

From supramolecular chemistry to nanotechnology: Assembly of 3D nanostructures*

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Abstract: Fabricating well-defined and stable nanoparticle crystals in a controlled fashion receives growing attention in nanotechnology. The order and packing symmetry within a nanoparticle crystal is of utmost importance for the development of materials with unique optical and electronic properties. To generate stable and ordered 3D nanoparticle structures, nanotechnology is combined with supramolecular chemistry to control the self-assembly of 2D and 3D receptor-functionalized nanoparticles. This review focuses on the use of molecular recognition chemistry to establish stable, ordered, and functional nanoparticle structures. The host–guest complexation of β -cyclodextrin (CD) and its guest molecules (e.g., adamantane and ferrocene) are applied to assist the nanoparticle assembly. Direct adsorption of supramolecular guest- and host-functionalized nanoparticles onto (patterned) CD self-assembled monolayers (SAMs) occurs via multivalent host–guest interactions and layer-by-layer (LbL) assembly. The reversibility and fine-tuning of the nanoparticle-surface binding strength in this supramolecular assembly scheme are the control parameters in the process. Furthermore, the supramolecular nanoparticle assembly has been integrated with top-down nanofabrication schemes to generate stable and ordered 3D nanoparticle structures, with controlled geometries and sizes, on surfaces, other interfaces, and as free-standing structures.

Keywords: nanoparticles; nanoparticle arrays; self-assembly; self-assembled monolayer; supramolecular chemistry.

INTRODUCTION

The advances in nanotechnology have provided a variety of nanostructured materials with highly controlled, interesting, and exceptional properties. Among these materials, nanoparticles sized between 1–1000 nm elicit an intense interest because of their unique optical, electronic, magnetic, catalytic, and other physical properties arising from the core material and the nanometer dimensions [1–5]. The ability to attach nanoparticles onto planar surfaces in a well-defined, controllable, and reliable manner is an important prerequisite for the fabrication of micro- or nanostructured devices suitable for the application in the field of (bio)nanotechnology. The stability and ordering of these nanoparticle structures are the most important features of such structures in order to achieve function for long-term applications.

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In general, there are two approaches to assemble nanostructured materials, namely, physical assembly and chemical assembly. Physical assembly techniques are based on the assembly of non-functionalized nanoparticles on surfaces by physical forces, such as convective or capillary assembly [6], spin coating [7], and sedimentation [8]. The physical assembly of nanoparticles generally results in relatively simple close-packed 2D or 3D particle arrays with limited stabilities.

Hence, coupling chemistries are being incorporated to direct and control the deposition of nanoparticles with surface functionalities onto a functionalized substrate. Control over functional groups at the surface of nanoparticles allows tailoring of the nanostructures in a predictable manner, resulting in the formation of functional, more complex nanostructured architectures on surfaces to meet the needs for specific applications such as in molecular electronics and biosensing [9]. Various chemical interaction strategies, e.g., covalent bonding [10], electrostatic forces [11], and host–guest interactions [12] have been employed to chemically govern the self-assembly of nanoparticles onto surfaces. Cross-linking of the neighboring particles with chemical forces by selective binding can further enhance the stability of nanoparticle assemblies [13]. These methods are anticipated to directly control the spatial distribution of nanoparticles across a large area in more complex patterns when combined with nanopatterning schemes.

The integration of particles into devices usually requires placing them in specific positions on surfaces. Hence, the combination of top-down patterning techniques, e.g., microcontact printing [14], transfer printing [15], nanoimprint lithography (NIL) [16], and photolithography [17] and bottom-up self-assembly is crucial in obtaining (submicron) patterned functional nanostructures on surfaces. The introduction of self-assembled monolayers (SAMs) on localized areas of a substrate allows straightforward further functionalization and directed assembly of nanoparticles. By using chemistry, specific binding can be introduced, allowing the control of nanoparticle assembly onto lithographic patterns. Wet-chemical self-assembly of nanoparticles is particularly attractive for the fabrication of nanoparticle-based nanostructures because of its compatibility with various kinds of substrates with complex shapes.

This review integrates nanotechnology and supramolecular chemistry to control the self-assembly of 2D and 3D receptor-functionalized nanoparticles. The aim is to generate stable and ordered 3D nanoparticle structures while using molecular recognition, both for establishing stability and order as well as creating a functionality of the resulting structure. The host–guest complexation of β -cyclodextrin (CD) and its guest molecules [e.g., adamantane (Ad) and ferrocene] are applied to assist the nanoparticle assembly. Direct adsorption of supramolecular guest- and host-functionalized nanoparticles onto (patterned) CD SAMs via multivalent host–guest interactions and layer-by-layer (LbL) assembly are demonstrated and characterized using a variety of techniques. The control over the reversibility and fine-tuning of the nanoparticle-surface binding strength in this supramolecular assembly scheme are extensively examined. Furthermore, the supramolecular nanoparticle assembly has been integrated with top-down nanofabrication schemes to generate stable and ordered 3D nanoparticle structures, with controlled geometries and sizes, on surfaces, other interfaces, and as free-standing structures.

CONTROLLED ASSEMBLY AND REVERSIBILITY OF SUPRAMOLECULAR NANOPARTICLE STRUCTURES

The supramolecular recognition properties of the nanoparticles is used to generate stable and ordered 3D functional nanostructures. CD is a natural host molecule for organic guest molecules, such as Ad and ferrocene, that forms specific and kinetically labile inclusion complexes in aqueous media via hydrophobic interactions (Fig. 1A). The binding constant (K_a) of a single CD-Ad interaction is $\sim 1 \times 10^5 \text{ M}^{-1}$. The noncovalent host–guest complexation of CD host molecules and its guest molecules have been applied to assist the nanoparticle assembly. The host or guest molecules were attached to the surface of various nanoparticles (including gold [12], silica [18,19], and polystyrene [20]) via coordinative or covalent bonding. The molecules with recognition properties on the surface of nanoparticles create

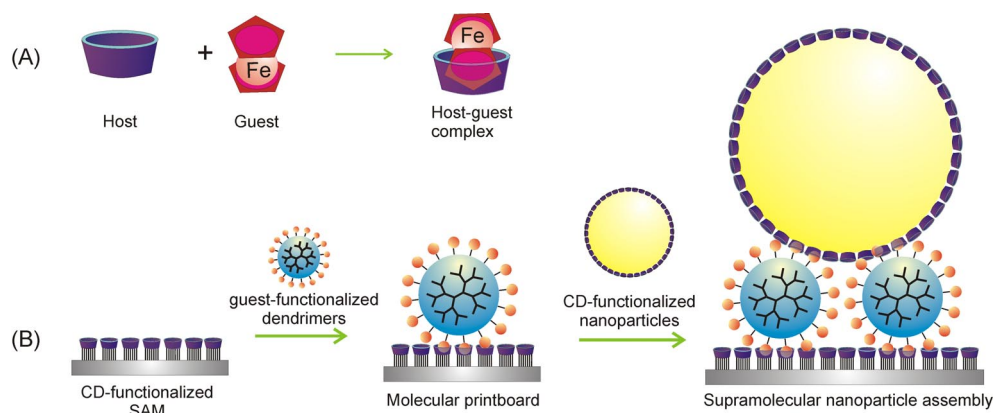


Fig. 1 Scheme of (A) one-to-one host–guest complexation, and (B) supramolecular nanoparticle assembly.

multiple binding sites that stoichiometrically increase the binding strength of the particles via multivalency [21]. CD-functionalized (gold, silica, and polystyrene) nanoparticles have been assembled onto CD SAMs, by using adamantyl- or ferrocenyl-functionalized dendrimers as supramolecular glue (Fig. 1B) [22], whereas ferrocenyl-functionalized nanoparticles were directly adsorbed onto CD SAMs via host–guest recognition [18].

The major advantages of using supramolecular chemistry is that fine-tuning of the supramolecular binding strength is feasible to ensure the organization of the nanoparticles into an ordered nanoparticle array while maintaining the strong binding affinity between the particles and the CD-functionalized surface. The controllable binding strength and reversibility of host–guest interactions are highly appealing for the assembly of ordered and stable functional nanoparticle architectures [23,24].

The adsorption and desorption of particles during the convective assembly on native oxide surfaces, with additional electrostatic interactions and with supramolecular interactions, were studied [20]. The packing density, order, and stability of the nanoparticle lattices were compared. The convective assembly of carboxylate-functionalized polystyrene particles on native SiO_2 surfaces displayed the best hexagonal close-packing (hcp). These structures can be easily desorbed from the surface by reducing the temperature below dew point. The electrostatically induced assembly led to disordered lattices because of the strong attractive particle–surface interactions. The supramolecular assembly was driven by multivalent host–guest interactions between CD-functionalized polystyrene nanoparticles (PS-CD) and ferrocenyl-terminated poly(propylene imine) dendrimers on CD SAMs. The supramolecular particle lattices, though very stable on the surface, fail to form perfect closely packed particle lattices because of strong supramolecular affinity between the nanoparticles and the substrate (Fig. 2A). Hence, fine-tuning of the specific chemical particle–surface and inter-particle interactions has been performed to ensure sufficient affinity of particles on surfaces and organization of particles into highly ordered arrays. By manipulating the number of interactions involved during the nanoparticle–surface interaction and the introduction of the competition during the assembly [20], highly ordered and stable CD-functionalized nanoparticle lattices were demonstrated (Fig. 2C).

The reversible attachment of nanostructures from surfaces is crucial, as structural modifications are often needed on a specific area of a nanostructure. The reversible attachment of CD-functionalized nanoparticles of different core materials and sizes has been demonstrated by using a stimuli-responsive ferrocenyl dendrimer as a multivalent “reversible supramolecular glue” for the association and (electrochemical) dissociation of nanostructures at the CD SAM (Fig. 3) [25]. The in situ adsorption and desorption of ferrocenyl dendrimers and Au-CD ($d \sim 3$ nm) nanoparticles onto and from the CD SAMs was monitored by combined surface plasmon resonance (SPR) spectroscopy and electrochemistry. The regeneration of the molecular printboard after prolonged electrochemistry was confirmed by a subse-

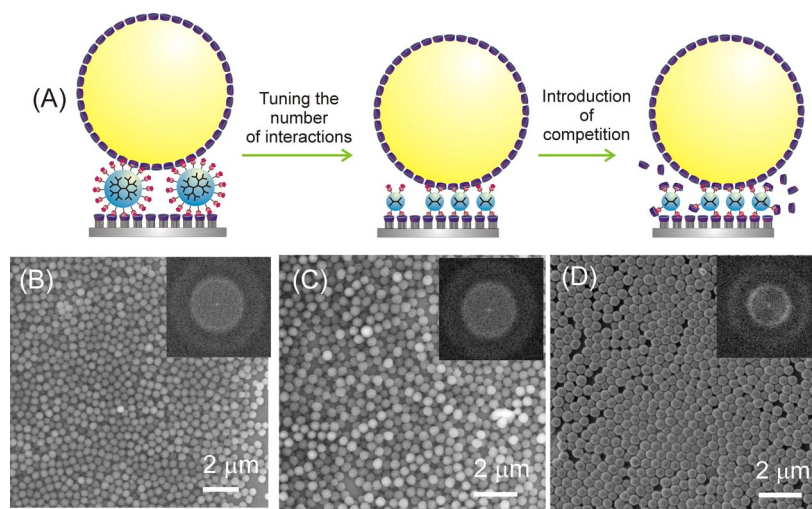


Fig. 2 (A) Scheme and (B–D) scanning electron microscopy (SEM) micrographs of particle lattices formed by fine-tuning the binding strength of the supramolecular nanoparticle assembly. Adapted from [20].

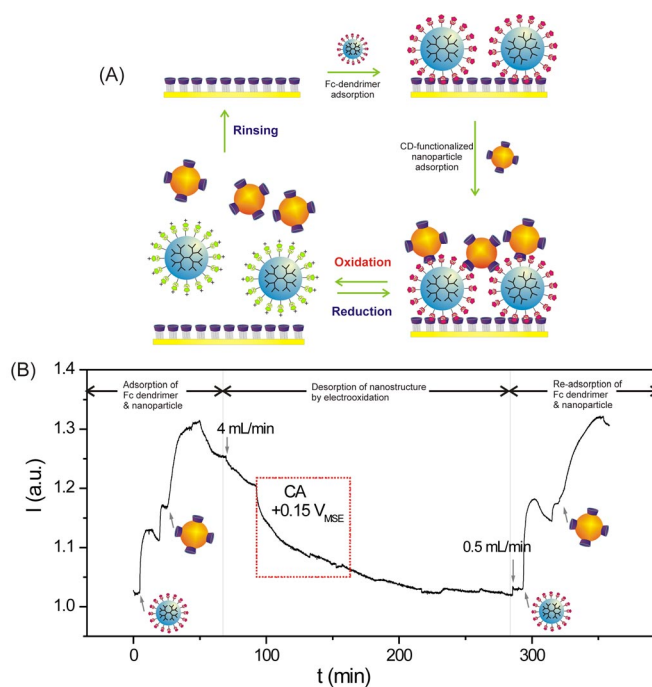


Fig. 3 (A) Illustration and (B) SPR sensogram of the adsorption and electro-oxidation-induced desorption of CD-functionalized nanoparticles onto and from CD SAMs with ferrocenyl dendrimers as reversible glue. Adapted from [25].

quent re-adsorption of ferrocenyl dendrimers and Au-CD nanoparticles. The size effect of the nanoparticle on the reversibility of the nanostructure attachment was examined by using larger nanoparticles, i.e., CD-functionalized silica nanoparticles ($\text{SiO}_2\text{-CD}$) of 60 nm. Similar electrochemically induced desorption showed the complete removal of a $\text{SiO}_2\text{-CD}$ nanoparticle layer from the surface by using ultrasonication to accelerate the desorption. Local desorption of nanoparticles was also observed by ap-

plying electrochemical oxidation to a specific area of a nanoparticle layer. The controlled and reversible supramolecular nanoparticle assembly has huge potential for the formation of functional, more complex nanostructured architectures.

PATTERNING OF SUPRAMOLECULAR NANOPARTICLE STRUCTURES

The integration of particles into devices usually requires high-precision arrangement of the particles on surfaces. Top-down nanofabrication techniques, e.g., microcontact printing [26] and NIL [27] have been combined with the self-assembly of nanoparticles in creating nanoparticle structures of desired geometries and dimensions. Patterned multicomponent hybrid (organic-metallic-inorganic) nano-objects were formed by alternately attaching host- and guest-functionalized nanoparticles in a LbL fashion onto nanoimprinted surfaces with complementary recognition properties (Fig. 4) [22]. It showed that the specific supramolecular assembly of nanoparticles is self-limiting, i.e., one nanoparticle layer per assembly step. Hence, the control over the thickness of supramolecular nanostructure can be manipulated at the nm-length scale by selecting the size of the nanoparticles and the number of deposited layers.

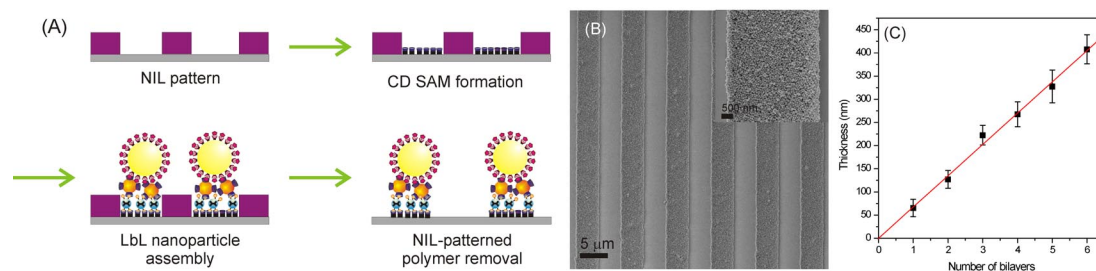


Fig. 4 (A) Scheme and (B) SEM image of the multicomponent nanostructures on NIL patterns. (C) AFM thickness of nanoparticle lines of 1–6 bilayers. Adapted from [22].

To this point, the nanoparticle structures were directly assembled onto a surface with complementary recognition properties. A new strategy of forming 3D nanoparticle structures with better crystallinity and stability has been developed by decoupling the nanoparticle assembly and supramolecular binding of nanoparticles into a sequential process. To begin, nanoparticles were physically assembled to form ordered nanoparticle crystals without stability. Subsequently, stability was introduced to the nanoparticle crystal by infiltration with supramolecular glue to bind neighboring nanoparticles into a stable entity. By incorporating the sequential processes with nanofabrication techniques, such as transfer printing, highly ordered and stable functionalized nanoparticle crystals have been transferred from the elastomeric poly(dimethylsiloxane) (PDMS) stamp to a target CD-covered substrate via host–guest interactions (Fig. 5) [28,29]. Depending on the geometry and size of the PDMS stamps, various 3D multilayered and single-layered nanoparticle structures were demonstrated. The stable, ordered supramolecular particle structures served as 3D receptors for the binding of complementary guest molecules. This strategy can potentially be utilized to create sensing channels for the detection, storage, and transportation of complementary molecules.

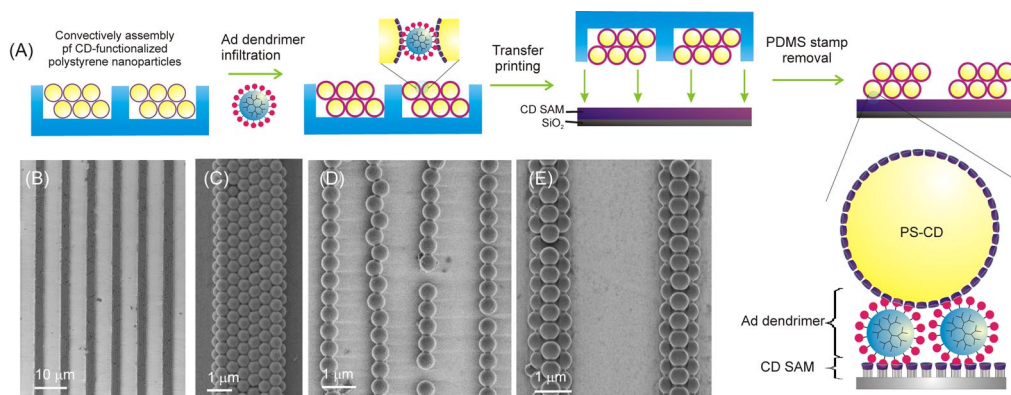


Fig. 5 (A) Scheme and (B–E) SEM images of the formation of 3D supramolecular nanoparticle crystals by combination of convective assembly, supramolecular glue infiltration, and transfer printing. Adapted from [28,29].

FORMATION OF FREE-STANDING NANOPARTICLE AND NANOCAPSULE STRUCTURES

Free-standing and freely suspended nanostructures with controlled composition and macroscopic robustness are crucial to match the needs for electronic or nanomechanical applications. The use of supramolecular nanoparticle assembly on surfaces has been extended to the formation of free-standing nanoparticle structures. Self-assembly of nanoparticles, templating, and (multicomponent) supra-

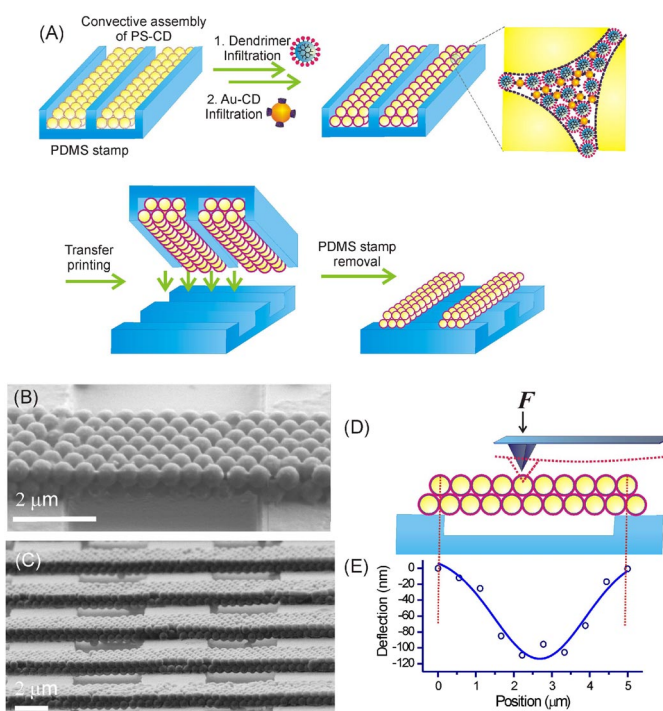


Fig. 6 (A) Scheme and (B–C) SEM images of the hybrid particle bridges on a topographically patterned CD SAM. (D–E) Scheme of an AFM bending test and an AFM force-deflection curve of the nanoparticle bridge. Adapted from [28,30].

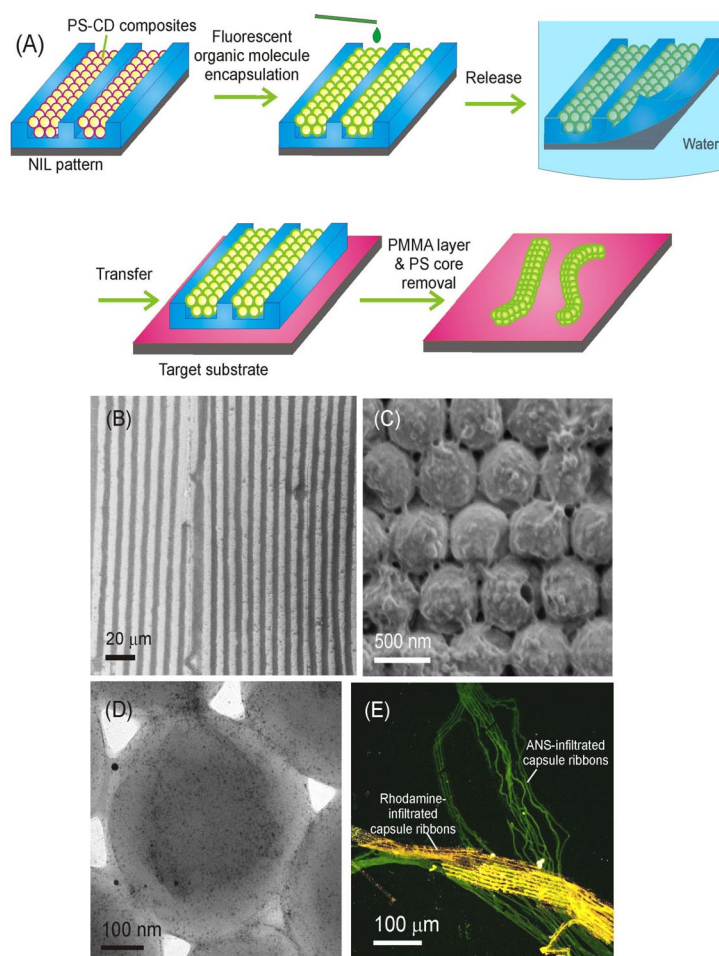


Fig. 7 (A) Scheme, (B–C) SEM, and (D) transmission electron microscopy (TEM) images of the free-standing hybrid hollow capsules. (E) Fluorescence microscopy image of the capsule ribbons overlapping structures infiltrated with fluorescence 8-anilino-1-naphthalenesulfonic acid (ANS) and rhodamine, respectively. Adapted from [31].

molecular glue infiltration were combined to obtain stable and ordered free-standing 3D nanoparticle structures (Fig. 6) and capsules (Fig. 7) with controllable sizes and geometries.

3D polystyrene nanoparticle composites were fabricated with Ad dendrimers and Au-CD as the supramolecular glues and assembled in a LbL fashion within the PS-CD crystal to yield nanoparticle composites. Free-standing hybrid polystyrene nanoparticle bridges were obtained by transfer printing of the hybrid structures onto topographically patterned substrates via host–guest interactions [28]. Atomic force microscopy (AFM)-based bending test measurements show that these nanoparticle bridges exhibited a classical position-dependent behavior of a homogeneous single-beam bridge with a bending modulus of 1.2 ± 0.4 GPa [28,30]. This is the first report on 3D and self-supported freestanding mesoscopic structures, bottom-up assembled from discrete and individual nanoparticles held together by intrinsically weak and dynamic supramolecular host–guest interactions. The ability to enhance the mechanical properties of free-standing particle bridges by supramolecular infiltration has initiated new perspectives for the formation of free-standing structures of desired shapes and sizes.

The sequential process was further exploited to form freely suspended porous capsule assemblies with specific functionalities (Fig. 7) [31]. Polystyrene particle composite structures were formed on NIL-patterned polymer templates by using self-assembly of particles and LbL assembly of supramolecular host- and guest-functionalized nanoparticles and dendrimers. The subsequent removal of the polystyrene cores of the hybrid particle structure resulted in the formation of macroscopic structures of interconnected porous capsules. The integrity, order, and functionality of the porous nanoparticle composites are preserved. These porous assemblies are capable of carrying fluorescent organic molecules.

CONCLUSIONS

This review illustrates the versatility of the combined supramolecular nanoparticle assembly and top-down fabrication techniques in creating 2D and 3D nanoparticle architectures. The incorporation of specific molecular recognition functionalities onto the surface of the nanoparticles allows the use of nanoparticles of arbitrary core material and size to form stable and ordered supramolecular nanoparticle structures, with a highly tunable and specific binding strength. In combination with the top-down fabrication techniques, 3D nanoparticle structures with well-defined geometries and sizes can be obtained. These supramolecular nanoparticle structures are ready to be used as 3D receptors for the application in sensing devices. The recognition function of the individual nanoparticles can be further engineered as a sensing tool in the subsequent assembly of complementary guest molecules or nano-objects.

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