangement, dielectric properties and filling density of structures. Pileni et al. studied the effect of silver (Ag) particle size and coordination environment on plasmon resonance through changes in the absorption spectrum [120], which were calculated based on Mie theory [121]. The formula for the absorbance (*A*) is as follows [122]:

$$A = CNl/2.303 \tag{2}$$

where C and N are the absorption cross-section and the number of particles per unit volume, respectively, and l is the optical pathlength.



Fig. 6. (a) Simulation of extinction spectra of superlattices with different degrees of polydispersity and a different mean size (top, 8.9 nm; middle, 19.8 mm; down, 39.1 nm), compared with the extinction curve (dashed lines) of the superlattice in solution. (b) Schematic diagram of different lattice planes for calculating the electric field. (c) Electric-field intensity plotted for the perfect superlattices and (d) an imperfect superlattice in which the particle polydispersity is 10% and the variation of the lattice site is 5%. The diameter of the spheres in the lattices is 40 nm, and the nearest-neighbor gap is 16.0 nm (25% Au). Scale bar is 100 nm. Reproduced with permission.[123] Copyright 2010, National Academy of Sciences of the United States of America

The decrease in particle size causes a reduction in the intensity and an increase in the peak width of the plasmon peak. Ross and coworkers used simulations to investigate the influence of size distribution on the optical properties of superlattices [123]. For smaller particles, the extinction intensity increased with polydispersity; for larger particles, broadening and red-shifting of the extinction peak were observed (Fig. 6a). Spheres with a small mean particle diameter behave in a quasistatic manner, resulting in an increased extinction intensity without alteration of LSPR location or breadth. In contrast, the nonquasistatic state in large mean diameter spheres, together with the greater extinction coefficients (compared with smaller spheres), increases the contribution of larger particles to collective extinction. In comparison with an ideally ordered lattice that has a uniform electric field distribution, the electric field intensity of the lattice with a more extensive size distribution has localized maximum and minimum values (Fig. 6b–d); thus, it is more challenging to reproduce the desired performance. Murray et al. found that self-assembly procedures have a "self-cleaning" function [124]; specifically, irregularly shaped NPs will be excluded from the superlattice during NP arrangement, thus facilitating the ability to attain a uniform size and shape of the basic structural unit constituting the superlattice. Compared with the traditional size precipitation method, the particle size distribution is smaller.

LSPR is greatly affected by the particle separation distance. Su and coworkers used the discrete dipole approximation to study the effect of spacing on near-field plasmon coupling between Au particles; they found that the plasmon resonance peak red-shifted with decreasing spacing [125]. In addition, the attenuation of the peak shift showed an exponential response as the particle spacing increased (Fig. 7a), consistent with the experimental results; this indicates the nature of the near-field plasmon coupling can be achieved by the electron tunneling generated in the particle gap, and the peak position offset is closely related to the gap size. Chen et al. reached a similar conclusion with respect to self-assembled Au superlattices by adjusting the ligand length to control the spacing, thereby precisely altering the extinction spectra of superlattices (Fig. 7b–d) [126].

In addition to particle size and spacing, the optical response also depends on the arrangement mode of nano self-assemblies. Zou studied the impact of positional disorder on the optical properties of superlattices by extending the discrete dipole approximation approach [127]; compared with an ideally aligned lattice, position disorder weakened the interactions between particles, resulting in a reduced peak intensity and blue shift. Murray et al. also demonstrated the red shift of SPR wavelengths, along with an increase in the local packing density of Au NCs in three binary NC superlattices (BNSLs) (Fig. 7e-f) [128]. The higher mean coordination number in the NaZn₁₃-packing mode was energetically favorable for near-field couplings; this led to lower energy resonance, compared with the resonances of the AlB₂ and CaCu₅ types. The arranged superstructure in the self-assemblies also change the dielectric constant of the environment, thereby affecting the position of the plasma peak. For isolated particles, an increase in the matrix environmental dielectric constant causes the plasmon peak to shift to a lower energy. As the self-organization changed from isolated Ag particles to 2D and then to 3D superlattices, the plasmon peak shifted to lower energy as the dielectric constant of the NP surroundings increased [120]. This shift could be ascribed to the change in the mean free path of the conduction electrons and the increasing filling volume fraction of self-assemblies that



Fig. 7. Influences of interparticle spacing and particle alignment. (a) Considering the short axes of 72-nm and 84-nm particles, the resonance peak shift decreases exponentially as the particle spacing increases. (b) The resonance peak position and the interparticle gap exhibit an exponential correlation; the inset shows the linear relationship between the interparticle gap and the thiolate chain length. (c) Field-emission-scanning electron microscopy images of Au nanoparticle (NP) superlattices (Au@C12, Au@C14, Au@C16, and Au@C18) with ligands of different lengths. The bottom is the length of 40 lattice periods (40a) of the NP superlattice. (d) Extinction spectra of superlattices with the same Au NP size but different ligand lengths (upper: C12; upper middle: C14; lower middle: C16; lower: C18). (e) Structural models of the corresponding projections of binary NP superlattices (BNSLs). (f) Normalized extinction spectra of Au anacrystals (NCs) in different packing densities in Au-Fe₃O₄ BNSLs (AlB₂: peak at 574 nm; CaCu₅: peak at 599 nm; NaZn₁₃: peak at 640 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (a) Reproduced with permission.[125] Copyright 2003, American Chemical Society. (b-d) Reproduced with permission.[126] Copyright 2008, American Chemical Society. (e-f)

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decrease the bandgap. Similarly, Lazarides et al. also found that the characteristics of the plasma peak also affected by the filling volume fraction of self-assemblies. They compared the absorption peaks of dispersed Au nanospheres and DNA-linked Au aggregates, in which red-shifting and broadening of the absorption peak in self-assemblies were obvious [129]. The aggregation-induced change in the plasmon peak of the Au colloid is a manifestation of the collective optical response, and the intensity of plasma peak increases with increasing volume fraction. Cheng and his research group proposed one-particle-thick 2D superlattices and termed "plasmene" nanosheets according to the naming rule of "graphene" [130–132]. The plasmene nanosheets exhibited plasmonic gap resonance and propagating nature of the excited plasmons. When investigating the nature of the propagating surface wave, they found that there was a metal-dielectric interface in which only vertically polarized plasmons were allowed to propagate.



Fig. 8. Influences of various factors on dielectric properties. (a) Real (bottom) and imaginary (bottom) effective refractive index changes with the particle filling rate tuned by interparticle spacing. (b) Real (bottom) and imaginary (top) longitudinal effective refractive index changes with the ellipsoidal NP aspect ratio. (c) Lattice arrangement of ellipsoid NPs and the corresponding three plane projections. Skin depth of the (d) longitudinal array and (e) transverse array with different volume fractions; the skin depth of the pure Ag metal is indicated by the gray line.

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Effective refractive index and skin depth

The self-assemblies will change the dielectric properties of materials [120], thereby affecting their optical properties, such as effective refractive index and skin depth [133,134]. Previous studies have found that the effective dielectric constant ε_{eff} in the aggregates is related to the particle filling volume fraction f [135,136]. The Maxwell-Garnett effective medium theory (EMT) describes the effect of the filling index in particle arrays as follows [137,138]:

$$\varepsilon_{eff} = \varepsilon_m \frac{\varepsilon(1+2f) + 2\varepsilon_m(1-f)}{\varepsilon(1-f) + \varepsilon_m(2+f)}$$
(3)

$$m = \sqrt{\varepsilon_{eff} \times \mu} \tag{4}$$

where ε_m is the dielectric constant of the substrate (e.g., silica [36]), ε is the dielectric constant of filled particles (e.g., Au NPs [37]). In Eq. (4), *m* refers to the complex refractive index, and μ is the permeability. Adjusting the interparticle spacing or particle size is the key to regulating the particle filling volume fraction in self-assemblies. However, affected by the arrangement structure, different crystals have limit densities. For example, the *f* of the *fcc* structured supercrystal is 0.74 [139], whereas the f of the AB₁₃ type binary superlattice is 0.69 [49]. Ross et al. plotted the effective refractive index of Au nanoparticle systems with different volume fractions simulated with EMT (Fig. 8a) [36]. The real part $(n_{\rm eff})$ of refractive index determines the phase velocity of light, and the imaginary part (k_{eff}) represents the absorption of the material. The imaginary effective refractive index was red-shifted with the increased Au volume fraction, revealing the weak dipole-dipole interactions. The $n_{\rm eff}$ exhibited a dispersive linear resonance corresponding to the maximum value of k_{eff} , and was much higher than the refractive index of water background when the volume fraction of Au was 20%.

For anisotropic particles, the aspect ratios of nanomaterials affect the packing density of the assembled structure in different planes, so as to realize the regulation of the dielectric constant. Ross et al. further demonstrated the effects of the particle filling rate, the aspect ratio of anisotropic NPs, and different array directions relative to incident light on the collective optical properties in an ordered

array [140]. The 3D superlattice exhibited distinct LSPR effects in different planes: ellipsoids oriented longitudinal to the incident field exhibited a strong LSPR related to the aspect ratio of ellipsoids, while a weaker LSPR was shown in transverse oriented ellipsoids. The above phenomenon is attributed to the difference in the projection of the superlattice on each plane. The lattice arrangement of the ellipsoid NP and the corresponding plane projection are shown in Fig. 8b. In direction 1 (left in Fig. 7b), the material response is independent of the aspect ratio of the ellipsoid; however, in directions 2 and 3 (middle and right in Fig. 8b), the response is polarization dependent. In the longitudinal oriented ellipsoids medium, the high aspect ratio increased the polarizability of Ag nanostructures, and the negative well of real parts of the effective dielectric function $(\text{Re}\{\varepsilon_{eff}\})$ deepened (Fig. 8c). In contrast, the polarizability of the ellipsoid in the transverse direction was significantly reduced, and the Re{ ε_{eff} } was minimally dispersive (Fig. 8d). The Ag ellipsoidal superlattice also showed tunable skin depths. For the longitudinally oriented ellipsoid medium, the imaginary parts of the effective dielectric function (Im{ ε_{eff} }) was greatest when the ellipsoids were on resonance, and the skin depths was close to 10² nm. The skin depths was $\sim 10^6$ nm when ellipsoids were off-resonance. The peak position of $Im\{\varepsilon_{eff}\}$ varied with the aspect ratio of the ellipsoids, and the optical performance of superlattice throughout the UV-visible-NIR could be divided into two states: transparent or optically thick. (Fig. 8e). Conversely, for transverse-oriented ellipsoids, the skin depths were high ($\sim 10^5 - 10^7$ nm) and the material could be considered transparent throughout the vis-NIR (Fig. 8f).

Anisotropy and polarization phenomena

The formation of anisotropically arranged structures in the selfassembly can lead to light polarization [141]. Quinten et al. calculated the light guiding ability of a linear chain of spherical Ag NPs; transmission in the direction parallel to the chain axis was enhanced, compared with transmission perpendicular to the chain alignment [142]. In that study, the strong polarization dependence of the transmission was attributed to the localized near-field intensity of the particles. Wang et al. reported the 3D assembly of needle-like



Fig. 9. (a) i) Illustration of the steps for synthesis of needle-like superparticles (SPs). ii) Diagram of the lateral alignment of SPs into a unidirectional line type on a solid substrate. iii) In the context of an excitation wavelength of 380 nm, the graph shows the relationship between photoluminescence (PL) intensity and manually rotated polarization angle. (b) i-ii) Plasmon peak shifts ($\Delta\lambda$) of two differently shaped particles at 0° and 90° polarization field (bottom: spherical particles; top: octahedral particles) when varying the particle spacing from 20 nm to 70 nm. Backscattering spectra show the difference in peak shift between spherical particles (top) and octahedral particles (bottom) with a particle spacing of 20 nm. iii-iv) Backscattering spectra of octahedral aggregates assembled in random (top) and aligned (bottom) patterns at 0° and 90° polarization field. (c) Plasmon coupling of 10-nm-radius Ag spherical dimers with a decreasing interparticle gap (from darkest to brightest curves: 50, 40, 30, 20, 10, 5, 4, 3, 2, and 1 nm) in the light polarized field, along and across the dimer axis; scale bar, 10 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (a) Reproduced with permission.[143] Copyright 2012, American Association for the Advancement of Science (AAAS). (b) Reproduced with permission.[145] Copyright 2017, American Chemical Society. (c) Reproduced with permission.[146] Copyright 2016, American Chemical Society

SPs consisting of two steps: nanorod micelle formation and the formation of needle-like SPs [143,144]. SPs can form unidirectional line patterns through a patterned template and tend to exhibit intense PL polarization (Fig. 9a).

Sun et al. prepared superlattices composed of anisotropic octahedral and isotropic spherical NPs under a DNA-programmable assembly; they found that the polarization-dependent peak-shift increased with decreasing interparticle spacing in the superlattices (Fig. 9b(i-ii)) [145]. When changing the polarization direction from alignment with the assembly axis to crossing the assembly axis, the backscattering spectra of a spherical particle assembly showed a blue shift of the peak leading to a negative $\Delta\lambda$ value ($\Delta\lambda = \lambda_{max}^{90} - \lambda_{max}^{0}$), whereas the superlattice composed of octahedral particles exhibited a positive $\Delta\lambda$ value. The different $\Delta\lambda$ value is attributed to the difference in polarization characteristics between octahedral particles and spherical particles (Fig. 9b(iii-iv)). For octahedral particles, tip-to-tip coupling along 90° is stronger than edge-to-edge coupling along 0° due to the smaller interparticle spacing. The bcc superlattice assembled by spherical particles showed a blue shift because of the differences in lattice sums for the two polarization directions. The polarization correlation disappeared for random orientations. Therefore, self-assemblies can effectively affect the polarization of the material by controlling the particle spacing and arrangement. The above phenomenon can be further demonstrated by a simplified dimer system to indicate the importance of particle arrangement for polarization applications [146]. When the incident field is applied along the axis (Fig. 9c(i,iii,v)) (in which the dipoles of particles are additive), a strong electromagnetic field arises in the gap because of the constructive interference between additive dipoles. Otherwise, the dipoles interfere destructively, thus weakening the electric field intensity in the gap when the incident field is vertical (Fig. 9c (iii,iv,vi)). Both constructive and destructive interferences can be adjusted by varying the gap distance in this instance, leading to different optical shifts. When the light illuminates along the array direction, the coupling effect increases as the particle spacing decreases, accompanied by a red-shift of the excitation peak and higher excitation efficiency. When the light illuminates perpendicular to the array direction, the excitation peak blue shifts and the excitation efficiency decreases as the particle spacing decreases.

Circularly polarized luminescence (CPL) occurs because of the superposition of two plane polarized waves of equal amplitude, which are perpendicular to each other in vibration direction. A chiral material can be stimulated to emit left-handed or right-handed CPL [147,148]. Recently, the assembled superstructures with circular dichroism have been confirmed to exhibit collective CPL characteristics, which have attracted increasing attention due to their specified properties and resultant wide applications [149-152]. Huo et al. assembled QDs on chiral host nanotubes to transfer their chiralities to achiral guest QDs, thus preparing an ordered structure with CPL [153]. The electrostatic and hydrogen-bonding interactions between the mercaptoalkyl acid ligands of QDs and amine groups hanging on the chiral nanotube were the driving force required for chiral architecture assembly. The well-ordered alignment of QDs along the chiral nanotube was critical for achievement of CPL; in contrast, the disassembled homologue induced strong emission (without CPL) under ultraviolet light irradiation (Fig. 10a). In addition, adjusting the conduction distance by changing the length of the mercaptoalkyl acid ligand on the OD is another important parameter to control the properties of the component CPL (Fig. 10b). Chiral conduction could only be achieved with short-chain ligands (C3 ligands). For ligands with longer alkane chains (C12 ligands), the chiral conduction was offset by the disorder of the alkyl chain.

Photoluminescence properties

The self-assembly structure leads to changes in PL properties, mainly from two aspects: exciton coupling and plasmon-exciton interactions. The exciton coupling can be described in terms of the Förster resonance energy transfer (FRET), which occurs in donor-acceptor (D–A) pairs separated by 2–10 nm. The FRET efficiency (*E*) is determined as follows [154]:

$$E = \frac{nR_0^8}{nR_0^6 + r^6}$$
(5)

where R_0 is the Förster distance, n is the mean number of acceptors interacting with one donor, and r is the separation distance of the D–A pair. FRET is the non-radioactive energy transfer between adjacent D–A pairs. As the D–A spacing decreases, the FRET efficiency increases, which leads to a shortened PL lifetime and red-shifting of the PL peak in the spectra. Compared with monodispersed NPs, the self-assembled structure has a smaller, more constant r and a limited particle size distribution, which leads to greater FRET efficiency and a narrower PL peak [155–157]. Luo et al. synthesized *fcc* CdSSe QDs SPs with preserved surface structure through thermally controlled emulsion-based selfassembly [158]. The importance of interparticle spacing for the collective PL properties was investigated by surveying the optical properties



Fig. 10. (a) A comparison of circularly polarized luminescence (CPL) spectra of quantum dots (QDs) assembled on chiral gel and unassembled QDs. (b) CPL spectra comparison of co-assembled materials with capping agents of different lengths. Reproduced with permission.[153] Copyright 2017, Wiley-VCH

of ordered SPs, random SPs, and ordered arrays, in which the mean interparticle distance successively increased. Supercompact SPs with well-defined crystallized domains can be created by compressing the QDs to sub-nanometer spacing via prostrating ligand conformation during thermal evaporation in the emulsion. The ordered SPs exhibited weaker intensity, red-shifted PL peaks, and shorter exciton lifetimes than did random SPs, because of the smaller interparticle spacing compared with disordered and ordered SP arrays (Fig. 11a). Recently, Baranov et al. found that CsPbBr₃ NC superlattices exhibited a greater PL red shift than did NCs in dilute solution and re-dissolved superlattices (Fig. 11b) [157]. To analyze the elements' contributions to the red shift, self-assembly on a tilted silicon wafer was adopted to obtain superlattices with various packing densities. Notably, the PL redshift occurred with the increased packing density of the superlattice. In addition, the author also found that as the packing density increases, the assembly exhibited stronger photoluminescence and light absorption.

The plasmon-exciton interaction will cause a wavelength shift of the PL emission [159], weakened PL, and a shortened PL lifetime [160]. The relationships of energy transfer with particle spacing and arrangement have also been studied in theory [161]. The plasmon resonance amplifies the electric field to transfer energy to the semiconductor, thereby inducing increased emission; otherwise, the emission decreases. In general, there is a consensus on the experimental data and calculated results relating to the energy transfer times according to the previously reported literature (Fig. 12b) [161,162]. The energy transfer rate largely depends on the interparticle spacing and lattice structure, such that the energy transfer time increases with the interparticle spacing. The energy transfer time also tends to vary with the number of coordination particles. Govorov *et al.* used a modified rate model to calculate the energy transfer time of structures with different Au particle coordination numbers under varying laser wavelengths [161] (Fig. 12a). They

found that under the same wavelength of laser, the greater the coordination number, the shorter the energy transfer time (Fig. 12c).

Gueroui and colleagues measured the intensity distribution of individual QDs and QDs-dsDNA-Au complexes to measure the quenching and charge transfer efficiency. They found that the plasma-exciton interaction in the Au-QD system obeyed a FRET-analogous behavior, and the associated energy transfer was inversely proportional to the sixth power of the distance [162]. Shevchenko et al. constructed self-assembled binary superlattices of CdSe QDs and Au NPs, and investigated the influence of the plasma-exciton interaction on PL properties [160]. Fig. 12d-e show that strong extinction and PL lifetime reduction occurred with the injection of Au NPs into the assembly, suggesting energy transfer from the CdSe QDs to the Au NPs.

Collective electronic and photoelectronic properties

Generally, the collective electrical and photoelectronic properties of superlattices are achieved through enhanced coupling and electron transfer between adjacent particles, which are always isolated by ligand molecules. Quantum mechanical coupling between the energy levels can be written in terms of coupling energy $h\Gamma$, where *h* is Planck's constant and Γ is the tunneling rate between two orbitals of adjacent NCs. NCs comprising metals or semiconductors use two electron transport mechanisms that are determined by the relationship between the thermal energy $k_{\rm B}T$ and coupling energy $h\Gamma$. When $h\Gamma \ll k_{\rm B}T$, the coupling mechanism is weak, such that wavefunctions are mostly localized at the particles. Consequently, the electronic transmission proceeds as sequential tunneling between points. Strong coupling occurs when $h\Gamma \ge k_{\rm B}T$, such that coherent wavefunctions expand throughout the NC to form a band of width $h\Gamma$ in the superlattices. The self-assembly technology enables the possibility of regulating electron transport



Fig. 11. (a) i) Different packing modes of QD assemblies with increasing interparticle distance and optical properties resulting from distinct electronic energy transfer events. ii) The PL lifetime of ordered SPs with the smallest interparticle spacing is significantly reduced, compared with the PL lifetimes of random SPs and ordered arrays. iii) Significant changes are evident in the PL peak and intensity of ordered SPs, disordered SPs, and the ordered array(b) i) The PL peak position of the superlattice solid material (red solid, right) shows a significant red shift, compared with monodispersed CsPbBr3 NCs (green solid, left) and re-dissolved superlattices (green dash, left). ii) The Emission wavelength of CsPbBr3 NCs in toluene and CsPbBr3 SLs on Si. iii) Schematic diagram of the preparation of various density superlattices and their optical images; iv) normalized PL spectra of superlattice solid material in different islands with increasing packing thickness, revealing an obvious red shift; and v) the self-absorption effect of materials with different n values in which solid lines are PL spectra and dotted lines are transmittance spectra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) Reproduced with permission.[157] Copyright 2019, American Chemical Society

by adjusting the interparticle spacing and packing structure to produce collective properties in both weak and strong coupling mechanisms. In this section, we outline the impacts of spacing and ordered structure on the collective properties, with respect to theoretical studies and experimental works. Weak electronic coupling mechanism and collective electronic tunneling

The self-assembled superstructures with adjustable spacings and various packing modes show collective electronic tunneling properties. In theory, electron tunneling between particles can generally be classified into two types: metal-insulator-metal junctions and



Fig. 12. (a) The scheme of different Au coordination conditions (Coordination numbers are 1, 2, 4, 6, respectively). (b) Comparison of literature data (blue symbols) with calculation results (red curve). (c) Energy transfer time of a CdSe NP with several Au particles in coordination. (d) Time-resolved fluorescence transients of a CdSe superlattice and a BNSL composed of CdSe and Au NCs. (e) Time-integrated fluorescence spectra of the CdSe superlattice, Au superlattice, BNSL composed of CdSe and Au NCs, and Si substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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metal-molecule-metal junctions. Amir Zabet-Khosousi et al. established a two-electrode model to investigate the electronic behavior between two nanoparticles, and confirmed that particle spacing plays a crucial role in electronic tunneling [163]. A tunneling junction model is shown in Fig. 13a. The tunneling rate in metal-insulator-metal junctions is determined as follows:

$$I = \frac{4\pi e}{\hbar} \int_0^{+\infty} \rho(E) \rho(E + eV_b) |T(E)|^2 [f(E) - f(E + eV_b)] dE$$
(6)

where ρ is the density of states of the electrodes, f(E) represents the possibility of discovering a full energy state in a metal electrode at energy E. $|T(E)|^2$ is the tunneling transmission possibility at energy E, and the calculation formula is as follows:

$$|I|^2 \approx e^{-2\kappa L},\tag{7}$$

where κ is the decay constant. Notably, $|T(E)|^2$ decreases exponentially with *L*, which is the barrier spacing between electrodes.

The tunneling rate in metal-molecule-metal junctions is described as a "superexchange" model that is based on charge transfer in a donor-bridge-acceptor system reported by McConnell [164]. The expression for the charge transfer rate k_{CT} is as follows [165]:

$$\kappa_{CT} \approx \exp(-\beta' r_{DA}),\tag{8}$$

where r_{DA} is the spacing between the acceptor and the donor, while β' is a parameter related to bridge length and energy.

The above theories are applicable to explain the electron tunneling effect between particles in the self-assemblies, and spacing is an important indicator for determining charge transfer rate, whether in metal-insulator-metal junctions or metal-molecule-metal junctions. Electron tunneling is the primary mechanism in alkanethiol self-assembled films [166]. Murray et al. studied the electronic conductivity of Au NP assemblies capped by alkanethiols of varying chain length in an attempt to establish a functional relationship between chain length and electron transfer. The conductivity possessed an exponential correlation with the chain length of alkanethiols. As the chain length increased, the conductivity decreased exponentially [167].



Fig. 13. Energy diagrams of a tunnel junction when applied to a. i) zero-bias voltage ($V_b = 0$) and ii) positive bias voltage ($V_b = 0$) between two electrodes. (b) Plot of the relationship between the logarithm of conductivity and the number of non-conjugated bonds in the connected molecule. (c)The current–voltage curves for (i) isolated Ag NPs, (ii) a two-dimensional (2D) lattice, and (iii) the 3D face-centered cubic (*fcc*) supercrystal of Ag NPs on an Au (111) substrate. (d) Conductivity of monoclinic (green, square) and triclinic (red, circle) single crystals assembled with two types of Au₂₁ NPs. (e) Schematic diagram of the height difference in tunneling barriers (shown as white solid squares) derived from interacting π - π pairs in ligands with different configurations, thereby changing the electronic conductivity for the two Au₂₁ NP supercrystals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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The influence of the assembly modes on electron tunneling has also been studied. When the electron undergoes point-to-point sequence tunneling, it charges the NPs, which require energy supplied with a large external bias voltage or high temperature to overcome the additional energy caused by the Coulomb repulsion between incoming electrons and existing electrons. Without this, Coulomb blocking will occur [168]. Pileni et al. also proved that a strong relationship has been established between the assembled structure and the collective electron tunneling properties, when investigating the electronic properties of Ag NPs undergoing different deposition processes on an Au substrate [169]. The current-voltage curves of the three deposited modes of Ag NPs are shown in Fig. 13c. The isolated NPs exhibited Coulomb blockade behavior (Fig. 13c(i)). When the NPs organized as an ordered 2D film, the tunneling current exhibited both metallic and Coulomb contributions, indicating that lateral tunneling between adjacent particles significantly contributed to the total electronic transport (Fig. 12c(ii)). Furthermore, the assembled 3D *fcc* supercrystal displayed linear ohmic characteristics and an almost flat dl/dV curve, compared with the isolated NP and 2D lattice (Fig. 13c(iii)). This behavior originated from enhanced dipole-dipole interactions along the vertical axis of the 3D assembly, which contributed to an enhanced tunneling effect. Wessels and coworkers found that an exponential decay function related the conductivity of assemblies of Au NPs and the number of non-conjugated bonds in

the linker molecules (Fig. 13b) [170]. The effect of alkyl chain length on electronic conductivity of monolayer-protected Au clusters can be described as follows [171]:

$$\sigma_{EL}(n, T) = \sigma_0 \exp[-n\beta_n] \exp[-E_A/RT], \qquad (9)$$

where *n* is the length of the ligands, β_n is the electronic coupling term corresponding to the length of the ligand, and E_A is the activation energy of conductivity (kJ/mol).

Wold and coworkers discovered that the junction resistance R has an exponential relationship with the electrode spacing [172], which is proportional to the length of alkanethiols between metal nanoparticles. The resistance is determined as follows:

$$R = R_0 \exp(\beta s),\tag{10}$$

where R_0 is the effective contact resistance, *s* is the length of the junction, and β is a measure of the transport efficiency related to structure, considering 1/length as the unit.

Parthasarathy et al. investigated the influences of structural factors on electronic transport in Au NC assemblies [173]. The voltage threshold of the ordered superlattice increased linearly with the array length, in contrast to the voltage threshold observed in disordered monolayers. Recently, Jin et al. achieved a hierarchical fibrous assembly of Au₂₁ NPs by precisely adjusting the site-specific surface hooks at the atomic scale. They found that counterions (such as [AgCl₂]⁻ and Cl⁻) could modulate the assembly of Au₂₁ NPs, and the electrical conductivity of monoclinic [Au₂₁(SR)₁₂(PCP)₂]⁺[Cl]⁻ supercrystals was approximately two orders of magnitude greater conductivity than the electrical of triclinic [Au₂₁(SR)₁₂(PCP)₂]⁺[AgCl₂]⁻ supercrystals, regardless of similar interparticle spacings (16.80 and 16.39 Å) [25]. The parallel-displaced π-stacking arrangement of ligands in the monoclinic [Au₂₁(SR)₁₂(PCP)₂]⁺[Cl]⁻ supercrystals could reduce tunneling barriers, facilitating electron conductance (Fig. 13d,e).

Strong electronic coupling mechanism and related collective properties

The two most common physical phenomena in strong coupling systems are the Mott insulator-metal transition (MIT) and the Anderson metal-insulator transition, both of which are influenced by the interparticle spacing and degree of order. Currently, research concerning strong coupling materials has focused mainly on metal chalcogenide QDs. Compared with bulk materials prepared by traditional methods, a QD artificial solid with programmed interparticle spacing and assembled modes can achieve band-like transmission, exhibiting enhanced conductivity and collective electronic properties that validate the mechanisms of MIT and Anderson metal-insulator transition. The MIT depends on the separation between NPs [174-176]. With decreasing distance between the surfaces of adjacent metallic spheres δ , wavefunction overlap increases. With further reduction in δ , the conduction gap caused by charging energy ($\varepsilon_e = e^2/C$) disappears, while the energy band generated by the overlap between NP wavefunctions promotes band-like transport and the MIT (Fig. 14a) [177].

The ease with which the electron moves from a particular position to a neighboring position is determined by the intensity of the transfer integral β . Markovich et al. revealed an MIT by tuning the interdot spacing by compression of a Langmuir monolayer of Ag QDs [177]. The QD solid underwent MIT when D/2r decreased from 1.3 to 1.1, and carried out inductive transport when D/2r approached 1.1, where *D* is the spacing between the centers of the QDs, and *r* is the radius of the QD. Remacle et al. discussed the influence of interdot spacing and the size fluctuation of particles on β , which is governed by the overlap of the wavefunction of neighboring particles (Fig. 14b) [178]. β decreases exponentially with an expanding lattice. $\Delta \alpha$ represents the fluctuation in orbital energy due to the size fluctuation ($\Delta R/R$). Eq. (9) describes the fluctuation in the transfer integral $\Delta \beta$

(indicated by the red line in Fig. 14d); it is influenced by the packing disorder $\Delta D/D$ and size fluctuation $\Delta R/R$, as follows:

$$\Delta\beta = \beta (D/2RL)[(\Delta D/D) + (\Delta R/R)]$$
(11)

The electronic state can be changed by adjusting the degree of disorder and coupling of the material. Fig. 14c displays a quantum phase diagram showing localized and delocalized electronic states in the 2D superlattice. The diagram is shown with fluctuations in the site energy disorder ($\Delta \alpha$), which is derived from fluctuations are related to coupling strength [178,179]. In a periodically arranged artificial crystal, the wavefunction of electrons extends throughout the crystal; however, the disorder destroys the lattice period, resulting in electron localization. Anderson found that the envelope of the wavefunction decays exponentially with increasing distance *r* when the disorder is sufficiently strong [180]. The relationship is determined as follows:

$$|\psi(r)| \propto \exp(-|r - r_0|/\zeta) \tag{12}$$

where r_0 is the center of the localized state and $_{\zeta}$ is the localization state.

The Anderson metal-insulator transition is determined by the comparison of coupling energy $h\Gamma$ and site energy dispersion $\Delta E_{\rm S}$. Disorder in the assembly can increase the site energy dispersion. When $\Delta E_{\rm S} > h\Gamma$, the strong coupling system divides into small, isolated zones where strong coupling remains. When $\Delta E_{\rm S} < h\Gamma$, the wavefunctions of the electrons remain in an extended state. Using a Pariser-Parr-People-type Hamiltonian, Remacle *et al.* studied the factors of electronic properties of QD assemblies by means of computation [181]. The array behaved as a Mott insulator at D/2r > 1.5. The electronic coupling was further strengthened with reduced distance. An Anderson-like transition was found from delocalization to positioning change at D/2r = 1.3, where *D* is the spacing between dots centers, and *r* is the average radius of dots.

Compared with traditional methods, self-assembly technology can create closely packed superlattices to compress the distance between points in QD solids. Murray et al. created an energy diagram of the QD superlattice (Fig. 14d) and found that as the interdot spacing decrease such that the wavefunctions of adjacent QDs overlap, they undergo a transition from a discrete electronic state to an extended electronic state (Fig. 14e) [182]. The electronic states split to form energy bands (Fig. 14f, left) because of the Pauli exclusion principle if the interdot spacing decreases further. Conversely, a regression to electron and hole states occur when individual QDs are present in uncoupled states with a large intervening distance (Fig. 14f, right). Fig. 14h simulates the real model with inhomogeneous dots distribution. Disordered QD organization leads to a distribution of barrier width and height among dots, which broadens the distribution of electronic states; additionally, higher coupling is required to bind these energy states together. Fig. 14g indicates the density of states in uncoupled QD solids (right) and coupled QD solids (left). The bandwidth of the electron and hole states increases for strongly coupled states because of their interaction. In addition, the disordered organization of QDs lead to Anderson localization. The reduction of the assembly distance produces an extended electronic state to make E_0 approach E_f , which effectively reduces the mobility gap and facilitates the band-like transmission [183].

Overall, self-assembly is a promising strategy to reduce the undesired positional disorder in materials, because the assembled procedures are always accompanied by self-purification and concentration in size distribution, especially during superlattice or SP formation requiring high uniformity. With the aid of self-assembly, the collective properties of enhanced band-like electron transport can be achieved [184–186]. Furthermore, the binary self-assembly method can involve combination of different materials to enhance conductivity. Murray *et al.* incorporated PbTe and p-type dopant



Fig. 14. (a) Illustration of the impact of interdot spacing on the metal-insulator transition of the QD superlattice. (b) Influence of position fluctuation and stacking disorder with varying interparticle spacing on the transfer integral β , charging energy *I*, cross capacitance γ , and energy of valence electron orbit *a*. (c) Phase diagram with coupling strength and disorder as independent variables with respect to the electronic state. (d) Schematic diagram of QD solids with reduced spacing. (e) Electronic states that gradually expand as the spacing decreases. (f) Degraded electronic state under large interparticle spacing (right); enhanced coupling (blue shadow) and splitting of extended electronic state (blue shadow) caused by short interparticle spacing (left). (g) Mid-gap trap state and energy distribution of QD solids in an uncoupled electronic state (left) and an enhanced coupling electronic state (left). (h) Effects of energy disorder and position disorder in an uncoupled electronic state (right) and an enhanced coupling state (left) for QD solids. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (a) Reproduced with permission.[177] Copyright 1999, American Chemical Society. (b) Reproduced with permission.[178] Copyright 2001, Wiley-VCH. (c) Reproduced with permission.[179] Copyright 2012, American Vacuum Society. (d-h) Reproduced with permission.[182] Copyright 2015, Springer Nature

 Ag_2Te into a BNSL through co-crystallization, which dramatically increased the conductivity of the material by nearly 100-fold, compared with the monocomponent assembly [187]. In subsequent research, Murray *et al.* further demonstrated manipulation of the conductivity over six orders of magnitude by doping with Au or Au/ Ag NCs at sizes similar to the host size [188].

Contact electrification (CE) and Wang transition

Contact electrification (CE) occurs when the distance between the two materials is shorter than bonding length. For self-assemblies, the building blocks are often not densely arranged due to the hindrance of surface ligands. However, in recent years, with the emergence of research work based on self-assembly under high pressure and removal of surface ligands in assembled particles, the CE phenomenon between particles cannot be ignored. CE can occur in all phases and is a basic phenomenon widely present in various interfaces, including solid-solid, solid-liquid, solid-gas, liquid-liquid, liquid-gas and gas-gas interfaces [189–191].

The mechanism of CE has been controversial in the past few centuries. Recently, Prof. Zhong-Lin Wang proposed for the first time that the CE between metal and dielectric could be perfectly described by using the Fermi level model and the surface state model [192,193]. CE will occur when the two materials are approaching to each other until the distance is less than the bonding length, that is, in the repulsive force region between adjacent atoms (Fig. 15a). The ultra-close distance between atoms under mechanical stress maximizes the overlapping of electron clouds, which weakens the potential barrier and allows electron transition from one atom to another, accompanied by the emission of photons (Fig. 15b) [194]. This electron transition model is also known as Wang Transition for CE. Wang Transition provides theoretical basis for studying supertightly packed superlattices, and the contact electrification induced

interface spectroscopy (CEIIS) can be used as an intuitive detection method to study the CE in superlattices.

Photoelectronic Properties

Additionally, self-assembly shows great promise for new photoelectronic device development. Modeling NCs through tight binding Hamiltonian and Monte Carlo simulation, Yang and co-workers drew the variation charts of fractal dimensions at the band center $(d_2(E = 0))$ according to energy disorder s/t_0 and positional disorder κg for different semiconductor NC superlattices, as shown in Fig. 16a-g [195]. The black line divides the chart into delocalized and localized states in the bottom left and top right corners, respectively. Thus, both energy and position disorders contribute to electron localization in different assembly structures. Furthermore, the relationships among critical energy disorder, critical location disorder, material structure dimension and coordination number were investigated (Fig. 16h). The solid line is a structure with a regular arrangement, and the dotted line is a random arrangement. They found that the disorder threshold of the 3D structure is higher than that of the 2D structure; the threshold of both 2D and 3D superlattices increases with the enhancing coordination number; the threshold of ordered superstructure is higher than that of disordered structure.

The efficiencies of photoelectronic devices are limited because of the prevent absorption of photons with sub-gap energies and attenuation of carriers excited by high-energy photons. However, sizecontrolled QD superlattices (QDSLs) can overcome these limitations. As described in Section 3.1, the compact arrangement in superlattices can enhance light absorption, compared with discrete NPs. Specifically, it causes a red-shift of the absorption spectrum and increased overlap with the light spectrum, thereby increasing the possibility of multiple exciton generation (MEG) and enhanced efficiency with regard to photoelectronic devices. Chang et al. performed a simulation study of MEG in Si QDSLs, which showed that the acceleration for 3D QDSL was



Fig. 15. (a) Interatomic potential between two adjacent atoms: little electron cloud overlapping occurs when the two atoms in attractive force region (left); strong electron cloud overlapping occurs when two atoms approach each other in the repulsive force region (right). (b) The corresponding 3D atomic potential energy model of two atoms. The strong overlap of electron clouds between two approaching atoms will lower the potential barrier between the atoms, and the electrons will be transferred from one atom to another, possibly accompanied by the emission of photons. This theory is called the Wang Transition. Reproduced with permission.[189] Copyright 2020, Wiley-VCH. Reproduced with permission.[190] Copyright 2021, IOP Publishing

1.9-fold greater than the acceleration of discrete particles (Fig. 17a(ii)) [196]. Dynamic electron-phonon coupling and a static density of states are both responsible for this enhancement through quantum resonance in the hyperstructured QDSL via manipulation of the interior nanospaces (A, B) (Fig. 17a). The 3D, 2D, and 1D QDSL, as well as an isolated QD, could be transformed by adjusting the A and B values. When A became small and *B* was large enough, the 3D structure changed to 2D structure. Conversely, when A was large enough and *B* became small, the 3D structure became 1D structure. The 3D structure transformed to 0D structure when both A and B became large enough. The effective charge separation in the SL suppressed the carrier Auger recombination and further improved MEG efficiency. When particles in the superlattice were positioned closer to each other, the enhanced quantum resonance promoted continuous density of states in the QDSL; thus, MEG was more likely to occur. Luo et al. fabricated compact and ordered QD SPs with 0.3-nm interparticle spacing through the emulsionbased bottom-up self-assembly, and realized band-like transport (Fig. 17b) [158]. Compared with random SPs and ordered arrays, the charge transfer ability was more obvious in ordered QD SPs. The ordered SPs exhibited collective photoelectric activity, and the surface photovoltaic signal of SPs was 8.5 times that of the loose self-assembled structure. The photoelectric activity of SPs was further verified

by photocatalytic degradation of Rhodamine B (RhB), and approximately 57% of RhB was degraded in 30 min by using ordered SPs, significantly better than random SPs (12%) and ordered arrays (6%).

Collective magnetic properties

Magnetic nanoparticles can self-assemble into ordered manner under the drive of ligands interactions or magnetic interparticle interactions, giving birth to new collective characteristics [197]. The associated collective magnetic properties are closely related to the supracrystalline structure, particle spacing and the order degree of the NPs [86,198,199], and are significantly different from disordered NPs [200,201].

Increase in barrier energy and blocking temperature

Compared with disordered assemblies, the zero field cooled (ZFC) peak is narrower for the ordered assemblies (Fig. 18a) [202], whereas the peak width of the ZFC curve is positively correlated with the distribution of the potential barrier E_b that involves anisotropic energy (E_a) and dipole-dipole interaction energy (E_{dd}) [52]. The anisotropy energy is determined as follows:



Fig. 16. Contour maps of the fractal dimension $d_2(E)$ at the band center $[d_2(E = 0)]$ with changing disorder of the onsite energy s/t_0 and disorder of position κg in different lattice structures that exhibit variation in the number of the most adjacent neighbors N: (a) sc = simple cubic lattice, (b) bcc = body-centered cubic lattice, (c) fcc = face-centered cubic lattice, (d) rcp = random close packing, (e) 2D honeycomb lattice, (f) 2D square lattice, and (g) 2D hexagonal lattice. N of rcp is evaluated by a cumulative pair distribution function. (h) Thresholds for the different number of nearest neighbors with disorder at g = 0 and s = 0. Reproduced with permission.[195] Copyright 2015, American Chemical Society

$$E_a = KV \tag{13}$$

where *K* is the anisotropy constant and *V* is the NP volume. Importantly, E_a does not influence E_b when using the same batch of NPs to prepare the ordered and disordered assemblies, considering the presence of constant magnetic anisotropy and identical NP size distributions. If different batches of NPs are used, the batch with a narrower size distribution exhibits a narrower peak on the ZFC curve [203]. The value of E_{dd} is partly related to the particle spacing, which has been confirmed by multiple models [204,205]. When the distance between two single domain magnetic particles is moderate, the energy barrier formula is as follows [205]:

$$E_{dd} = \frac{m_1 \cdot m_2 - 3(m_1 \cdot r)(m_2 \cdot r)}{4\pi\mu_0 r^3}$$
(14)

where *m* is the magnetic moment and \hat{r} is the unit vector of particle spacing. Furthermore, E_{dd} is inversely proportional to r^3 . *m* and \hat{r} are vector units; thus, the dipole interaction of assembled NPs is sensitive to the detailed geometric arrangement of NPs. The ordered assemblies have narrower particle spacing and more regular periodic arrangement, leading to a narrower distribution of E_{dd} . Without the variation in E_a , the effect of self-assembly on E_{dd} is the main cause of a narrow E_b distribution and ZFC peak.



Fig. 17. (a). i) Schematic diagram of 3D, 2D, and 1D Si₂₉H₂₄ QDSL, as well as an isolated Si₂₉H₂₄ QD. ii) Time-dependent double exciton populations created by multiple exciton excitations in 3D, 2D, and 1D QDSL, as well as an isolated QD. (b), simulated electric field distribution in i) ordered SPs, ii) random SPs, and iii) ordered arrays. iv) Schematic diagram of light degradation mechanism using Rhodamine B (RhB) with order SPs. v) Surface photovoltaic responses of the three materials; ordered SP (red) exhibits a stronger surface photovoltaic signal intensity, compared with the random SP (blue) and the ordered array with large spacing (black). vi) Computed relative transfer efficiency of the excited QD to the adjacent QD, in terms of the distance between particles in ordered SPs, random SPs, and ordered arrays. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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Dipole-dipole interactions also lead to an increased blocking temperature (T_B). The Vogel-Fulcher model is commonly used to describe the assembly of interacting NPs, as well as T_B :

$$\ln\left(\frac{\tau_{\rm m}}{\tau_0}\right) = \frac{E_{\rm a}}{k_{\rm B}(T_{\rm B} - T_{\rm int})} \Leftrightarrow T_{\rm B}$$
$$= (1/\ln\left(\frac{\tau_{\rm m}}{\tau_0}\right))\frac{E_{\rm a}}{k_{\rm B}} + T_{\rm int} = T_{\rm b_0} + T_{\rm int}$$
(15)

$$T_{\rm int} = \frac{A}{r^3} \tag{16}$$

where $k_{\rm B}$ is the Boltzmann's constant, $\tau_{\rm m}$ is the time scale of the measurement, $\tau_0 \sim (10^{-9} \text{ to } 10^{-11} \text{ s})$, $T_{\rm b_0}$ is the blocking temperature when there is almost no dipole interaction among NPs, $T_{\rm int}$ is the increase in the blocking temperature caused by the dipole interaction, and *A* is a constant.

Fleutot et al. used LB technology to synthesize a uniform highdensity 2D Fe₃O₄ array. Fig. 18b fits the data according to Eq. (16). As the particle distance decreased, the dipole-dipole energy increased, leading to the increased blocking temperature [206]. In addition to the dipole-dipole energy, the blocking temperature is also affected by changes in the magnetic anisotropy barrier. Farrell et al. studied the effect of particle size on the blocking temperature in 2D Fe₃O₄ arrays; they found that a larger particle size could contribute to higher blocking temperature [207]. According to Eqs. (13) and (15), a larger particle size increased the magnetic anisotropy barrier energy, thereby increasing the blocking temperature. Moreover, the assembled 2D arrays had a specific shape anisotropy, the blocking temperature of the assembled monolayer and multilayer was higher than the blocking temperature of the powder. In the disordered powder sample, magnetization reversal could occur in any direction, thereby reducing the energy barrier of magnetization reversal. However, the magnetization reversal in 2D arrays was mainly realized by in-plane rotation. The shape magnetic anisotropy of single-layer NPs was stronger than the shape magnetic anisotropy of multilayer NPs, which raised the anisotropy barrier [208]. The results also explained why the blocking temperature of single-layer NPs was higher than that of multilayer NPs, and both were higher than the blocking temperature of disordered powder.

Changes in hysteresis loop

The shape changes of hysteresis loop are usually related to the coercivity, remanence ratio (ratio of residual magnetization M_r and saturation magnetization M_s), and the rate of magnetization that increases with the applied magnetic field strength. The effects of assembled structures on coercivity will be discussed in the next section; and the following section mainly discusses the influence of self-assembly on the remanence ratio, which further influences the shape of the hysteresis loop curve. The theoretical remanence is determined as follows:



Fig. 18. (a) Zero field cooled (ZFC) curves of disordered (black line) and ordered (red line) 3D assemblies. Insert: Raw ZFC (dashed line) and field-cooled (full line) curves. (b) Fitted curve for the blocking temperature and negative cubic value of interparticle distance (a^{-3}) of 2D and powered samples. (c) Reduced remanent magnetization of the assembled supercrystal (black squares) and disordered (red cycles) samples at different particle diameters, measured at T = 5 K. (d) Coercivity of magnetic particles as a function of particle size. (e) Schematic illustration of the unit cell of (left) *fcc* and (right) *fct* 3D FePt supercrystals. (f) Comparison of coercivity among NPs with different structures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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$$M_{\rm r} = M_{\rm s} \exp\left(-t/\tau_{\rm N}\right)$$

$$\tau_{\rm N} = f_0^{-1} \exp\left(-KV/k_{\rm B}T\right)^{\prime}$$
(17)

where f_0^{-1} is a constant related to the Larmor precession frequency of the magnetic moment [207]. Stronger magnetic anisotropy and larger NPs will increase τ_N and further increase the remanence ratio.

The hysteresis loops of self-assembled 2D arrays are usually squarer and sharper [209]. The shape change of the hysteresis loop curve is generally accompanied by the change of remanence ratio, whereas a higher remanence ratio in the self-assembly contributes to a squarer hysteresis loop. Concurrently, the assembled superstructures can quickly reach saturation magnetization under a smaller external magnetic field, which sharpens the hysteresis loop. Zhang et al. proved that the remanence ratio of the monolayer is greater than that of the multilayer due to the higher anisotropy constant (K) in monolayer 2D array, thus creating a squarer hysteresis loop curve [208]. Notably, a higher remanence ratio can also be achieved by increasing the NP diameter. Yang et al. synthesized fcc ε -Co NP supracrystals by evaporation self-assembly; they found that the reduced remanence increased in accordance with the NP size (Fig. 18c) [210]. Furthermore, the presence of BNSLs can modify the shape of the hysteresis loop by controlling the type and proportion of binary components (Fig. 19a–d) [49]. It is worth noting that the shape of the hysteresis loop is not a simple linear superposition of the two components; in addition, the magnetic coupling effect inside the assembly has an obvious impact on the hysteresis loop shape [49,211].

Increase in coercivity

For monodisperse magnetic NPs, the coercivity increases gradually to a maximum value with decreasing particle size, then rapidly decreases to zero with further reduction in particle size [212]. The size of NPs used for assembly is usually small. Especially when the size of NPs is below the critical diameter of the single domain grain, it corresponds to the point at which the thermal agitation energy breaks through the magnetic anisotropy energy, resulting in a superparamagnetic regime. Therefore, most of the small-sized magnetic NPs exhibit a superparamagnetic state with almost no coercivity. The approach to improve coercivity can be achieved by self-assembly of these magnetic NPs (Fig. 18d).

The increase in coercivity means that higher energy is required to overcome the magnetization reversal energy (KV) of magnetic NPs. The coercivity can be improved by synthesizing hard magnetic units, such as FePt alloys with large uniaxial magnetocrystalline anisotropy $[K_{\rm u} \cong 7 \times 10^6]/{\rm m}^3]$. Medwal et al. fabricated a hexagonal close-packed FePt array, and realized the control of coercivity at different annealing temperatures [213]. It is worth pointing out that the change in coercivity in the above-mentioned work is mainly due to thermal annealing that changes the internal structure of the NPs: from a chemically disordered fcc phase with a low magnetic anisotropy constant to a chemically ordered face-centered tetragonal (fct) phase with high magnetic anisotropy (Fig. 18e). From the aspect of atomic structure, it is impossible to determine which atom occupies an individual site in the fcc unit; however, the *fct* phase has an explicit arrangement of alternating atomic layers of Fe and Pt along the c-axis. The spin-orbit coupling and hybridization between Fe and Pt contribute to a large anisotropy constant (K) and thus increase the coercivity of FePt alloys [214,215]. The above principle may have reference significance for the regulation of the coercivity of the binary assembly structure. It is reported that the magnetocrystalline anisotropy is also affected by the shape and alignment of NCs [216,217], which further alters the coercivity. Tadic et al. found that the coercivity of self-assembled α -Fe₂O₃ with ellipsoidal morphology significantly improved (~35 times higher than irregular hematite nanoparticles and ~4 times higher than hematite nanoplatelets), because the increase in shape anisotropy with this form inducing the formation of multidomain magnetic structures [217].



Fig. 19. Magnetization hysteresis loops of various SPs measured at 100 K: (a) *fcc* CoFe₂O₄ NCs; (b) *fcc* Fe₃O₄ NCs; (c) AB₁₃-type CoFe₂O₄-Fe₃O₄ BNSLs; and (d) disordered CoFe₂O₄-Fe₃O₄ SPs. Reproduced with permission.[49] Copyright 2018, American Chemical Society.

In addition to increase *K* by using the abovementioned methods, increasing the volume of NP can also improve coercivity. Dolci et al. used a copper-catalyzed alkyne-azide cycloaddition "click" reaction to promote the assembly of iron oxide magnetic NPs. They compared the magnetic properties of several iron oxide NPs with different diameters and found that the coercivity increased with the diameter of self-assembled NPs, resulting from an increase in the magnetization reversal energy that must be overcome [218]. Sawano et al. reported the synthesis of Co₃O₄-Fe₃O₄ nanocube bilayers by stacking antiferromagnetic Co₃O₄ nanocubes on ordered ferrimagnetic Fe₃O₄ monolayers, using evaporation-assisted self-assembly technology [219]. They also synthesized a Co₃O₄-Fe₃O₄-Co₃O₄ trilayer sandwich structure via layer-by-layer manipulation. The exchange coupling effect between the antiferromagnetic nanocubes and ferromagnetic nanocubes led to significantly greater coercivity. Specifically, the layered structure increased the coercivity through enhancement of exchange coupling at the interface. The coercivity enhancement of assembled structure was greater than core-sell structure and random arrangement of Fe₃O₄ and Co₃O₄ nanocubes, indicating that the ordered structure provided by self-assembly promotes exchange coupling and further increases the coercivity (Fig. 18f).

Collective mechanical properties

Collective mechanical properties produced by self-assembled superstructures have been discovered, such as vibrational coherence [220], adhesion properties [221], improved hardness, and Young's

modulus [222]. In self-assembled superstructures, the materials exhibit enhanced mechanical properties when the particle spacing is almost unchanged but the ligand length increases or the ligand density increases [223,224]. The high value for Young's modulus originates from the collective resonances because of strong interactions between ligands confined to a limited space between NPs. Strong interactions between larger inorganic PbS cores are presumed to facilitate closer interparticle spacing (e.g., from 2, 1.9, and 0.9 nm to 4.7, 7.1, and 13 nm large PbS NCs, respectively), and increase the elastic modulus and hardness of self-assembled PbS NCs (Fig. 20a, b); thus, the self-assembled materials exhibit better behavior, compared with drop-casted film [225]. In addition, the crystallinity of the building block also affects the mechanical properties of the assembly. Pileni et al. found that compared with supercrystals comprising polycrystalline NCs, singledomain materials assemblies showed a higher Young's modulus [226,227], which was attributable to the different degrees of ordering in the supercrystals. The supercrystals assembled from single-domain NCs possessed better orientation, resulting in stronger face-to-face interaction between the NCs; whereas their counterparts assembled by polycrystalline units are randomly oriented, which reduces the intergranular interaction and lowers Young's modulus.

Furthermore, the self-assembled close-packed structure can disperse the stress more uniformly to enhance its modulus and hardness. Gauvin et al. used a dimension model of the stress-strain relationship to investigate the mechanical behavior of *fcc* superlattices (Fig. 20c, d) [227]. Here, E_{macro} is defined as the effective macroscopic Young's modulus of the *fcc* superstructure, determined as follows:



Fig. 20. (a) Elastic modulus and (b) hardness of an ordered single-component (SC) superlattice and drop-cast film comprising particles of various sizes and components. (c) Schematic diagram of connecting *fcc* rigid spheres array with diameter *D* through compliant junctions. The force *F* is perpendicular to the (111) plane. (d) The thickness *h* and half width *r* of the three compliance nodes of the tetrahedral sub-element are squeezed under the applied load *F*, resulting in a thickness reduction of δ while the rigid spheres do not deform. (e) Elastic modulus and hardness of the iron oxide/oleic acid nanocomposites with increasing annealing temperature. Inset shows nanoindentation during measurement. (f) Adhesion of Au NP films with increasing packing densities shows an exponential correlation.

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$$E_{macro} = 3\sqrt{3}B\pi r^2/(h(D+h)),$$
 (18)

where *r* is the junction radius, *h* is the thickness of compliant junctions, and D is the diameter of the rigid sphere. The formula indicates that the Young's modulus of the supercrystal is proportional to the junction area within neighboring NCs. The radius of the compliant junction rincreases with increasing crystallinity, which explains why the Young's modulus values of single domain ε -Co and *hcp*-Co were an order of magnitude greater than the Young's modulus of amorphous Co. Liu et al. synthesized hierarchical, intrafibrillar mineralized collagen (HIMC) through the co-assembly of nano-hydroxyapatites and collagen molecules [228]. nHAs were deposited uniformly and orderly inside the collagen fibers to form a periodic structure of ~67 nm, with light- and dark-contrast zones under TEM. The hierarchical assembly structure of inorganic crystals/biomacromolecules was conducive to strain transferal: nHAs could sustain high tensile stress, while the collagen domains were able to withstand shear stress. Therefore, HIMC hardly produced cracks under the vertical force of 6 N, and crack propagation was observed in the nonhierarchical structure due to stress concentrations.

Dreyer *et al.* demonstrated an effective approach to exceptional isotropic mechanical properties through a crosslinking process during annealing treatment [229]. As the annealing temperature increased, crosslinking occurred between the original stacking of oleic acid links; this contributed to a stiff and strong covalent backbone, which reinforces the short bond in the supercrystal to yield greater elastic modulus and hardness, as shown in Fig. 20e. Moreover, using LB technology, Lin *et al.* discovered that the adhesion force was sensitive to the packing density in self-assembled Au nanostructures (Fig. 20f) [221]. The different stacking modes in self-assembly structures also affect the mechanical properties of the material. Xue *et al.* induced the self-assembly of Eu₂O₃ nanosheets through solvent evaporation to form face-to-face and interlocked-junction superstructures (Fig. 21) [230]. They found that the mechanical properties of both superstructures were better than the

mechanical properties of a random structure, because fewer structural defects were present. Additionally, the interlocked-junction provided added shear stress and resistance to stabilize the metamaterial, such that it exhibited mechanical properties better than the properties exhibited by the face-to-face structure.

In suit SAXS measurements under pressure provide a monitor tool to study the collective mechanical properties of NPs superstructures [231]. Bian et al. found that PbS NCs in a bcc superlattice exhibited higher structural stability than similar particles assembled in a fcc mode [232]. The fcc mode exhibited a rock-salt/orthorhombic phase transformation at 7.0 GPa, while the transition pressure was up to 8.5 GPa for bcc allotrope. The in situ high-pressure SAXS data revealed that the orientational ordering in bcc mode with ligand rearrangement lowered the total free energy of entire ordered nanostructure, resulting in higher capacity to absorb mechanical energy. The mechanical properties of NPs superstructures are determined mainly by the relatively weak interactions between soft ligands that attached on the surface of NPs. A molecular dynamics simulation proved that short ligands contributed to large elastic moduli in alkanethiol-grafted AuNPs superlattice [233]. On the basis of this concept, a stress applied method was invented to compress and study the stiffness of the superstructures by uniaxial compression of the ligands between NPs.

Other properties

Compared with simple physical mixing materials, self-assembled binary superstructures can enhance electrocatalytic and photocatalytic activities by promoting the synergistic effect [84,234]. In addition, assembled particles are better able to maintain their structural integrity, thereby greatly improving catalyst stabilities during the reaction process [235,236]. Self-assembled materials with excellent photothermal performance could be used for interfacial solar evaporation [237,238]. Furthermore, self-assembled materials deposited on substrates with good electrical conductivity show high



Fig. 21. Schematic diagrams of the stress performance of Eu_2O_3 nanosheets superstructures and building bricks. (a) The top half of the panel shows a schematic diagram of the test of mechanical characteristics. The bottom half of the panel illustrates the strain-structure relationship analyzed by the unit cell model, showing transverse strain or shear strain around the side of the nanosheets (σ_{rF} or σ_{rL}), friction resistance (τ), and squeezing or stretching within the faces (σ_{c-FF} or σ_{c-IL}). (b) Path models of the implemented force by a singlecrystal nanosheet (*s*-NSt) and faultycrystal nanosheet (*f*-NSt) are indicated with white arrows. In *f*-NSt, no stress concentration phenomenon such as the phenomenon in *s*-NSt occurs, mainly because of the redistribution of stress caused by the amorphous phase that produces a uniform loading force. Reproduced with permission.[230] Copyright 2020, Wiley-VCH

sensitivity and resistance to high relative humidity; thus, they are good candidates for manufacturing high-performance sensors [239]. Compared with membranes made using conventional technology, self-assembled nanomembranes have a regular arrangement and high pore density, which facilitate water flow. Moreover, due to the good compatibility of self-assembled materials, the incorporation of highly ion-selective materials can further improve the selective permeability of nanomembranes [240]. The highly sophisticated assembly modes bring about special aggregation, such as chiral superstructures. Generally, the chiral arrangement of NCs superstructures can be realized through the chiral soft templates [241–243]. The isotropic or anisotropic nanoparticles assembly could behave chiral properties in plasmonics, luminescence, and magnetics [244–248].

Applications of self-assembled superstructures

As discussed earlier in this review, the excellent structural properties of self-assembled superstructures provide extraordinary functionality for various device applications. Self-assembled materials thus show great potential for addressing challenges experienced by conventional technologies and advancing new developments in science and engineering fields.

Optical applications

Compared with traditional sensors, plasmon components as sensors are used to detect molecules at a smaller dose and concentration [249]. An example is the exploitation of self-assembled Au NPs to achieve enhanced SERS under an electromagnetic field in the superstructures. For example, Kotov and colleagues demonstrated the potential for metamaterials to serve as intracellular probes by means of in-situ Raman spectroscopy; they found that the SERS intensity was dependent on superlattice structure [250]. Moreover, Au metamaterials offer a good substrate for SERS [56,251,252]. Matricardi et al. self-assembled a series of 2D plasmonic supercrystals with different lattice parameters using topographically patterned polydimethylsiloxane molds, which showed enhanced SERS intensity compared with random layers and inhomogeneous assemblies (Fig. 22a) [30]. In addition, precise control of the stacking layers of Au NPs from monolayer to trilayer format



Fig. 22. (a) Au NP superlattices with different lattice parameters and their SERS intensities under 785-nm excitation of the Raman probe 4-acetamidothiophenol. (b) Schematic diagram of wrinkle-assisted self-assembly of patterned Au@Ag nanobrick plasmonic arrays. (c) Simulated electric-field amplitude distribution of spherical and planar Au NP arrays. Reproduced with permission.[254] Copyright 2015, Wiley-VCH.

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generates interlayer synergistic effects between NCs. Using EISA, Ling et al. found that Ag supercrystals with a double lattice structure are 3.3fold more efficient than homogeneous Ag superlattices [92]. Large-scale manufacturing technology of plasma superlattices is currently in development. Chu et al. used evaporation-assistant self-assembly of Au nanorods to prepare millimeter-level 3D superlattice arrays and retained excellent SERS sensitivity with the superlattice materials [10]. Recently, Gu et al. introduced wrinkle-assisted self-assembly to fabricate 1D and 2D macroscopic superlattice materials exhibiting enhanced uniform distribution of near-field confinement (Fig. 22b), which comprised an important contribution to the practical application of plasmon arrays as SERS substrates [8]. Notably, the application potential in the field of light absorption has received considerable interest because of the enhanced extinction effect of superlattice materials, as well as the red shift of the plasmon resonance band. Considering the enhancement in dipole coupling between assembled units, self-assembled superstructures exhibit broadband absorption, which is important for photovoltaic devices [253]. Moreover, assembled superstructures with curved surfaces exhibit stronger electric field enhancement than do flat surfaces, supporting stronger light absorption (Fig. 22c) [254]. Si et al. fabricated Fresnel lens with ~23% focusing efficiency using previously mentioned plasmene nanosheets [131]. The additional Huygens' effects from plasmene-constituent building blocks contribute to the high focusing efficacy. The superiority of using bottom-up self-assembly process to build the ultrathin optical devices lies on providing freedom in tuning its plasmonic properties simply by adjusting sizes, shapes, and orientations of constituent building blocks.

Electrical applications

Self-assembled superstructures have demonstrated remarkable attributes in a wide range of electrical applications. Compared with traditional methods, self-assembly is easier with respect to forming materials with a specific pore structure, which is crucial in the electrode reaction and has been widely used to prepare electrode materials [14]. First, the pore structure can resist the influence of volume changes in the electrode reaction, thus contributing a robust electrode with high stability. Second, the pore structure is beneficial to the



Fig. 23. (a) Diagram and scanning electron microscopy image of magnetic mesoporous nanochains. (b) Representative microscopy images of differentiating osteoclasts (stained in purple). (c) Quantitative proportion of trap-positive area for different materials with or without an external magnetic field. In vivo T2-weighted magnetic resonance images of (d) before and (e) after injection of magneto-fluorescent SPs; clear tumor visualization can be observed after injection of magneto-fluorescent SPs. (f) Pre-injection and post-injection T2 relaxation times for the tumor region. Inset shows a typical transmission electron microscopy image of the core-shell magneto-fluorescent SP with highly ordered *fcc* superlattice fringes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.) (a-c) Reproduced with permission [262] Copyright 2014, Springer Nature.

transfer and storage of substances. For example, Wang et al. assembled ultrathin MoS₂ layers to construct mesoporous tubular architectures that promote the transportation and storage of matter, resulting in excellent lithium storage electrochemical performance [255]. Moreover, the inherent collective electric properties of the self-assembled structure (i.e., the excellent electron delocalization ability) are suitable for electrical applications. Considering the structural characteristics of self-assembled materials, Jiao et al. prepared 3D interconnected superlattice electrode materials with excellent electrochemical performance by carbonizing surface-coating oleic acid ligands and acidetching Fe₃O₄ supercrystals templates [236]. Recently, Li et al. obtained monolayer supertubes based on a confined epitaxial assembly of Fe₃O₄ nanocubes within the channels of anodic aluminum oxide templates, exhibiting the structure-performance relationship of lithium-ion storage [28]. The robust electron mobility of self-assembled materials can be exploited to manufacture high-performance photoelectronic devices. However, the insulated organic ligands introduced during selfassembly affect electron migration. Self-assembled superstructures can promote band-like transport after removal or exchange of long alkyl ligands. Based on this strategy, Lee and collaborators assembled CdSe/CdS nanocrystalline solids to realize ultrahigh electron mobility by ligand exchange with a molecular metal chalcogenide complex In₂Se₄^{2–}, enabling the creation of a photodetector with all-inorganic nanocrystalline arrays [186]. With the exceptions of frequently used CdSe and PbSe NCs, InP or InAs NCs with low toxicity can be utilized in the self-assembly strategy to fabricate field-effect transistor devices after inorganic ligand exchange to improve the electron mobility [185].

Catalytic applications

The collective properties of self-assembled superstructures have achieved excellent results in catalytic applications. By exploiting enhanced light absorption and red shift for the self-assembled structure, Wang et al. obtained a catalyst by self-assembled porphyrin building blocks through π - π stacking and metalation with better stability and a longer electron-hole pair lifetime in the photocatalyzed hydrogen evolution [256]. In addition, self-assembly could trigger synergistic effects between components, leading to cascade catalysis. The heterostructure of nanotube arrays synthesized by electrostatic self-assembly exhibited enhanced solar-powered photoelectrochemical water splitting ability. Zeng et al. created cooperative synergy among Au_x clusters, graphene QDs, and TiO₂ nanotubes to enhance charge transfer by promoting the separation of photogenerated electron-hole pairs [103]. Yang et al. used 10 nm Pt nanoparticles and CeO₂ nanoparticles as building blocks to self-assemble a Pt-CeO₂ double-layer membrane structure on a silicon wafer through LB technology. Through the close combination of the Pt-CeO₂ and the Pt-SiO₂ interface, it effectively formed the tandem catalytic interface with methanol and ethylene as reactants, and the selectivity to propionaldehyde was greater than 94% [257]. Recently, 2D ultrathin transition metal carbide sheets with high electrocatalysis properties were reported through a versatile bottom-up self-assembly by exploiting gelatin hydrogel as a scaffold [43]. Carbonization of the scaffold was essential for conductivity; the presence of a metal-rich hybrid carbide exhibited synergistic effects with excellent hydrogen evolution reaction efficiency.

Biomedical applications

Mertz et al. synthesized a self-assembled protein capsule with negligible cytotoxicity [258]. Compared with polymer capsules, selfassembled capsules showed good mechanical stability and decompose when exposed to external stimuli; thus, they had great potential with respect to the fabrication of custom architectures for biomedical applications. The electrostatic interaction drove the layer-by-layer self-assembly of electrolyte multilayer capsules to enfold a CaCO₃ microparticle loaded with protein antigen, which could be used for vaccine development and design against intracellular pathogens (e.g., Mycobacterium tuberculosis and human immunodeficiency virus) after dissolving the inorganic core [259]. Wan et al. synthesized 1D magnetic mesoporous Fe₃O₄@nSiO₂@ mSiO₂ nanochains (Fig. 23a) through a magnetic field-assisted interface co-assembly method, which showed high sensitivity to the external magnetic field, as well as easy alignment and rotation [58]. Under a rotating magnetic field, internalized magnetic nanochains helped to generate a shearing force inside of bone marrow-derived macrophages that enhanced the interaction between the cell and loaded zoledronate (a medication for treatment of bone diseases) in silica shell mesopores. Regardless of drug presence, blank magnetic nanochains also exhibited excellent ability to inhibit osteoclast differentiation under an external magnetic field; this was further improved when zoledronate was loaded in the nanochains (Fig. 23b, c). Considering the collective optical properties of metamaterials, the self-assembled Au vesicle structure synthesized by Lin et al. showed strong absorptivity in the near-infrared region of 650-800 nm because of plasmonic coupling between adjacent Au NPs in vesicular membranes [260]. After encapsulating photosensitive Ce6 within the Au vesicles, they showed a cooperative effect in photothermal/ photodynamic therapy under continuous irradiation with a singlewavelength laser. Moreover, multifunctional vesicle nanocarriers possessed high solubility and stability in aqueous solutions, as well as good biocompatibility; they were especially suitable for biomedical applications. Self-assembled magnetic materials reportedly have better T_2 relaxation than monodispersed materials [261]. Chen and collaborators demonstrated the assembly of Fe₃O₄NPs@CdSe-CdS QD binary SPs to form a colloidal magneto-fluorescent SP with a thin layer of silica, which allowed versatile surface functionality and biocompatibility [262]. The *fcc*-close-packed magnetic core was subsequently surrounded by a shell of semiconductor fluorescent QDs, thus combining magnetism and fluorescence functionality for a multiphoton/magnetic resonance dual-mode imaging probe (Fig. 23d-f). Qiao et al. designed a gold SP@MOF structure for surface enhanced Raman scattering substrate in detection of lung cancer biomarkers [263]. In this structure, the inner gold SP provided electromagnetic hotspots for enhanced Raman scattering, while the outer MOF shell served as a shielding case to curb the decay of electromagnetic field intensity and facilitated the absorption of target molecules.

Conclusion and Outlook

As a promising direction in the field of nanotechnology, self-assembled superstructures are increasingly used to customize and enhance material properties and functionality. Here, we have discussed several important aspects of the structure-activity relationships of self-assembled superstructures, including the distance between assembled units and disorder regarding NP position and size. The aim of this review is to set the stage for exploring the structure-activity collective properties of self-assembled superstructures. However, preparation of high-quality functional superstructures in a controlled manner and detailed understanding of the self-assembly mechanisms are still challenges in the coming years.

i. Multicomponent Assemblies with Tailored Properties

Self-assembly provides a tailored, bottom-up approach to the design of functional materials. The fabrication process would not only be limited to the assembly of monocomponent building blocks, but also, reference to self-assembled structures in the nature, require diverse reconfigurable units to follow a predetermined hierarchical sequence. Although we have a good grasp on the method of controlling multiple self-assembly, fundamental works are required to understand the synergistic effect between different NCs in assembled superstructures. Just like the artistic creation, the artist not only needs colorful pigments, it is also necessary to consider the matching and synergy between different colors to present great paintings. The multiple self-assembly brings NCs with different energy band structures together. The success of carrier migration depends on whether the energy levels match between the two types of NCs, which means that the transmission of carriers is directional: once electrons can transmit from particle A to particle B, it is difficult for them to transfer back to particle A under the same conditions. Based on this, we speculate that anisotropic self-assembly (such as layer-by-layer, core-shell structure) is more conducive to the generation of cascaded energy levels, resulting in collective performance. On the contrary, isotropic assembly with uniform distribution of different particles is difficult to cause extensive interparticle communications. Moreover, whether the co-assembly of materials with optical, electrical and magnetic properties will promote their respective performance or to be dragged down by each other remains to be studied in the future. In addition, changes in other properties derived from position disorder or different self-assembled structures affect the collective properties of the material product. A notable example is the Anderson insulator: despite the small intervals in the assembled units, the disorder-related changes in energy level can shield against the generation of collective properties. Growing interest in the structure-activity relationships would promote the development of customized functional materials based on assemblies. Especially in biomedical applications, we can imagine that in the future, functions such as fluorescence imaging, Raman detection, MRI, photothermal and photodynamic therapy can be integrated into one assembly to achieve multi-mode, simultaneous diagnosis and treatment.

ii. Enhancement of the Interparticle Communication

There is a contradiction existing in the self-assembled superstructures: surface ligands play a crucial role in inducing the assembly, but hinder the electronic communication in the subsequently function performance. The insulating ligand shell increases the interparticle spacing and block coupling between neighboring nanoparticles. The challenge comes as how to enhance the electronic communication between nanoparticles to trigger the collective properties while maintaining the ordered assembled superstructure. Several subsequent processing including heat treatment, ligands removal, and ligands exchange are introduced to facilitate the electronic coupling between the adjacent NPs. The annealing or high-heat thermal treatment were reported to bring atomically coherence of QDs with high charge mobility, and graphitization of organic ligands supplied great electronic channels for interparticle interactions [264-266]. When the particle spacing in the superlattice decreases, the enhanced quantum resonance will promote the formation of continuous density of states in QDSL; making MEG (multiple exciton excitation) more likely to occur. The ligand removal strategy also brings some disadvantages, including the destruction of the surface atomic structure of inorganic NCs and the increased sensitivity to oxygen and water in the environment without the ligand protection. Ligand exchange and grafting of biological, optical, electrical, and magnetic responsive ligands could be introduced into self-assembly system to promote coupling and trigger collective properties. Short organic bidentate ligands (such as ethanedithiol, ethylene diamine and mercaptopropionic acid) and inorganic conductive ligands (such as molecular metal chalcogenide complexes, chalcogenides, halides anions, hydrochalcogenides, nitrosonium tetrafluoroborate and aryldiazonium tetrafluoroborate) could be introduced to replace the original capping ligands with aliphatic chains for metallic and semiconducting nanoparticles [267–274].

iii. Exploration of the self-assembly mechanism

Multidisciplinary efforts are required to construct a quantitative theoretical framework describing the self-assembly system, from experimental techniques to mechanism understanding. We have already known that the interparticle forces between building blocks are the basis for the construction of self-assembled superstructures, however the evolution process of ordered structure is still a "Black Box". The ordered assemblies supported by covalent and hydrogen bonds is relatively easy to understand, because both covalent and hydrogen bonds are directional and saturated. It is still confusing how a weak, short-range force, such as van der Waals interaction and Coulomb force, that has neither directionality nor saturation can induce a long-range ordering supercrystalline structure. Although we can seek explanations from the perspective of thermodynamics, a theory that can unify microscopic forces and mesoscopic structures is still lacking. Therefore, the in situ metrologies should be extensively developed to characterize the driving interactions, kinetics and structures during the assembly process by employing like fast sub-diffraction microscopy techniques or time-resolved neutron or synchrotron X-ray scattering resources [275]. The development of computational chemistry provides us with another perspective. At present, some classic methods, such as Monte Carlo, self-consistent field theory, dissipative particle dynamics, are used to simulate the self-assembly behavior of nanoparticles. As the most commonlyused model, the Monte Carlo simulation simplifies nanoparticles to hard spheres. This theoretical calculation that does not consider the charge, chemical composition and ligand structure may deviate from the experimental results. With the increase of computing power, it is believed that in the future, computer simulations can more accurately quantify self-assembly parameters and predict the impacts of their structural parameters on the collective properties.

CRediT authorship contribution statement

Cong Li: Investigation, Writing – original draft. **Xiaoyun Qin:** Investigation, Writing – original draft. **Zhenghao Zhang:** Writing – original draft, Formal analysis. **Yujia Lv:** Formal analysis. **Shengwei Zhang:** Formal analysis. **Yijie Fan:** Formal analysis. **Shiyuan Liang:** Formal analysis. **Bowen Guo:** Formal analysis. **Zhou Li:** Writing – review & editing. **Yan Liu:** Writing – review & editing. **Dan Luo:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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