JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Synthesis and Integration of Fe-soc-MOF Cubes into Colloidosomes via a Single-Step Emulsion-Based Approach

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Supporting Information

ABSTRACT: Bottom-up fabrication of complex 3D hollow superstructures from nonspherical building blocks (BBs) poses a significant challenge for scientists in materials chemistry and physics. Spherical colloidal silica or polystyrene particles are therefore often integrated as BBs for the preparation of an emerging class of materials, namely colloidosomes (using colloidal particles for Pickering stabilization and fusing them to form a permeable shell). Herein, we describe for the first time a one-step emulsion-based technique that permits the assembly of metal–organic framework (MOF) faceted polyhedral BBs (i.e., cubes instead of spheres) into 3D hollow superstructures (or "colloidosomes"). The shell of each resultant hollow MOF colloidosome is constructed from a monolayer of cubic BBs, whose dimensions can be precisely controlled by varying the amount of emulsifier used in the synthesis.

The targeted assembly of fundamental building blocks (BBs) into functional complex architectures has become a multidisciplinary topic, attracting interest in the areas of chemistry, physics, and materials science.[1,2] In particular, the development of tailor-made hollow micro- and nanostructures has recently been investigated due to their potential application in photonic devices, drug delivery, chemical sensors, energy storage and release, and catalysis.[3−7] Accordingly, procedures for fabricating hollow structures have been extensively developed and are based on two major templating methods, i.e., hard and soft.[6]

A specific class of superstructure named "colloidosomes" has emerged on the basis of the soft-templating method.[8−18] Colloidosomes are microcapsules or microspheres with shells consisting of close-packed colloidal particles or partially fused colloidal particles that self-assemble at the surface of emulsion droplets. Spherical solid particles are traditionally used as primary BBs to stabilize the emulsion droplets, and the colloidosomes are produced either by mixing immiscible solutions or by controlling the flow of immiscible fluids in microfluidic devices.[8−18] To date, the majority of colloidosome reports focus on well-known nonporous inorganic materials [e.g., spherical silica or polystyrene (PS) beads], and therefore their porosity is dictated by the interparticle spacing and voids between neighboring solid spheres. Accordingly, the development of hybrid organic–inorganic colloidosomes from highly porous metal–organic frameworks (MOFs) represents a promising alternative to introduce periodically disturbed isopores and thus access to tunable, controlled, and functionalized porosities. This is due in part to the unique attributes of MOFs, such as their hybrid nature, modularity, ultrahigh surface areas, tunable porosity, and mild synthetic conditions.[19−26] It is pertinent to mention that a limited number of reports pertaining to the fabrication of MOF hollow structures have appeared recently in the open literature.[27−30] For example, [HKUST-1, i.e., $Cu_3(BTC)_2(H_2O)_3$] hollow capsules and ZIF-8 hollow spheres were prepared by employing a soft interfacial formation technique and hard-templating method (with PS beads as sacrificial cores), respectively.[27,28] Lately, the spray-drying technique and two-step emulsion-based method were employed successfully to construct various MOF hollow spherical superstructures but mainly based on the assembly of nonuniform BBs.[29,30] Nevertheless, to the best of our knowledge, the open literature does not contain any reports on the fabrication of MOF colloidosomes via a single-step emulsion-based approach, likely due to the fact that the preparation of uniform BBs is a pertinent challenge and not straightforward.[31]

Among the developed synthetic protocols, the solvothermal method assisted by continuous stirring is regarded as one of the most effective approaches to obtain highly uniform nanometer- or micrometer-sized MOFs. In fact, our group recently reported a unique synthetic pathway to precisely control the uniformity and morphology of (In, Ga)-**soc**-MOF materials and successfully produce large area 2D superlattices using various polyhedral BBs (e.g., cubes, truncated and dodecahedral cubes).[31] Inspired by these results and the rapid development of colloidosomes, we continued our quest toward the deliberate formation of MOF colloidosomes, because this novel 3D integration would represent a fundamental challenge for both general colloidal chemistry and advanced architecture of MOF materials.

Received: April 22, 2013
Published: July 3, 2013

dx.doi.org/10.1021/ja403994u | J. Am. Chem. Soc. 2013, 135, 10234−10237

Herein, we report for the first time, a facile and efficient one-step, emulsion-templating approach to prepare Fe-**soc**-MOF hollow colloidosomes with a monolayer shell comprised exclusively of cubic BBs. Notably, the formation of Fe-**soc**-MOF BBs and resultant hollow superstructures takes place in a consecutive fashion during the one pot synthesis, similar to the previously reported one-step synthesis of gold hollow colloidosomes,[7] and totally distinct from traditional protocols where the BBs are usually prefabricated prior to their assembly into the final colloidosomes, i.e., a two step synthesis.[8−18,30]

Monodisperse BBs are a prerequisite for the construction of superstructures, and therefore in this project, we first optimized the experimental conditions in the presence of organic structure-directing agents (SDAs) and surfactants that permit the fabrication of uniform Fe-**soc**-MOF faceted polyhedral BBs (i.e., cubes).[31] For instance, under solvothermal reaction conditions, *tert*-butylamine was chosen as SDA to regulate the crystal growth, while polyvinylpyrrolidone (PVP) was adopted as surfactant to control the morphology and uniformity of the final pure phase of Fe-**soc**-MOF cubes. Indeed, monodisperse cubic BBs, with an average edge length of ∼900 ± 100 nm, were obtained with this synthetic route. Owing to the uniformity of the product, a 2D superlattice was readily formed in isolated locations via the oriented attachment mechanism (Figure S1) with permanent engagement among the BBs.[5,32,33] The powder X-ray diffraction (PXRD) pattern (Figure S1) for the resultant product is in good agreement with that of the calculated M^{III}-**soc**-MOF (e.g., M = In and Ga),[31,34] which confirms the homogeneity and formation of the pure phase, submicrometer-sized In-**soc**-MOF analogue, i.e., Fe-**soc**-MOF cube crystals (in this study).

Interestingly, during the preparation of Fe-**soc**-MOF cubes we observed spontaneous spherical organization of the cubes (i.e., the formation of MOF colloidosomes), when PVP was substituted with polyoxyethylene (20) sorbitan trioleate (tween-85). The driving force for controlling the relative size of the hollow colloidosomes was proven to be dependent upon the amount of tween-85 added, i.e., the diameter of the emulsion droplet decreased with increased concentration.[35,36] This trend is exemplified in Figure S2, where large (10−20 μm) and small (3−5 μm) Fe-**soc**-MOF hollow colloidosomes were prepared by adding 0.01−0.03 and 0.05 mL of tween-85, respectively. It should be noted that the relatively larger Fe-**soc**-MOF hollow colloidosomes prepared by adding 0.01 mL of tween-85 are less rigid, compared to those prepared by adding 0.03 mL of tween-85, which is probably due to ineffective stabilization of the hollow superstructures when a smaller amount of tween-85 is used in the respective synthesis.

Figure 1 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images for the as-synthesized small hollow colloidosomes assembled from uniform cubes (edge length of ∼310 ± 10 nm). The estimated inner cavity diameter was found to be in the range of 3−5 μm (Figure 1a−e), which is about 100 times smaller than the MOF hollow spheres synthesized by the aforementioned interfacial formation technique with which the MOF shell was grown continuously.[27] The inner cavities of the hollow superstructures were clearly identified in both SEM (Figure 1e) and corresponding TEM images (Figure 1f). Accordingly, the partially broken hollow colloidosomes reveal that the shell is composed of a monolayer of Fe-**soc**-MOF cubes with a wall thickness corresponding to the average edge length of the assembled cubes.

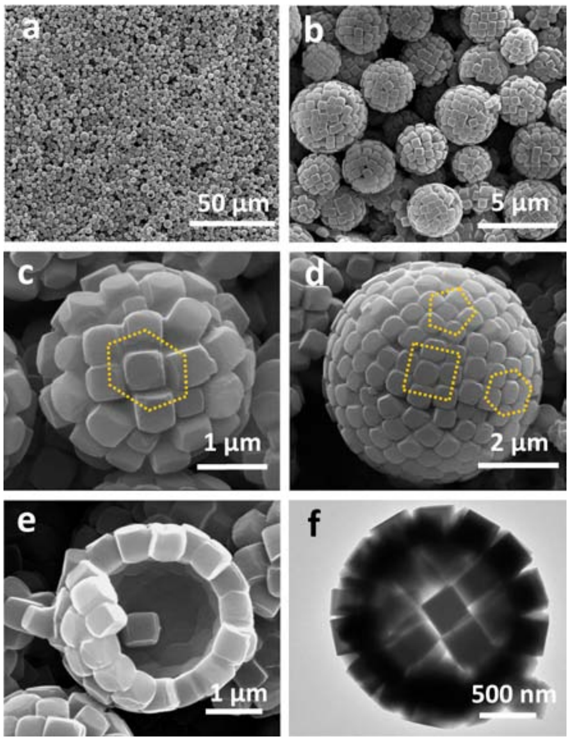

Figure 1. Small Fe-**soc**-MOF hollow colloidosomes prepared by adding 0.05 mL of tween-85: (a−e) SEM and (f) TEM images.

The PXRD pattern (Figure S4a) for the as-synthesized small hollow colloidosomes agrees well with that for the In-**soc**-MOF single crystals,[31,34] which confirms the formation of crystalline Fe-**soc**-MOF hollow colloidosomes by this one-step emulsion-templating method.

Conversely, the large hollow colloidosomes shown in Figure 2 were prepared by adding a reduced amount of tween-85 (i.e., 0.03 mL instead of 0.05 mL; Figures 2a−e). The shell also consists of a monolayer of cubic BBs (310 ± 10 nm); however, the diameter of the colloidosomes was in the range of 10−20 μm. Notably, this is still at least 20 times smaller than the MOF hollow spheres grown by the biphasic method.[27] It is to mention that the morphology of the colloidosomes remains unaltered under heat treatment up to 520 °C under N_2 flow and stepwise heating in a TGA measurement (see Figure S4b).

Due to the limitation of the general emulsion method, the resultant Fe-**soc**-MOF hollow colloidosomes exhibit a relatively broad size distribution. This is particularly evident in the case of the large hollow colloidosomes.[13,37] Since the monodisperse Fe-**soc**-MOF cubes form a monolayer shell, we can approximate the number of constituent Fe-**soc**-MOF cubes from the SEM images to be 30−200 units/BBs (Figure 1b−d) and 1400−2800 (Figure 2c−d) units/BBs per sphere, for the small and large hollow colloidosomes, respectively.

Figure 3 illustrates the evolution process of these hollow colloidosomes and our proposed mechanism of formation. First, emulsified droplets were formed by vigorously stirring the precursor mixture at room temperature with the assistance of tween-85 (soft template for the subsequent step). Monodisperse Fe-**soc**-MOF cubes were obtained after heating the mixture at 120 °C for 40 min in the presence of *tert*-butylamine. Then the as-synthesized cubes spontaneously self-assembled at the interface of the spherical droplets to form monolayer shells encapsulating the soft-templates (Figure S5); a process driven

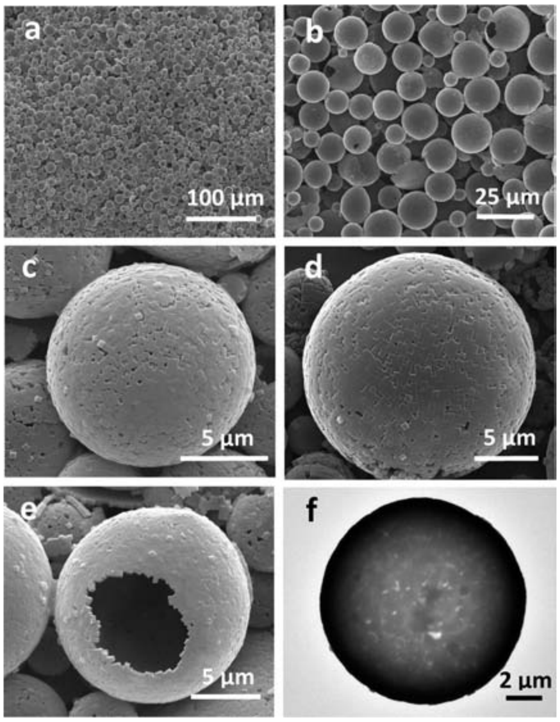

Figure 2. Large Fe-**soc**-MOF hollow colloidosomes prepared by adding 0.03 mL of tween-85: (a–d) SEM and (e) TEM images.

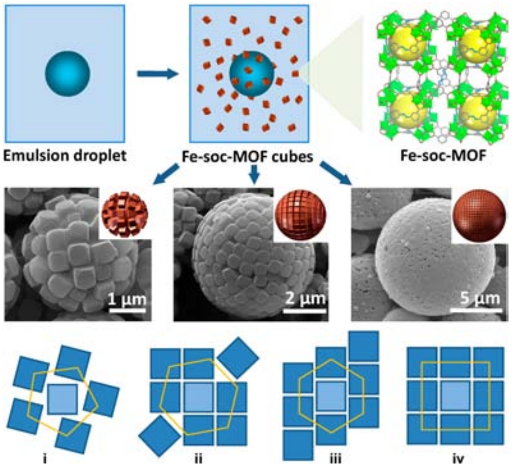

Figure 3. Schematic illustrations of synthesis and integration of Fe-**soc**-MOF cubes into hollow colloidosomes, the crystal structure of Fe-**soc**-MOF (top right panel), and basic polygons (i–iv, bottom panel) that form the single-shelled hollow colloidosomes; the central cubes inside the polygons are indicated in light blue.

by the reduction in the total interfacial energy. Prolonged solvothermal treatment was found to yield more colloidosomes with robust shells, probably due to the decomposition of tween-85 into alkylated oleate moieties which in turn assist locking the cubes into position (see Figure S6).[38,39] Hollow colloidosomes with a shell composed of a monolayer of Fe-**soc**-MOF cubes were finally formed after evaporation of the droplets.[9−14]

A careful examination of the surface topology of these colloidosomes indicates that a number of basic polygonal (geometric) arrangements are required for the cubic BBs to assemble into a colloidosome (Figure 3). The presence of two key/central polygons, i.e., five- (pentagons, Figure 3i) and six-membered rings (hexagons, Figure 3ii), permits the formation of a curved surface, as observed in the well-known fullerenes (e.g., C_{60} and C_{70}). Such organized polygonal domains are clearly present in our study, where the small Fe-**soc**-MOF colloidosomes have more cube/BB surfaces exposed (Figures 1, S2 and S3). In the case of the large colloidosomes, two additional polygons are present, and consequently, a flatter surface is evident (Figure 3iii,iv). Note that the latter two types of organizing "patches" are often observed in 2D superlattices assembled from cubic BBs. While types i and ii are required for the generation of a curved surface, the assembly of polygons types iii and iv permits a closer contact among the neighboring cubic BBs and thus reinforces the overall structural integrity of the material. In fact, integration with "oriented attachment" among the cubes has been observed in large colloidosomes through the latter two types of arrangements (Figure 2). It should also be mentioned that these polygons are distorted, because the cubic BBs are structurally anisotropic in terms of generating lateral connectivity within the monolayer shell organization.

In an effort to explore potential applications of these hollow MOF colloidosomes, low-pressure gas adsorption measurements were conducted on the exchanged and fully evacuated (@165 °C) Fe-**soc**-MOF cubes and small hollow colloidosomes. Indeed, the permanent microporosity of the small hollow Fe-**soc**-MOF colloidosomes was confirmed from the fully reversible type-I argon adsorption isotherm (Figure 4).

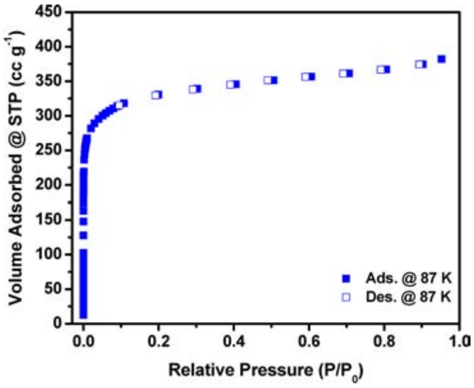

Figure 4. Argon adsorption isotherm at 87 K for the small Fe-**soc**-MOF hollow colloidosomes.

The apparent BET (Langmuir) surface area and total pore volume were estimated to be 1100 m^2/g (1210 m^2/g) and 0.49 cm^3/g, respectively. It should be noted that, although we utilized different surfactants (i.e., PVP vs tween-85) to obtain the monodispersed Fe-**soc**-MOF cubes and organized hollow Fe-**soc**-MOF colloidosomes, the resultant products were found to exhibit very similar gas adsorption behaviors (Table S1). Therefore, the entrapped organic phase on the surface of the hollow colloidosomes is minimal and does not appear to hinder access to the micropores. Nevertheless, the lower framework density of the Fe analogue affords higher uptakes relative to the isoreticular In-**soc**-MOF.[31] More advanced applications of these hollow MOF colloidosomes is in progress. For example, one objective is to discern ways to seal the remaining gaps between neighboring BBs (e.g., with "fillers"), so that such MOF "colloidosomes" can be utilized as a new type of microreactor providing all-angle access to the resultant submicrometer-sized inner voids (central space) of the colloidosomes via the MOF microporous system.

In summary, we have successfully developed a facile solvothermal approach for the fabrication of submicrometer-sized monodisperse Fe-**soc**-MOF cubes and their subsequent integration into 3D superstructures. For the first time, we have demonstrated the feasibility of integrating colloidosomes with controllable central space and shell thickness composed of highly porous MOF materials, using a monolayer of functional cubic BBs (as opposed to conventional spheres) via a continuous synthesis-cum-organization route. Owing to the fact that MOFs have been extensively investigated in the fields of drug delivery, controlled storage and release, active-material encapsulation, and catalysis, among others, the newly developed MOF superstructures in this work may serve as a novel structural platform for the above potential applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

PXRD, TGA curves, SEM images, and gas adsorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge financial support from King Abdullah University of Science and Technology (KAUST), Saudi Arabia and National University of Singapore (NUS), Singapore. The authors also would like to thank Kexin Yao and Lan Zhao in KAUST for productive discussion and TEM measurements.

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