Ostwald Ripening: A Synthetic Approach for Hollow Nanomaterials

Hua Chun Zeng*

Department of Chemical and Biomolecular Engineering, Faculty of Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Abstract: Fabrication of nanomaterials with hollow interiors is an important research area in nanoresearch, owing to their potential applications in photonic devices, drug delivery, material encapsulation, ionic intercalation, surface functionalization, nanocatalysts, membrane nano reactors, and many other technologies. The common preparative methods for this new class of materials can be broadly divided into hard and soft template-assisted syntheses. In recent years, furthermore, the interest in template-free techniques for these materials has also increased, as the new processes involved in these techniques are relatively simple and less demanding, compared to the template-assisted processes. In this short review, we will introduce the application of a well-known physical phenomenon of crystal growth – Ostwald ripening – in the fabrication of hollow nanomaterials. It has been demonstrated that formation of the interior spaces of nanostructures depends on the aggregative states of the primary crystallites during the synthesis. With this new development, many inorganic nanomaterials with interior spaces can now be fabricated in solution media together with the materials synthesis. Different types of Ostwald ripening observed in this synthetic approach have been reviewed. In particular, various geometric structures and configurations prepared with these methods have been discussed. The prepared hollow materials also allow further compositional and structural modifications under the similar process conditions. Future directions in this research area are also discussed.

INTRODUCTION

In recent years, fabrication of nanomaterials with hollow interiors has received increasing attention in nanoscience and nanotechnology owing to their potential applications in photonic devices, drug delivery, material encapsulation, ionic intercalation, surface functionalization, nanocatalysts, and membrane nanoreactors, etc [1-7]. In response to the technological requirements, there have been numerous methods in place [1-17]. These methods can be broadly divided into two types: hard template and soft template approaches, where solid materials such as anodic alumina membranes or mesoporous silicas and soft templating materials such as ionic or non-ionic surfactants, polymers, or organic ligands have been utilized as structural guiding matters or reagents [7-17]. In addition to these two common approaches, template-free methods have also attracted great interests because of their process simplicity and methodological flexibility [18-24]. For example, many chemophysical processes have been found to be efficient in creating interior spaces for nanomaterials without assistance of the templates [18-24]. Among them, the approach through Ostwald ripening is a recent advancement which shows great flexibility to generate different types of hollow crystallite aggregates [21-24].

Ostwald ripening is a physical phenomenon that has been well known for more than a century [21, 22]. According to the IUPAC's terminology (IUPAC Compendium of Chemical Terminology, 2nd edition, 1977), this process refers to “the growth of larger crystals from those of smaller size which have a higher solubility than the larger ones” [25, 26]. For colloidal particles formed in solution media, there are many chemical equilibriums existing between the solid–liquid interfaces under each experimental setting. Because of non-uniformity of crystallites, concentrations of solutes (or growth nutrients) across the bulk solution vary. The homogenization of these concentration gradients will lead to complete dissolution of smaller crystallites as a result of the growth of the large crystallites [22]. As this process involves matter relocation, one may use it as a new means for generation of interior space for the crystallite aggregates. In this connection, it is conceivable that the cavity will be generated in a location where crystallites are smaller and/or less compact when the Ostwald ripening proceeds [22]. Likewise, more complex interior spaces can also be attained if the size distribution and aggregative patterns of as-formed primary crystallites are tiered. In most cases, however, large crystallites can be considered to be essentially immobile while the smaller ones are undergoing mass relocation through a solid–solution–solid process [21-24]. In this short review article, we will use some recent investigations in this area to introduce basic concepts and methodologies of this new synthetic approach for creating hollow interiors of nanomaterials.

OSTWALD RIPENING AND HOLLOW STRUCTURES

Symmetric Hollowing. The application of Ostwald ripening mechanism in fabrication of hollow nanostructures was proposed for the first time in a recent synthesis of anatase phase TiO2 where a TiF4 solution (1.33–2.67 mM) was used as a titanium source and hydrolysis of this compound in aqueous solution led to the formation of spherical anatase crystallite aggregates [21]. According to the Scheme (a) of Figure 1, it is believed that the crystallites located in the central part of the spherical aggregates are smaller or less dense compared to those in the outer parts, and thus they will be dissolved and re-deposited on the outer parts, resulting in formation of hollow spheres [21]. Figure 2a shows a transmission electron microscopy (TEM) image of TiO2 nanospheres synthesized with that method. It has been found that the shell structure such as thickness and texture can be further tailored by varying the process time and temperature. In general, longer reactions and higher temperatures favour the evacuation of the central crystallites and produce thinner shell structures. Furthermore, it has also been revealed that some inorganic or organic additives can also help the ripening processes during which these chemical entities act as ion carriers in the observed mass transport. On the basis of the crystal textures of the shell structure, it is found that the central crystallites dissolve in a direction perpendicular to the shell surface, which corresponds to a shortest distance between interior and exterior spaces. As a result, the final crystallites in the hollow spheres show an elongated shape (i.e., nanorod-like structure), in addition to the larger crystal size observed. Due to the dynamic processes of the Ostwald ripening, there are plenty of channels available in the shell structure which can remain unblocked for mass transport as long as the ripening proceeds [21].

The unique shell structures promises potential applications of this type of nanospheres. For example, they can be treated as inorganic nanoreactors or nanocontainers. On the other hand, the hollow structures of this type can be used as a primary matrix for incorporating a second or even a third phase of materials. In principle,
A desired solid phase or a surface phase can be introduced through the channels of the shell to the central space or directly deposited on the external shell surfaces [21]. Using this route of synthesis, nanocomposites or nanohybrids can be fabricated, which will be addressed shortly in the modifications of these hollow materials.

**Core-Shell and Multi-Shelled Structures.** Similar to the symmetric Ostwald ripening for central space formation, complex core–shell structures (Scheme (b), Fig. 1) and multi-shelled structures (Scheme (c), Fig. 1) can also be obtained. However, the formation of these more complex spherical structures depends on an oscillative aggregation of nanocrystallites along the radial direction. Shown in Figure 2b, it had been found recently in the synthesis of ZnS core–shell structure that surface crystallites act as nucleation sites for the creation of the space between the core and shell. The ZnS was synthesized in an aqueous solution of zinc nitrate (Zn(NO₃)₂·6H₂O) and thiourea under hydrothermal conditions (at 180°C for different times) [22]. During the solid evacuation, crystallites immediately below the surface region are transported to these surface sites. Since the shells and cores have the same chemical constituents, the resultant structures are called “homogeneous core–shell”. If the sizes of primary crystallites in the cores are not exactly the same, hollowing of core can still take place, which will thus give even more complex space patterns. This hollowing process had also been demonstrated in the formation of multi-shelled ZnS very recently using a similar approach [22].

**Asymmetric Hollowing.** The Ostwald ripening processes discussed above all proceed in a symmetric manner (Fig. 1), because all the crystallite size (and/or density) variations in the respective aggregates are concentric. It is understandable that the spaces created in Ostwald ripening process might not be in the center if the primary crystallites are packed in an asymmetric manner in the starting aggregates. In such cases, the Ostwald ripening will take place predominantly in certain sides of an aggregate, and the process associated can thus be termed as “asymmetric Ostwald ripening”. The observation of this hollowing process had been recently made in a solution synthesis of spinel oxide of cobalt (Co₃O₄) core–shell structures [22]. In that work, a solution prepared from cobalt nitrate (Co(NO₃)₂·6H₂O), ethanol, ammonia (30 wt% in water), and sodium hydroxide (NaOH) was hydrothermally heated at 100°C for varied times (12–24 h) [22]. As displayed in Fig. 3, the cores of Co₃O₄ are located towards one side while the overall structures still maintain spherical. The spaces generated in this process must correspond to the regions where primary crystallites were either small or less dense, considering the nature of Ostwald ripening. On the basis of the above examples and discussion, it is now understood that the primary aggregative state of crystallites from the synthesis plays an important role in determining the shape and location of the interior spaces of final products, although other synthetic parameters may also contribute to or alter the hollowing processes.

**Coupling with Chemical Reactions.** In the above cases, the Ostwald ripening processes proceed upon an existing solid phase, and chemical compositions of crystallite aggregates are not changed.
before and after the hollowing. In fact, chemical conversion of a solid phase to the other can also be coupled into the Ostwald ripening. Recently, this process had been elucidated with the fabrication of Cu$_2$O hollow nanospheres, whose product morphology is shown in Fig. 4 [23]. In that synthesis, discrete nanocrystallites in CuO phase were formed firstly from a copper nitrate solution (Cu(NO$_3$)$_2$·3H$_2$O in N,N-dimethylformamide solvent) at 150–180°C under hydrothermal conditions [23]. Subsequently, the nanocrystallites self-aggregate into spherical structures. Because of a small degree of hydrolysis of Cu$_2$O nanospheres (TEM image) formed from a reductive reaction. Nevertheless, the resultant product is Cu nanocubes instead of normally known spherical aggregates, it has been found that the CuO nanocrystallites were firstly reduced to Cu$_2$O which then self-attached each other according to their crystallographic directions (i.e., oriented attachment), resulting in faceted porous CuO nanocubes. The solid evacuation of these nanocubes continued, and a hollow interior space was formed because of an Ostwald ripening process. The Cu$_2$O nanocubes produced in this way are shown in Fig. 5 [24]. The formation of cubic aggregates of Cu$_2$O is attributed to the presence of more water in the synthesis. In other words, water stabilizes the [100], [010], and [001] crystal planes of the Cu$_2$O nanocrystallites which allows an aggregation through oriented attachment. Replacing water with ethanol, similar processes and products were observed. Therefore, it is apparent that high temperature and polarity of solvent used in synthesis are important parameters for the formation of single-crystalline Cu$_2$O nanocubes. Similar to those observed in Cu$_2$O nanospheres, their further reduction to metallic Cu$^0$ is also possible with a prolonged reaction. Nevertheless, the resultant product is Cu nanocubes instead of Cu nanospheres [23].

**Polyhedral Hollow Structures.** Sphere possesses a highest degree of symmetry. For this reason, the aforementioned crystallites all have a spherical morphology in their random aggregations in order to reduce their surface-to-volume ratios and thus to lower their system energies. Nevertheless, no all small crystallites are aggregated into spherical structures, because of other crystal growth processes. For example, oriented attachment refers to a special kind of crystal growth in which small crystallites attach each other through their suitable crystal planes or facets along the same crystallographic directions [27-31]. In this sense, the final aggregates can be considered as larger single crystals built from the pristine crystalline units despite presence of defects and voids. In principle, Ostwald ripening can also take place and create interior spaces for these single-crystalline products. The combined process of both oriented attachment and Ostwald ripening has been recently demonstrated in the synthesis of hollow nanocubes of Cu$_2$O and Cu$.^0$. In that work, CuO phase was prepared from a copper nitrate solution (Cu(NO$_3$)$_2$·3H$_2$O in N,N-dimethylformamide solvent), together with some water, under hydrothermal conditions (150–200°C) [24]. Instead of normally known spherical aggregates, it has been found that the CuO nanocrystallites were firstly reduced to Cu$_2$O which then self-attached each other according to their crystallographic directions (i.e., oriented attachment), resulting in faceted porous CuO nanocubes. The solid evacuation of these nanocubes continued, and a hollow interior space was formed because of an Ostwald ripening process. The Cu$_2$O nanocubes produced in this way are shown in Fig. 5 [24]. The formation of cubic aggregates of Cu$_2$O is attributed to the presence of more water in the synthesis. In other words, water stabilizes the [100], [010], and [001] crystal planes of the Cu$_2$O nanocrystallites which allows an aggregation through oriented attachment. Replacing water with ethanol, similar processes and products were observed. Therefore, it is apparent that high temperature and polarity of solvent used in synthesis are important parameters for the formation of single-crystalline Cu$_2$O nanocubes. Similar to those observed in Cu$_2$O nanospheres, their further reduction to metallic Cu$^0$ is also possible with a prolonged reaction. Nevertheless, the resultant product is Cu nanocubes instead of Cu nanospheres [23].

**Fig. (4).** Cu$_2$O nanospheres (TEM image) formed from a reductive conversion of spherical aggregates of CuO nanocrystallites, followed by an Ostwald ripening process (Chang et al. [23]).

**Fig. (5).** Single-crystalline Cu$_2$O nanocubes (TEM image) synthesized from a combined process of oriented attachment and Ostwald ripening of Cu$_2$O nanocrystallites (Teo et al. [24]).

Based on the above observation, it is believed that in addition to the cubic crystal system, crystallites with other crystal systems can also undergo a combined process of oriented attachment and Ost-
Au core size and conducting photocatalytic reactions. In this regard, hollow spheres, there are plenty of interstitial spaces (channels) that can be modified by anchoring a second or even a third chemical phase. For example, the pure anatase TiO$_2$ hollow spheres prepared from the Ostwald ripening have been used as a catalyst support for Au nanoparticles in fabrication of Au/TiO$_2$ nanocatalysts [33]. With the assistance of organic linkers in this self-assembly process, the Au particles of 2–4 nm in size can be uniformly distributed onto the external surfaces of TiO$_2$ nanospheres, as displayed in Figure 6b. Besides less material consumption in the hollow structures, it should be pointed out that this hollow support material has lighter weight and thus a better solid–liquid suspension can be prepared when considering its applications in solution phase. The resultant catalysts have been tested in photodecomposition of organic dyes (e.g., methyl orange) in aqueous solutions. Due to the nanocomposite nature of these catalysts, excellent catalytic performance has been elucidated under UV-illumination [33].

CONCLUDING REMARKS

We have reported in this short review about the recent new development in fabrication of hollow nanomaterials via Ostwald ripening. It has become clear that this template-free route allows us to pursue various structural architectures in a stepwise manner. One important feature of this synthetic approach is that the process can be carried out entirely in solution media and thus it can be analogous to the conventional organic total synthesis, where every part of an organic compound is added one at a time according to pre-designed synthetic schemes. For this reason, Ostwald ripening has become promisingly one of the major tools for synthetic architecture of inorganic nanomaterials, although the controllability of the interior spaces still needs to be exploited [22, 34].

As illustrated in this short review, spherical shape will be adopted mainly for those aggregates formed from less organized crystallites [22]. On the other hand, polyhedral structures will be the main crystal morphologies for well organized building blocks such as those aggregated through an oriented attachment process. It is expected that the interior spaces created in these polyhedral structures will also have non-spherical voids because the inner crystal planes and external crystal planes should belong to the same family [24]. Concerning a further improvement of this approach, initial organization of crystallites should be considered as an important issue, since it determines the ultimate architecture of interior space. Future research in pre-organization as well as aggregative state of crystallites should be pursued. In particular, more attention should be paid to generation of different interconnections among as-synthesized primary crystallites.

Research activities should also be directed to the organization of another class of building units, i.e., surfactant-capped inorganic nanocrystallites. In the assemblies of these organic-inorganic composite building blocks, interconnection among the primary units through van der Waals interaction of organic ligands or surfactants on the surfaces is expected. In this connection, partial (or complete) removal of these surface species and producing permanent bindings for the aggregated crystallites require more exploitative efforts. Furthermore, general colloidal chemistry and related assembling environments such as structures of micelles and vesicles may determine overall structures of the final products that undergo a hollowing process [34].

In extending the above synthetic methods, it has been anticipated that hollowing processes take place also in non-crystalline solids such as sol-gel derived materials upon the aging processes where crystallization and recrystallization are often coupled together. Nevertheless, their transformation processes could also be describable through Ostwald ripening mechanism. However, this is
an area which is understudied. In this regard, transforming intermediates of this type of softer matters should be examined, as the mechanisms involved could be different from other soft-template assisted hollowing processes [34].

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