



Self-assembly of inorganic nanoparticles mediated by host-guest interactions

Di Li, Limin Qi *

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China



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ABSTRACT

The use of host-guest interactions to direct the controllable self-assembly of inorganic nanoparticles has aroused intensive interest in recent years. Through deliberate surface modifications of inorganic nanoparticles, the recognition between host and guest molecules drives the dynamic self-assembly of nanoparticles, leading to fascinating assembly behaviors such as stimulus-responsive and reversible self-assembly. In this review, we first briefly introduce the structures and properties of the typical host molecules, such as cyclodextrins, cucurbit[*n*]urils, calix[*n*]arenes, and pilla[*n*]arenes, and their supramolecular complexes with guest molecules, which have been frequently employed in nanoparticle assembly. Then, recent advances in the approaches toward precise control over the dynamic self-assembly processes of inorganic nanoparticles based on rational regulation of host-guest interactions are summarized with special emphasis on the assembly strategies. Furthermore, the potential applications of the self-assembly systems involving host-guest interactions in sensing and catalysis are highlighted. An outlook on future developments in this field is also provided.

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1. Introduction

Self-assembly is the process by which individual components spontaneously arrange themselves into ordered structures or patterns, which is prevalent in nature, and involves many objects ranging from small molecules to large planets. In particular, the self-assembly of inorganic nanoparticles has stimulated intensive interest in recent years because ensembles of nanoparticles can exhibit unique collective properties in addition to the novel size-dependent properties of individual nanoparticles, and self-assembly provides a simple and powerful method for producing nanoparticle ensembles with tunable structures and properties in a controllable manner [1,2]. The self-assembly of nanoparticles can be realized either in solutions or at various interfaces (e.g., the gas-solid, liquid-solid, gas-liquid, and gas-liquid-solid interfaces), yielding diverse nanoparticle ensembles including discrete assemblies (colloidal clusters or artificial molecules) and large-scale assemblies such as one-dimensional (1D) chains, two-dimensional (2D) sheets, and three-dimensional (3D) superlattices [3,4]. Recently, much attention has been paid to the controlled self-assembly of large-scale nanoparticle superlattices with complex structures and finite colloidal clusters with well-defined structures. Particularly, there is growing interest in the employment of patchy or anisotropic particles as nanoscale building blocks to construct superstructures with symmetries that are unattainable with conventional spherical particles [5–8]. For example, Mirkin and co-workers [9] successfully assembled

DNA-functionalized gold triangular bipyramids into clathrate architectures, which are the most sophisticated architectures made via programmable assembly. Our group recently achieved the shape-directed self-assembly of gold nanoarrows adopting a unique concave geometry into sophisticated 2D and 3D supercrystals with unprecedented architectures [10].

On the other hand, more and more efforts have been devoted to the realization of dynamic nanoparticle assemblies as they can increase diversity of nanoparticle ensembles, enable functional tuning and optimization of superstructures, facilitate integration with microscale technologies, and mimic biological systems [11]. These dynamic assemblies are generally characterized by some novel features such as switchable structures, stimuli-responsive properties, and adaptive or self-healing characteristics, which endow them with potential applications in sensing, catalysis, microreactors, stimuli-responsive optoelectronic devices, drug delivery vehicles, and energy harvesting. For example, Klajn and co-workers [12] used different azobenzene-decorated nanoparticles to realize the precise regulation of the reversible self-assembly based on the photoisomerization of azobenzene groups. The generated dynamically self-assembling nanoflasks exhibited reversible trapping and reaction acceleration, which can be useful for studying chemical reactivities in confined environments. Among the various approaches toward dynamic nanoparticle self-assembly, the self-assembly of inorganic nanoparticles based on mutual recognition between host and guest molecules has been demonstrated to be a convenient and efficient strategy [13]. Through desirable modifications of the nanoparticle surface with either host or guest molecules, the self-assembly can be readily achieved by mixing the differently functionalized nanoparticles

* Corresponding author.
E-mail address: liminqi@pku.edu.cn (L. Qi).

or adding additional guest or host molecules. Moreover, if the host-guest interactions are sensitive to certain chemicals and external fields, stimuli-responsive self-assembly and reversible self-assembly may be realized by the introduction of chemical or field-based stimuli. Therefore, the controllable self-assembly of inorganic nanoparticles can be realized in an efficient manner by selecting and designing suitable host and guest molecules combined with desirable stimuli. In this regard, more and more supramolecular host-guest systems have been applied to the self-assembly of varied nanoparticles along with the improvement in the methods for decorating nanoparticles surface with host or guest molecules [14,15]. Furthermore, the applications of the dynamic nanoparticle self-assembly involving host-guest interactions in technologically important fields including sensing and catalysis have been explored.

In this review, recent advances in the development of self-assembly of inorganic nanoparticles mediated by host-guest interactions are summarized. As nanoscale building blocks, the nanoparticles specially refer to functional inorganic nanoparticles, such as noble metal nanoparticles, quantum dots, and magnetic nanoparticles, which have unique functional characteristics. After the discussion of the assembly methods and mechanisms based on different supramolecular host-guest systems, the potential applications in sensing and catalysis are highlighted.

2. Host-guest interactions involved in nanoparticle assembly

Supramolecular system generally refers to a molecular entity that contains two or more different components or a large number of identical components combined through weak intermolecular interactions. The field of supramolecular chemistry focuses on the noncovalent interactions between molecules that give rise to molecular recognition and self-assembly processes [16]. Since the Nobel Prize in Chemistry in 1987 was awarded to the outstanding achievements in supramolecular chemistry, significant progress has been made in this area; particularly, the Nobel Prize in Chemistry in 2016 was awarded to the design and synthesis of molecular machines, another prominent contribution in supramolecular chemistry [17]. Traditionally, supramolecular chemistry has focused predominantly on systems at equilibrium; however, more recently, kinetics-controlled self-assembly processes dictated by the assembly pathway are attracting increasing interest [16].

Among the many branches of supramolecular chemistry, the application of supramolecular host-guest interactions in the realization of controllable self-assembly of inorganic nanoparticles is becoming topical. Particularly, utilizing specific recognition and reversible characteristics of the supramolecular systems has emerged as a powerful strategy for realizing stimuli-responsive and reversible assembly of nanoparticles. The host and guest molecules can be attached to the surface of two different nanoparticles, respectively, and then the controllable assembly of the nanoparticles can be induced by the recognition between the host and guest molecules. Alternately, the surface of the nanoparticles can be modified with one kind of host (or guest) molecules, and then the molecules that can simultaneously recognize two or more host (or guest) molecules are added into the system to induce the assembly. A wide variety of synthetic organic receptors including cyclodextrins, cucurbit[*n*]urils, calix[*n*]arenes, and pilla[*n*]arenes have been used as host molecules to control the self-assembly of nanoparticles because they can be massively synthesized and feature a great versatility toward chemical modifications [18,19]. In this part, we briefly introduce the structures and properties of the typical host molecules frequently employed in nanoparticle assembly.

Cyclodextrins (CDs), the semi-natural product obtained by enzymatic starch degradation, are a class of widely studied supramolecular host molecules. CDs form the cyclic structure by a number of D-glucose units coupled through α -1,4-glycosidic linkages. The common α , β and

γ -CDs have a structure like a cone-shaped cavity with a height about 7.9 Å and consist of 6, 7 and 8 units, respectively (Fig. 1A). The inner diameters of the cavities are about 5.7 Å, 7.8 Å and 9.5 Å, respectively. Because of the highly reactive hydroxyl groups, it is easy to introduce many functional groups to these native CDs platforms. The CDs have a hydrophobic cavity and a hydrophilic outer surface, and a hydrophobic small molecule can enter the cavity of the CDs due to hydrophobicity and forms a stable supramolecular inclusion with a higher binding constant. In particular, the interactions between CDs and some guest molecules, such as surfactants and various azobenzene molecules have been extensively studied [20]. Among all the guest molecules, azobenzene derivatives play an important role in the photo-responsive self-assembly of nanoparticles because of their unique photo-isomerization behaviors. Namely, the linear, nonpolar trans-isomers can form an inclusion complex with α - and β -CD in high binding constants; after UV irradiation, they change themselves to the polar and bent cis-isomers, which cannot fit in the cavity [21].

CB[*n*]s ($n = 5-8, 10$) are highly symmetrical pumpkin-like structures with negatively charged carbonyl rims and a hydrophobic cavity, which are produced by the acid-catalyzed condensation reaction of glycoluril and formaldehyde [22] (Fig. 1B). CB[6] was reported firstly among the CB[*n*] homologues, but the low solubility and poor functionality limited its applications. Then the progress in the synthesis brought the appearance of CB[5] and CB[7], which showed moderate solubility in water compared to the even counterparts. The development of the direct oxidation of CB[*n*]s allowed the introduction of reactive hydroxyl groups into CB[*n*], which made the further decoration possible. In a manner similar to CDs, the cavity of CB[*n*]s is a hydrophobic environment. Furthermore, because of two negatively charged carbonyl-laced portals, CB[*n*]s can accommodate hydrophobic cationic species, especially positively charged ammonium cations. While CB[5], CB[6], and CB[7] can usually bind only one guest molecule inside their cavities, the larger homologue CB[8] can accommodate more than one guest at one time to form ternary complexes.

Calix[*n*]arene homologues are a class of phenol-derived cyclic oligomers, which can be prepared by tuning temperature and base concentration conditions of the base-induced oligomerization between phenols and formaldehyde. The use of different types of bases results in different numbers of aromatic rings (n). All the homologues have good solubility in organic solvents. The phenolic moieties can act as active sites in reactions, which bring a series of functional groups to them [23]. The phenolic moieties can act as electron-donating groups to form host-guest complexes with cationic molecules through cation/ π interactions (Fig. 1C).

As compared to the typical host molecules mentioned above, pillar [*n*]arenes, which are composed of phenolic moieties, have characteristic highly symmetrical pillar-shaped structures (Fig. 1D). As the latest reported macrocyclic compounds, pilla[*n*]arenes combine many features of typical macrocyclic compounds discussed above, making them structurally similar to CB[*n*], calix[*n*]arenes, and highly functionalized CDs. Their phenolic moieties provide many active sites to ensure the further functionalization; meanwhile, the electron-rich cavities enable them to act as host molecules for various electron-deficient guests or neutral molecules to induce self-assembly [24].

3. Self-assembly of nanoparticles involving host-guest interactions

While the self-assembly of macrocycles themselves have potential applications in biology, medicine and materials science due to their specific recognition and reversible characteristics, the self-assembly of nanomaterials mediated by host-guest interactions based on macrocycles is attracting more and more attention. Through the surface modifications of nanoparticles, the recognition between host and guest molecules drives the dynamic self-assembly of nanoparticles, leading to nanoparticle ensembles with tunable structures and collective properties.

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