Fullerene nanopottery : shaping and interconnecting hollow nanostructures

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SINGAPORE

**Fullerene Nanopottery: Shaping and Interconnecting Hollow
Nanostructures**

HAN Fei

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

Fullerene Nanopottery: Shaping and Interconnecting Hollow Nanostructures

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in partial fulfillment of the requirement for the degree of Doctor of Philosophy

2019

Special Statement

The work presented in this thesis was completed under the supervision of professor CHEN Hongyu.

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Authorship Attribution Statement

This thesis contains material from **1** paper published in the following peer-reviewed journal in which I am listed as the first author.

Some parts in Chapter 3 and 4 is published as F. Han, R. Wang, Y. Feng, S. Wang, L. Liu, X. Li, Y. Han, and H. Chen, On Demand Synthesis of Hollow Fullerene Nanostructures. *Nature Communications*, 10, 1548 (2019). DOI: 10.1038/s41467-019-09545-8

The contributions of the co-authors are as follows:

- Prof. Chen Hongyu provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Feng Yuhua.
- I co-designed the study with Prof. Chen and performed all the laboratory work at the School of Physical and Mathematical Sciences, Division of Chemistry and Biological chemistry. I also analyzed the data.
- All microscopy (unless mentioned in the following points), including sample preparation, was conducted by me in the above facility for Analysis, Characterization, Testing and Simulation.
- Dr Wang Ruoxu and Wang Shaoyan assisted in the taking some of the SEM images.
- Dr Liu Lingmei, Dr Li Xinghua, and Prof Han Yu assisted in the collection of EELs mapping and HR-TEM images.

Chapter 6 is in manuscript as F. Han, R. Wang, B. Chen, H. Liu, S. Wang, W. Xu, H. Zhang, Y. Feng, and H. Chen, Dimerization and Tetramerization of Fullerene Hollow Cavities

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- Dr Wang Ruoxu, Wang Shaoyan, and Xu Weichang assisted in mechanism study.
- Dr Chen Bo, and Prof. Zhang Hua assisted in the collection of EDX mapping and HR-TEM images.
- Liu Huanzhi helped in the construction of mathematic models.

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Abstract

My work has been largely focused on developing a methodology to fabricate fullerene hollow nanostructures, namely, nanopottery. It is a method to build, expand, and connect hollow compartments via a stepwise liquid templating strategy. Hollow nanostructures have been extensively used in materials, chemistry, and medicine. However, it is synthetically extremely difficult to increase their structural complexity. We bring pottery, the simplest and oldest method of making hollow structures, to the nanoscale, for the design and stepwise synthesis of hollow nanostructures.

As the first step, in chapter 2, we established a three-solvents system: IPA, xylene, and DMF, for the controllable deposition of fullerene materials. Metal@fullerene core-shell nanoparticles were synthesized and studied as a model system. In the following chapter 3 and 4, we demonstrated that in the above system, the liquid nature of *m*-xylene droplets template can be exploited to the synthesis of fullerene hollow nanostructures with tailored shapes, for example, bowl, bottle, and cucurbit, etc. The liquid templates permit stepwise and versatile manipulation, which would lead to modular assembly of hollow nodes and junctions into interconnected hollow system. Such stepwise shaping, addition, and connection are the fundamental operations in pottery, which could greatly expand the synthetic freedom for designing complex hollow nanostructures and interconnected systems. Last but not least, we provided critical regio-selectivity for this system in chapter 5. With the precise controlling of the nanobowls' opening size, the exposed area of droplet template can be precisely controlled to govern the extent of nanobowl self-assembly. A larger exposed area would allow more nanobowls to be assembled, so that steric hindrance as in organic chemistry was created among the bowls.

In short, my work demonstrates the dexterity in manipulating liquid droplets for templating fullerene hollow structures. Importantly, through the studying of its underlying mechanism, it also opens a window for the synthesis of complex hollow systems with the soft templates. In comparison to the literature works, our understanding of the mechanism allows rational design of the structures, and further using the geometrical shapes of the hollow structures to create regio-selectivity. The knowledge of creating critical selectivity around the droplets as synthetic handles, and adding appropriate material at the appropriate time point is critical for elevating the synthetic freedom in a complex system (beyond simple and conventional).

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List of Abbreviations

DMF:	Dimethylformamide
IPA:	Isopropanol
DLS:	Dynamic light scattering
EDX:	Energy dispersive X-ray
TEM:	Transmission electron microscopy
SEM:	Scanning electron microscopy
NP/NPs:	Nanoparticle/Nanoparticles

Chapter 1: Introduction

The ultimate goal of nano-synthesis is to create sophisticated components and eventually functional devices or nano-robots, just as the build of complex machines or robots in macroscopic world. However, it is unrealistic to use hands or tools to directly manipulate objects at the nanoscale, making the synthetic advances become the bottleneck for next stage exploration of nanotechnology.¹ Scientists cannot examine the property or test the application of a nanostructure, until the synthetic skills are in place to make it. During this process, as the methods become more sophisticated and the products become more complex in structure, serendipity would play a less important role. Without understanding the underlying mechanism, exploring the multi-dimensional parameter space by using try and error would be more difficult than finding a needle in a haystack.

Huge efforts have been devoted to this area in recent decades. Studying the synthesis of hollow nanostructures is of particular interests, due largely to their fantastic structures,^{2,3} unique property,⁴ and broad applications.⁵⁻⁷ To make advances in nano-synthesis and to polish the synthetic skills, we must go beyond the conventional structures and systems to acquire new synthetic capabilities. In order to learn from the traditional methodologies, design principals, and underlying mechanisms, commonly used approaches for hollow nanostructure synthesis is summarized. We believe such discussion would be of great help to consolidate our understandings and improve the flexibility to create new structures and synthetic pathways.

Fullerene is a star species that has been widely studied since its discovery in 1980s. However, as they would be readily crystallized upon precipitate,⁸ it is extremely difficult to tune the morphology of fullerene nanostructures via conventional approaches, which greatly limits their applications. We attempted to break the limit of traditional synthetic methods, and thus, as the first step, an overview of synthesizing fullerene nanostructures is presented.

Inspired by previous works, we are now committed to give a comprehensive insight into their basic properties and synthetic strategies in this chapter.

1.1. Fullerene, fullerene derivatives, and their applications

As one of the most important materials in carbon family, fullerene and its derivatives have attracted continuous interests since the initial discovery of C₆₀ molecules. In nanoscience, due to the wide applications and unique properties of fullerene and its derivatives, thousands of scientific works on fullerenes have been reported in recent decades. Particular efforts have been made to explore the synthesis of fullerene nanostructures due to their unique morphology and optoelectronic property.^{9,10} These features make the materials are promising in the application of optical devices,¹¹ organic solar cells,¹² superconductors,¹³ and organic thin films,¹⁴ *etc.*¹⁵⁻¹⁷ From the view of nano-synthesis, in order to seek for possibilities to overcome conventional systems, we need to study the basic properties of fullerenes, and then typical synthetic strategies of their nanostructures.

1.1.1. C₆₀ and C₇₀

A molecule of fullerene is consisted by single and double bond connected carbon atoms. The molecules usually have the shape of hollow sphere or ellipsoid, which are made up of closed mesh with fused rings of five to seven atoms. These molecules could be expressed in short with their chemical formula C_n, in which n is the number of carbon atoms contained in the molecule. Among the fullerene materials, those with simplest molecular structures such as C₆₀ and its homologue C₇₀ are most widely studied, and a series interesting properties have been found in the field of chemistry, physics, and materials.^{18,19} Moreover, the C=C bonds contained in fullerene molecules provide valuable opportunities for the functionalization of fullerene species, bringing their derivatives to the sight of scientists.

C_{60} and C_{70} are the two most abundant fullerenes. C_{60} , the earliest discovered fullerene molecules in 1985, has a structure similar to a soccer ball, in which 60 carbon atoms locate at each vertex of the molecule (Figure 1.1a). C_{70} serves as the earliest discovered homologue of C_{60} , having a rugby ball structure that consist of 70 carbon atoms (Figure 1.1b). Due to the unique enclosed spherical molecular structure of C_{60} and C_{70} , they have exceptional optical and electrical properties.²⁰

Figure 1.1. Molecular structures of (a) C_{60} , (b) C_{70} , and (c) PC₆₁BM.

C_{60} has outstanding optical properties because of its highly molecular nature in solid phase and the high molecular symmetry that gives rise to forbidden transitions, strict selection rules, and unique excitonic phenomena at the absorption edge.²¹ Tutt and Kost reported the first observation of non-linear optical limiting property of C_{60} and C_{70} in a solution phase.²² The experiment was carried with a 8 ns pulsed laser at a wavelength of 532 nm. When the incident light had an intensity of $100 \text{ mJ}\cdot\text{cm}^{-2}$ or slightly higher, C_{60} solution in toluene could clamp the transmitted fluence at $\sim 65 \text{ mJ}\cdot\text{cm}^{-2}$. Solution of C_{70} showed similar optical limiting behaviors: the output fluence can be clamped at $350 \text{ mJ}\cdot\text{cm}^{-2}$ in C_{70} solution in toluene. Hence, a typical application of C_{60} and its derivatives is optical limiters, which is usually combined with optical sensors to protect them from being damaged by over-bright light sources.²³ Importantly, the C_{60} doped materials also have excellent optical performance. For instance, Zidan et al. prepared C_{60} doped acetylene-dicarboxylic acid (ADC) polymer with unique non-linear optical property.²⁴ The material was prepared via a mild heated reflux of the ADC polymer and pristine C_{60} powders. The measurements of its optical property were carried with

a Z-scan measurement under the radiation of continuous wave laser (wavelength 635 nm). The as-measured non-linear absorption coefficient and the non-linear refractive index was 10^{-8} cm²/W and 10^{-3} cm/W, respectively.

Besides optical properties, C₆₀ and C₇₀ also have exceptional electrical properties, being widely applied in the field of semiconductor and superconductor.²⁵ Both C₆₀ and C₇₀ are an excellent n-type semiconductor with the activation energy varied from 0.1 to 0.3 eV,²⁶ being extensively used in high current density diode,²⁷ solar cells,²⁸ and so on.²⁹ Before the discovery of C₆₀ superconductivity, a pioneer research reported that the conductivity of C₆₀ and C₇₀ could be adjusted from semiconductive to conductive when doped with alkali metals.³⁰ After this work, such a property was further studied by the same group at a lower temperature. Hebard et al. reported the first case of superconductive potassium-doped C₆₀ film in 1992,³¹ in which the film was demonstrated to be superconductive at 18 K. The doping process was carried out at 433 K, by placing the mixture of C₆₀ and alkali metal vapor in sealed tubes. To avoid the dissociation of samples, the tube was placed either in high vacuum or under a partial pressure of helium. With similar methods, C₆₀ can be doped with other alkali metals such as rubidium and cesium.³² The alkali-doped C₆₀ materials have a general formula A₃C₆₀, and could reach a highest superconductive temperature of 40 K.³³

1.1.2. Fullerene derivatives

Chemical modification of simple fullerenes like C₆₀ and C₇₀ has become one of the major fields of fullerene chemistry. Due to the presence of spherical π electron surface, fullerene molecules usually have abundant electrons distribution around their surface, and thus, addition, cycloaddition, and electrochemical reaction have become the most popular synthetic approaches to open the double bonds in fullerene molecules.³⁴ With these methods, various functional groups could be decorated onto the molecules. Typical fullerene derivatives like

phenyl-C₆₁-butyric acid methyl ester (PCBM or PC₆₁BM), phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM), C₆₀F₆₀, and embedded fullerenes have been successfully synthesized. Comparing with the original fullerene molecules, chemical modifications could lead to property changes in solubility, optical property, and thermal conductivity,³⁵ etc.,^{36,37} making the derivatives of fullerene being extensively used in high efficiency solar cells, photocatalysis, solid lubricants, and optoelectronic devices.³⁸

PCBM or PC₆₁BM, an ester derivative of C₆₀, is the earliest synthesized fullerene derivatives in 1990s. It is also one of the most widely studied fullerene derivatives. PC₇₁BM was then synthesized via the same method. Both PC₆₁BM and PC₇₁BM can be prepared by refluxing a mix solution of 5-phenyl-5-(p-toluenesulfonyl hydrazino) valeric acid methyl ester and C₆₀/C₇₀ in *o*-dichlorobenzene.³⁹ Benefits from its high hole mobility, PC₆₁BM is the most efficient fullerene-based electron donor until now. This feature makes the organic solar cells (OSC) based on PC₆₁BM and P₃HT become the most efficient OSC for a long time (2005-2010).^{40,41} A traditional P₃HT-PC₆₁BM solar cell has a layered heterojunction structure that consisted of glass supporting, PEDOT-PSS modifier, and an active layer containing P₃HT and PC₆₁BM (Figure 1.2a). Importantly, in 2018, PC₆₁BM solar cells with a heterojunction perovskite structure reached a power conversion efficiency of 20.43% with a fill factor of 83.4%.⁴² The authors prepared a p-i-n type solar cell with a planar structure of FTO/NiO/CH₃NH₃PbI₃/PC₆₁BM/PPDIN₆/Ag layers as shown in Figure 1.2b. Different from the traditional PC₆₁BM perovskite solar cell, an amino-functionalized perylene di-imide polymer (PPDIN₆) was inserted between the PC₆₁BM/Ag layer to reduce the battery trap density, thereby facilitating electron extraction and suppressing electron recombination at the layers' interface.

Figure 1.2. Typical cell structure of a (a) P₃HT and PC₆₁BM heterojunction, and (b) PC₆₁BM solar cell with a heterojunction perovskite structure.

1.2. Synthesis and application of fullerene nanostructures

In the past decades, a number of popular synthetic methodologies have been reported for the synthesis of fullerene nano/micro-structures, such as precipitation method, templating techniques, slow evaporation of solvents, and chemical vapor deposition (CVD) methods. Among them, synthesis in solution phase has attracted particular attentions due to their simple steps, ease of scaling up, and diversity of synthesized structures' morphology.⁴³

As pure fullerenes like C₆₀ and C₇₀ are extremely easy to crystallize upon precipitation from a good solvent, liquid phase precipitation is commonly adopted for their synthesis.⁴⁴ With it, fullerene nano/micro-structures with a variety of morphologies (e.g., space structures from 1D to 3D) could be rationally designed and synthesized. The shape and size of the fullerene nanostructures critically depend on the synthetic route, and hence, to break the limit of current systems, a comprehensive study into their synthetic strategy is necessary.

In solution phases, direct precipitation method is the most straightforward methodology for preparing fullerene nanostructures. It can be done within one-step: the fullerene is dissolved in a good solvent first, and a poor solvent is then added to reduce its solubility, giving solid precipitate with pre-designed shapes.⁴⁵ Usually, the precipitation of fullerene is a seeded-

growth process, leading to the crystalline structure of the products. For example, Jin and co-workers reported the synthesis of highly uniformed C₆₀ nanorods with this method,⁴⁶ in which C₆₀ nanorods were synthesized via the direct addition of IPA (poor solvent) into the C₆₀ solution in toluene. The nanorods have a prism-like morphology with a hexagonal cross-section, and their length can be controlled by changing the addition rate of IPA. HR-TEM characterizations suggest the nanorods have a *fcc* crystalline structure. It is noteworthy that similar strategy is applicable not only for fullerene materials, but also for other organic materials.^{47,48} Therefore, there should be greater potential for applying this strategy to a broader range of materials or solvent systems.

Liquid-liquid interfacial precipitation (LLIP) method is a derivative of direct precipitation method, providing a more controllable route for the synthesis of fullerene nanostructures. It employs liquid interfaces of the two solvents simultaneously as the nucleation sites for crystals and the restriction for the nucleation sites. This synthetic strategy was first report by Miyazawa et al. for the synthesis of crystalline C₆₀ nanowhiskers,⁴⁹ in which the interface between the C₆₀ solution in toluene and IPA is used as the nucleation site. A subsequent study from this group reported that LLIP method can be used for the synthesis of more complexed fullerene structures.⁵⁰ In this case, 2D C₆₀ nanosheets with different sizes and shapes were synthesized at the interface between alcohol and C₆₀ solution. When different good/poor solvent combinations were used, for example, CCl₄/IPA or toluene/*tert*-butyl alcohol, C₆₀ rhombi or hexagons with uniform sizes and shapes were obtained as shown in Figure 1.3b & c, and Figure 1.3d & e, respectively. Moreover, this strategy can be used for the synthesis of other fullerene structures, such as C₇₀ tube and nanowhiskers,⁵¹ or fullerene flowers. For instance, Kim et al. prepared mix fullerene flowers with a modified LLIP method,⁵² in which the products were formed at the interface between ethanol and a mix solution of C₆₀ and C₇₀ in mesitylene.

Figure 1.3. (a) Schematic illustrating the synthetic route of C_{60} nanosheets with LLIP methods. (b-g) the synthesized nanosheets with different morphologies and different routes. Reprinted and modified from ref. 44 with permission. Copyright © 2013, John Wiley and Sons.

Though a systematic study has yet to be reported, but it is generally agreed that the construction of fullerene nano/micro-structures with different morphologies would lead to enhanced properties or brand-new applications.^{3,44} For example, fullerene materials are sp^2 -rich species, and are able to selectively interact with electron-rich species. Unique applications can be achieved when this feature is combined with specific structures. Ariga et al. reported the fabrication of “Hole-in-Cube” fullerene (C_{70} and C_{70} derivatives) crystals via a modified LLIP method,⁵³ in which a size-tuneable hole was introduced at the central and each surface of fullerene cubes (Figure 1.4b-e). Due to the cubes are made up of sp^2 -rich carbon materials, these open-hole cubes could selectively recognize graphitic carbon particles among polymeric resin particles: the graphitic carbon particles can be trapped within the hole, while the polymer particles stays out (Figure 1.4a).

Also, the π -electron rich property of fullerene materials can be combined with hollow nano/micro-structures to achieve elevated performances.⁵⁴ A recent report showed that hollow

fullerene nanostructures showed excellent vapor sensing performance for recognizing acid vapors.⁵⁵ The hollow materials were prepared by chemical etching of C_{60}/C_{70} crystals in solution phases. When being used on a quartz crystal microbalance as chemical sensors, they could selectively detect and adsorb formic or acetic acids from a mixture of aromatic vapors (benzene or toluene). Due to the high specific surface area brought by hollow nanostructures, their sensing performance is much better than solid fullerene materials. Similarly, sensing performance improvements for aromatic compounds can be observed on nanoporous tubes of fullerene crystals.⁵⁶

Figure 1.4. (a) Schematic illustrating the synthetic route of “Hole-in-Cube” fullerene crystal. (b, c) SEM images of the synthesized nanocrystals. (d, e) TEM and HR-TEM images of the as-prepared nanocrystals, respectively. Reprinted and modified from ref. 53 with permission. Copyright © 2017, American Chemical Society.

In short, C_{60} is probably the most studied fullerene material in the field of nanosynthesis, and the liquid precipitation method serves as an effective methodology for their synthesis. Despite great efforts, due to the sparing solubility of C_{60} or other unmodified fullerenes in most non-aromatic solvents and the large size of fullerenes molecules,⁵⁷ the controllable synthesis of solid fullerene nanostructures is still difficult. Only few solvents combinations can be used for the synthesis (good solvents like aromatic solvents and CCl_4 ;

poor solvents like alcohol), and most fullerene nano/micro-structures have simple symmetric structures. To increase the structural complexity, e.g., break the symmetry, is still a great challenge, not to mention synthesis more sophisticated structures. These problems have remained unsolved for over a decade. The lacking of synthetic capability greatly limits the application of fullerene materials. Hence, exploring new synthetic approaches beyond the conventional systems are in great demand.

1.3. Overview of hollow nanostructure synthesis

Hollow nanostructures with inner void space and functional shells are of critical significance in nanoscience. For instance, in the field of catalysis, hollow nanostructures can be used as supporting materials or directly as catalysts due to their high surface to volume ratio and low density,⁵⁸ which give high catalytic efficiency. On the other hand, the cavities could be adopted as nanocontainers to hold goods or reagents, which enable the application of hollow nanostructure as drug delivery carriers and nanoreactors.^{59,60} Furthermore, exploiting different functional materials to generate synergistic effect with the hollow structure can bring about a variety of important applications such as sensing and energy storage.^{61,62} Briefly, hollow nanostructures offer an additional direction for the rational design of novel functional material and application.

Despite the great structural advantages demonstrated by hollow nanostructures, there are still lots of room for improvements. The ultimate use of hollow structures can be found in biology, where cells and the various organelles are essentially smart hollow systems. Their structural precision, diversity, stability and flexibility are so far difficult to emulate. Their shells (*i.e.* cell membrane, etc.) are highly sophisticated, not only as a physical barrier separating and protecting the content, but also capable of regulating materials exchange and signaling, and

facilitating merging and splitting.⁶³ Most importantly, the various hollow compartments could form a highly integrated system and jointly complete the desired functions.

To realize the great promise of hollow nanostructures, synthetic advances are in urgent demand. Obviously, we cannot use any objects that are beyond the current synthetic skills, which are the foundation and prerequisite for any applications. It requires the synthetic methods to be more reproducible, versatile, scalable, and to yield more complex nanostructures with a broader scope, but the current nanofabrication capabilities still far from such basic demands. We should develop new synthetic concepts and methodologies beyond the conventional systems. To do so, we have to gain experience from the past methodologies and strategies. In this part, we start from different synthetic approaches, typically, the template synthesis and self-template (or template-free) synthesis, to analyze their characteristics and applicable conditions. Then, further understanding of the similarities and differences between these methods is summarized and discussed.

1.3.1. Concept of template methods

Templating method is a straightforward approach for the synthesis of hollow structures. Generally, it is based on a ready-made mold to produce morphologically similar objects. In macroscopic world, the template method has been widely used in manufacturing, such as metal casting and injection molding. Typically, liquid form of metal or polymer is injected into a mold with desired shape. After solidification and removal of the template, the resulting object retains the form of the templating mold, allowing multiple copies to be mass produced with structural consistency. Finally, the template must be disassembled so that the product can be retrieved. In most cases, the mold remains intact and can be reused.

Similar as the procedures in macroscopic world, the general strategy for templated preparation of materials at the nanoscale contains the following three steps (Figure 1.5): (1)

template preparation, (2) coating target materials onto the template to obtain the desired shapes, and (3) removal of the template (when necessary).⁶⁴ Such a methodology is mostly used to synthesis hollow nanostructures. Benefits from the pre-synthesized templates, the synthesized structures have a well-defined size and shape.

Figure 1.5. Schematic illustrating the hard template synthesis process. Reprinted and modified from ref. 64 with permission. Copyright © 2016, American Chemical Society.

Most of the templating syntheses of nanostructures are carried with a colloidal solution, and the combination of template and target materials usually rely on a “bottom-up” self-assembly or coating process. The target material is often dissolved in solution in the form of molecular and ionic precursors or directly as nanoparticles (NPs), so that they can diffuse and uniformly deposit on/in the template. Instead of directly injecting the new materials into the mold, one has to rely on the intrinsic properties of molecules or ions, in order to “guide” them to the template. For deposition on the surface of template NPs, usually one can exploit the kinetics of heterogeneous nucleation, and to cause conformal coating, the wetting of the desired material on the template NPs have to be considered.⁶⁵ After nucleation and growth, the desired material eventually solidified on the template with a copied shape.

Overall, our introduction on templated synthesis is divided according to the type of templates used. As shown in Figure 1.6, the type of templates can be classified into colloidal and non-colloidal.⁶⁶ Among the colloidal templates, typical examples on hard (colloidal) templates will be introduced in cases of both chemical and physical templating. Then, as a special kind of non-colloidal templates, synthesis based on soft materials will be introduced.

Last but not least, as a special kind of synthetic methodology, self-template and template-free method will be introduced, as well.

Figure 1.6. Classification of the commonly used template types.

1.3.2. Deposition of target materials

As mentioned previously, after template preparation, the first step is the deposition of target materials. Several methods have been successfully applied to this process, varying with the different templates and desired target materials. Typical methodologies include the layer-by-layer (LbL) assembly, sol-gel process, electrodeposition, chemical reduction, and physical coating methods.

LbL assembly is a popular coating methodology in colloidal solution based on electrostatic interactions, in which shell formation involves a step-wise alternating absorption of contrary charged materials. It serves as an effective way for the deposition of both organic and polymeric hollow nanostructures.⁶⁷ For instance, Caruso et al. reported the synthesis of mono-dispersed hollow micelles with lipid bilayers via the LbL method.⁶⁸ It is also the first case on the synthesis of hollow nanostructures with a hard template. As illustrated in Figure 1.7e, negative charged polystyrene (PS) NPs with a diameter of 640 nm were employed as the hard template, and a thin layer of positive charged poly-(diallyl-dimethylammonium chloride)

was deposited onto their surface. The positive charged film was used for the subsequent deposition of SiO₂ NPs (size around 25 nm). After the removing of PS core with either THF dissolution or calcination, hybrid polymer-silica hollow spheres were obtained (Figure 1.7c and d). Simply by changing the number of polymer-silica layer deposition cycles, the thickness of the shell is tunable from ~10 to over 200 nm.

Figure 1.7. (a, b) SEM and TEM images of the PS template with a layer of silica. (c, d) SEM and TEM images of the as-prepared hollow structures. (e) Schematics illustrating the procedures for preparing the inorganic hollow spheres by using PS NPs as the template. Reproduced and modified from ref 69 with permission.

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Moreover, the LbL assembly could be used for the deposition of target material onto soft templates, e.g., onto liquid droplets. A typical synthetic example was reported by Khapli's group.⁶⁹ In their work, hollow polyelectrolyte (PE) capsules were synthesized via the LbL assembly in a water-cyclohexane emulsion, with the droplets of cyclohexane served as soft templates. As a start, a small amount of poly-(styrene-sulfonate) (PSS) was added to the mixture of cyclohexane and water, followed by vigorous sonication. Then, poly-(allylamine

hydrochloride) (PAH) was added and adsorbed onto the droplet surface to form the second layer. The droplets of cyclohexane were frozen to avoid coalescence, and they were evaporated to give the hollow capsules with the size ranging from 10-15 μm .

Besides LbL assembly, sol-gel process also serves as an effective methodology for the coating step. The sol-gel process is commonly used for the preparation of bulk nano/micro-sized materials from small molecules.⁶⁴ It is widely used in the deposition of oxides layers, for example, in the deposition of titanium oxides and silicon oxide layers. In this method, the template particles are dispersed into the precursor colloidal solution (sol, Figure 1.8). And the latter process involves hydrolysis and deposition of the precursor phase at the template surface that resulting in the sol-gel of target product.⁷⁰ Under the certain conditions of drying and curing, the gel further precipitated out, forming a shell covering around the template particles. Occasionally, before the coating process, certain functional groups are deployed onto the templates to modify their surface properties. With this method, the interfacial energy between the two phases (template and shell material) could be adjusted for better deposition.⁶⁵ For instance, Tissot and co-workers reported the preparation of hollow silica nanospheres with silanol groups modified PS as the template.⁷¹ Silicon hydroxyl, amine group, and assisted-surfactant like poly-(vinylpyrrolidone) (PVP) are also frequently used ligands for the surface modification.⁷² Due to the limit from its synthetic principle, sol-gel process is usually adopted for hard template synthesis.

Figure 1.8. Illustration of typical sol-gel synthetic procedures. Reproduced and modified from ref 70 with permission. Copyright © 2013 Elsevier Science.

Also, electrodeposition such as electrophoretic deposition, electroplating (for metals), and electro-polymerization (for conducting polymers) are frequently used as the deposition method. For electrodeposition, a preliminary step would be surface modification of the template, which provides available binding sites for the following nucleation and growth.⁶⁶ For instance, Lei and co-workers prepared silver nanosphere arrays with the electrophoretic deposition methodology.⁷³ In this work, a layer of PS spheres (diameter around 700 nm) was used as the template. The PS template was placed at the cathode of the electrophoresis, and coated with a thin layer of silver first. The electrophoresis was carried in silver colloidal solution that contains ~10 nm sized silver NPs. The surface roughness of the as-prepared silver spheres was tuned via current density and plasma etching. Xu and co-workers synthesized a poly-pyrrole (PPy) film with hollow nanohorn arrays via electro-polymerization method.⁷⁴ Micelles of toluenesulfonic acid containing pyrrole monomers is used as the soft template. The

shape of the micelles was tuned via the potential and the pH value of the reaction solution and thus, the morphology of the PPy films could be controlled.

In addition, chemical reduction methods like hydrothermal reduction, microwave reduction, and ultrasonic reduction can be used to plat a layer of materials onto the template surface. Among these methods, hydrothermal reduction is extensively used in the colloidal templated synthesis of hollow nanostructures. It has unique advantages in scalability, product crystallinity, and good generality in synthesizing various morphologies.⁶⁶ Hydrothermal synthesis can be applied in a wide range of materials, for example, metal/metal oxides, carbon-based materials, and ceramics. Recently, Lou et al. reported the preparation of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanospheres with a one-step hydrothermal reaction (Figure 1.9).⁷⁵ The synthesis employed silica as the hard template and LiOH solution as the chemical lithiation reagent. Start from bare silica spheres, a layer of titanium dioxide was deposited onto the silica template via a sol-gel process. A hydrothermal reaction was then carried to lithiate the TiO_2 shell and to dissolve the silica core, giving the mesoporous hollow spheres (Figure 1.9d-g).

Figure 1.9. (a) Schematic showing the synthetic steps of mesoporous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ hollow spheres; SEM (b) and TEM (c) images of the $\text{SiO}_2@\text{TiO}_2$ NPs, and their HR-TEM images (d,e); SEM (f) and TEM (g) images of

Li₄Ti₅O₁₂ hollow spheres. Reproduced and modified from ref 75 with permission. Copyright © 2013, John Wiley and Sons.

Chemical methods are not the only approaches for the deposition process. Physical coating methods like physical and chemical vapor deposition (PVD and CVD) and spin coating has been widely used for the direct coating of target materials. These methods are usually used for the fabrication of ordered arrays or templating on a flat surface.⁶⁴ For instance, Wang et al. prepared hollow carbon-SnO₂ nanosphere array through the CVD methodology.⁷⁶ Benzene vapor was deposited against silica sphere templates via CVD to form the carbon shells. Then, SnO₂ NPs were deposited onto their surface via a solution phase reduction method. Moreover, CVD can be accompanied with the thermal reduction process to produce more sophisticated structures. Yin et al. synthesized porous silica nanotubes with the CVD method.⁷⁷ The synthesis employs mesoporous anodic aluminum oxide (AAO) as the template, and the poly-(dimethylsiloxane) (PDMS) was thermally heated and decomposed to obtain the silica vapor which could be deposited onto the AAO template.

1.3.3. Hard template synthesis

Hard template specifically refers to some rigid micro/nanoscale stuffs that can be used for the deposition of target materials, for example, silica, polymer, ceramics, carbon, NPs, and even plant fibers.⁶⁴ It is noteworthy that polymer frameworks with high crosslinks are considered as hard templates, while those with low degree of crosslink can be used as soft templates, such as micelles by block polymers. In this part, we will start with introducing typical kinds of hard templates according to their different compositions. At the end, the advantages and disadvantages of hard template synthesis will be discussed.

1.3.3.1. Commonly used hard template

Polymer NPs are probably the most widely used hard template. Among them, PS and its derivatives are commonly used because it is often easy to selectively remove them after the deposition of target materials. As mentioned in Chapter 1.3.2, the first report on the templated synthesis of hollow nanostructures was carried out with PS template.⁶⁸ Such a strategy appears to be general, and hollow nanostructures of other materials could be readily synthesized with it. For instance, Caruso and co-workers prepared titania hollow nanospheres by using negatively charged PS particle as the templates,⁷⁸ and the chelating compound titanium bis-(ammonium lactate) dihydroxide (TALH) was adopted as the precursor. Roughly, the positively charged poly-(diallyl dimethylammonium) chloride (PDADMAC) and negatively charged PSS was sequentially deposited onto the PS surface via a LbL assembly manner (Figure 1.10a). Then, TALH was added to the colloidal solution of polymer coated PS to form the last layer. Finally, a calcination treatment was carried out to form the titania hollow nanospheres (Figure 1.10b-e).

Figure 1.10. (a) Schematic showing the synthetic route of titania hollow nanospheres. The grey dots represent the precursor of TALH. TEM images of the as-prepared hollow spheres with seven-layer pairs of TALH and

PDADMAC (b-c), and their HR-TEM image. Reproduced and modified from ref. 78 with permission.

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Except for polymer NPs, silica is another class of popular hard templates. It has unique advantages in cheap price, high uniformity, widely adjustable particle size, and ease of preparation.⁷⁹ Usually, solid silica NPs with their size ranging from 40-1.5 μm can be prepared via the “Stöber method”.⁸⁰ Hyeon et al. fabricated hollow nanospheres of palladium by applying solid silica NPs as the template.⁸¹ The surface of silica NPs was first functionalized with 3-(trimethoxysilyl) propyl methacrylate to facilitate the adsorption of palladium precursor ($\text{Pd}(\text{acac})_2$). Then, the Pd hollow spheres were obtained by heating the mixture to 250 °C for 3 h, followed by adding an etchant.

Carbon-based materials have been extensively employed as the hard templates in the fabrication of hollow structures due to their unique features, including ease of preparation and removal, and their low cost.⁷⁹ Importantly, the porous structure of carbon materials provides valuable opportunity for the adsorption of synthetic precursors, so that the shell growth could be greatly facilitated. Employing solid carbon sphere as the template, Titirici and co-workers reported a one-pot synthesis of hollow metal oxides nanospheres through a hydrothermal methodology.⁸² In this case, D-glucose monohydrate was used as the carbon precursor. It was dissolved in water together with the metal salts. The mix solution was transferred into an autoclave, heated to 180 °C for 24 h, and calcinated to form the metal oxide hollow spheres. During the heating process, carbon spheres with a hydrophilic surface formed first. Then, the metal ions were adsorbed onto their surface to become the new shell. A variety of hollow spheres can be synthesized with this methodology, including but not limit to CuO, CeO₂, Co₃O₄, MgO, NiO, and Fe(III) oxide.

Metal NPs can be used as hard template, as well. A general strategy in using it as the template is to make core-shell NPs (metal@shell) first, followed by removing of the metal

core.⁸³ The type of metal core includes but not limit to the NPs of gold, silver, Pd, Pt, Cu, and metal oxides, etc.⁶⁶ The relevant work has been reported by Marinakos and co-workers,⁸⁴ in which poly-(N-methyl-pyrrole) and poly-pyrrole hollow capsules were prepared by using gold NPs as the template. Au NPs with their diameter around 5-200 nm were filtered through a porous membrane. The initiator of the reaction, $\text{Fe}(\text{ClO}_4)_3$ aqueous solution was then added onto the membrane. The polymerization reaction on the gold NPs surface was initiated when vapor of the monomer diffused through the membrane. After the shell formation, the Au core was removed via the addition of etchant solution (mixture of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and KCN).

Besides polymer, silica, and metal NPs, inorganic or complex salts could be adopted as the hard template of hollow structures, as well.⁸⁵ For example, Chen et al. reported the fabrication of mesoporous silica hollow spheres with diameter around 50-70 nm by using size tunable CaCO_3 NPs as the templates.⁸⁶ In this work, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was used as the silica precursor, which was heated to form a layer of silica on the template surface. The CaCO_3 core was removed through the etching of HCl. The synthesized silica spheres have a shell thickness around 10 nm. Also, Yin et al. applied the nanorods of a complex, $[\text{Ni}(\text{N}_2\text{H}_4)_3](\text{NO}_3)_2$ as the template to fabricate hollow silica nanotubes.⁸⁷ By tuning the aspect ratio of the nanorods, the corresponding aspect ratio of the resulting nanotubes could be readily controlled. The silica was deposited onto the nanorods via a sol-gel process to form a core-shell structure. Then, the complex nanorods could be removed via the addition of strong acid like HCl, leaving silica nanotubes.

1.3.3.2. Limitations of hard template

Due to its straightforward synthetic strategy, hard template method is the most widely used methodology in the synthesis of hollow nanostructures. However, there are significant limitations and challenges during the using of this synthetic strategy.

The first problem comes from the separation of template and product. As mentioned previously, the hard template method requires physical separation of template and product, and there is a lack of methods to do the separation. Usually, the template could only be removed by chemical etching, calcination, or dissolving in a solvent.⁶⁶ It is often hard to evaluate if the template has been completely removed, particularly considering the interface layer with the product, which is important for the surface properties.

In terms of the synthetic steps, the hard template methods mainly have drawbacks in two aspects. On one hand, it requires multi-step and tedious treatments, where the errors in each step would accumulate and lead to low yield. This is particularly problematic for nano-synthesis, as the steps have yet to be optimized. On the other hand, the synthesized structures with hard template methods critically depends on the shape of template. The final products only replicate the shape of template. It should be noted that it is hard to fabricate a template with arbitrary shape as desired. In the field of nanomaterials, there are few available shapes to choose from and the templating method does not create new morphologies. From the point of view of advancing synthetic skills, hard template method is less interesting.

1.3.4. Soft template synthesis

Recently, the strategy of soft template synthesis has attracted continuous interests for the construction of hollow nano/micro-structures. Just as its name implies, a soft template is usually a fluid substance, for example, droplets in an emulsion, vesicles or micelles, and gas bubbles, etc.⁸⁸ Comparing with the hard one, as the liquid droplets and air bubbles are easy to vaporize upon drying, only the coating process is necessary in most soft template synthesis. Hence, such a synthetic strategy provides a more facile approach for the preparation of hollow structures. As the shape of fluid substance could be readily modulated, it also provides more possibilities to increase the structural complexity of hollow structures. Now, the soft template

synthesis could be applied for the synthesis of carbon-based, organic, polymer, silica (SiO_2), and oxides hollow structures, etc.⁶⁴

1.3.4.1. Emulsion-based soft template

I. Definitions and classifications

Usually, an emulsion can be produced by a mixture of two or more immiscible liquids, and it is defined as a dispersion of the droplets of one liquid in a second liquid. According to the definition, an emulsion system usually contains a dispersed phase and a continuous phase.⁸⁹ An emulsion can be classified according to the different polarities of dispersed phase and continuous phase: a direct emulsion is the dispersion of oil-in-water (O/W), and a reverse emulsion is the dispersion of water-in-oil (W/O). The definition of 'oil' and 'water' is not strictly limit to their literal meaning. The oil can be any liquid with a low polarity, and the water can be any liquid with a high polarity.

The size of droplets in an emulsion have a wide distribution, usually from 10 nm to 100 μm , providing opportunities for the templating of hollow structures with different sizes. In order to use emulsion droplets as the template, at the first, emulsion droplets have to be steadily dispersed in solution. Usually, the dispersed phase droplets in the continuous phase are thermodynamically unstable, and tend to gather small droplets into large droplets, and then produce stratification.⁹⁰ However, even though the droplets are not in an equilibrium position, the emulsion can be kept at a metastable state, with their droplets remain integrity for an extended period if their surface is stabilized by surfactants/amphiphilic molecules to reduce the interfacial tension.⁶⁵

To obtain hollow nanostructures, in most cases, it requires the use of the interface between dispersed phase and continuous phase to deposit materials onto the surface of emulsion droplets, which is similar to hard-templating method. As mentioned in chapter 1.2.2.,

there are some typical coating processes could be applied, for instance, LbL assembly and in-situ polymerization for polymer hollow structures, sol-gel coating and hydrothermal deposition for inorganic hollow structures (e.g., metallic and non-metallic oxide), and interfacial precipitation for organic hollow structures, etc.⁹¹⁻⁹³ After that, the liquid core can be readily removed by adding solvents or evaporation.

II. Direct emulsion synthesis

Direct emulsion can be used for the preparation of polymeric, inorganic, and organic hollow nanostructures with various morphologies, such as capsules, spheres, balloons, and hollow tubes.⁶⁴

There are two major strategies for the preparation of hollow polymeric structures with a direct emulsion system. The first method is a two-step synthesis, which includes a polymerization and a swelling process.⁹⁴ Starting from an emulsion contains the monomers (oil, dispersed phase) and water (continuous phase), the emulsion needs excessive surfactant to form the micelles and to stabilize the droplets (Figure 1.11a). The micelles would serve as nanoreactors for the polymerization, which is able to convert the monomers into polymer particles. This methodology was first reported by Rohm et al. to prepare hollow polymeric spheres.⁹⁵ In this work, carboxylate NPs were synthesized via the above steps, and the hollow structures were then produced by an osmotic swelling process. Finally, under a base condition, the ionization of the carboxylate NPs gives the hollow structure (Figure 1.11b-d).

Figure 1.11. (a) Schematic illustrating the synthetic process of the hollow carboxylate nanospheres. (b-d) TEM images of the hollow spheres with different void space. Reprinted and modified from ref. 95 with permission. Copyright © 2000, American Chemical Society.

Different from the two-step synthesis, recently, a one-step emulsion method is reported for the simplified synthesis of hollow polymeric structures. Luo and co-workers prepared hollow polymeric nanostructures via an interfacial radical emulsion polymerization reaction (reversible addition-fragmentation chain transfer, RAFT).⁹⁶ The as-prepared hollow structure is highly crosslinked and non-collapsed. In their synthesis, through the deployment of amphiphilic RAFT agents, the polymerization reaction is restricted at the interface of the liquid droplets and the water phase. The polymer shells are produced via the living growth of the polymer chains during polymerization, which allows the growth of the polymer shell with ultra-high extent of crosslinking, and thus, it could prevent the collapse of the hollow nanostructures during drying.

Moreover, inorganic hollow nanostructures can be obtained with the direct emulsion synthesis. Through the using of a hydrothermal reaction or a sol-gel process, inorganic materials are deposited onto the droplets via hydrogen bonds or electrostatic force. A typical

example was reported by Zoldesti and co-workers,⁹⁷ in which monodispersed silica hollow nanostructures such as capsules, balloons, and spheres could be reasonably synthesized (Figure 1.12). In this case, an O/W emulsion was obtained via mixing dimethyl-diethoxysilane with water, giving droplets with the size of 0.6-2 μm . Then, silica was deposited onto the droplets via mild hydrolysis and condensation of tetraethoxysilane (TEOS). Morphology of the as-prepared hollow structures were adjusted by tuning the thickness of the silica shells: the particles cannot maintain the spherical shape upon drying when they had a thin shell, and thus, collapsed structures were obtained (Figure 1.12f). With similar emulsion system, it is noteworthy that other inorganic hollow nanostructures such as TiO_2 and ZnO can be prepared via a sol-gel deposition process, as well.^{91, 95}

Figure 1.12. TEM images of silica hollow nanostructures synthesized with direct emulsion templating methodology. (a-d) silica hollow capsules with different size and shapes. (e, f) silica microballoons. Reprinted from ref. 97 with permission. Copyright © 2005, John Wiley and Sons.

III. Reverse emulsion synthesis

Synthesis carried in a reverse emulsion system are typically employed in the synthesis of hollow inorganic (e.g., metal oxides/sulfides) and polymeric nanostructures.

Hollow structures of inorganic materials can be synthesized in a reverse emulsion system via interfacial precipitation reactions. A typical example comes from Yu and co-workers,⁹⁹ in which a W/O reverse emulsion consisted by CS₂ and water was adopted for the synthesis of CuS hollow spheres. CuSO₄ and Na₂S were used as the source of Cu²⁺ and S²⁻. A surfactant, Triton X-100, was dissolved into the aqueous solution of CuSO₄ to stabilize the emulsion droplets, and hence the Cu²⁺ ions were restricted in the aqueous phase (Figure 1.13a). Then, with the slow addition of Na₂S solution in CS₂, solid CuS gradually formed at the surface of the water droplets due to the reaction between Cu²⁺ and S²⁻. The accumulation of solid CuS finally formed the hollow shell structures (Figure 1.13b-d). The as-prepared CuS spheres have a diameter around 200 nm, and a shell thickness around 20-30 nm.

By using suitable surfactants or functional membranes, hollow polymer nanostructures can be prepared from a reverse emulsion system, as well. Cheng and co-workers prepared hollow poly-(N-isopropylacrylamide) capsules with the aid of hydrophobically modified Shirasu-porous-glass membrane (SPG) and a W/O system consist of water kerosene.¹⁰⁰ SPG is a kind of microporous glass that has been widely applied in industrial fields like emulsification and filtration. After the emulsification process, the polymerization reaction was initiated by UV light. The synthesized microcapsules have the size around 10 μm, and a morphology similar to broken balloons.

Figure 1.13. (a) Schematic illustrating the formation process of the CuS hollow spheres. SEM (b) and TEM (c) image of the hollow spheres, respectively, and their SAED pattern (d). Reprinted and modified from ref. 99 with permission. Copyright © 2007, John Wiley and Sons.

IV. Double emulsion synthesis

Through the combination of emulsion and reverse emulsion system, more complicated synthetic system could be obtained for preparing hollow nanostructures. For instance, a double emulsion like water/oil/water (W/O/W) could be generated either by ultrasonic irradiation, or dispersing a reverse emulsion with a water solution, or by microfluidic technique.^{101, 102}

Among these methods, the dispersion of a reverse emulsion with a water solution is the most straightforward method to obtain a double emulsion. For example, Fujiwara et al. synthesized hollow silica microcapsules through an interfacial reaction in a W/O/W system.¹⁰³ The double emulsion was prepared via the addition of a W/O reverse emulsion consist of n-hexane and water into another aqueous solution (WP2). The surfactant Tween 80 and Span 80 was pre-added into WP2 to stabilize the emulsion droplets. During the escaping of the oil

droplets, silica would precipitate out and deposit along the W/O/W interface, giving silica microcapsules. The size of the silica microcapsules critically depends on the volume ratio of water to *n*-hexane to WP2, as this ratio would determine the sizes and shapes of the emulsion droplets. By using a similar synthetic strategy, hollow silica spheres with a hierarchical structure were obtained by this group.¹⁰⁴

1.3.4.2. Vesicles & micelles based soft template

A major problem in soft template synthesis is that nucleation at the fluid-fluid interface is difficult when the interface is located at the contact part between the continuous phase and the dispersed phase.¹⁰⁵ An effective solution is introducing surfactants or amphiphilic molecules at the interface. By doing so, the interface could be stabilized due to the reduced interfacial tension. Although not in equilibrium, emulsions can be metastable with the droplets retaining their state for an extended period. It may also be helpful in increasing the effective interaction between surface-modified core and shell material, which is preferred in homogeneous interface nucleation.

The assembly of surfactants or amphiphilic molecules in pure solvents would form vesicles or micelles. These molecules could pack into mesostructures when their concentration exceeds the critical micelle concentration. Morphology of the mesostructures could be controlled via several factors, for example, temperature, pH value or ionic strength of the solution, the concentration of surfactant, and the addition of ligands.¹⁰⁶ Also, the geometrical property of the amphiphilic molecules can influence the packing structures via steric effect. These factors lead to the various structures and shapes of the vesicles/micelles, providing templates with a variety of morphologies for templating hollow nanostructures.

A vesicle itself can be seen as a hollow structure formed by the self-assembly of amphiphilic membrane/molecules. With micelles/vesicles as soft templates, the hollow

structure of desired materials can be obtained by depositing materials on the surface. The coating process occurs at the functional interface between micellar molecules and surrounding solution, in which special sites are provided for the deposition of materials. Micellar templates and precursors of target materials are usually combined through electrostatic interactions and hydrogen bonds. After this, target materials could self-assemble or nucleate at the interface. They are finally solidified to become the shape of the vesicle templates to form hollow nanostructures.

Amphiphilic molecules like PDADMAC, dimethyl-dioctadecylammonium bromide (DODAB), sodium dodecyl benzenesulfonate (SDBS), and cetyltrimethylammonium bromide (CTAB) have been extensively used to form micelles in the fabrication of hollow nanostructures with a single shell.¹⁰⁷ Theoretically, it is also possible for all the layers of a multi-layered vesicle to become the growth sites, which would lead to multi-shell structures. For instance, by using the micelles of CTAB as soft template, Wang and co-workers reported the first preparation of hollow Cu₂O yolk-shell structures with double, triple, and quadruple shells.¹⁰⁸ In this case, multi-layered CTAB micelles were obtained by adjusting the concentration of CTAB in water phase. As shown in Figure 1.14, CTAB micelles were first generated in the solution. Then, clusters of Cu-Br formed through the electrostatic interaction between Cu²⁺ and Br⁻, which would lead to an excess of Cu²⁺ at the interface between the hydrophilic end of CTAB and the aqueous solution. Finally, the solid Cu₂O shell was obtained via the reduction of Cu²⁺. Similar as the synthesis of single-shelled hollow structures, hollow spheres of Cu₂O with multiple shells could be obtained via the templating of CTAB micelles that have multiple bilayers (Figure 1.13a (3)). Cu₂O could deposit on both layers of this structure, leading to the growth of multi-shelled structures.

Figure 1.14. (a) Schematic illustrating the synthetic route of multi-shelled Cu_2O hollow spheres. TEM image of hollow Cu_2O spheres with a single shell (b, d), and their HR-TEM image (c) (inset: the corresponding SAED results); (e) TEM image of double-shelled Cu_2O hollow spheres. Reprinted and modified from ref. 108 with permission. Copyright © 2007, John Wiley and Sons.

1.3.4.3. Other types of soft template

Except for the soft template synthesis based on emulsion and micelle/vesicle templates, different hollow nanostructures can be obtained via either gas bubble template or electrospray methods, as well.⁷⁹

Typically, synthesis employs gas bubbles as the template involves three steps: (1) the generation/distribution of gas bubbles within a liquid phase; (2) the initial deposition/adsorption of shell materials onto the surface of these bubbles; and (3) the subsequent growth/aggregation of the shell materials. There are several factors governing the templating effect of gas bubbles, including temperature, surface charge, formation rate of bubbles, particle size, and hydrophobicity of the materials.¹⁰⁹ Several different approaches could be employed for the production of gas bubbles, such as acoustic cavitation methods, chemical reactions, hydrothermal approaches, and blowing of gas into liquid phases.

Pumping gas into a liquid system is the most direct approach for the formation of gas bubbles. Han and co-workers synthesized hollow calcium carbonate spheres through the

pumping of CO₂ gas into an aqueous solution of calcium chloride.¹¹⁰ In this synthesis, bubbles of CO₂ played the roles of both soft template and the reactant. CO₂ molecules were transformed to become CO₃²⁻ ions via a hydration reaction, which could initiate the subsequent reaction with Ca²⁺. Finally, the precipitated CaCO₃ was adsorbed and attached onto the surface of gas bubbles, giving the hollow structures. Peng et al. prepared semiconductive ZnSe hollow spheres through the using of nitrogen gas bubbles as the soft templates (Figure 1.14).¹¹¹ In this work, Se²⁻ ions were formed as the first step through the reduction of SeO₃²⁻ ions with the presence of hydrazine. During the pumping of nitrogen gas, the selenium ions could then react with the Zn²⁺ ions to form small ZnSe nanocrystals, which were subsequently aggregated onto the surface of the gas bubbles to form the hollow spheres (Figure 1.15). With the size of the as-prepared ZnSe hollow spheres were around 3 μm, they also have a crystalline shell with a thickness around 300 nm. The small ZnSe nanocrystals consisting the shell have tunable sizes from 5-100 nm, indicating the good controllability of this method.

Electrospray has become a popular method in the synthesis of both hollow and non-hollow nanostructures, for example, nanospheres, nanofibers, and other inorganic-organic hybrid hollow nanostructures. Though this method also employs liquid droplets as the soft template, it is usually classified as “other types soft template”, as the experimental steps of this methodology are a bit different from other liquid droplet-based soft template synthesis.

The first step of an electrospray method is the injection of reactant solution into an electrospray atomizer via a stainless-steel capillary tube. Then, the liquid is forced and distorted into a sharp cone through the changing of its surface tension with a strong static electric field (Figure 1.15d).¹¹² Under the help of high voltage electric field, the cone-shaped liquid is dispersed into small charged droplets and splashed out. Eventually, desired nanostructures could be obtained on a collection substrate after the solvents evaporation. The generation of hollow nanostructures is usually caused by the evaporation of solvents within enclosed

structures or/and additional ripening processes. The morphology of as-prepared nanostructures is determined by the environment temperature, the strength of electric field, the flow rate of reactant solution, and the concentration/composition of the material precursors.

Figure 1.15. (a) Schematic illustrating the producing process of ZnSe nanospheres. Reprinted from ref. 111 with permission. Copyright © 2003, John Wiley and Sons.

In 1990s, Rulison and co-workers successfully fabricated yttrium oxide hollow nanospheres via electrospray method.¹¹³ In this work, concentrated solution of hydrated $\text{Y}(\text{NO}_3)_3$ in IPA was pumped into the electrospray atomizer for the electrospray process. The $\text{Y}(\text{NO}_3)_3$ was then pyrolyzed under a high temperature to obtain the hollow structures. Another typical example comes from Du and co-workers.¹¹⁴ They reported the fabrication of BiFeO_3 hollow spheres via a two-step electrospray method. As the first step, solid NPs made up of Fe_2O_3 and Bi_2O_3 were prepared through electrospray method. Then, the solid NPs were converted to hollow spheres by reacting the two phases under a high temperature (forming BiFeO_3). Size of the as-prepared hollow spheres distributed from 50 to 200 nm, and their shell thickness is around 20 nm. In a follow-up work from this group, similar strategy can be used

for the preparation of double-perovskite $\text{Bi}_2\text{FeMnO}_6$ hollow spheres (Figure 1.16a-c), as well.¹¹⁵

Figure 1.16. SEM images of $\text{Bi}_2\text{FeMnO}_6$ hollow spheres synthesized with different spraying time: (a) 10 min; inset: agglomeration of the NPs; (b) 1 h; inset: typical hollow sphere that is elliptical due to surface shrinkage; and (c) typical cracked porous hollow sphere. (d) Schematic illustrating the basic principle of electrospray method. Reprinted from ref. 115 with permission. Copyright © 2011, Elsevier.

1.3.4.4. Soft vs. hard

There are a number of commonalities between soft and hard template synthesis. For instance, in both syntheses, the coating of shell materials on template surface should form a conformal coating, and thus well-defined core-shell structures. To this end, establishing strong bonding interactions between the template surface and the shell materials needs to be considered when designing a synthesis.⁶⁵ Also, the template removal method has to be selected

according to the template composition. Following that, three points need to be considered while designing a template synthesis: 1) The template material should be decomposed to small molecules or ions. 2) The shell should have permeability so that the etching reagent and the decomposed products could diffuse through. 3) The shell should be rigid enough to survive the etching, purification, and drying processes.

Indeed, in many cases, the capillary force during drying is the dominant factor in causing shell collapse,¹¹⁶ which is the drawback of both hard and soft templates. Nevertheless, comparing to hard template, soft template synthesis is much preferred in nano-synthesis in terms of simplified synthetic steps, reduced cost, and potential to enhance structural complexity. As the liquid or gas templates can be readily removed via evaporation, it could avoid the separation problem in hard template synthesis, so that the surface properties of the products will not be influenced by the template. By combining the evaporation and the separation steps, it could also simplify the synthetic procedures, making the soft template synthesis possess unique advantages in reducing production cost and the ease of scaling up. Moreover, the simplified synthetic steps could avoid the accumulation of errors in each synthetic step, leading to a high yield of the products.

Most importantly, beneficial from the fluid nature of soft templates, it offers additional possibilities to construct new and complex nanostructures comparing with the hard one. The morphology of hollow structures is directly determined by the engaged templates, whereas available hard templates with non-spherical morphologies are quite rare. It is also certainly difficult to manipulate their shapes after the encapsulation of shell materials. Thus, a hard template synthesis always creates structures with simple and similar shapes as the templates. In contrast, the fluid nature of soft templates (e.g., emulsion droplets or vesicles) permits versatile manipulation of their shapes. For instance, Huang et al. reported the growth of bottle-like structures with the slow evaporation of the solvents within the nanobowls.⁹² The vesicle

templates of the bowls slowly extended due to the expanding and escaping of the interior solvents to form the bottleneck. Another example comes from Wang's group:¹¹⁷ the enclosed micelle templates gradually swelled with the addition of polymer blocks, and finally cracked to create an opening. Although the controllability of template manipulation is quite weak up-to-now, it still provides us a possibility: If such manipulation processes can be systematically controlled, scientists will be able to continuous shaping and adjusting the morphology of hollow nanostructures, which would be extremely helpful in expanding their synthetic freedom and creating more complexed structures. While it may pose great challenges, the unique advantages of soft templates indeed provide valuable opportunities to overcome the conventional synthetic systems.

1.3.5.Template-free synthesis

To expand the synthetic toolbox and to simplify the synthetic steps, how to spontaneously form a hollow structure via template-free methods has attracted continuous attentions, as well. In industry manufacturing, it is hard to imagine how to naturally build a commodity without using a mold, but such phenomenon is widespread in nature: if a seed is planted and provided with suitable growth conditions, fantastic plants can be obtained; air bubbles could spontaneously expand when rising from the deep sea; caused by the comprehensive effect of internal and external forces on the earth's surface, there are various landforms on the earth. Similarly, it would be extremely useful if we could know how NPs react with the surrounding environment to spontaneously form different hollow structures. In the following, to know more about the hollowing mechanism, we will analysis the mechanism of several major types of template-free synthetic approaches, such as Ostward ripening, galvanic replacement, and Kirkendall effect.

1.3.5.1. Ostwald Ripening

Ostwald ripening is a phenomenon describes the evolution of structure and morphology of solid particles or gels in colloidal solution system as time goes on. In 1896, this phenomenon was first investigated by Wilhelm Ostwald and subsequently defined as: dissolution of small crystals or particles and the redeposition of the dissolved species onto the surface of larger crystals or particles.¹¹⁸ The ripening phenomenon originates from the heterogeneity of the system: the smaller particles with higher surface energy have stronger tendency to dissolve, and the dissolved matters are more inclined to deposit on the surface of the large particles to make it thermodynamically stable.⁶⁵

In recent years, the self-templating method based on Ostwald ripening has been extensively developed to prepare hollow structures. It is worth noting that the ripening process by itself does not produce a cavity inside the particle. However, according to the concept of ripening, channel or mode of material exchange inside and outside the particles can be exploited to form hollow nanoparticles. Typically, preparing hollow nanostructures via Ostwald ripening involves two unique steps: the gradually dissolution of the particles' interior, and the re-deposition of the dissolved matters onto the outer surface of the particles (Figure 1.17).¹¹⁹

The driving force to make small NPs smaller and large ones larger is the difference of their surface energy. The mechanism of ripening in the construction of hollow structures should also be derived from the non-uniformity of crystallites. Therefore, it is essential that the primary particle for ripening should be amorphous, as a form of crystallite aggregates composed of large and small grains. Amorphous particles used for Ostwald ripening are not only limited to inorganic solids like metal, metal oxides, hydroxides, and sulfides, but also extended to polymer and metal-organic frameworks (MOFs), and other organic molecular crystals.¹²⁰

Figure 1.17. Schematic illustrating a typical process of hollow structure formation via Ostward ripening.

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Also, considering that the cavity would be produced at the position where crystallites are smaller or less compact when the Ostwald ripening proceeds, the size and concentration gradients of small and large “grains” should distribute increasingly from the interior of the particle to surface. This means crystallites in the particle center are smaller and pack more loosely than those of exterior, leading to the complete dissolution of central small crystallites and the growth of the exterior large crystallites, generating interior cavities via Ostwald ripening. During the ripening, the small and non-compact amorphous crystallites at the central of the particles will be dissolved and re-deposited onto the exterior large crystallites, resulting in mass transfer between the solid interior and outside solution.¹²¹ As the ripening is a dynamic process, there are a number of available channels in the shell to avoid them being blocked from material transport.

Applying Ostwald ripening in the preparation of hollow spheres was first reported by Zeng et al. in 2004.¹¹⁹ Solid hollow anatase TiO₂ spheres were obtained with the hydrolysis of TiF₄ under hydrothermal conditions via a straightforward “one-pot” approach. The solid TiO₂ spheres were consisted by a number of smaller crystallites. As the crystallites located at the center of the spheres can be approximated as smaller spheres that have a higher curvature, their higher surface energy (comparing with those at the outer surface) would make them easy to be dissolved during the reaction. The hollowing effect was then observed with a prolonged incubation.

1.3.5.2. Galvanic Replacement

Galvanic replacement has become an effective template-free method for the preparation of hollow nanostructures. With it, metal hollow structures with well-controlled sizes and shapes, porous walls, and tunable elemental compositions can be readily synthesized. The driving force of a galvanic replacement reaction comes from the electrochemical potential difference between the two metals at anode (reducing agent) and cathode (oxidizing agent).¹²² The method was initially reported by Xia et al., for the fabrication of Au nanostructures.

In a typical synthesis, solid nanostructures of anode metals are synthesized first. Then, when the anode metal contacts with the ions of cathode metal, the redox reaction would start at the site of its surface where surface energy is highest, such as defects and stacking faults.¹²³ With the oxidation of anode metal, its ions slowly dissolve into the solution, leaving a small hole at its surface (step 1 & 2 in Figure 1.18a). At the same time, the reduction product of cathode metal ions would deposit onto the anode surface, forming a thin layer. This new layer prevents the underneath anode metal from contact with the cathode metal ions, so that the primary small hole serves as the only active site for the dissolution of anode metal. During the reaction, alloy of two metals would be formed as a homogeneous alloy is thermodynamically more stable than a mixture of chemically segregated metals (step 3 & 4 in Figure 1.18a). The formation of alloy elevates the anode reduction potential, thus reducing the rate of the whole reaction. Finally, the anode metal within the hole is thoroughly eliminated and an alloy shell is left in the solution. The loophole on the shell can eventually be filled as a result of the continuous deposition of cathode metal atoms, hence a complete hollow shell is successfully synthesized.

Figure 1.18. (a) Schematic illustrating the structural changes at different stages of a galvanic replacement reaction between HAuCl_4 and silver NPs in an aqueous solution. (b) TEM image of the reaction products in (a), and their SAED pattern (d). (c) HR-TEM image showing the edge of a gold nanosphere. Reprinted and modified from ref. 123 and 124 with permission. Copyright © 2002, American Chemical Society, and Copyright © 2013, John Wiley and Sons.

It is worth emphasizing that if there are excessive metal ions in the solution, the galvanic replacement reaction will continue, which is destructive to the hollow structures (last step in Figure 1.18a). Xia et al. were the first to report the preparation of hollow nanostructures with galvanic replacement in 2002.¹²⁴ The synthesis employs the galvanic replacement reaction between HAuCl_4 and pre-synthesized silver NPs in an aqueous solution. The silver NPs were oxidized by HAuCl_4 , giving gold nanostructures with well-defined hollow spaces and single-crystal shells (Figure 1.18b-d).

1.3.5.3. Kirkendall Effect

Kirkendall effect typically refers to the movement of the interface between two metals that occurs as a result of the difference in diffusion rates of the metal atoms. Observations of unequal material flows during inter-diffusion offer the first evidence for the vacancy-mediated

bounce of atoms being the prevailing mechanism for diffusion in crystal materials.¹²⁵ The flow of matter is balanced via the moving of vacancies, which would coalesce to become larger cavity when there is excess amount of vacancies.

In metallurgy or macroscopic production, the present of Kirkendall cavities in metal materials is considered as a hazard. However, at the nanoscale, the Kirkendall effect shows great potential for the synthesis of hollow nano/micro-structures. In a typical synthesis, solid nanocrystals containing at least one component is prepared first.¹²⁶ A second component is reacted with the crystal to form the outer shell layer. Due to the block of the new shell, direct reaction between the two components is limited. Further reaction could only proceed via the diffusion of ions or atoms through the shell. Then, vacancies are obtained through the outward diffusion of the solid core, which would eventually coalesce into larger cavities via nanoscale Kirkendall effect (Figure 1.19). The first successful preparation of hollow nanostructures with the Kirkendall effect was reported by Yin et al. in 2004, in which hollow cobalt spheres with a crystalline shell were synthesized.¹²⁷

Figure 1.19. Schematic illustrating a typical formation process of hollow nanostructures via Kirkendall effect.

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1.3.6. Summary of current methods

The major approaches of synthesizing hollow nanostructures can be classified into template and template-free synthesis, both of which have drawbacks in different aspects.

From the view of synthesis, most of the templating methods in the literature, including hard and soft template, are essentially methods that involve coating and etching of the existing NPs to create hollow nanostructures with similar shapes. Though the discovery of template-free synthesis greatly expands the toolbox of hollow structure synthesis, these methods can only be applied to certain conditions. For example, synthesis via Ostwald ripening and Kirkendall effect can only be realized in solution phase, and they have strict prerequisite for their reactants; the application of galvanic replacement is strictly limited to metal and metal oxides. It is still a great challenge for scientists to advancing the synthetic skills and lift the structural complexity.

There should be greater potential for the templated synthesis strategy, especially for the soft template synthesis. Though it has a major drawback that it offers less control over the uniformity of final products, as the morphology of soft templates is hard to be tuned as a fluid. Nevertheless, this fluid nature provides us a unique opportunity to create sophisticated structures beyond current systems. For instance, liquid droplets permit stepwise and versatile manipulation of their shapes. This characteristic provides a straightforward approach in breaking the symmetry and controlling the morphology of resulting hollow structures. Similar features have been preliminary observed. Yi et al. adopted hydrolyzed amphiphilic silane molecules to squeeze the water droplet out of a nanobowl to form a hollow bump at its top,¹²⁸ suggesting the droplets could retain their fluid nature in a synthesis. However, it is difficult to use mechanical devices to directly manipulate the shape of nano-sized droplets, making the potential of liquid droplets in hollow structure synthesis has yet to be developed. Despite few cases can be referenced, it is likely that this feature of soft templates could open a window for the synthesis of hollow nanostructures.

1.4. Summary

In this chapter, we give a brief overview on the synthesis of fullerene nano/micro-structures and hollow nanostructures. The properties of fullerene materials were introduced to provide basic knowledge foundation for their synthesis. Then, typical strategies of hollow structure synthesis based on template and template-free methodology and their underlying mechanisms have been systematically summarized and analyzed.

On the basis of the above case studies, a comparison of hard and soft template synthesis has been made. Although soft template synthesis has unique advantages in simplified steps, reduced costs, and ease of template removal, it still has great room for improvement. Theoretically, the fluid nature of soft templates could provide us the ability of continuous shaping of the templates and hence the morphology of hollow structures, which is promising for the development of new synthetic capabilities. We expect such an introduction could give a big picture on the fields, as well as support the development of synthesizing hollow structures with enhanced complexity and novelty.

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Chapter 2: Controlling the precipitation of fullerene:

Synthesis of metal@fullerene core-shell structures

As bare fullerenes have poor solubility and ease of crystallization in most non-aromatic solvents,¹ it is usually difficult to control their precipitation process in solution phase, which has become a major challenge that limiting the synthesizing their nanostructures. In this chapter, we attempted to establish a solvent system for the controllable precipitation/deposition of fullerene materials. To directly observe and monitor the deposition process, we started from the synthesis of metal@fullerene core-shell NPs, in which different fullerene materials such as C₆₀ and C₇₀ could be gradually deposited onto the metal core to reflect the effectiveness of the method. Through the adjustment of the precipitation time and the solvent combinations, the synthesized core-shell structures have tunable core materials, shell thickness and shapes. Due to the high refractive index of the fullerene shell, large red-shift of UV-Vis plasmonic absorption of Au@C₆₀ NPs was observed. Such a synthesis serves as a useful model system for the study of controllable precipitation of fullerene materials.

2.1. Introduction

2.1.1. Typical process of liquid-phase precipitation

The precipitation of a material in solution phase is essentially a nucleation and growth process, and different materials share the similar process regardless of their compositions.² In a typical process, free atoms or molecules (monomers) can be released via either a chemical reaction or a physical process, for example, the reducing of solubility. Then, the gradually joining of these free atoms or molecules gives the final solid particles.

Such a process has been well described with the classic theory of nucleation and growth.^{3,4} A plot of the monomer concentration against time is drawn as shown in Figure 2.1a.⁵

The monomers need to overcome an energy barrier to nucleate, which would force them to accumulate in solution, and hence, making the solution becomes oversaturated.⁶ When the oversaturation increases to a certain level, stable nuclei form in solution via a homogeneous nucleation process (nucleation stage). The formation of nuclei could only last for a short period as the homogeneous nucleation would consume the growth material, making the oversaturation drops under the critical level. Then, due to the energy barrier of heterogeneous nucleation is lower than that of homogeneous nucleation, the deposition of the monomers onto the existing nuclei becomes energetically favorable (Figure 2.1d), and the growth could continue so long as the solution is oversaturated.

Figure 2.1. (a) Schematics illustrating the change of monomer concentration against time, which show the initial accumulation of the monomers, the nucleation stage, and the subsequent growth; (b) A burst homogeneous nucleation of the monomers; (c) A continual homogeneous nucleation with an excess of

monomers; d) heterogeneous nucleation on the pre-existing seeds. Reprinted from ref. 5 with permission.

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Obviously, monomer concentration is the factor governing the whole nucleation or precipitation process. To get mono-dispersed particles, the use of more or concentrated start material is usually not a wise choice.⁷ The high concentration would lead to a high oversaturation at the beginning, and thus a prolonged nucleation stage. The extra monomers would contribute to the formation of more nuclei rather than nucleate onto the existing particles. Hence, the nuclei form at a later stage would have less growth time, which leads to the poly-dispersed particles (Figure 2.1c). To increase the size uniformity, the formation rate of monomers needs to be kept at a lower level to compress the homogeneous nucleation period and to promote heterogeneous nucleation on the existing nuclei. After the initial homogeneous nucleation stage, the monomer concentration should be kept between the saturation level and the homogeneous nucleation concentration. Thus, all the nuclei are designed to form at a similar time point and to grow at a same rate.⁵

2.1.2. Challenges in controlling the precipitation of fullerenes

However, scientists met troubles when applying the above principle to control the formation of fullerene nano/micro-structures in liquid phase. A two-phase system is widely used for the synthesis: fullerene materials are dissolved in a good solvent first, and a poor solvent is directly added to form the desired structures.⁸ Reducing of solubility is the driving force that makes the fullerene molecules precipitate out of the solution. A major challenge of this strategy comes from the poor solubility of bare fullerenes in most non-aromatic solvents (Table 2.1).^{9,10,11} Hence, traditional solvent systems always employ aromatic solvents like *m*-xylene and toluene as the good solvent, and alcohol like ethanol and IPA as the poor solvent. As fullerenes have extremely low solubility in alcohol, the oversaturation point is much easier

to be achieved. Although some works reported the synthesis with non-aromatic solvents such as CCl_4 ,¹² similar problem cannot be completely solved due to the huge solubility difference between good and poor solvents (typically, 2-3 orders of magnitude). Thus, fullerene materials are tend to have high oversaturation once a poor solvent is added, leading to the formation of products with poly-dispersed sizes.

Table 2.1. Solubility of C_{60} , C_{70} , and PC_{61}BM in a variety of solvents (273 K).^{9, 10, 11}

Solubility (mg/mL)	C_{60}	C_{70}	PC_{61}BM
Xylenes	4.9	-	-
M-xylene	1.4	3.98	16
CCl_4	0.32	-	-
DMF	0.027	0.04	-
Chloroform	0.016	0.0021	-
Cyclohexane	0.036	0.08	-
IPA	0.0041	0.0021	-
Ethanol	0.0008	-	-
Water	1.3×10^{-11}	10^{-10}	-

A number of attempts have been made to solve this problem. The most popular one is the liquid-liquid interfacial precipitation (LLIP) synthesis reported by Miyazawa group,^{13,14} which is a modification from the direct precipitation method. After the dissolution of fullerenes in a good solvent, the poor solvent was gently added onto the top of the fullerene solution to form an interface of good/poor solvents. Thus, the complete mixing of two solvents is limited, so that the nucleation of fullerenes could be restricted at the interface to slow down the rapid increasing of fullerene oversaturation. This method is able to control the prompt nucleation of fullerenes, but the interface of two miscible solvents is usually not stable enough, which would reduce its controllability. Moreover, the nucleation of fullerenes is strictly limited at the interface, making this method cannot be readily combined with other synthetic methods to

change the morphology of products. Though great efforts have been devoted, it is still a challenge to get well control and further understanding in this area.

2.1.3. Design principles of the experiments

Hybrid nanostructures typically refers to structures that have two or more domains with different compositions. They have attracted much interest as they could show combined properties of each component.¹⁵ Sometimes, new or improved properties can be obtained due to the coupling of components.¹⁶ Core-shell NPs is one typical class of hybrid nanostructures formed through evenly deposition of shell materials on the core NPs. Typical core NPs such as metal-metal,¹⁷ metal-oxide,^{18,6} and metal-polymer core-shell NPs have been successfully synthesized.^{19,8} Among them, NPs with a plasmonic metal core and an organic shell are particularly interesting,^{20,9} due to their expected combined fascinating properties. Fullerene is one important and unusual type of organic molecules. Due to their unique spherical structure, they have excellent optical, redox and optoelectronic properties.²¹ Despite many efforts, fullerene-based hybrid nanostructures have been rarely reported due to the difficulties in controlling the precipitation of fullerene species in liquid phase.

To successfully fabricate the fullerene-based hybrid NPs, there are two critical issues to be considered. The first one is the quick homogeneous nucleation of fullerene materials. We attempted to use C₆₀ as an example, and to prevent its quick precipitation by adding a “buffer solvent” that has relatively poor (but not so poor, typically between the order of magnitude of xylenes and IPA) solubility of C₆₀. A frequently used solvent combination for the synthesis of C₆₀ nanostructures, xylenes and IPA, was selected as the good and poor solvent, respectively. DMF was chosen as the “buffer solvent” because the solubility of C₆₀ in it exactly drops between that of xylenes and IPA (Table 2.1). We expected that such a solvent system could provide a solution for the controllable precipitation of C₆₀.

The other problem is the affinity between metal seeds and fullerene molecules. Usually, modifying C₆₀ molecules with certain functional groups such as thiol group (-SH) is a common while effective way to solve this problem. However, after functionalization, the properties of bare C₆₀ may be affected, for example, the solubility in aromatic solvents, redox properties, and electrochemical behaviors.^{22, 23} In some cases, even get lost as much as two orders (e.g., the solubility). To avoid the possible negative effect, we selected bare C₆₀ molecules as shell material for the synthesis of core-shell NPs. Au NPs have a number of empty orbitals on their surface, which are able to form Au- π interactions with the sp² electrons in benzene.²⁴ Hopefully, the rich sp² electrons on the surface of C₆₀ molecules could bond with Au NPs via similar mechanism, so that bare C₆₀ molecules should be able to directly deposit onto the Au NPs to form a core-shell structure. Also, an unpublished result from our group found that Au NPs that are prepared from citrate (c-Au NPs) have good stability in DMF, suggesting they could be an ideal core material in the solvent system of DMF, xylenes, and IPA.

2.2. Materials and methods

2.2.1. Materials

Pristine C₆₀, C₇₀ powders (purity 99% for each), xylenes (98%) and anhydrous DMF (99.8%) were purchased from Sigma-Aldrich. *M*, *o*, *p*-xylene (Analytical Reagent, A.R.), 1,2,4-trimethylbenzene (A.R.), toluene (A.R.), CCl₄ (A.R.), ethanol (absolute) and IPA (A.R.) were purchased from Beijing Chemical Agent Ltd., China. All the chemicals were used without further purification. The following experiments could be reasonably reproduced without referencing other literatures.

2.2.2. Methods

Characterization: TEM images were obtained on a JEOL JEM-1400 electron microscopy at an accelerating voltage of 80-100 kV. Thermogravimetric analysis (TGA) data was obtained via a TGA Q500 thermogravimetry analyzer. An Apple iPhone is used to take the photographs of the reaction solution.

UV-Vis characterizations: UV-Vis characterizations were carried on a Cary 100 UV-Visible spectrometer. The mixture of 0.2 mL sample solution and 0.8 mL DMF was taken, mixed, and used for all the measurements.

TEM sample preparation: 300 μ L of the sample solution was taken and centrifuged at a speed of 2500 rpm for 8 minutes. Then, the supernatant was removed, and the precipitate was dropped on a copper grid that had been pre-treated under oxygen plasma (with a Harrick Plasma cleaner) for 20 s to remove the dusts. The sample was completely dried in flow air or in oven for at least 1 h.

Preparation of Au@C₆₀ and Au@C₇₀ core-shell NPs: Gold NPs with different sizes were prepared from sodium citrate and HAuCl₄ solution according to the literature method.²⁵ 1 mL of the above Au NPs solution was taken and centrifuged at 3000 rpm for 10 minutes. The supernatant was removed and 1 mL of DMF was added to the precipitate. The precipitate was dispersed in DMF through vortex. After this, 50 μ L of fullerene solution in xylenes (2 mg/mL for C₆₀ and 5 mg/mL for C₇₀) was added to the mixture with vortex. Finally, 400 μ L of IPA was added dropwise with vortex. The mixture was sealed and incubated at room temperature for 20 h to obtain the core-shell NPs.

Preparation of Au@C₆₀ NPs with a crystalline shell: The other steps of this part are exactly same as the previous one, the only difference is the solvent of C₆₀ was changed to *p*-xylene or 1,2,4- trimethylbenzene, and the concentration of C₆₀ was increased to 2.5 and 5 mg/mL, respectively. After an incubation of 16 h at room temperature, Au@C₆₀ core-shell NPs with

thick amorphous shells were obtained. After another incubation of 72 h, the amorphous shell became crystalline.

Preparation of metal@C₆₀ core-shell NPs: The steps of this part are exactly same as the previous one, the only difference is the metal core materials were changed from Au NPs to Pd nanocubes, Au nanorods, Ag NPs, and 15 nm Au NPs. The Ag NPs were prepared from PVP in aqueous phase. The 15 nm Au NPs were prepared according to literature method with only two rounds of HAuCl₄ aqueous solution were added.²⁵ For the synthesis of Au@C₆₀ core-shell NPs with a 15 nm Au NPs core, only 30 μ L of C₆₀ solution in xylenes was used.

2.3. Results and discussions

2.3.1. Synthesis of Au@C₆₀ core-shell NPs

In a typical synthesis (Figure 2.2a), pre-synthesized c-Au NPs (55 nm in diameter) were concentrated via centrifugation. They were then separated from water phase, and re-dispersed into DMF under vigorous vortex to avoid the aggregation of hydrophilic c-Au NPs in hydrophobic xylenes. A clear red solution was obtained after the re-dispersion. Concentrated C₆₀ solution in xylenes (1.5 mg/mL) was slowly added into the Au-DMF solution to avoid the quick precipitation of C₆₀. The red solution turned dark immediately after the addition of dark purple C₆₀ solution. Finally, IPA was slowly added to the mixture to reduce the C₆₀ solubility to a lower level to facilitate the deposition of C₆₀. The mixture was sealed and incubated at room temperature to obtain the Au@C₆₀ core-shell NPs.

2.3.1.1. Properties of Au@C₆₀ core-shell NPs

Thin shells coated on Au NPs were observed at 4 h (Figure 2.2b). At the same time, the solution became darker and gradually shifted from dark purple to light blue. In the following reaction, the shells increased in thickness and evenly coated on the Au cores. At 30 h, typical core-shell

Au@C₆₀ NPs with obvious core and shell contrast were observed (Figure 2.2d). Each Au NPs was fine-encapsulated by the C₆₀ shell, forming uniform concentric core-shell structure. The C₆₀ shells had uniform thickness around 30-40 nm, which is the limit of their thickness. The overall diameter of the core-shell NPs distributed from 150 to 180 nm. Unlike fine nanocrystals formed in other C₆₀ nanostructures, the C₆₀ shell appears to be highly amorphous. The color of the solution finally became clear green at 30 h (Figure 2.2e). The UV-Vis spectra also showed obvious red-shift of Au plasmonic absorptions (Figure 2.3b). Since no aggregation of the NPs was observed, the large red-shift of absorption peak should be resulted by the high refractive index of thick C₆₀ shell ($n=2.2$, 600 nm), suggesting the Au NPs were indeed functionalized by C₆₀.

Figure 2.2. (a) Schematics illustrating the preparation of Au@C₆₀ core-shell NPs. (b-d) TEM images of Au@C₆₀ core-shell NPs reacted for 4, 16, and 30 h, respectively. (e) Photograph of the reaction solution before (left) and after reaction (right).

To confirm the relationship of C₆₀ shell thickness and the UV-Vis absorption shift, and to get details of the formation process of Au@C₆₀ NPs, a kinetic study was carried out. The change of solution color, UV-Vis spectra and C₆₀ shell thickness were continuous recorded. A

series of Au@C₆₀ NPs samples with different shell thickness were isolated at different time. Their corresponding TEM images were collected to get a precise control on the shell thickness. We note that the synthesis of core-shell NPs was carried out under the same conditions except for the incubation time. As shown in Figure 2.3a, with the increasing of the incubation time, the solution color gradually changed from purple to blue purple, blue, blue green, and finally a clear dark green solution was obtained after 20 h.

Figure 2.3. Studies on the formation process of Au@C₆₀ NPs. Photographs and the corresponding TEM image of typical NPs reacted for different time (a), and their respective UV-Vis measurements (c). (b) UV-Vis measurements of the sample solution reacted for 0 (black) and 20 h (red), respectively. (d) Increase of the C₆₀ shell thickness with reaction time. Scale bars are 50 nm.

Such a trend was further confirmed by TEM images. The corresponding TEM images at different time stage were shown under each photograph (Figure 2.3a). From dark red to purple, blue purple and blue colored samples, the thickness of C₆₀ shell continuously increased. No obvious thickening of the shell was observed upon prolonged incubation over 30 h (Figure 2.3d), indicating most of the C₆₀ had been precipitated out. The thickest shell was observed at the green color stage. We note that no obvious aggregation of Au or Au@C₆₀ NPs was observed

within all time scale, indicating that the color change was completely induced by the increasing of shell thickness. As shown in Figure 2.3c, when the C₆₀ shell grew thicker, the UV-Vis absorption of the core-shell NPs continuously red-shifted from 547 to 616 nm, consistent with the color change. Meanwhile, the absorption intensity also increased with the increasing of shell thickness. From this series results, it is conceivable that the red-shift in absorption peak was indeed caused by the high refractive index and thickening of the C₆₀ shell. For core-shell NPs, the shift of core absorption due to the formation of shell is common phenomena.^{26,8a} However, such an obvious red-shift have never been observed before. This significant and tunable red-shift in UV-Vis absorption should be a useful property in plasmonic-related applications.

In order to get further understanding about how the thickness of C₆₀ shell contribute to Au core absorption peak shift, finite-difference time-domain method (FDTD) was applied for calculating the absorption of Au@C₆₀ in a mix solvent of DMF and IPA ($D_{Au}=60$ nm, $n_{DMF}=1.43$, $n_{IPA}=1.375$). Figure 2.4a and b show a series of experimental and simulated Au@C₆₀ UV-Vis absorption spectra, in which the C₆₀ shell thickness is set at 0 (bare Au NPs), 5, 10, 15, 20, 25, 30 and 40 nm, respectively. The two images show almost the same red-shift trend and interval for different C₆₀ shell thickness. We note that there is about 10 nm error between experimental and FDTD results (Figure 2.4c), which is likely caused by the approximated refractive index and the solvent ratio.

Figure 2.4. FDTD simulation of the UV-Vis absorption of Au@C₆₀ NPs. (a) experimental data and (b) simulation results; (c) error comparison of the experimental and simulation results.

2.3.1.2. Mechanism study

In term of the C₆₀ shell formation on Au seeds, the attachment of the first layer of C₆₀ molecules should be a critical step. Generally, bare C₆₀ molecules and c-Au NPs are not compatible because C₆₀ is highly hydrophobic as its all carbon component, while c-Au NPs are hydrophilic. There must be interactions between C₆₀ and Au surface other than simple Van der Waals interactions to stabilize the core-shell NPs.

It is well-known that some transition metal atoms with empty orbitals can form dp- π bonds with molecules containing π electrons, including Au. Previously, complexes of Au and olefin (or other aromatic molecules) have been reported with dp- π interactions.²⁴ C₆₀ is a special molecule with delocalized π electrons, which could form dp- π complexes with transition metals like Pd and Pt (Figure 2.5d).^{24, 27} Thus, the formation of weak dp- π bonds between Au and bare C₆₀ molecules should be the main reason for the spontaneous attachment of C₆₀. As this dp- π

interaction is quite weak, it needs some time to complete the formation of C₆₀ monolayer on Au seeds' surface. In our case, because C₆₀ is hardly dissolve in DMF, the addition of C₆₀ solution into Au-DMF solution can promote the attachment of C₆₀ on Au seed as a result of the decreased solubility in mix solution. The addition of IPA promotes the deposition of more C₆₀ by further decreasing its solubility.

In comparison, C₆₀ could only form fine crystals themselves with the presence of Au NPs in other solvents such as DMSO and alcohol (Figure 2.5a and b, respectively). Such a result agrees well with our synthetic design (in chapter 2.1.3), as the presence of DMF could provide a buffer between good and poor solvent to avoid the prompt homogeneous nucleation and self-nucleation of C₆₀, which is successful. This result demonstrated that the property of solvents could play a critical role in controlling the nucleation and growth mode of solutes therein. For the subsequent growth of thick C₆₀ shell, π - π and hydrophobic-hydrophobic interactions between C₆₀ molecules should be the key reason.²⁸

The highly amorphous C₆₀ shell can be explained from the solvent effect during the formation of crystals. In the liquid-phase synthesis of molecular nanocrystals, the using of different solvents always leads to the formation of crystals with different morphologies.⁵ For instance, in the synthesis of C₆₀ nano/micro-structures, when the good solvent of C₆₀ is changed from *m*-xylene to CCl₄, the morphology of resulting crystals would change from nanorod to nanosheet.^{29,30} The underlying reason of this effect is that the solvent molecules could participate in the packing of molecules during the formation of nanocrystals, and the embedded solvent molecules could influence the nearby bonding and packing of the crystals.⁵

In terms of the solvent effect during the packing of fullerene molecules, Wang et al. gave systematical studies to the influence of embedded solvent molecules, which they name it as "co-solvent effect".^{12,31} They used the selective etching of C₆₀ nanosheets to demonstrate that *m*-xylene could lead to the *hcp* packing of C₆₀ molecules, and CCl₄ could lead to the *fcc*

packing; and when the two good solvents are simultaneously presented within a solvent system, both crystal phases would be destabilized by embedding two kinds of solvent molecules. In a follow-up work, Ariga et al. further demonstrate the presence of co-solvent effect in C_{60} nanorods, nanoplates, and C_{70} nanocubes, suggesting the widespread presence of this effect in fullerene species.³² Although at the molecular level, how different solvent molecules could interact with fullerene molecules in crystal phases are still unclear, the works in literatures provide solid support on the unique effect of solvents embedment in the packing of fullerene molecules.

Figure 2.5. (a, b) TEM image of nanostructures formed by using ethanol and DMSO instead of DMF, respectively. (c) TGA measurement of the Au@C₆₀ NPs. (d) Au- π (arene) interactions.²⁴

Similarly, in our case, xylene molecules are likely to be packed together with the C_{60} molecules. As xylenes is a mixture of *m*, *p*, and *o*-xylene, the presence of different xylene molecules would generate co-solvent effect, leading to the simultaneous presence of different packing modes of C_{60} molecules. Thus, the competing formation of different crystal phases

finally leads to the poly-crystalline shells (that is, the amorphous shells). The evidence of embedded solvents existence can be obtained from Thermal gravity analysis (TGA, Figure 2.5c). The weight losing rate of the sample became flat from 250-350 °C, suggesting the completely escaping of the solvents. At 300 °C, the weight of the samples reduced about 3%. As the melting point of C₆₀ is 600 °C, this weight loss should come from the losing of solvents embedded in the C₆₀ shell.

2.3.2. Tuning the shell morphology

Results in the above parts suggest our synthetic design was successful. The deposition of C₆₀ was successfully controlled via a DMF “buffered” solvent system. To examine the effectiveness of our design principle in controlling the rate of fullerene precipitation (with DMF), we attempted to further tune the morphology of the C₆₀ shell by changing the good solvents.

When *m*-xylene was used as the good solvent, due to the reduced solubility of C₆₀ in *m*-xylene, its concentration was decreased to 0.6 mg/mL. Serious aggregated Au NPs with extremely thin C₆₀ shells were obtained (Figure 2.6a). When CCl₄, another solvent that has low solubility of C₆₀, was used for the synthesis, only bare Au NPs, very thin C₆₀ shells, and tiny C₆₀ crystals were obtained (the concentration of C₆₀ was reduced to 0.2 mg/mL, Figure 2.6f). When *o*-xylene was used, self-nucleated C₆₀ particles were observed together with the core-shell NPs (Figure 2.6b). The core-shell NPs had thick shells. When toluene was adopted for the synthesis, thin C₆₀ shells in irregular shapes were obtained as shown in Figure 2.6e. The modified solvent systems had similar reaction time and phenomena, suggesting the overall mechanism was not changed.

Interestingly, when *p*-xylene and 1,2,4-tri-methylbenzene were used as the good solvent with a higher concentration of C₆₀ (2.5 and 5 mg/mL, respectively), a pro-longed incubation of

76 h gave core-shell NPs with a crystalline shell (Figure 2.6c and d). With one Au NP at the center, the obtained structures have approximated hexagonal cross-section and octahedral shapes (from TEM and SEM images, respectively, Figure 2.7d-f). The cubic morphologies should be caused by the different viewing directions of the particles under TEM.

We attempted to further analysis the formation mechanism of the crystalline shells. We noticed that the complete deposition of C₆₀ molecules onto the Au NPs requires more than a day to become a complete shell, no matter the shell is amorphous or crystalline. Normally, the formation of core-shell NPs based on reduction, hydrolysis or polymerization of the precursors should need longer time than that of molecule direct deposition.^{5,20} In contrast, in our cases, the buffer effect of DMF leads to long C₆₀ growth time. The growth time of crystalline shells are even longer, suggesting a ripening mechanism might be involved at the later stages of their growth.

Figure 2.6. (a-f) TEM images of nanostructures formed by using *m*-xylene, *o*-xylene, *p*-xylene, 1,2,4-trimethylbenzene, toluene, and CCl₄ as the solvent of C₆₀, respectively.

To know more about the formation process of the crystalline shells, their growth intermediates were trapped as shown in Figure 2.7. Core-shell NPs with thick amorphous shells were observed together with some small C_{60} particles at 16 h. Then, with the nucleation of C_{60} from the solution, the shells became thicker, and the C_{60} particles increased in diameter (28 h). At 60 h, with the reducing of the amorphous C_{60} particles, core-shell NPs with apparently angular shells and much larger sizes were obtained (Figure 2.7c), which finally developed to regular cubic shells after another 16 h.

Figure 2.7. Reaction intermediates of core-shell NPs with a crystalline shell (with 1,2,4-tri-methylbenzene as the good solvent). (a-d) TEM images of the samples reacted for 16, 28, 60, and 76 h, respectively. (e) SEM image of the products in (d), and a typical NPs (f). Scale bars are 200 nm for (a) and 500 nm for (b-f).

Such a process appears to be an Ostwald ripening mechanism. C_{60} is extremely easy to form crystals when its saturated or near saturated solution in good solvents is added into a poor solvent. According to our synthetic design, DMF could slow down the fast-homogeneous

nucleation of C₆₀. However, C₆₀ cannot completely dissolve due to the low solubility therein. It is possible that when C₆₀ solution was added into Au-DMF solution, some C₆₀ molecules attached on Au seeds surface via weak dp- π interaction, while others form tiny amorphous particles that could slowly grow larger. As the tiny C₆₀ particles are metastable, ripening with crystalline Au@C₆₀ NPs should be an energy favored process. Therefore, when a large amount of C₆₀ could be adapted in a pure good solvent (solubility of C₆₀ is 5.9 mg/mL in *p*-xylene and 17.9 mg/mL in 1,2,4-tri-methylbenzene, much larger than that of other good solvents),^{9,11} the excess C₆₀ would precipitate out in a faster rate, leading to the rapid growth of the initial amorphous shell and the amorphous C₆₀ particles (28 h vs. 16 h). The tiny C₆₀ particles re-dissolve and eventually disappear to become the crystalline shells via a ripening process. Usually, ripening is a time-cost process as it is a slow deposition-dissolve, re-deposition and re-dissolve equilibrium, making the reaction requires several days to be completed.

2.3.3. Other metal@fullerene core-shell NPs

To check whether this solvent system is suitable for other metal core or fullerene species, we attempted Pd nanocubes, Au nanorods, Ag NPs, and 15 nm Au NPs as the core materials. The C₆₀/C₇₀ shells were coated under the same condition as Au@C₆₀ NPs. As shown in Figure 2.8, the above core materials were successfully encapsulated within thick fullerene shell. For Pd nanocubes and Au nanorods (Figure 2.8a and b), unlike previous single encapsulated Au NPs, aggregated core NPs inside C₆₀ shells were observed. This may due to that CTAB is partly soluble in DMF, and thus cannot well stabilize the NPs. Except for C₆₀, C₇₀ can be uniformly deposited onto Au cores as well, giving Au@C₇₀ core-shell NPs (Figure 2.8e). These results indicate (1) the as-designed mix solvents synthesis strategy is suitable for the controllable precipitation of fullerene materials; (2) it is suitable for the synthesis of various metal@fullerene core-shell NPs by using bare fullerene as shell materials. Hopefully, this

strategy may also be extended to other materials, for example, the core of metals or metal oxides, and the shell of other organic materials, though in some cases pre-surface modification may need before the deposition.

Figure 2.8. TEM image of Different core-shell NPs: (a) Pd nanocube@C₆₀; (b) Au nanorod@C₆₀; (c) Ag NPs@C₆₀; (d) 15 nm Au NPs@C₆₀; and (e) Au NPs@C₇₀.

2.4. Summary

In this chapter, we did a preliminary exploration on the controllable precipitation of fullerene materials in solution phase. A three solvents solubility buffer system was designed for this purpose, and the series of experimental results confirm that our design was successful. With it, bare fullerenes could be slowly deposited onto the surface of different metal NPs. Such a gradual deposition provides us a valuable opportunity for convenient observation of the precipitation process.

As a model system, C₆₀/C₇₀ molecules can grow into uniformly thick shells on Au NPs, forming Au@fullerene core-shell NPs. Due to the high refractive index of C₆₀, plasmonic absorption of Au@C₆₀ NPs showed large red-shift. Importantly, through the tuning of reaction time, the deposition of C₆₀ can be precisely tuned, leading to the Au@C₆₀ NPs with controllable shell thickness. To our best knowledge, they are the only typical fullerene core-shell nanostructures with thick and tunable shell thickness. Except for Au NPs, Ag NPs, Pd nanocubes, and Au nanorods can also be used as the core NPs, indicating the excellent generality of this system. Such a new solvent system not only develops a facile route to control the deposition of fullerene materials, but also provides us the possibility of creating structures with increased complexity and controllability.

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Chapter 3: Shaping fullerene hollow nanostructures

Hollow nanostructures are widely used in chemistry, materials, bioscience, and medicine,¹ but their fabrication remains a great challenge. We bring pottery, the oldest and simplest method of fabricating hollow containers, into the nanoscale (nanopottery). By exploiting the liquid nature of the *m*-xylene template, fullerene hollow nanostructures of tailored shapes, such as spheres, bowls, and bottles, are readily synthesized. The liquid templates permit stepwise and versatile manipulation and hence, the synthesized structures could be readily shaped. As a proof-of-concept application, we create nano-containers for the selective incorporation of hydrophobic NPs. This methodology expands the synthetic freedom for hollow nanostructures, and opens a window for the using of emulsion liquid as the soft templates.

3.1. Introduction

Pottery brings the dawn of manufacturing in human history. With it, one can readily design, build, and assemble hollow containers with shapes tailored for various applications. But this important concept has yet to be emulated in nanoscience. Hollow nanostructures have found applications in catalysis,¹ nanoreactor,² energy storage,³ and drug delivery.⁴ Despite the progresses in application, the fundamental synthetic capabilities remain at a primitive level. Most hollow nanostructures are enclosed spheres,^{5,6} and to create an opening is still a great challenge. An opening serves as a channel of material exchange, which could play critical roles in cargo loading and release, or serve as a junction to restrict material flow.⁷ For this reason, hollow nanostructures with an opening (e.g., nanobowls) are widely used as nanocontainers, nanoreactors, and nanomotors.⁸ However, further increase of structural complexity, such as

creating a nanoflask, is extremely difficult,^{9,10} not to mention creating more sophisticated shapes and systems.

According to the geometry, hollow nanostructures are divided into spheres, cubes, tubes, bowls, etc. A variety of methods have been developed for their synthesis, including template method, Ostwald ripening, galvanic replacement, and Kirkendall effect. Among these methods, soft template synthesis is widely adopted due to its advantages in simplified steps, reduced costs, and ease of template removal. The soft template synthesis uses fluid such as liquid droplets or air bubbles as the template for the growth of hollow nanostructures. Due to the presence of surface tension, most fluid droplets are spherical in open air or liquid phase. Hence, the resulting hollow cavities always have a spherical shape. For instance, hollow spheres of metal or metal oxides, polymers, silica, carbon, and other organic materials have been successfully and extensively prepared (Figure 3.1).^{6,11,12} However, more complexed shapes are rarely reported with this methodology. As it is unrealistic to directly manipulate the shapes of nano-sized droplets, the symmetry of spherical template is hard to be broke.

Indeed, there are a limited of methods to break the symmetry of hollow nanostructures, although some efforts and successes have been achieved over the past years. For instance, Wang's group reported the synthesis of silica nanobottles through the squeezing of liquid droplet templates out of the nanobottles to create openings and short bottlenecks;¹⁴ Li et al. reported the fabrication of porphyrin nanobowls and bottle-like nanostructures, in which the solvent inside the vesicles were evaporated to create openings;⁷ and Fu et al. reported the creation of irregular openings on C₆₀ nanospheres via the escaping of their internal gas bubbles.¹⁵ Despite the interesting structures achieved, the underlying design principles of the above methods are either cannot be readily applied to a wider class of materials, or too complex to be precisely controlled, making the synthesis and applications of hollow structures are limited to rudimentary demonstrations. Advancing the synthetic skills in in urgent demand.

Figure 3.1. (a) A typical synthetic process of hollow spheres with a soft template methodology. Typical morphology of hollow spheres with different materials: (b) Au; (c) silica; (d) TiO₂. Reprinted and modified from ref. 6 (for a and b), 11 (for c), and 12 (for d) with permission. Copyright © 2004, 2009, and 2013, American Chemical Society.

In the synthesis of hollow nanostructures, to create asymmetric hollow nanostructures is of particular interest due to their unique applications. In macroscopic world, asymmetric hollow structures are the most widely applied hollow structures. Similarly, creating asymmetric hollow structures at the nanoscale would be a promising path for creating new functions: in the above synthetic cases of asymmetric hollow nanostructures, the as-prepared silica nanobottles could be used as nanoreactors, and nanomotors;¹⁴ the porphyrin nanobowls and bottles have unique conducting behaviors under a bias voltage;⁷ and the irregular C₆₀ nanospheres can be adopted as electrocatalytic sensor for biomolecules.¹⁵ Although some interesting applications have been reported as a preliminary exploration of asymmetric hollow nanostructures, we have

to point out that it is still a great challenge to break the symmetry of hollow nanostructures, due largely to the lack of synthetic capability.¹³ From the view of synthetic methodologies, difficulties not only come from symmetry breaking, but also from the site-selective growth of hollow spaces, and the selective deposition of shell materials.

In the previous chapter 3.2, we demonstrated that the precipitation of fullerenes can be precisely controlled via a three-solvents and two-phases system that is made of IPA, xylene, and DMF. In this system, xylene is the good solvent of fullerenes, IPA is the poor solvent, and DMF is a buffer of solubility. As a demonstration, Au@C₆₀ and Au@C₇₀ core-shell NPs with different shell shapes and thickness were successfully prepared. In this chapter, we attempt to apply this solvent system to a wider kinds of fullerene materials that has yet to be reported in a hollow form, to realize the controllable synthesis of complexed hollow structures.

In short, we report a facile synthetic methodology: nanopottery, where fullerene hollow nanostructures with tailored openings and shapes can be created within one-step (Figure 3.2a and b).¹⁶ Through this method, two main morphological controls on hollow nanostructures were made, including tunable opening sizes on nanobowls and tunable bottlenecks on nanobottles. The core synthetic capability comes from the stepwise manipulation of liquid droplet template, which is also the focus of mechanistic study (Figure 3.2c). As a proof-of-concept application, we constructed nanocontainers for the selective incorporation of different hydrophobic metal NPs.

Figure 3.2. Schematics illustrating the concept and design. (a) Models of pottery, and (b) TEM images of their corresponding nanostructures created with nanopottery. (c) Schematics illustrating the synthesis steps. Scale bars are 200 nm.

3.2. Materials and methods

3.2.1. Materials

Pristine C_{60} (98%) and C_{70} (99%) powders, phenyl- C_{61} -butyric acid methyl ester (PCBM, 99%) and anhydrous DMF (99.8%) were purchased from Sigma-Aldrich. *M*, *o*, *p*-xylene (Analytical Reagent, A.R.), toluene (A.R.), ethanol (absolute) and IPA (A.R.) were purchased from Beijing Chemical Agent Ltd., China. Deionized water (resistance > 18.2 $M\Omega/cm$) was used for all the reactions unless annotated. All the chemicals were used without further purification. The following experiments could be reasonably reproduced without referencing other literatures.

3.2.2. Methods

Characterization: TEM images were obtained using a JEOL JEM-1400 electron microscopy at an accelerating voltage of 80-100 kV. SEM images were obtained with a field-emission scanning electron microscopy (FE-SEM, model JEOL 7600F) at an acceleration voltage of 5 kV. SAED and HR-TEM data was obtained with a JEOL JEM-3010 TEM at 300 kV. HAADF-STEM images and EELs spectrums were obtained with a FEI-Titan ST electron microscope operated at 300 kV. An Apple iPhone is used to take the photographs of the reaction solution.

DLS measurements: DLS data was obtained with a machine model ZEN 5600 from Malvern under a back-scattering mode (at a scanning angle of 173°). For DLS measurement, 1 mL of the sample solution was injected to a four sides transparent glass cuvette, and then capped to avoid volatilize of solvent.

Raman spectroscopy: Raman spectrums were obtained with a machine model DXR3xi from Thermal Scientific under a 785 nm laser. For Raman measurements, 1 mL of the sample solution was taken and centrifuged at a speed of 12 g for 15 min. Then, the supernatant was removed, the precipitate was extracted and dropped onto a slice of quartz glass. The sample was quickly heated to 85 °C to be completely dried.

TEM sample preparation: 0.3 mL of the sample solution was taken and centrifuged at a speed of 8 g for 10 min. Then, the supernatant was removed, and the precipitate was dropped on a copper grid that was pre-treated under oxygen plasma (with a Harrick Plasma cleaner) for 20 s to remove the dusts. The sample was dried in flow air for 1 h. Samples for HR-TEM were prepared on ultra-thin copper grids, and were completely dried in oven at 80 °C for 0.5 h.

SEM sample preparation: The above TEM samples were collected for SEM characterization. To improve the samples' conductivity, they were coated with a thin layer of gold with an Edwards Sputter Coater for 33 s.

Preparation of fullerene nanobowls/bottles/spheres: Pristine C₆₀ powders were dissolved in *m*-xylene with a concentration of 0.80 mg/mL (for the synthesis using *o*-xylene as the solvent, the concentration is 2.2 mg/mL; for *p*-xylene and toluene as solvent, the concentration is 1.2 mg/mL; for the synthesis using PCBM or C₇₀ as shell material, the concentration is 14.5 and 2.4 mg/mL, respectively). 40 µL of the above solution was added to 1 mL DMF dropwise (rate varies from 3 µL/s to one shot) with vortex, and 400 µL of IPA was added to the mixture slowly with vortex. The mixture was then sealed and incubated at room temperature. After 18 h, C₆₀ nanobowls with different opening sizes or enclosed hollow spheres were obtained, and C₆₀ nanobottles could be obtained after another 24 h (using the C₆₀ nanobowls with a small opening).

Preparation of fullerene nanobottles in water doped DMF: The steps of this part are exactly same as the previous one, the only difference is the DMF was pre-doped with water before the synthesis. The volume ratio of DMF:Water can be arbitrarily varied from 1000:0 to 1000:30. According to the different volume ratio, nanobottles can be obtained after an incubation of 16-28 h at room temperature.

Preparation of fullerene nanobowls without IPA: The steps of this part are exactly same as the previous one, the only difference is the absence of IPA. The volume of C₆₀ solution in *m*-xylene was increased to at least triple as the previous to guarantee the successful preparation. The reaction needs a longer period of incubation at room temperature (more than 28 h) to obtain the bowls.

Incorporation of metal NPs. Ag NPs were synthesized using the literature method.¹⁷ Fe₃O₄ NPs were purchased from Ocean Nanotech. Co NPs were purchased from Strem Chemicals. Solution of metal NPs was mixed with the C₆₀ solution in *m*-xylene (0.80 mg/mL) according to the ratio as shown in Table 3.1. The mixture was used to synthesize nanobowls or bottles without changing the steps.

Table 3.1. Volume ratio of metal solution and C₆₀ solution.

	Ag NPs	Fe ₃ O ₄ NPs	Co NPs
V _{metal} :V _{C60}	1:200-1:500	1:400-1:800	1:100-1:200

Scale-up the synthesis: The synthesis of fullerene nanobowls can be directly scaled-up to up to 30 times as the original dimensions without changing the synthetic steps. For example, for a 30 times' scale-up, the volume of each reactant was changed to 1.2 mL fullerene solution, 30 mL DMF, and 12 mL of IPA.

3.3. Results and discussions

3.3.1. Synthesis of C₆₀ nanobowls

In chapter 2, we demonstrate that DMF is an effective solvent that is able to slow down the fast nucleation of fullerenes when combined with IPA and *m*-xylene. As a demonstration of this three-solvents system, Au@C₆₀ core-shell NPs were synthesized with a shot of C₆₀ solution in xylenes added into Au-DMF solution (Figure 2.2 and 3.3a), followed by IPA. Interestingly, when two shots of C₆₀ solution were continuously added into the Au-DMF solution, for example, when 20 μ L C₆₀ solution in *m*-xylene was added first and then 20 μ L C₆₀ solution in *o*-xylene, hollow nanostructures resemble bowls were obtained together with the core-shell NPs (Figure 3.3b).

Wondering whether these nanobowls can be synthesized without Au NPs, we did the synthesis without gold, and kept all other reaction conditions unchanged. As a result, nanobowls with different sizes were obtained as shown in Figure 3.3c. Further control experiments confirmed that this synthesis could be done when using *m*-xylene as the solvent of C₆₀, and different solvents would influence the size and shapes of these nanobowls. If C₆₀ solution in two different solvents were sequentially added, a mixture of big and small bowls would be obtained (Figure 3.3c and d). As no emulsification is observed during the synthesis,

it appears that a template-free mechanism is involved for the nanobowl formation, which is rare. As this synthesis employs a completely new solvent system, it should be useful to study its underlying formation mechanism.

Figure 3.3. TEM image of (a) Au@C₆₀ core-shell NPs; (b) the mixture of Au@C₆₀ NPs and the nanobowls; (c) C₆₀ nanobowls with two different sizes and their large area SEM image (d).

We optimized the preparative condition of the nanobowls. In a typical synthesis, C₆₀ solution in *m*-xylene was added dropwise to DMF with vortex to avoid fast precipitation. IPA was then added to reduce the solubility of C₆₀. With the proceeding of the reaction, the solution changed gradually from nearly colorless to light yellow, indicating the slow nucleation of C₆₀ (Figure 3.5k). After 18 h, hollow C₆₀ hemispheres resembling bowls were obtained, with uniform size and opening. We note that after the reaction there was no precipitate at the bottom. All the particles floated in solution, indicating the low density of the nanobowls. When the rate of C₆₀ solution addition was increased (from 3 to 5, 10 and 20 $\mu\text{L/s}$), the half-shell changed

towards complete sphere, with the size of their opening decreased from 181 ± 20 to 102 ± 13 , 77 ± 12 , and 41 ± 8.5 nm, respectively. Direct TEM characterization of the products confirmed the successful synthesis of bowl-like nanostructures in an extremely high yield (Figure 3.4a-d and f-h). When the rate of C₆₀ solution addition was increased to one-shot, enclosed hollow spheres were obtained. DLS measurements of different samples further confirm the formation of the hollow nanostructures in solution phase.

Interestingly, for nanobowls with a small opening (e.g., 41 nm), prolonged incubation (>18 h) led to gradual outward extension of the C₆₀ shell, giving short tube-like protrusions, which eventually developed into long straight bottlenecks (17 ± 3 nm at 18 h, 31 ± 3 nm at 24 h, 59 ± 6 nm at 36 h, 116 ± 18 nm at 72 h, and 119 ± 23 nm at 108 h, Figure 3.5a-d). With the bottleneck consistent in width with the nanobowls opening, the overall structures resemble bottles or vases. During the growth, the bottle wall also increased in thickness, indicating the non-selective deposition of C₆₀ at its outer surface (Figure 3.5j). The formation of bottlenecks critically depends on the size of nanobowls' opening. No bottlenecks were observed when the opening was over 77 nm, even after incubation for several days.

Figure 3.4. (a-e) TEM images (top row) of typical C₆₀ nanobowls with decreasing opening size and their corresponding SEM images (bottom row); scale bars are 100 nm for TEM images, and 200 nm for SEM images. (f-h) Large area TEM images of nanobowls with different opening size. (i) TEM image of hollow spheres.

DLS measurements of the bottles further confirm the formation of bottleneck in solution phase (Figure 3.5i). It is possible that the critical factor is the small opening's ability to restrict the material flow from the inside of the nanobowls (vide infra). High-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) results show that the C_{60} shell in these hollow structures is amorphous (Figure 3.5e and f), which is same as the amorphous shell in the $Au@C_{60}$ core-shell NPs. The as-prepared hollow structures have high stability: when being transferred into water, the nanobottles were not damaged after vigorously sonication for 1 h; the shape of the nanobottles remained unchanged after heat treatment at 80 °C for 24 h; and the nanobowls could be stored in the original preparative solution for at least 3 months.

Figure 3.5. (a-d) TEM images of nanobottles incubated for 18, 24, 36, and 72 h, respectively. (e, f) SAED and HR-TEM image of the nanobottle. (g) SEM image of nanobottles incubated for 72 h. (h) Dependence of nanobottles' neck length on incubation time. (i) DLS measurement of particle size distribution of nanobottles incubated for 18 h (blue) and 72 h (red). (j) Dependence of nanobottles' shell thickness on incubation time. (k) Photograph of the nanobottle solution: at the very beginning of the reaction (left), and reacted for 36 h (right);

the two photos were pieced together. (l) Schematics illustrating the formation of the nanobottles. Scale bars are 100 nm for TEM images and 200 nm for SEM images; error bars indicating standard deviation.

3.3.2. Mechanism Study

3.3.2.1. Confirm *m*-xylene droplet as template

Considering the low solubility of C₆₀ in *m*-xylene/DMF/IPA, the amount of C₆₀ making up the bottleneck appears to be too much, given the maximum solute allowed in the small cavity of the initial nanobowls. Thus, we initially hypothesized that solid amorphous C₆₀ is the template, which eventually disappeared after ripening. However, DLS results showed instant formation of 100 nm droplets/particles after mixing C₆₀ solution in *m*-xylene with DMF (Figure 3.6d). When IPA was added, their size rapidly increased to over 120 nm. By the end of 150 min, the size increased to ~170 nm. The gradual growth of the particles argues against the solid template hypothesis. We then found that *m*-xylene is only partially miscible with DMF,¹⁸ suggesting the droplets of *m*-xylene might be the real template. To explore the effect of *m*-xylene, we ran a mock reaction by mixing *m*-xylene, DMF, and IPA according to the ratios used and in the absence of C₆₀. The mixture appeared to be transparent, but clear Tyndall effect could be observed with green laser (Figure 3.6a and c). DLS results further confirmed the formation of droplets with diameter around 140 nm (Figure 3.6e). We speculate that the reason why no emulsification was observed might be the refractive index of the three components is too close ($n = 1.430$ for DMF, 1.377 for IPA, and 1.497 for *m*-xylene). Hence, it is more likely that *m*-xylene droplets (containing some DMF and IPA) are the main template, whereas the C₆₀ precipitate in the droplets may provide the materials for the growth of bottlenecks.

Figure 3.6. Photographs of the mock reaction with the mixture of (a) DMF and *m*-xylene; (b) DMF, *m*-xylene, and IPA, and (c) emulsion obtained after adding 10% volume of water into the mixture in (b). (d) DLS measurements reflect average particle diameter change in the first 150 min of the reaction. (e) DLS

measurements of *m*-xylene droplet size distribution in the emulsion in (b). TEM images of (f, g) C₆₀ nanobottles synthesized in water pre-doped DMF (reacted for 36 h); (f, g) contains 1.2%, and 2% volume of water, respectively.

Given the hypothesis, we attempt to extend the liquid template, and thus promote the formation of the resulting bottleneck. We introduce water, a solvent that has extremely low solubility of C₆₀, into the system. Water is miscible with DMF and IPA and immiscible with *m*-xylene.¹⁹ It is expected to increase the polarity of the DMF/IPA phase, thus promoting the phase separation of *m*-xylene droplets from it (Figure 3.6c). Hence, the formation of more droplets and the faster deposition of C₆₀ would lead to the bottleneck extension. When the DMF used for nanobottle synthesis was pre-doped with water (1-2% V/V), the resulting nanobottles have longer bottlenecks (160-190 nm) within a shorter period (36 h), matching with our expectations (Figure 3.6f and g). We noticed that the bottleneck formed at a later stage always has thin thickness. Thus, there are two nucleation sites for C₆₀: one selectively along the opening extending the shells, and the other non-selectively at the outer surface making the shells thicker. Such a strategy also provides a faster route to nanobottle synthesis.

3.3.2.2. Intermediates study

To know more about the formation of the above hollow structures, growth intermediates of the nanobowls were trapped. The intermediates showed a large number of irregular clusters at 1 h, which should be the drying pattern of oversaturated C₆₀ in solution (Figure 3.7a). Then, thin half-shells could be recognized at 2 h (outer diameter ~170nm, Figure 3.7b), with paste-like substance wrapped in the cavity. From 3 h and onwards, the half-shells grew thicker and gradually became more complete with reduced opening size. At the same time, the paste-like substance inside the shell, possibly xylene-solvated C₆₀, reduced in volume, and eventually disappeared. As the outer diameter of the half-shell increased, the diameter of its inner cavity remained almost unchanged (~140 nm), suggesting that the deposition of C₆₀ mostly occurs at

its outer surface. It appears that the deposition cannot occur within the droplet, but has to be assisted by the outer solution.

Also, we note that the selectivity for one opening per particle is extremely high. We did not find a single example with more than one opening. It is because that the growth of C_{60} shell always starts from the rim of the opening and extends along the boundary with the opening reducing in size. Such gradual extension avoids multiple openings. In comparison to the heterogeneous nucleation at the rim of opening, the homogeneous nucleation at the droplet-solution interface would be less favorable.

Figure 3.7. TEM images of C_{60} nanobowls (a-f) formation intermediates reacted for 1, 2, 3, 5, 6, and 20 h, respectively.

3.3.2.3. Proposed mechanism

Based on these facts, we propose a coherent mechanism that is consistent with all observations: when C_{60} solution in *m*-xylene was added into DMF, the reduced solubility

excludes most xylene and C₆₀ from the DMF phase. The *m*-xylene solution is highly dispersed when mixed with DMF/IPA, forming tiny droplets that merge together to become the initial template of the bowls/bottles. As the *m*-xylene is only partially miscible with DMF, the formation of droplet template is expected to be slower than that of two immiscible liquids, leading to the uniform size of the droplet template (just like the crystal growth). Then, the addition of IPA further reduces the solubility, allowing extensive growth until the exhaustion of C₆₀.

The addition rate of C₆₀ solution determines the initial degree of C₆₀ oversaturation. As faster addition leads to more C₆₀ precipitate along the droplets, it determines the completeness or opening size of the initial thin shell. There are two nucleation sites: the non-selective growth at the outer surface depends on the C₆₀ concentration, which is a factor of the initial addition and the material exchange from inside of the xylene phase, minus the consumption by the growth. The selective growth at the rim of the opening is slow, as its collection area is much smaller than the outer surface. Hence, nanobowls with initial larger opening undergo faster material exchange and faster depletion of the C₆₀ paste. Only those with small opening could prolong the ripening process, so that their opening would be able to slowly close in and then form bottlenecks (more evidences are provided in chapter 4.3.2).

During the formation of bottlenecks, the highly-dispersed *m*-xylene droplets would gradually merge at the exposed liquid surface of the bowls. The merging with the remaining xylene droplets at the later stage of growth is expected to be much slower. Such slow merging would cause the liquid to slowly exceed the rim of the bowls, forcing the C₆₀ shell to gradually extend outward, and form the straight bottlenecks (Figure. 3.51). In other words, the bottleneck becomes straight when it is templated by many stages of thin layers. At the same time, the C₆₀ paste in the *m*-xylene phase (that is, in the cavity of the bowls) may slowly dissolve into the DMF/IPA phase and re-deposit to give more stable C₆₀ domain. This would allow C₆₀ in the

paste to move into the ripening cycle, and its low solubility explains the long growth time of the bottlenecks.

Obviously, according to the above mechanism, the critical step for the formation of bowls/bottles is the short mixing process of C_{60} solution and DMF. After this, IPA only plays the role of facilitating C_{60} precipitation. Therefore, we hypothesis that as long as the solubility of C_{60} is low enough, or its oversaturation is high enough after the initial mixing with DMF, the nanobowls could be obtained even without the IPA. To test on this hypothesis and to maximum the chance of simplifying our synthetic system, we attempted to do the synthesis without IPA. When IPA was directly removed from the synthesis, no nanobowls could be obtained even after an incubation of several days. However, when the C_{60} solution was added with an increasing volume (120 μL , without changing the volume of DMF), nanobowls with thin shells were obtained after an incubation of 36 h (Figure. 3.8a-c). By increasing the volume of C_{60} solution to 240 and 480 μL , their shell thickness slightly increased form ~ 20 nm to 30 nm, suggesting more C_{60} could precipitate out within a certain period, agreeing well with our hypothesis. We noticed that by increasing the volume of C_{60} solution, the paste-like C_{60} within the bowls also increased in volume. This is likely because the C_{60} become more concentrated as its volume increases, making more solvated C_{60} could form within the nanobowls.

Figure 3.8. TEM images of C_{60} nanobowls obtained without IPA. (a-c) Addition of 120, 240, and 480 μL of C_{60} solution into DMF, respectively.

Furthermore, though C₆₀ molecules are usually stable under room temperature,²⁰ it would be a better support to the above mechanism if we could demonstrate that no chemical modification of the C₆₀ molecules happened. To this end, Raman spectrum and UV-Vis spectrum of the C₆₀ nanobowls were measured. The Raman spectra were obtained using a 785 nm laser at room temperature. Both commercial C₆₀ powders and the C₆₀ nanobowls had only one intense Raman absorption peak at 1470 cm⁻¹ (Figure 3.9a), which is exactly consistent with the Raman shift of C₆₀ in literature.^{21,22} The consistency of Raman shift and the absence of newly formed peaks after the reaction suggest there are no new chemical bonds formation. The peak of commercial C₆₀ powders had a sharper bump than that of the bowls, which is likely caused by the higher crystallinity of the powders (comparing with the highly amorphous nanobowls).

Figure 3.9. (a) Raman spectrum of C₆₀ nanobowls (black) and commercial C₆₀ powders (red) measured at 296 K. (b) UV-Vis spectrum of nanobowls reacted for 0 h (black) and 22 h (red).

Additionally, UV-Vis spectrum of C₆₀ nanobowls reacted for 22 h showed three absorption peaks/bands (Figure 3.9b): one strong and sharp peak appeared around 330 nm, one small peak appeared around 410 nm, and another broad band appeared at 500-600 nm. The position and the shape of the three peaks are well-consistent with the peak of C₆₀ in literature.²³

Comparing to the initial stage, the UV-Vis spectrum after reaction had exactly the same peak position, indicating the C₆₀ was not chemically modified. The decreased peak intensity after reaction should be caused by the nucleation of C₆₀ from the solution.

3.3.3. Incorporation of metal NPs

Due to the high stability of these hollow nanostructures, as a proof of concept, we tried to construct nanocontainers with the hollow structures. The different solvent environment in and outside the hollow structures provides an opportunity for selective loading of NPs. Hydrophobic NPs that can be well dispersed in *m*-xylene, for example, Fe₃O₄, Co, and Ag NPs, were mixed with C₆₀ solution in *m*-xylene. They are expected to be trapped in the xylene droplets, and thus retained in the cavity. Figure 3.10a and e show Ag and Fe₃O₄ NPs trapped in nanobowls; Figure 3.10b and c show Co and Fe₃O₄ NPs in nanobottles. Elemental mapping of these containers confirmed the successful incorporation (Figure 3.10f-h and j, k). The incorporated NPs can be released either by transferring the containers into fresh DMF (or other solvents that have higher solubility of C₆₀) followed by a 1 h vigorous sonication, or by re-dispersing the containers into a good solvent of C₆₀ (e.g., xylene).

In contrast, when hydrophilic NPs, for example, citrate-stabilized Au NPs dispersed in DMF were used, they could only attach to the outer surface of the nanobottles (Figure 3.10d), agreeing well with our synthetic design. The hydrophobic NPs are expected to prefer the xylene phase than the DMF/IPA phase. The same could be said for any C₆₀ precipitated in our method. Hence, the selective incorporation of the NPs could support the selective localization of C₆₀ paste in the cavity, as discussed in the above mechanism. Such an incorporation-release model provides a plausible way for the future application of these hollow structures in the cargo loading and releasing of other hydrophobic substances. Importantly, considering the excellent biocompatibility of C₆₀ and its derivatives,^{24,25} for smaller molecules that could readily pass

through the opening, the slow release rate allowed by the single opening may lead to potential applications in sustained drug release and drug delivery.

Figure 3.10. TEM images of C_{60} (a) nanobowls holding Ag NPs; (b) nanobottles holding Fe_3O_4 NPs; (c) nanobowls holding Co NPs; (d) hydrophilic Au NPs stay out of the nanobottles. (e) High-angle annular dark field (HAADF) image of nanobowls holding Fe_3O_4 NPs, and its elemental mapping (f-h). (i) HAADF image of nanobowls holding Ag NPs, and its elemental mapping (j, k). (l) Electron energy loss spectroscopy (EELS) of nanobowls holding Fe_3O_4 NPs. Scale bars are 200 nm for TEM and HAADF images, and 50 nm for elemental mapping profiles.

3.3.4. Generality

The principles of nanopottery are expected to be generally applicable, though the conditions for different shell formation would need slightly alternative design. For instance, nanobowls could be created when the *m*-xylene solvent was changed to *o*-xylene, *p*-xylene, and toluene (Figure. 3.11a-c). When *o*-xylene is used as the solvent, nanobowls with much smaller size and large openings were obtained (diameter 161.0 ± 9.3 nm, opening size $81.1 \pm$

11.3 nm), likely due to the larger solubility of C₆₀ in these solvents. IPA could be replaced by ethanol or methanol, and nanobottles or hollow spheres were obtained (Figure. 3.11d and e). In comparison, the modified solvent systems have similar reaction time, color change, and Tyndall effect, suggesting unchanged mechanism. We noticed that different particle sizes were obtained when different good solvents were used (e.g., ~160 nm for *o*-xylene, ~220 nm for *m*-xylene, ~180 nm for *p*-xylene, and ~310 nm for toluene). It is possible that the different miscibility of the solvents (with DMF) could influence their initial diffusion process.¹⁸ Hence, the formation of liquid droplet templates was affected, producing liquid droplets with different size distributions.

In addition to C₆₀, other fullerene group materials like C₇₀ and PCBM (phenyl-C₆₁-butyric acid methyl ester) can also give similar hollow structures, by directly replacing C₆₀ in the reaction (Figure. 3.11f-h). The C₇₀ nanobowls can easily grow additional bottlenecks, giving cucurbit-like structures. The higher solubility of PCBM or C₇₀ requires higher concentrations and longer reaction time, but the general phenomena remain unchanged. Importantly, the above results serve as an extra evidence for the proposed mechanism. When solvents that have larger solubility of C₆₀, or when fullerenes that have larger solubility in *m*-xylene were used, the synthesized nanobowls have a large opening, because their higher solubility reduces the initial degree of fullerene oversaturation even when a more concentrated fullerene solution was added. Hopefully, this synthetic strategy can be used to synthesis hollow nanostructures of other fullerene/fullerene derivatives with only slightly alternative design, as well.

Figure 3.11. TEM images of C_{60} hollow structures obtained with (a-c) *o*-xylene, *p*-xylene, and toluene as the good solvent of C_{60} , respectively; (d) ethanol as the poor solvent of C_{60} , hollow spheres; (e) methanol as the poor solvent of C_{60} , mixture of hollow spheres and nanobottles; (f) PCBM nanobowls with very large opening; (g) C_{70} nanobowls; (h) C_{70} nanocucurbits.

3.3.5. Scale-up the synthesis

The preliminary successful incorporation of metal NPs in section 3.3.3 suggests the as-prepared hollow structures may have applications in nanocontainer and drug delivery. Most of the applications require a sample mass of milligram level,^{10,25} but our original methods could

only produce several micrograms sample a time (roughly, 2-3 μg). To reduce the difficulties in the application of these hollow materials in future, we have demonstrated that the synthesis of C_{60} nanobowls can be directly scaled-up to up to 30 times as the original dimensions without changing the synthetic steps.

As shown in Figure 3.11, the scale-up from 5 to 10, and 30 times gave similar nanobowls. The overall morphology, uniformity, and shape of the bowls were not influenced in a scaled-up reaction. The as-prepared nanobowls usually have a larger opening, even when the C_{60} solution was added with a much faster rate. This is likely to be caused by the modified diffusion condition: When there is an increased volume of DMF, the instant C_{60} oversaturation would be much lower at the moment of addition, leading to fewer C_{60} precipitate along the droplets surface, and hence a large opening. At the same time, as the *m*-xylene is partly miscible with DMF, the increasing of DMF volume also influences the formation of emulsion droplets, making the nanobowls have a relatively smaller size. After an incubation of a week to make the C_{60} precipitate as much as possible, hollow materials were obtained with the mass of 11, 23, and 70 μg with a scale-up of 5, 10, and 30 times, respectively. The results of scale-up provides solid foundation for the application of these hollow materials. Hopefully, more nanobowls can be obtained by slightly modifying the reaction conditions to promote the nucleation of the C_{60} , for example, pre-doping the DMF with water, increasing the volume of IPA, or reducing the volume of DMF.

Figure 3.11. TEM images of (a-c) nanobowls synthesized with a scale-up of 5, 10, and 30 times as the original dimension.

3.4. Summary

Fullerene and its derivatives have strong electron-accepting ability and excellent non-linear optical properties,²⁶ being widely applied in lithium battery, solar cell, photoconductive devices, and photocatalysis.^{27,28} However, to create hollow fullerene nanostructures or precisely control the shape of fullerene structures remains a great challenge, which greatly limit the application of fullerene materials. The new synthetic control provides precise and sophisticated structures with high surface area, opening new possibilities for further synthetic design or applications.

With the three-solvents system that is made up of DMF, IPA, and *m*-xylene, we developed the soft template synthesis of hollow nanostructures towards a wider class of material, better shape controllability, and more complexed structures. In the conventional nanosynthesis, continual modification of a structure is extremely difficult. Most NPs cannot be easily reshaped once the synthesis is completed. While liquid droplets can readily reshape by right, the colloidal droplets have monotonous spherical shape, due to the need to minimize their surface. Indeed, it has been almost impossible to manipulate the shape of nanodroplets. In

contrast, with the designed three-solvents system, this work of nanopottery demonstrates the dexterity of liquid droplets in shape control, and the use of them as template for a variety of hollow C₆₀ nanostructures. As a proof-of-concept application, hydrophobic NPs could be selectively retained in the cavities. Such stepwise expansion or addition are the basic skills of pottery, which would offer enormous synthetic freedom for the field.

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Chapter 4: Interconnection of hollow fullerene nanostructures

Interconnected hollow systems are ubiquitous in modern life, which could realize the functions beyond individual hollow cavities by connecting them together. Typical examples include blood vessels, plumbing systems, and tunnel networks. However, the capability of connecting hollow spaces has yet to be realized at the nanoscale. During this process, considering the need to avoid barriers among the hollow compartments, such a capability cannot be readily adapted from the existing methods for assembling solid NPs.¹ Our works in previous chapters prove that the liquid nature of soft template can be used for the expansion of hollow nanostructures. Now, we go one step further on manipulating the shape of liquid droplets template, and the capability of connecting hollow spaces is brought to nanoscale. Hollow fullerene nanostructures such as cucurbits are readily synthesized and interconnected via the stepwise expansion and merging of *m*-xylene droplet template. This synthetic strategy greatly expands the synthetic freedom for hollow nanostructures, building a bridge from isolated hollow structures to interconnected hollow systems.

4.1. Introduction

4.1.1. Common methods of nano-assembly

Assembly of NPs or other nanostructures has become a major approach to create new superstructures or to explore new applications. Despite the great progresses in manipulating the shapes of individual NPs,^{2,3} the growing demands for the scalable organization of nanostructures, especially in the area of energy conversion coatings, biomedical devices, and environmentally friendly catalysts,⁴ cannot be readily fulfilled by the shaping of individual

NPs.⁴ The capability of precise assembling nanostructures is necessary for the application requirements. To this end, difficulties not only comes from controlling the movement of nanostructures, but also from the lacking of driving force and the fault tolerant during massive assembly.⁵ The nano-assembly methods can be classified via the type of driving forces, for example, the assembly via non-covalent interactions, external fields, evaporation of solvents, and template methods.^{5,6} The rapid development of nano-assembly provides scientists scalable superstructures with reduced processing costs and energy efficiency.

The spontaneous organization of NPs or other nanomaterials via non-covalent interactions is a common phenomenon. With the retaining of their original individuality, the interparticle forces provide an exceptional opportunity for dimensional transformation of nanomaterials from nanometer to micron, and even to millimeter.⁷ This widespread interaction make it becomes the most extensively adopted driving force for nano-assembly. For instance, Chen's group reported the chain assembly of colloidal Au NPs via hydrophobic interactions of polymer shells.⁸ The Au NPs were coated with PSPAA to form a core-shell structure, followed by a re-dispersion to obtain the 1D double-line chain structures (Figure 3.1). In 2018, a follow-up work from this group reported the selective dimerization of Au@PSPAA core-shell NPs, reaching a high yield of 65%.⁹ Except for hydrophobic interactions, other frequently used non-covalent interactions in nano-assembly include charge repulsion, Van der Waals interaction, and hydrogen bond.¹⁰ However, most non-covalent interactions are weak and reversible, which lead to unique difficulties in controlling shapes, fault tolerant, and elevating the yield of assembly products.

Figure 4.1. (a) Schematics illustrating the assembly process. (b-d) TEM images of Au@PSPAA core-shell NPs (b), and double-line chains before (c) and after (d) purification. Reprinted from ref. 8 with permission.

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4.1.2. Interconnection: a higher level of assembly

Interconnected hollow systems are playing important roles in macroscopic world. Connecting hollow spaces can often bring about qualitative advance in property, for example, joining tubes into channel systems; connecting a condenser with a flask; and assembling space capsules into a station. A major difference between interconnection and direct assembly comes from the situation of hollow spaces before and after. A direct assembly could only lead to the re-arrangement of isolated hollow compartments, while an interconnection would lead to the connection and expansion of original hollow spaces, just as the difference between a pile of steel tubes and an interconnected channel system in macroscopic world.

Likewise, assembling hollow compartments at the nanoscale would be a promising path for creating new functions. However, such capability remains a blank at the nanoscale. To start on the problem, the elemental step would be connecting hollow nodes and junctions, which cannot be readily adapted from the existing methods for assembling solid NPs, particularly considering the need to avoid barriers among the compartments. To this end, unique challenges come from that direct aggregation would lead to side-by-side arrangement of their shells, which would eventually become the barriers between the compartments.¹¹ To do away with the barrier, interconnection requires site-selective docking of the openings and welding of the resulting subunits, making the process even more challenging.

Adapted from the works in previous chapter, we could do more with the liquid droplets template. We report a facile synthetic methodology, where hollow fullerene nanostructures with tailored opening and shapes can be readily created (Figure 4.2). Importantly, the method allows flexible interconnection of hollow units, advancing from individual hollow units to multi-compartment vessels. The core synthetic capability comes from the stepwise manipulation of liquid template and the regio-selectivity allowed by the single opening, both of which are the focus of mechanistic study. As a proof-of-concept application, we construct multi-compartment nanocontainers for the selective holding and isolation of different hydrophobic NPs within a hollow system.

We note that some mechanism/discussion/data in this chapter is the mutual evidence of the mechanism in Chapter 3.3.2, which will be annotated when necessary.

Figure 4.2. (a) Models of pottery, and their corresponding nanostructures created with nanopottery (b); (c) Schematics illustrating the addition of nodes or junctions, and (d) interconnection of hollow structures. Scale bars are 200 nm.

4.2. Materials and methods

4.2.1. Materials

Pristine fullerene powders (C_{60} , 99%) and anhydrous DMF (99.8%) were purchased from Sigma-Aldrich. *m*-xylene (Analytical Reagent, A.R.), and isopropanol (IPA, A.R.) were purchased from Beijing Chemical Agent Ltd., China. Deionized water (resistance $> 18.2 \text{ M}\Omega/\text{cm}$) was used for all the reactions unless annotated. All the chemicals were used without further purification. The experiments could be reasonably reproduced without reference of other literatures.

4.2.2. Methods

Characterization: TEM images were obtained using a JEOL JEM-1400 electron microscopy at an accelerating voltage of 80-100 kV. SEM images were obtained with a field-emission scanning electron microscopy (FE-SEM, model JEOL 7600F) at an acceleration voltage of 5 kV. SAED and HR-TEM data was obtained with a JEOL JEM-3010 TEM at 300 kV. HAADF-STEM images and EELs spectrums were obtained with a FEI-Titan ST electron microscope operated at 300 kV.

DLS measurements: DLS data was obtained with a machine model ZEN 5600 from Malvern under a back-scattering mode (at a scanning angle of 173°). For DLS measurement, 1-1.2 mL of the sample solution was injected to a transparent four sides glass cuvette, and then capped to avoid vaporization of solvents.

TEM sample preparation: 0.3 mL of the sample solution was taken and centrifuged at a speed of 8 g for 10 min (for bowls, bottles, and cucurbits with less than two cavities), or at a speed of 2 g for 15 min (for more complexed structures). Then, the supernatant was removed, and the precipitate was dropped on a copper grid that was pre-treated under oxygen plasma (with a Harrick Plasma cleaner) for 20 s to remove the dusts. The sample was dried in flow air for 1 h. Samples for HR-TEM were prepared on ultra-thin copper grids, and were completely dried in oven at 80 °C for 0.5 h.

SEM sample preparation: The above TEM samples were collected for SEM characterization. To improve the samples' conductivity, they were coated with a thin layer of gold with an Edwards Sputter Coater for 33 s.

Preparation of individual fullerene hollow nanostructures (bowls/bottles/spheres): Pristine C₆₀ powders were dissolved in *m*-xylene (concentration 0.80 mg/mL). 40 µL of the above solution was added to 1 mL DMF dropwise with vortex. Then, 400 µL of IPA was added to the mixture slowly with vortex. Finally, the mixture was sealed and incubated at room

temperature. After 18 h, C₆₀ nanobowls with different opening sizes were obtained, and C₆₀ nanobottles could be obtained after another 24 h (using the C₆₀ nanobowls with a small opening).

Preparation of fullerene nanobottles/bowls in water doped DMF: The steps of this part are exactly same as the previous one, the only difference is the DMF was pre-doped with water before the synthesis. The volume ratio of DMF:Water can be arbitrarily varied from 1000:0 to 1000:30. According to the different volume ratio, nanobottles/bowls can be obtained after an incubation of 16-28 h at room temperature.

Interconnection of individual hollow nanostructures: Individual hollow nanostructures were synthesized in water doped DMF according to the above steps. 1.2 mL of the sample solution was taken and enriched to certain times (via a 10 min centrifugation at 16g; then remove certain volume of the supernatant followed by the re-dispersion of precipitate). Then, 24 μ L (or less) C₆₀ solution in *m*-xylene (0.75 mg/mL) was quickly added to the mixture with vortex. The mixture was sealed and incubated for 16 h at room temperature to obtain the interconnected structures.

Construction of multi-compartment nanocontainers: Ag NPs were synthesized using the literature method.¹² Fe₃O₄ NPs were purchased from Ocean Nanotech. Solution of metal NPs was mixed with the C₆₀ solution in *m*-xylene (0.80 mg/mL) according to the ratio as shown in Table 4.1. The mixture was directly used to synthesize nanobowls without changing the steps. After the formation of nanobowls holding metal NPs, a second round of C₆₀ solution in *m*-xylene that contains another kind of metal NPs was added ($V_{C60+metal}/V_{nanobowl} = 1:39-1:49$). The mixture was incubated at room temperature for another 18 h to obtain the multi-compartment nanocontainers.

Table 4.1. Volume ratio of metal solution and C₆₀ solution.

	Ag NPs	Fe ₃ O ₄ NPs
V _{metal} :V _{C60}	1:200-1:500	1:400-1:800

Fitting of the function: The function between the cavity size of cucurbits (y) and the volume of m -xylene (x) was obtained with the fitting function in Microsoft Excel 2019.

4.3. Results and discussions

4.3.1. Continuous addition of hollow nodes and junctions

A major discovery in the previous chapter is that we demonstrate the dexterity of liquid droplets in shape control, and the using of them as template for hollow C₆₀ nanostructures with various morphology. Now, we attempted to further manipulate the shape of liquid droplets, utilizing their liquid nature to realize more complexed morphology control.

Based on the existing nanobowls and bottles, we attempt to extend the template, and thus the resulting hollow structure, by adding additional C₆₀ solution in m -xylene to the nanobowl solution. After 20 h, a second hollow compartment grew along the original nanobowls' opening, forming a two-node, cucurbit-like structure (Figure 4.3b). With further additions of C₆₀ solution, similar nodes can be sequentially added, giving interconnected hollow structures with exactly three, four, and five nodes (Figure 4.3c-e and g-h). Such structures with exact number of connected hollow compartments are unprecedented. The arrangement of the nodes is roughly straight, with the opening often occurring at the far end. The wall thickness of the nodes decreases in sequence, with the newly grown one being the thinnest. Thus, there are two nucleation sites for C₆₀: one selectively along the opening extending the shell coverage, and the other non-selectively at the outer surface making all shells thicker.

Figure 4.3. TEM images of (a) typical C₆₀ nanobowl, and (b-e) nanocucurbits with 2-5 nodes, respectively. (f) Schematics illustrating the formation of the node. (g, h) SEM images of nanocucurbits with two and three nodes. (i) A plot showing the linear relationship between the cavity diameter and the cubic root of the xylene volume. (j, k) TEM images of long-neck cucurbits with different neck length. (l) SEM image of long-neck cucurbits with neck length of 95 nm. (m) Addition of a node on long-neck cucurbits. (n-q) C₆₀ nanocucurbits obtained with the

addition of 50, 30, 15, and 3 μL of C_{60} solution, respectively. Scale bars are 200 nm. Error bars indicate standard deviation.

When the C_{60} solution of the second addition was changed from 40 μL to 50, 30, 15, and 3 μL , the inner diameter of the second node changed accordingly (Fig. 4.3i and n-q). The correlation between them can be fitted with the following function (1), in which the cavity size (y , in nm) is proportional to the cubic root of xylene volume (x , in mL). Combining with the proposed mechanism in the previous chapter (see chapter 3.3.2.3), this correlation gives a strong support that the nodes are indeed templated by *m*-xylene droplets.

$$y = (A\sqrt[3]{x} + B)10^{-7} \quad (A = 616.34, B = -79.44, R^2 = 0.98) \quad (1)$$

The second nodes have uniform size distribution, just like the uniformity of nanobowls/bottles in the previous chapter. This indicates that the nodes were formed by gradual merging with a large number of tiny droplets, as opposed to random merging with only a few large droplets, which would lead to nodes with large size variation. We note that the bottleneck connects with the initial bowl with a smooth curve (Figure 4.5h), whereas the cucurbit shows an abrupt turn at the connecting point (Figure 4.5i). The former is consistent with a slow growth of the liquid domain, whereas the latter shows a rapid growth, that is, relative to the rate of shell formation.

When the C_{60} solution of the second addition was further reduced in volume, a much smaller and straight node that resembles a bottleneck was obtained, with only a smooth curve at the connecting point (Figure 4.3p). On these bases, we believe that the highly dispersed droplets in this system (see chapter 3.3.2.3 for details) would have a different behavior when there is a fresh addition of C_{60} xylene solution. During the growth of cucurbits, the newly added xylene droplets could gradually merge at the exposed liquid surface of the bowls/cucurbits. In contrast to the merging with the remaining xylene droplets during the growth of bottleneck, the merging of xylene droplets in a fresh addition is expected to be much faster. In other words, a

round node is formed when the liquid droplet grows much faster than the hardening of the C₆₀ shell, whereas the bottleneck becomes straight when it is templated by a slow merging of droplets. Hence, the growth of liquid domains in nanobottles can be viewed as the accumulation of many stages of thin layers (Figure 3.5l vs. 4.3f).

4.3.2. Study the mechanism with second addition

To know more about the formation of the nanocucurbits, their growth intermediates were trapped. The intermediates showed paste-like substance at the nanobowls' opening at 1-3 h, which should be the drying pattern of xylene-solvated C₆₀ (Figure 4.4b-d, similar as that of the bowls in Figure 3.7a-c). Then, with the reducing of the paste, the new wall became recognizable, and slowly extended outwards from the opening, apparently along the curved edge of the second xylene droplet. As it grew thicker and larger, the new opening closed in and eventually a near-spherical node emerged (13 h, Figure 4.4f-h). During this process, there was no barrier covering the original opening or the later junction between the two compartments. This result supports our hypothesis, as the new xylene domain is expected to quickly merge with the original droplet, forming a connected liquid phase (Figure 4.3f). The transport of C₆₀ from the inside to the opening, and the material exchange with the outer solution keeps the opening open. Thus, it is conceivable that having an opening at the far end of the cucurbits would allow a straight and optimal diffusion path. This explains the coherent orientation of the openings in the cucurbits (Figure 4.3b-e).

We realize that the second growth is a convenient method for trapping the solution species, thus avoiding the inherent ambiguity from the drying process. As shown in Figure 4.5a and b, the second addition of C₆₀ solution in *m*-xylene to nanobowls gave additional nodes, but the opening at the cucurbit junction was kept as wide as the initial nanobowls. When the second addition occurred earlier at 6 h, as opposed to the typical 16-18 h, cucurbits with wider

junctions were obtained (Figure 4.5b). For nanobottles, when the second addition occurred at 3, 6, and 15 h, the trapped intermediates showed cucurbits with decreased opening size at the junction (from ~85 to 45 nm, Figure 4.5c-e). Hence, there are clear trends that: (1) the opening size decreases with time; and (2) the bottleneck only occurs after the opening is reduced to a critical size.

Figure 4.4. (a-h) TEM images of C_{60} nanocucurbit formation intermediates reacted for 0.5, 1, 2, 3, 5, 7, 10, and 13 h, respectively. Scale bars are 200 nm.

After the second growth on nanobottles, an additional node was found at the far end of the bottleneck, giving long-neck cucurbits (Figure 4.3j-l). The selective addition at the bottleneck and the sharp turn at the connecting point supports the above mechanisms. The openings of the long-neck cucurbits have random orientation, unlike those without bottlenecks (Figure 4.3b-d). The restriction by the narrow bottleneck is expected to disrupt the diffusion path of the material exchange, causing the opening to deviate from the straight path. Compare with the original nanobottles, their neck length remained unchanged after the node growth (50 and 100 nm). The bottleneck serves as a junction between the nodes, and additional junctions and nodes can be easily added by repeating the steps of neck growth and node growth (Figure 4.3m, 4.5f and g). The level of structural precision achieved is amazing: not only are we able

to control the exact number of hollow compartments but also the presence of junction and its length.

For comparison, second addition was added to the completely enclosed C_{60} hollow spheres (those were synthesized in chapter 3.3.1), only after 3 h of reaction. No shell extension occurred for those spheres, and instead, the excess C_{60} formed small hollow spheres (Figure 4.5j). This result proves the critical role of nanobowls opening in the node growth: it not only allows the material exchange across the phases but also provides accessible area for the merging of droplets. The results in this part further support the observations and mechanisms in chapter 3.3.2.3: (1) The growth of hollow nanostructures is essentially a slow extension of the existing shells along the spherical *m*-xylene droplets template; (2) The opening size on the final structures critically depends on the completeness or opening size of the initial thin shell; and (3) Only bowls with small openings could prolong the ripening process to form the bottlenecks (Figure 4.5a).

Figure 4.5. (a) Schematics illustrating the process of shell extension. TEM images of (b) second addition products of nanobowls reacted for 6 h; (c-e) second addition products of nanobottles reacted for 3, 6, and 15 h,

respectively; (f, g) typical long-neck cucurbits with different neck length; (h) gradual curve at the connecting point for bottlenecks vs. (i) sharp turn at the connecting point for nodes growth, and (j) second addition products of enclosed spheres reacted for 3 h. Scale bars are 100 nm.

4.3.3. Interconnection of hollow units

In the TEM images, we note that the nanobowls, bottles, and cucurbits often arrange closely in a circle/curve with their openings pointing inward (Figure 4.6a and b, and Figure 3.4f and g). This unusual alignment cannot be explained by random aggregation of the particles during drying. We speculate that they were assembled around a *m*-xylene droplet, which connects with the xylene domain inside the hollow units. This extra droplet may form at the initial stage of drying and eventually evaporated to leave a circular arrangement of the hollow structures.

We attempted to cause C₆₀ growth around this hypothetical droplet. Water-doped DMF (1% V/V) was used to reduce the solubility of C₆₀, and the nanobowls used as the starting material were enriched to four times of the normal concentration, to enhance the probability of aggregation. After second addition of C₆₀ solution in *m*-xylene, interconnected structures were obtained. As shown in Figure 4.6c and 4.7d, the dimers of nanobowls contain a shared hollow compartment as the node connecting the two nanobowls. When the nanobowls were replaced with nanobottles, connected trimers and tetramers were obtained in addition to dimers (Figure 4.6g-i), probably because the presence of bottlenecks reduced the mutual steric hindrance. When the nanobottles were not enriched, only dimers were formed (Figure 4.6l), agreeing with the concentration effect. In the products, the monomers are often well separated from each other surrounding the central node (Figure 4.6g), with no direct contact between them. It is a clear proof that the monomers did not aggregate by direct contact, but via the mediating droplets at their openings.

Figure 4.6. TEM images of (a, b) C_{60} nanocucurbits and bottles arranged in a circle; (c) dimers of connected nanobowls; (d) connection between a dimer of nanobowls and a nanobottle; (e) dimers of connected nanocucurbits; (f-h) dimers, trimers, and tetramers of nanobottles, respectively; (i) tetramers of nanobottles with a large node; (j) multimers of cucurbits (enriched to 6 times of the original concentration); (k) large area dimers of connected nanobowls; (l) large area dimers of nanobottles with a small node, and (m) a typical dimer in (l). (n) Schematics illustrating the interconnection of nanobottles via the droplet merging. Scale bars are 200 nm.

Nanocucurbits could also be used as monomers for similar interconnection, giving a five-node structure with a single opening at the central node (Figure 4.6e). Same as above, the

size of the newly formed node could be adjusted by changing the volume of C_{60} solution during the second addition (Figure 4.6h and i). We attempted to interconnect more cucurbits by further enriching their concentration to 6 and 8 times of the normal concentration, and multimers of cucurbits were obtained as shown in Figure 4.6j and 4.7a & b, respectively. We note that the number of interconnected cucurbits is different between each multimer: some of the multimers have more than ten cucurbits, while others may have only four to six. Also, there were some non-connected cucurbits being left in the sample. We speculate that the merging of the droplets on these cucurbits allows more units to be assembled, but they do not have enough time to finish this process due to the repaid formation of the C_{60} paste within the droplets. Similarly, this might be the reason why these bowls cannot be interconnected at the first-round addition of C_{60} solution into DMF. A control experiment showed that no interconnection was observed after the addition of C_{60} solution into nanobowls that were synthesized in water-doped DMF with no IPA addition (with a lot of C_{60} paste in the bowls, Figure 3.8b and c), which could partly support this mechanism.

Moreover, when dimers of nanobowls were mixed with nanobottles, more complex multi-compartment vessels were obtained (Figure 4.6d). These experiments provide proof-of-concept that various hollow structures could be interconnected, so long as their internal xylene domains could be linked via a new xylene droplet followed by C_{60} over-growth (Figure 4.6n). Such a phenomenon is unprecedented in soft template synthesis, as the fluid nature of soft templates has never been used for extending or assembling of hollow structures. The multi-nodal structures are stable under normal centrifugation and transfer processes, or under heat treatment at 80 °C for at least 24 h. They could be stored for months in the original preparative solution both for interconnected bowls and bottles (Figure 4.7c and d).

Figure 4.7. TEM images of (a) multimers of cucurbits (enriched to 6 times of the original concentration) and their SEM image (b); (c) interconnected nanobottles after 3 months storage. (d) SEM image of interconnected nanobowls after 3 months storage. Scale bars are 200 nm.

4.3.4. Multi-compartment nanocontainers

Due to the high stability of these multi-compartment hollow nanostructures, as a proof of concept, we tried to construct multi-compartment nanocontainers with different substances held and isolated in the separate pockets. Similar as the design principle in chapter 3.3.3, the different solvent environment in and outside the hollow structures provides an opportunity for selective loading of NPs. With the methodology in the previous chapter, we synthesized nanobowls incorporating hydrophobic Fe_3O_4 NPs first. The as-prepared containers were

applicable for subsequent node growth (Figure 4.8a), suggesting the merging of *m*-xylene droplets was not influenced by the incorporated NPs inside. Its elemental mapping profiles and HAADF images confirm the successful incorporation and the growth of a second node (Figure 4.8b-f).

Further experiments showed that when different NPs were mixed in the multiple round's addition of C₆₀ solution, they can be found in the separate compartments of the resulting cucurbits. For instance, Figure 4.8g shows that the Fe₃O₄ NPs are trapped in the bottom node, whereas the Ag NPs in the upper node are consistent with their sequence of addition. Elemental mapping of this multi-compartment container further proves the successful incorporation and isolation of the NPs in the separate compartments (Figure 4.8h-l). This selective positioning of the NPs could support the xylene template mechanism during the growth of cucurbits, as the hydrophobic NPs are supposed to move along with the merged droplets. Otherwise, NPs in the second-round addition would be left out of the cucurbits. The different incorporated NPs can be simultaneously released either by transferring the containers into fresh DMF (or solvents that have slightly higher solubility of C₆₀) followed by a 45 min vigorous sonication, or by re-dispersing the containers into a good solvent of C₆₀ (e.g., xylene).

The multi-compartment nanocontainer provides a model system for the selective incorporation and isolation of different substances within a hollow nano-system, which cannot be readily realized with existing structures. When different small molecules are loaded into the different cavity of the containers, their single opening would allow gradually and sequentially release of these molecules. Considering the excellent biocompatibility of C₆₀ and its derivatives,^{13,14} this feature may lead to new modes of long-time segmented drug delivery. Different drugs can be sequentially loaded into the container, and released at certain condition to save the troubles of multi-doses or injections.

Figure 4.8. (a) TEM image of a typical C_{60} nanocucurbit with Fe_3O_4 NPs in the first cavity and an empty second cavity, its HAADF image (c), and (b, d-f) its elemental mapping profiles of C, Fe, and O; (g) TEM image of multi-compartment nanocontainers with Fe_3O_4 NPs in the bottom node and Ag NPs in the upper, and its elemental mapping (h-l). Scale bars are 200 nm for TEM images.

4.4. Summary

In this chapter, on the basis of the solvent system of fullerene nanopottery (DMF, *m*-xylene, and IPA), we reported a methodology to realize the precise interconnection of hollow nanostructures with the help of water. More specifically, we developed the capability to build, expand, and interconnect hollow compartments with the manipulation of liquid templates. Our understanding of the growth mechanism allows rational design for the C_{60} hollow nanostructures. Through the studying of the mechanism, our knowledge of creating critical selectivity around the droplets as synthetic handles, and adding appropriate material at the appropriate time point is critical for elevating the synthetic freedom in a complex system (beyond simple and symmetrical shapes).

Generally, the liquid templates permit stepwise and versatile manipulation and hence, modular assembly of nodes and junctions leads to interconnected hollow systems. The material exchange between the *m*-xylene droplet and the external solution leaves a single opening that renders the critical regio-selectivity for subsequent modifications of the template, and thus hollow nanostructures. The liquid nature of the template allows continual structural modifications: gradual expansion of the xylene domain leads to a straight bottleneck, whereas direct addition leads to an extra spherical node. The processes can be repeated to give hollow structures with exact number of nodes, and bottleneck can be designed between any of the nodes. Merging the exposed xylene domains can connect bowls, bottles, or cucurbits together, forming multi-compartment vessels. Different hydrophobic NPs could be selectively retained in the cavities with their positions precisely located. Such stepwise expansion, addition, and connection could provide enormous synthetic freedom for designing complex hollow structures and interconnected systems. Considering the wide applications of hollow nanostructures in catalysis, energy storage, and medicinal,¹⁵⁻¹⁷ the methodology to realize accurate synthetic control and elegant structures has the potential to broaden their applications in a wide range of fields.

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Chapter 5: Assembly of fullerene hollow cavities with precise stoichiometry

Rational and precise assembly of nanostructures is the preliminary step towards the scalable design, preparation, and production of complex nanodevices, just as the coupling chemistry is to organic synthesis. However, to specifically assemble the dimers of solid NPs in solution phase still remains a great challenge, as the random aggregation cannot be completely limited via current regio-selective methods,¹ not to mention the precise assembly or connection of more complexed nanostructures. While in the previous chapters we had overcome the difficulty of interconnecting hollow nanostructures via a stepwise merging of liquid droplets template (fullerene nanopottery),² the degree of interconnection precisions is still imperfect without high-purity products. Now, we attempted to introduce steric hindrance, a popular and powerful regio-selective method in organic chemistry, to the nanoscale to interconnect fullerene nanobowls with precise stoichiometry. On this base, a mathematical model was constructed to simulate and explain the detail of the merging process and the steric effect, and to support the proposed mechanism.

5.1. Introduction

Nano-synthesis is similar to organic chemistry in that the advance of synthetic capability is the main goal of the field. Organic chemistry is essentially an art of precision molecular assembly, where steric hindrance and charge effects are the main tools of regio-selectivity.³ With these tools, the well-controlled molecular reactions create myriads of organic compounds such as medicine, polymer, and consumer chemicals that have significant impacts to human life.

The ultimate goal of nano-synthesis is to create sophisticated components and eventually functional nanodevices. As known from the macroscopic assembly of machines, a prerequisite would be the regioselective synthesis of nanostructures, that is, to break the high symmetry of NPs, and to extend or modify their structures at specific locations. However, it is unrealistic to use hands or tools to directly manipulate objects at the nanoscale. One must rely on the intrinsic properties to remotely control the growth or assembly processes,^{4,5} making this field similar to organic chemistry. Despite great efforts, regioselective methods are still rare and the level of synthetic control is still rudimentary. For example, charge repulsion among NPs could limit the stoichiometry of the assembled structures;^{6,7} and the ligand patches on NPs could be exploited for their selective assembly.^{8,9}

Dimer of NPs as the simplest and most fundamental assembled structure has been extensively studied as a model of nano-assembly.^{10,11} Despite many efforts, to control the movement of NPs and guide their assembly remain a great challenge. The traditional approach is to create asymmetric NPs, and to guide their assembly via external fields or ligand interactions, so that their asymmetric surface properties could be utilized for directional assembly.^{6,9,12} The purity of such synthesis is typically low, possibly due to the inhomogeneity of the synthesized NPs, the unclear boundary of the ligand patches, and the lack of docking precision during the assembly,^{13,14} making large-area views of high purity samples (> 70%) are only produced via purification methods.^{15,16} Hence, improving the regio-selectivity during assembly is in high demand.

Steric control as a powerful method in organic chemistry has hardly been explored at the nanoscale. The proceeding reports involve mostly the steric effects brought by bulky ligands on the NPs surface,^{17,18} but the size of ligands is often too small to influence the assembly. In the crossed assembly of nanorods reported by Liz-Marzán et al., both the bulging heads of the dumbbell-shaped rods and the bulky ligand patches on their surface play

significant roles in the directional assembly,¹⁹ and the synthesized nano-dumbbell dimers were not completely restricted within a single form (Figure 5.1). We believe that there should be greater potential in exploiting the steric effects to reduce the by-products, control conformations,²⁰ and create more sophisticated nanostructures.

Figure 5.1. (a) Schematic illustrating the steric effects driven assembly of nano-dumbbells into a cross-like arrangement. (b) Distribution of nano-dumbbells shapes at the different stages. (c) TEM image of crossed dimers of nano-dumbbells. Reprinted and modified from ref. 19 with permission. Copyright © 2012, American Chemical Society.

In chapter 4, we bring the capability of interconnecting hollow units to the nanoscale. Here, in this work, we report precise dimerization of hollow fullerene nanostructures, reaching 94% purity of dimers in one-step. The regio-selectivity is achieved via the control of the steric hindrance: by changing the relative size of the exposed liquid domain and the hollow hemisphere (nanobowl), the available area of the docking sites could be readily modulated (Figure 5.2b and c). The merging of the liquid domain is highly favorable and irreversible; the nanobowls have clear boundary; and their depth could be precisely controlled. These features lead to the high-purity assembly products. Tetramerization of the bowls gives 81% purity of tetramers. A mathematical model is constructed to describe the initial merging process, and to

support the proposed mechanism. We believe this new synthetic strategy and the precise structural control would open a new possibility of applying steric effects to achieve regio-selectivity in the field of nano-synthesis.

Figure 5.2. Schematics illustrating (a) the influence of steric hindrance and the corresponding assembly products; and (b) and (c) the steric allowed and hindered assembly of a third nanobowl, respectively. Scale bars are 200 nm.

5.2. Materials and methods

5.2.1. Materials

Pristine fullerene powders C₆₀ (98%), C₇₀ (99%), phenyl-C₆₁-butyric acid methyl ester (PCBM, 99%), and anhydrous DMF (99.8%) were purchased from Sigma-Aldrich. *M*-xylene (Analytical Reagent, A.R.), and isopropanol (IPA, A.R.) were purchased from Beijing Chemical Agent Ltd. Deionized water was used for all the reactions unless annotated. All the chemicals were used without further purification. The experiments could be reasonably reproduced without reference of other literatures.

5.2.2. Methods

Characterization: TEM images were obtained using a JEOL JEM-1400 electron microscopy at an accelerating voltage of 80-100 kV. SEM images were obtained with a field-emission scanning electron microscopy (FE-SEM, model JEOL 7600F) at an acceleration voltage of 5-8 kV. SAED, HR-TEM, HAADF-STEM images, and Energy-dispersive X-ray spectroscopy (EDX) spectrums were collected on a JEOL JEM-3010 transmission electron microscope at 300 KV. An Apple iPhone 8 is used to take the photographs of the reaction solution.

TEM sample preparation: 0.3 mL of the sample solution was taken and centrifuged at a speed of 8 g for 10 min (for bowls and reaction intermediates), or at a speed of 2 g for 15 min (for interconnected structures). Then, the supernatant was removed, and the precipitate was dropped on a copper grid that was pre-treated under oxygen plasma (with a Harrick Plasma cleaner) for 20 s to remove the dusts. The sample was dried in flow air for 1 h. Samples for HR-TEM were prepared on ultra-thin copper grids, and were completely dried in oven at 85 °C for 0.5 h.

SEM sample preparation: The above TEM samples were collected for SEM characterization. To improve the samples' conductivity, they were coated with a thin layer of gold with an Edwards Sputter Coater for 33 s.

DLS measurements: DLS data was obtained with a machine model ZEN 5600 from Malvern under a back-scattering mode (at a scanning angle of 173°). For DLS measurements, 1-1.2 mL of the sample solution was injected to a transparent four sides glass cuvette, and then capped to avoid vaporization of solvents.

UV-Vis characterizations: UV-Vis characterizations were carried on a Cary 100 UV-Visible spectrometer. The mixture of 0.2 mL sample solution and 0.8 mL DMF was taken, mixed, and used for all the measurements.

Preparation of fullerene nanobowls/spheres (opening sizes controlled via concentration):

Pristine fullerene powders were dissolved in *m*-xylene. 40 µL of the above solution was added to 1 mL DMF dropwise with vortex. Then, 400 µL of IPA was added to the mixture slowly with vortex. Finally, the mixture was sealed and incubated at room temperature. After 18 h, fullerene nanobowls with different opening sizes were obtained. For C₆₀, the concentration changed from 1.1 to 0.6 mg/mL; for C₇₀, the concentration changed from 2.8 to 1.6 mg/mL; for the nanobowls consisted by the mixture of fullerenes, the concentration can be chose from any of the following ranges without changing other steps: 0.9-0.6 mg/mL for C₆₀, 2.4-1.0 mg/mL for C₇₀, and 6.0-2.0 mg/mL for PCBM.

Synthesis of dimers/tetramers/multimers of the bowls: Fullerene powders were dissolved in *m*-xylene (concentration for the dimers: 5.5 mg/mL PCBM, 0.35 mg/mL C₆₀, and 0.7 mg/mL C₇₀; for the tetramers: 4.9 mg/mL PCBM, 0.25 mg/mL C₆₀, and 0.65 mg/mL C₇₀; for multimers (9-12 bowls): 4.5 mg/mL PCBM, 0.2 mg/mL C₆₀, and 0.6 mg/mL C₇₀; for multimers (16 bowls): 3.5 mg/mL PCBM, 0.2 mg/mL C₆₀, and 0.6 mg/mL C₇₀). 50 µL of the above solution was added to 1 mL DMF quickly with vortex, and 400 µL of IPA was added to the mixture slowly with vortex. The mixture was then sealed and incubated at room temperature. After 18-24 h, the respective structures could be obtained (the reaction time needs to be slightly increased with the decreasing of fullerene concentration).

Interconnection of individual hollow nanostructures: Individual hollow nanostructures were synthesized in water doped DMF according to the above steps. 1.2 mL of the sample solution was taken and enriched to certain times (via a 10 min centrifugation at 16g; then remove certain volume of the supernatant followed by the re-dispersion of precipitate). Then, 24 μL (or less) C_{60} solution in *m*-xylene (0.75 mg/mL) was quickly added to the mixture with vortex. The mixture was sealed and incubated for 16 h at room temperature to obtain the interconnected structures.

Construction of the mathematical model: The mathematical model that describes the initial merging process of the bowls and to explain the absence of trimers was established via MATLAB 2017 (student version). The approximate solution of the equations was obtained via finite difference method.

5.3. Results and discussions

5.3.1. Dimerization and tetramerization of fullerene nanobowls

In a typical synthesis, the mix solution of C_{60} , C_{70} , and PCBM in *m*-xylene is added to DMF and then IPA. With reduced solubility, the solution changes gradually from clear light orange to turbid (Figure 5.4e), indicating the slow nucleation of fullerenes. After 18 h, the products are isolated by centrifugation. Their TEM images show high-purity dimers (93.6% out of 233 particles surveyed, Figure 5.3g), where two nanobowls are interconnected through a shared hollow section, with a small opening in the middle section. The sample contains almost no trimers (0.1%) and 6.3% of monomers. DLS measurements show particles with average diameter around 400 nm, consistent with the TEM results. The UV-Vis spectrum of the product shows absorption peaks at ~ 330 and 480 nm, which can be attributed to C_{60} and PCBM. Comparing to the initial stage, the UV-Vis spectrum has decreased intensity after the reaction, likely due to the nucleation of fullerene from the solution. EDX mapping of the dimers shows

overlapped distribution of carbon and oxygen (Figure 5.3j-l). As the oxygen is observed only in the shell, it indicates the presence of PCBM in the shells.

Figure 5.3. (a) Schematics illustrating the dimerization process. TEM images of (b-f) typical formation intermediates of the interconnected nanobowls' dimer reacted for 5, 10, 13, 16, and 20 h, respectively; and (g) large area view of the dimers. (h) SEM image of the dimers. (i) HAADF image of a typical dimer, and its EDX

mapping results (j-l). (m) DLS measurements of particle size distribution of pure C₆₀ nanobowls (red) and the dimers (blue). (n) UV-Vis spectra of the dimers reacted for 1 h (blue) and 20 h (red). (o) Histograms of the dimers in (f). Scale bars are 200 nm.

In our previous work,² only pure C₆₀ was used to synthesize hollow structures, and an emulsion of DMF/IPA and *m*-xylene is employed for the synthesis. With the stepwise expanding and merging of *m*-xylene droplet template, C₆₀ hollow nanostructures could be interconnected into multi-compartment vessels. In contrast, here we use a mixture of fullerenes, so that the extent of interconnection could be readily controlled, giving high purity assembly products.

As this synthesis employs the same emulsion system as the previous works, we believe the dimers are also templated via *m*-xylene droplets. They have the shape of dimers because their templates are formed by the merging of two smaller droplets. Hence, the product structure would suggest the sequence of growth and assembly stages: if the merging happens before the shell growth, we would expect a completely merged droplet; if a complete shell forms first, merging would not occur and only isolated hollow cavities would be obtained. Therefore, the actual condition has to exist between the two extremes: only when the merging occurs half way during the shell growth, we would obtain partially merged products as shown in Figure 5.3f. The retaining of the half-shell at the two ends, and the growth of shells in the middle section are only consistent with the third scenario.

To investigate the growth process, intermediates of the dimers were trapped (Figure 5.3b-f and Figure 5.4a-d). At 6-8 h, monomers of the nanobowls were closely arranged in pairs with their openings pointing to each other. In the following reaction, the distance between the bowls slowly increased (from ~20 to 115 nm, 10-20 h); and the solid section between the two bowls gradually expanded with increasing thickness, leaving a small opening on it. Such an expansion cannot be explained with a solid template mechanism, as the solid template cannot expand between the bowls. In our previous works,² the *m*-xylene droplet template increased in

volume via the slow extraction of remaining droplets from the solution, leading to the gradual growth of the C₆₀ shell (see chapter 3.3.2.3 for details). Now, it is likely that the liquid template trapped between two bowls expands via a similar process (Figure 5.3a), making the fullerene shell gradually extend along the merged droplet (Figure 5.4g). At the same time, the existing shell increased in thickness due to the continuous deposition of oversaturated fullerenes. The absence of barrier in the hollow region and the curved edge of the hollow section further support the liquid template mechanism. The observations in intermediates show a clear trend of nanobowl self-assembly.

Figure 5.4. TEM images of (a-d) reaction intermediates of dimers reacted for 7, 10, 13, and 20 h, respectively. (e) Photographs of the nanobowl solution at the very beginning of the reaction and reacted for 20 h; (f) SEM image of a typical intermediate with paste-like substance at the middle. (g) Schematics illustrating the extension of fullerene shell along the merged droplets. Scale bars are 200 nm.

As the assembly is driven by the merging of xylene droplets, we speculate that a larger opening of the bowls would lead to a larger exposed area of the liquid, so that more nanobowls are expected to be assembled. In our previous work, the opening of a nanobowl is determined by the initial degree of C₆₀ oversaturation, and we control it by changing the addition rate of C₆₀ solution.² Now, we attempted to directly tune the degree of oversaturation and hence the

opening size by reducing the concentration of fullerene solution to reach a better controllability. When the concentration of each fullerene was reduced, (C_{60} from 0.35 to 0.25 mg/mL, C_{70} from 0.70 to 0.65 mg/mL, and PCBM from 5.5 to 4.9 mg/mL), tetramers of nanobowls were obtained as shown in Figure 5.5a and g. The samples came with a high purity of tetramers (81%), few dimers and trimers (12.3% and 5.2%, respectively), and barely any pentamers (0.8%). Similar as the dimers, the tetramers contain a hollow section connecting the bowls. The opening size of the bowls in tetramers significantly increased compare with that of the dimers (from ~85 to 120 nm), agreeing with our synthetic design. In the sample reacted for 24 h, the opening of the tetramers became clearly observable (Figure 5.5b). Similar as the dimers, UV-Vis spectra of the tetramers also showed decreased intensity after the reaction. DLS measurements showed particles with average diameter around 600 nm, suggesting the assembly indeed happened in solution phase.

Intermediates of the tetramers showed similar observations as the dimers. At the initial stage, monomers of the bowls were observed with some mud-like solid distributed at the center of three or four bowls (6 h, Figure 5.5f). From 12-24 h, the distance of four bowls increased with the growth of the hollow section. Hence, it is conceivable that the tetramerization of the bowls should be a merging driven self-assembly process, as well. It is likely that the paste-like solid is the drying pattern of the xylene-solvated fullerenes in the merged droplets (for the hypothesis on xylene-solvated fullerenes, see chapter 3.3.2.3 and 4.3.2). In contrast, if the solid comes from non-merged droplets, it should evenly distribute in the cavity of each bowl. We note that the cavity of the nanobowls in the intermediates usually have a larger diameter than that of the dimers/tetramers. It is possible that fewer C_{60} in the droplets could escape during drying with the reduced opening size in the middle section, which would make the shells thicker.

Figure 5.5. TEM images of (a) tetramers of nanobowls reacted for 18 h and their histogram (f); and (b) a typical tetramer reacted for 24 h with an obvious opening. (c) HAADF image of a typical tetramer, and its EDX mapping results (d, e). (g) SEM image of the tetrahedral shaped tetramers. (h) DLS measurements of particle size distribution of tetramers reacted for 0.5 hour (red) and the tetramers reacted for 24 h (blue). (i) UV-Vis spectra of nanobowls (blue) and tetramers (red). (j) Schematics illustrating the formation of spatial tetrahedral shaped tetramers. Scale bars are 200 nm.

We attempted to reduce the mutual steric hindrance among the bowls by further reducing their opening size, so that more nanobowls are expected to be interconnected. When the concentration of mix fullerene solution was further reduced, interconnected structures containing 9-12 nanobowls were obtained (Figure 5.6a), and the max number of interconnected nanobowls is around 16 (Figure 5.6c). It is worthy to mention that no trimers could be obtained

during the whole process. All of the multimers have a small opening in the middle section. In these multimers, the opening of the nanobowls increased in sequence (Figure 5.6f-i), agreeing well with our synthetic design. Similar as the dimers and tetramers, elemental mapping of carbon and oxygen indicates the existence of PCBM in multimers (Figure 5.6d and e). As PCBM has the highest solubility among the three fullerenes, it is possible that the multimers are made up of mix fullerene.

Figure 5.6. (a) TEM images of the assembly product of 9-12 bowls, and (b) their SEM images. (c) HAADF image of a typical assembly product of 16 nanobowls, and its EDX mapping results (d, e). (f-i) TEM images showing the opening changes in the nanobowls in the assembly products of 16, 12, 4, and 2 nanobowls, respectively. Scale bars are 200 nm for (a-e) and 100 nm for (f-i).

5.3.2. Mechanism study

5.3.2.1. Mathematical models describe the merging process

Obviously, the synthesis is carried without suitable ligands; and there should be no charged ions adsorbed on the surface of fullerene shells. Therefore, the steric repulsion caused by the opening of the nanobowls should be the only possible explanation for the high selectivity. Nanobowls with a small opening would cover its droplet template more completely, leaving a small exposed area for the merging. After the merging of droplets in two nanobowls (for dimers), there would be no enough exposed area for a third bowl (Figure 5.2b and c), and thus, regio-selectivity bring by steric repulsion like molecular reactions is produced, leading to a high assembly precision.

Interestingly, tetramers of nanobowls have tetrahedral shapes, and multimers with more bowls have near spherical shapes (Figure 5.6a and b). This is because the merging of droplets is a spatial process. Due to the limit of steric, a symmetrical, round shape would make each bowl occupies least space in the product, allowing more bowls to be assembled in a multimer. The merged droplets have a spherical shape due to the surface tension, leading to the resulting spherical arrangement of the bowls. This fact further demonstrates the interconnected structures were not assembled during drying. Otherwise, hemispherical or planar structures would be observed due to the restriction from the copper grid.

To provide a better theoretical support for the above mechanism, a mathematical model is set-up to describe the initial merging process of the bowls. The shell thickness of the nanobowls can be ignored at the initial growth stage, and each bowl is viewed as a spherical crown (depth h , Figure 5.7b). It closely grows along the spherical xylene droplets (radius r). After the merging of n droplets/bowls, a big spherical droplet (radius R) with the bowls closely covering its surface would form at the middle (Figure 5.7a). Hence, the relationship of R and h

can be described by function (1), and A is the volume of liquid reserved by each bowl after merging (Figure 5.7b):

$$\frac{4}{3\pi R^3} = \frac{4}{3\pi r^3} - nA \quad (1)$$

$$\text{Where, } A = \pi h^2 \left(r - \frac{h}{3} \right) - \pi H^2 \left(R - \frac{H}{3} \right)$$

$$\text{and, } H = R - \sqrt{r^2 + h^2 - 2rh}$$

Figure 5.7. (a) Schematics illustrating the merging of n bowls, and a typical bowl with their depth $h > r$ (b) and $h < r$ (c). (d) A geometrical model for the merging of a fourth bowl onto a trimer of the bowls.

This model can be used to explain the absence of trimers. When there are three bowls assembled into trimers ($n=3$, geometrical center at O_1-O_3), the relationship of R and h can be described with function (2), which is obtained from the cross section of the trimers. When the

radius of the droplets (r) that template the bowls is approximated to 49 nm according to the experimental value, the depth of the bowls h_0 could be solved from function (1) and (2) with a finite difference method, in which $h_0=69.54$ nm, and $R=51.37$ nm. At this condition, the three bowls could most closely cover the merged droplet, leaving a smallest exposed area for the subsequent merging. Figure 5.7d is the geometrical model of the trimers plotted according to the above parameters, in which each bowl is an approximated 7/10 spherical crown. We note that trimers cannot form when $h < h_0$ due to the mutual steric repulsion among the bowls; and the bowls would float on the merged droplet when $h > h_0$, leading to a greater chance for the subsequent merging. A space rectangular coordinate with x , y , and z -axis is set-up as shown in Figure 5.7d, with the sphere center of merged droplet (O) as the original point. The respective coordinates of O_1 - O_3 can be obtained as following:

$$3R^2 = 4(2rh - h^2) \quad (2)$$

$$O_1 (-\sqrt{3}/2D, 1/2D, 0); O_2 (\sqrt{3}/2D, 1/2D, 0); O_3 (0, -D, 0), \text{ where } D=|OO_1|$$

When there is a fourth bowl approaching the trimers along the sterically allowed direction (z -axis), the coordinate of its geometrical center is $O_4 (0, 0, Z)$. It is easy to get $Z=Z_0=\sqrt{4r^2 - D^2}$ when this bowl's approaching is completely hindered by the other three. In the experimental condition, when $r=49$ nm, $Z_0= 86.42$ nm ($Z_0 < r+R$), indicating the outer liquid surface of the trimer and the fourth bowl could overlap. This result reveals that once a trimer could form in solution, even though the three bowls could cover the merged droplet as tightly as possible, a fourth bowl/droplet would still be able to merge with it to form a tetramer. Moreover, it is noteworthy that there should be another condition in this model: when the opening of the bowls is large enough, it is possible that the depth of the bowls is smaller than the radius of its droplet template ($h < r$, Figure 5.7c), whereas now the three bowls cannot closely cover the merged droplet, leaving a larger exposed liquid surface for the subsequent merging. We note that for any value of r , the corresponding value of h_0 , R , D , and Z_0 will be

linearly changed, indicating this calculated result will not be influenced by the experimental errors in measuring r .

5.3.2.2. Study the merging details

The presence of steric supports that the nanobowls formed prior to the formation of multimers. Otherwise, the steric hindrance among the bowls cannot be influenced via the completeness of the bowls. To confirm the correlation between concentration and the completeness of the bowls, we attempted to study this via simplified mock reactions. Fullerene solution with different concentration was added to DMF with vortex, and then IPA. When C_{70} solution is used, C_{70} nanobowls were obtained after 22 h (Figure 5.9c), with uniform size, shapes, and openings. When its concentration was increased from 1.6 to 2.0 mg/mL, similar as the trend in multimer formation, the half-shell changed towards complete sphere, with the size of their opening decreased from ~60 to 115 nm, respectively (Figure 5.9b). When the concentration was further increased to 2.8 mg/mL, enclosed hollow spheres were obtained (Figure 5.9a). Similarly, the opening of C_{60} nanobowls could also be adjusted with this strategy (Figure 5.8).

The results of mock reaction agree well with the trend in nanobowl self-assembly. The correlation between the opening size and fullerene concentration could be explained with a mechanism extends from our previous work. Previously, the completeness of nanobowls critically depends on the initially formed thin half-shells, which completeness is determined by the initial degree of fullerene oversaturation. This factor was controlled via the addition rate of fullerene solution in the previous work. Now, the concentration of fullerene solution could directly determine this factor: A higher concentration leads to more fullerene quickly precipitate along the droplets, forming a relative complete thin shell with small opening, and *vice versa*. Thus, when fullerene solution with a lower concentration is used, or when the

fullerene material has a high solubility (e.g., PCBM), a wider opening is observed due to the initial large opening.

Figure 5.8. TEM images of (a-d) C_{60} nanobowls with different opening size, and their corresponding SEM image. Scale bars are 200 nm.

Hence, comparing with the synthesis with pure C_{60} , it is possible that having three kinds of fullerenes with increased solubility ($PCBM > C_{70} > C_{60}$,^{21,22} Table 2.1) could maintain a high oversaturation of fullerenes, and thus promoting the growth of the middle hollow section. To test this hypothesis, we attempted to do the synthesis with the mix solution of only two fullerenes. For instance, when the mix solution of C_{60} and PCBM (0.5 and 5 mg/mL, respectively), or C_{70} and PCBM (1.2 and 5 mg/mL, respectively), or C_{60} and C_{70} (0.5 and 1.2 mg/mL, respectively) were used, only nanobowls with their openings pointing to each other were obtained (Figure 5.8d-g), agreeing with our synthetic design. EDX analysis of the bowls that made up of C_{60} and PCBM further confirmed the existence of both materials (Figure 5.9m-o). HR-TEM and SAED results show that the shell in these nanobowls is amorphous (Figure 5.9j-l). When more concentrated mix solution was used, for example, when the concentration of C_{60} and PCBM was increased to 0.7 and 6.5 mg/mL, the shell of nanobowls could slightly

extend with a prolonged incubation to 38 h, giving bottle-like structures (Figure 5.8h). The formation of bottleneck indicates the critical role of high fullerene oversaturation in facilitating the shell extension.

Figure 5.9. TEM images of (a-c) C_{70} nanobowls with different opening size. (d) SEM image of nanobowls with the mixture of C_{60} and PCBM as the shell materials, and their TEM image (e). (f, g) TEM image of nanobowls with the mixture of C_{60} and C_{70} , C_{70} and PCBM as the shell materials, respectively. (h) Bottle-like structures

obtained by using the concentrated mix solution of C₆₀ and PCBM. (i) Nanobowls obtained by using the mix solution of less PCBM and more C₆₀ and C₇₀; inset: a typical nanobowl in this sample. (j, k) HR-TEM and SAED image of a nanobowl in (e). (l) HAADF image of a typical nanobowl in (e), and its EDX mapping results (m-o). Scale bars are 200 nm for TEM and SEM images, and 100 nm for HAADF and EDX mapping images.

In the synthesis of dimers, we found that DLS measurements of the samples reacted for 0.5 h showed particles with diameter around 400 nm (Figure 5.5h), which is significantly larger than that of the individual bowls. It indicates that the droplets merging happens at the very beginning of the reaction. To study the details of the merging process, we attempted to promote the merging in dimer formation by double the volume of mix fullerene solution. After 10 minutes, intermediates of this modified synthesis were taken for SEM and TEM characterizations. The sample solution was directly dropped onto the copper grid and quickly dried in flow air to avoid the merging induced by centrifugation and drying.

Merged spherical particles stayed in pairs were observed as shown in Figure 5.10a and b, which cannot be produced via random aggregation. Thus, they are likely to be the drying pattern of the merged droplets/nanobowls. The particles were then observed in-detail at a high magnification, in which a Janus thin shell can be distinguished (inset of Figure 5.10b). After reacted for another 1 h, the intermediates showed obvious bowl-shaped particles with paste-like solid remaining in the cavity (Figure 5.10c). The diameter of these particles was slightly smaller than the diameter of individual nanobowls in dimers (~185 nm vs. 225 nm), indicating that they are indeed the drying pattern of the merged droplets. The formation of dimers was not affected by changing the reaction condition, and high-yield dimers were obtained at 18 h (Figure 5.10d). In this sample, we speculate that the increasing volume of fullerene pastes in the hollow cavities is caused by the increased fullerene concentration in the whole system, which would lead to a higher fullerene oversaturation, and thus inhibit the outward ripening of solvated fullerene in the droplets. The retained fullerene pastes also leads to the increased shell thickness.

Figure 5.10. (a) SEM image of the dimer intermediates reacted for 0.5 h (synthesized by double the volume of mix fullerene solution), and its corresponding TEM image (b); inset: a typical drying product in this sample. (c) SEM image of the dimers reacted for 1.5 h. (d) TEM image of the dimers in (a) that reacted for 18 h. Scale bars are 200 nm.

5.3.2.3. Proposed mechanism

On these bases, we believe the formation of individual nanobowls should be similar as our previous works. When fullerene solution is added, thin fullerene half-shells quickly form along the *m*-xylene droplets due to the reducing of solubility. The addition of IPA further

reduces the solubility, allowing the extension of the existing shell. Then, the half-shells (bowls) are assembled through the rapid merging of exposed droplets. The completeness or the opening size of the bowls could determine the exposed area of the droplets, and hence the steric hindrance. A larger opening size would lead to a larger exposed area, allowing more nanobowls to be assembled. Moreover, a longer merging time is required to assemble more nanobowls (>4), but the quick shell extension at the initial growth stage would prevent nanobowls from merging, which explains the uneven numbers of the bowls in multimer formation. After the merging, there are two nucleation sites for the oversaturated fullerene: one selectively along the opening of the bowls extending the shell, and the other non-selectively at their outer surface to increase the thickness. The former selective growth is typically slow, as its collection area is much smaller than the outer surface, which requires a high fullerene oversaturation to make it happen. The continuous ripening of solvated fullerene keeps the opening open. Due to the high fullerene concentration (comparing with that of pure C₆₀), only a small opening can be left for the multimers.

5.3.3. Shape effects in pure C₆₀ structures

Besides the steric effects brought by the shape of mixed fullerene nanobowls, the shape of other hollow units could influence the connection results in nanopottery, as well. For instance, in the interconnection of C₆₀ nanobowls in water-doped DMF, the interconnection could only be observed at an enriched concentration of at least two times (Figure 5.11a-c), which is different from that in nanobottles or cucurbits, and no interconnection can be obtained without enrichment. As the synthesis was carried in the same solvent system, we believe the overall interconnection mechanism of C₆₀ nanobowls is also a merging-driven assembly, exactly same as the interconnection of other hollow units. Thus, the only difference between these conditions is the shape of hollow units.

Figure 5.11. TEM image of (a) C₆₀ nanobowls synthesized in water-doped DMF, before interconnection; (b) successful interconnection of C₆₀ nanobowls after enrichment (2 times); and (c) failed interconnection products without enrichment. (d) Schematic illustrating the different volume change behaviors between nanobowls and bottles. Scale bars are 200 nm.

Comparing with the bare droplets on nanobowls and bottles, it is likely that the merging of droplets on nanobowls could happen, but the thick shell of the nanobowls did something that limits the merging process. In the mechanism discussed in chapter 4.3.3, we believe the merging is limited by the formation of C₆₀ paste within the droplets. Due to the droplets are surrounded by thick shells, it may need some time to exceed the rim of the opening to start the merging (Figure 5.11d). Comparing with the direct formation of bare, accessible droplets on nanobottles, those on nanobowls do not have sufficient time to merge due to the repaid formation of the C₆₀ paste. Increasing the bowls' concentration would reduce the distance

among the bowls and increase their chance of merging within this short time. Similar shape effects bring by the thick shell of nanobowls also agrees with the results in Figure 4.3i and q, in which no cucurbits (only bowls) could be obtained when the volume of C₆₀ solution in second addition was fewer than 5 μ L.

5.4. Summary

Assembly of hollow nanostructures involves unique challenges in that direct aggregation would lead to side-by-side arrangement of their shells, which eventually become the barrier between the compartments.²⁰ To do away with the barriers, interconnection would require site-selective docking of the openings and welding of the resulting subunits, making the process even more challenging. Without a breakthrough in this fundamental step, building an interconnected hollow system would be impossible. Here, we demonstrate that the merging of liquid droplets can be used as the driving force for the precise docking and interconnection of fullerene hollow units, and the geometrical shapes of the nanobowls is adopted to provide the critical regio-selectivity. This methodology greatly expands the synthetic freedom for hollow structures, moving one step close to the synthesis of complex interconnected hollow systems. Importantly, it provides theoretical support for the future using of steric hindrance in creating critical regio-selectivity in nano-synthesis.

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Chapter 6: Summary and outlook

6.1. Summary

In summary, my research has been focusing on the synthesis of fullerene hollow nanostructures via a stepwise liquid templating strategy: nanopottery. The method allows continuous modification of fullerene hollow structures: With the gradual expansion of the liquid domain, hollow nodes and junctions can be sequentially added to the existing hollow structures; With the merging of droplet templates, hollow units can be readily assembled into hollow systems; Importantly, steric hindrance can be generated by controlling the shape of nanobowls and hence the exposed area of the liquid droplets, which is able to create critical regio-selectivity for the assembly.

In chapter 2, a three-solvents, two-phases system that is made up of IPA (or other alcohol), xylene (or trimethylbenzene), and DMF is constructed for controllable precipitation of fullerene materials. Due to the fast nucleation rate of bare fullerene materials caused by their sparingly solubility in most non-aromatic solvents, the controllable synthesis of fullerene nanostructures in a solution phase remains a great challenge. We showed that the rapid nucleation of fullerenes (C_{60} and C_{70}) can be effectively controlled with the help of DMF, a solvent that has a relatively low (but not too low) solubility of fullerenes. As a model system, metal@fullerene core-shell NPs with tunable core materials, shell thickness and shapes were synthesized. Unique properties were then found for these NPs: Large red-shift of UV-Vis absorption is observed for Au@ C_{60} core-shell NPs.

In the following chapter 3 and 4, we apply this solvent system to the designing of hollow fullerene nanostructures (nanopottery). The buffer effect of DMF allows gradual precipitation and growth of fullerene hollow structures. The *m*-xylene droplets serve as extendable soft template that allows continual extension of fullerene shells: gradual expansion of the droplets

leads to a straight bottleneck, while the fast expansion leads to an extra spherical node (cucurbits); merging the exposed liquid droplets could assemble the hollow units (e.g., bowls, bottles, and cucurbits), forming interconnected hollow systems. These processes can be repeated as long as the exposed liquid domain is not completely sealed. Such stepwise expansion, growth, and connection are the fundamental operations of pottery, which could greatly elevate the synthetic freedom for designing hollow nanostructures. As proof-of-concept applications, we demonstrate that the multi-compartment structures can be used as the vessels for selective incorporation of hydrophobic metal NPs within a hollow system. Most importantly, with this strategy, we demonstrate that the nano-sized droplets can be readily manipulated, suggesting the fluid nature of soft templates can be adopted for hollow structure synthesis in the future works.

In chapter 5, we provide critical regio-selectivity for this system, to realize precise structural control during the assembly process. Through the accurate control over the opening size or the completeness of the bowls, the exposed area of the droplet template can be tuned to govern the extent of nanobowl assembly: a larger opening would lead to a larger exposed area, which would allow more nanobowls to be assembled together and *vice versa*, so that steric hindrance like that of in organic chemistry was created among the bowls. Such steric hindrance exists not only in mix fullerenes, but also can be observed in pure fullerene hollow structures (e.g., C₆₀ bowls and cucurbits), suggesting it may have great potential in generality.

In short, our strategy of nanopottery not only brings the capability of interconnecting hollow structures to nanoscale, but also opens a window for the soft template synthesis of hollow nanostructures. In nanoscience, the capabilities of creating cubes, rods, hollow structures, etc., at the time of their initial discovery, have inspired lots of interests in the community, and many discoveries followed since then. In our works, C₆₀, C₇₀, and PCBM is the first model system for molecular nanostructures synthesis where the new synthetic control

is established. Current results indicate that the mechanism of using liquid droplets for continual extension of hollow compartments (in the fabrication of cucurbits and bottles) and for joining bowls, bottles, and cucurbits appears to be general, which could lead to subsequent works in diverse directions.

6.2. Outlook

Using the nanopottery as a main platform, follow-up works can be started from two aspects: generality/synthetic study and application exploration. Typically, synthetic works focus on extending this strategy to a wider class of materials, such as aggregation-induced emission (AIE) crystals and inorganic materials; and application study focuses on exploring the applications or property enhancements brought by the hollow morphology of these materials, for example, in nanodevices, energy storage, and drug delivery.

6.2.1. Generality

Due to the large specific surface area of hollow nanostructures, they are extensively used in energy storage, catalysis, nanoreactors, and drug delivery.¹ Despite the great progresses in applications, the fundamental synthetic capability remains at a primitive level: Most hollow structures are hollow nanospheres,² and to increase their structural complexity is extremely difficult. With the methodology of nanopottery, various hollow structures of fullerene or fullerene derivatives could be readily built, assembled, and interconnected. This highly-controllable methodology brings huge synthetic freedom for the field.

According to current data and results, there are possibilities to extend our synthetic strategy to a wider class of materials for the purpose of exploring new or enhanced properties. Some unpublished results from our group indicate that the design principle of this methodology appears to be general. In addition to C₆₀, C₇₀, and PCBM, the method can be extended to

inorganic materials: hollow silica spheres, bottles, cucurbits, dumbbells, and iron oxide nanobowls and bottles were generated via a similar stepwise liquid templating strategy (Figure 6.1). Although some minor adjustments need to be made for different materials, this primary successful in expanding our methodology to inorganic materials could demonstrate its great potential. Future works can be started from either inorganic materials such as metallic and non-metallic oxides, and organic molecular nanocrystals that has yet to be synthesized in a hollow form, such as AIE and polycyclic aromatic hydrocarbon like perylene and pyrene.

Figure 6.1. TEM images of (a-d) silica hollow spheres, bottles, dumbbells, and long-neck cucurbits, respectively; and (e, f) Fe_3O_4 nanobowls and bottles, respectively.

6.2.2. Applications

Fullerene and its derivatives have found applications in lithium battery, organic solar cell, photoconductive device, and photocatalysis, etc.^{3,4} Among them, due to the strong ability of electron transfer of fullerenes, pioneer exploration on their lithium storage property had

reported impressive results: a charge-discharge capacity of 1373 mAh/g and 773 mAh/g was achieved (Figure 6.2a and b).⁵ Such a capacity is more than double the theoretical capacity of commercial graphite (372 mAh/g), and even higher than the theoretical capacity of graphene (744 mAh/g). However, all of the traditional fullerene materials are micron-sized solid structures with limited surface area (Table 1).^{5,6} For instance, only commercial fullerene powders (size from 1 to several microns) were used in the above lithium battery studies. In comparison, with our synthetic strategy, hollow fullerene structures (e.g., bowls and bottles) with diameter of 100-200 nm could be generated, which could greatly lift their specific surface area. This is not only likely to bring their lithium storage ability to a higher level, but also helps in exploring the property enhancement that require high surface area, for example, in organic solar cell and photocatalysis.⁷

Figure 6.2. (a) Cycling discharge-charge performance of C₆₀ and different C₆₀ derivatives for lithium batteries, and coulombic efficiency of carboxyl C₆₀ at 0.1 C; (b) cycling stability of C₆₀ and different C₆₀ derivatives for lithium batteries at a rate of 1 C. Reprinted and modified from ref. 5 with permission. Copyright © 2017, Elsevier.

In terms of the applications in lithium battery, the future study can be divided into three parts: Scale-up the reaction, device set-up, and capacity test. Starting with the above discussed lithium battery system,⁵ the commercial fullerene powders could be directly replaced to our hollow materials. Hence, the first step is scale-up the synthesis for a micro-battery filling. As

the hollow structures could be synthesized with a high yield, and the synthesis contains only one step, it provides us the possibility to direct scale-up the reaction. Currently, a 50 times' scale-up has been realized, taking an important step for the study. Then, a coin cell device can be established according to literature methods.⁵ Cyclic voltammetry (CV), capacity test, cycling discharge-charge performance, and stability test can be used to examine the battery performance. Upon successful, mechanism leads to the capacity improvements can be studied as a next step.

Alternatively, there are a number of applications/properties closely associate with the materials' specific surface area.^{8,9} Among them, fullerenes have excellent performance in organic solar cell and photocatalysis.⁴ Property improvements in these areas can be studied as a back-up plan.

Table 6.1. Surface areas of C₆₀ and C₆₀ derivatives obtained by BET

Sample	Surface Area (m ² /g)
C ₆₀	1.69 ± 0.14
Carboxyl C ₆₀	3.58 ± 0.25
Ester C ₆₀	23.00 ± 3.76
Piperazine C ₆₀	53.97 ± 0.30

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Appendix: Publication list

1. **Han, F.**; Wang, R.; Feng, Y.; Wang, S.; Liu, L.; Li, X.; Han, Y.; Chen, H. On demand synthesis of hollow fullerene nanostructures, *Nat. Commun.* **2019**, 10, 1548.
2. **F. Han**, Y. Feng, H. Liu, R. Wang, S. Wang, W. Xu, B. Chen, H. Zhang, and H. Chen "Dimerization and tetramerization of fullerene hollow cavities." *in submission*, **2020**.
3. Wang, X.; Liu, S.; Cao, S.; **Han, F.**; Wang, H.; Chen, H. Stacked bowls by tandem self-assembly, *Macromolecule* **2019**, 52, 6698-6703.
4. S. Wang, Z. Lai, **F. Han**, D. Su, R. Wang, H. Zhang, H. Wang, and H. Chen "Solvent exchange as a synthetic handle for controlling molecular crystals." *Carbon* **2020**, 160, 188-195.
5. **Han, F.**; Chen, H. Fullerene nanopottery: Design and assemble hollow structures, *ChinaNano 2019*, China Beijing, Abstracts (RSC Best poster award).
6. **Han, F.**; Chen, H. Fullerene nanopottery: Design and assemble hollow structures, *14th Sino-US Forum on Nanoscale Science and Technology 2019*, China Changsha, Abstracts (golden award).
7. **Han, F.**; Chen, H. Fullerene nanopottery: Design, shaping, and interconnecting hollow nanostructures, *MRS Fall Meeting 2018*, USA Boston, Abstracts.
8. **Han, F.**; Chen, H. Fullerene nanopottery: Design and assembly of hollow nanostructures, *SICC10 2018*, Singapore, Abstracts.
9. J. Jia, G. Liu, W. Xu, X. Tian, S. Li, **F. Han**, Y. Feng, X. Dong, and H. Chen " Fine-tuning the homometallic interface of Au-on-Au nanorods and their photothermal therapy in NIR-II window." *Submitted to Angew. Chem. Int. Ed.*
10. M. Yan, B. Zhong, **F. Han**, H. Wang, and H. Chen "A general and controllable strategy for synthesizing organic nanocrystals." *Submitted to J. Mater. Chem. A.*