Fabrication and application of inorganic hollow spheres

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Received 25th April 2011
DOI: 10.1039/c1cs15103g

Inorganic hollow spheres have attracted considerable interest due to their singular properties and wide range of potential applications. In this critical review, we provide a comprehensive overview of the preparation and applications of inorganic hollow spheres. We first discuss the syntheses of inorganic hollow spheres by use of polymers, inorganic nonmetals, metal-based hard templates, small-molecule emulsion, surfactant micelle-based soft-templates, and the template-free approach. For each method, a critical comment is given based on our knowledge and related research experience. We go on to discuss some important applications of inorganic hollow spheres in 0D, 2D, and 3D arrays. We conclude this review with some perspectives on the future research and development of inorganic hollow spheres (235 references).

1. Introduction

Monodisperse hollow spheres have attracted considerable interest in the past few decades due to their well-defined morphology, uniform size, low density, large surface area, and wide range of potential applications. For instance, the large fraction of void space in hollow structures has been used to load and control releasing systems for special materials, such as drugs, genes, peptides, spiceries, and biological molecules. They can also be used to modulate refractive index, lower density, increase the active area for catalysis and adsorption, improve particles' ability to withstand cyclic changes in volume, and expand the array of imaging markers suitable for early detection of cancer. Inorganic hollow spheres have special optical, optoelectronic, magnetic, electrical, thermal, electrochemical, photoelectrochemical, mechanical, and catalytic properties, suggesting that they comprise a more common, more diverse, and probably richer class of materials than organic hollow spheres.

Beginning with the pioneering work carried out by Kowalski and colleagues at Rohm and Haas, a variety of chemical and physicochemical strategies, including heterophase polymerization/combined with a sol–gel process, emulsion/interfacial polymerization methods, self-assembly techniques, and surface living polymerization process have been used to prepare inorganic hollow spheres.

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employed to prepare inorganic hollow spheres. In particular, the template method is the most common. In this method, at least two steps are usually indispensable. First, the templates must be modified to give them the ability to coax inorganic precursors (salts or alkoxides) onto the surface of the template core. Then, after the inorganic shell is decorated outside the scaffold, the templates must be eliminated in some way, leaving behind a hollow shell. Generally, templates can be divided into hard and soft templates. When hard templates (e.g., SiO$_2$, C spheres, polymers, metal particles) are employed, the structure of the hollow product is similar to that of the template, with a well-defined and monodisperse morphology. However, the removal of the templates by either thermal (sintering) or chemical (etching) means is very complicated and energy-consuming. As for soft templates (bacteria, droplets, vesicles, and more), although it is relatively easier to remove the templates, the morphology and monodispersity of the as-prepared hollow products are usually poor due to the deformability of the soft template. Although the drawbacks in these template strategies seem to be inherent and insurmountable, some novel techniques that seem to overcome them, such as sacrificial templates, modified soft templates, etc., are emerging. Another important development in the preparation of inorganic hollow spheres is called the template-free method, such as the Ostwald ripening process, which not only combines the advantages of hard- and soft-template methods but also avoids their pitfalls. Recent reviews have provided a comprehensive description of these methods for fabrication of inorganic hollow spheres, from multilevel hollow spheres to non-spherical, even one-dimensional (1D) hollow structures.

In order to avoid overlapping reviews, this article will mainly focus on the syntheses and applications of inorganic hollow spheres rather than any non-spherical and 1D hollow structures. We will first discuss the syntheses of inorganic hollow spheres with polymer, inorganic nonmetal, and metal-based hard templates and small-molecule or oligomer emulsion, surfactant micelle-based soft-templates, and template-free approaches. For each method, we provide critical comments based on our knowledge and related research experience. Then we will introduce some important applications of the inorganic hollow spheres (0D) and two-dimensional (2D) and three-dimensional (3D) arrays of inorganic hollow spheres. Considering the rapidly expanding body of literature in the field, the list of examples provided in this review is by no means exhaustive, some excellent papers reporting novel approaches and applications are even omitted. Representative works were selected from the most recent literature available, with exceptions made only for special cases. The intent is to give the readers a critical discussion of the syntheses and applications of inorganic hollow spheres. Finally, we conclude this review with some perspectives on the future research and development of inorganic hollow spheres.

2. Hard template strategy

Hard templates are widely used to fabricate inorganic hollow spheres. Many compounds, such as polymeric, inorganic nonmetallic, and metallic particles, can be used as hard templates. The final shape and size of the inorganic hollow sphere are essentially dependent upon the templates.

2.1 Polymer template-based methods

Template against polymer colloids is probably the most common approach to produce hollow spheres. Two methods in particular are used to fabricate hollow spheres with homogeneous, dense layers. One is templating against colloid polystyrene (PS) and its derivatives as the particles to fabricate SiO$_2$, SnO$_2$, magnet (ccp-Co, hcp-Co, Co$_3$O$_4$, a-Fe, Fe$_3$O$_4$, and a-Fe$_2$O$_3$), metal–metalloid Ni–B, Ni(OH)$_2$, and others. In its typical procedure, the PS template particles are coated in solution either by controlled surface precipitation of inorganic molecule precursors (SiO$_2$, TiO$_2$, etc.) or by assembly and photoelectric properties of organic–inorganic nanoparticles, hollow inorganic particles, development of functional coatings and films.

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direct surface reactions utilizing specific functional groups on the cores to create core-shell composites. The PS template particles are then removed by selective dissolution in an appropriate solvent or by calcination at elevated temperature in air, leaving behind hollow spheres. Bourgeat-Lami et al. synthesized PS latex particles bearing silanol groups on the surface via emulsion polymerization using 3-(trimethoxysilyl)propyl methacrylate as a functional co-monomer.43 These PS colloids were then transferred into aqueous ethanol solution by solvent exchange, wherein the co-condensation of the silanol groups with tetraethoxysilane (TEOS) was carried out via an ammonia-catalyzed sol-gel process, causing composite particles with PS cores and SiO2 shells. Hollow SiO2 spheres were obtained by thermal degradation of the PS cores at 600 °C. Yang and Lu et al. first described a new approach to the generation of inorganic hollow spheres using a template of the core-shell PS gel particles synthesized by an inward sulfonation with concentrated sulfuric acid.44 They also successfully prepared double-shelled TiO2 spheres with a kind of special hollow spheres polymer as a template.45,46 This special hollow template composite was composed of hollow PS spheres containing a thin hydrophilic inner layer and transverse channels of poly (methyl methacrylate)–poly (methacrylic acid) (PMMA–PMA). As shown in Fig. 1, when the hollow sphere template was first treated with sulfuric acid, the sulfonation took place in the exterior shell surface, the interior shell surface, and the transverse channels. This sulfonation of the hollow spheres enhanced the hydrophilicity of the spheres and provided a suitable graft surface for adsorption or forming complexes with a large variety of functional components, such as metal ions, metal oxide precursors, and organic precursors. Using TiO2 as an example, the sulfonated hollow spheres were immersed into a Ti(OBu)4 sol to coat a layer onto both the inner and outer interfaces of the hollow spheres. The existence of PMMA–PMA transverse channels on the PS shell acted as the entrance for the TiO2 sol. The double-shelled TiO2 hollow spheres were obtained after the intermediate PS layer was removed by a solvent. Following a similar procedure, the same authors successfully prepared carbon,45 TiO2, BaTiO3 and SrTiO3 hollow spheres.48

Ma et al. used porous polystyrene-divinyl-benzene (PS–DVB) spheres as templates to synthesize multi-shelled spheres and sphere-in-sphere structures by modifying the post-calcination process.49 The temperature during the preheating process directly affects the final structures of TiO2 spheres. Except for using PS and its derivatives as templates, melamine formaldehyde can also be used to prepare hollow spheres based on noble metal oxides and magnetic oxides.50

Another method, termed the layer-by-layer (LbL) self-assembly technique, has become an attractive topic of investigation ever since it was first developed by Caruso et al.51,52 The principle of this process is based on the electrostatic association between alternately deposited, oppositely charged species. Multilayered shells are assembled onto submicrometer-sized colloidal PS particles by the sequential adsorption of polyelectrolytes and oppositely charged nanoparticles. Upon calcination of the obtained core-shell particles, uniform-sized hollow spheres of various diameters and wall thicknesses can be generated from a variety of inorganic materials, including SiO2,51,52 TiO2,53 Mn2O3,54 zeolite,55 and other materials.56

In polymer template-based methods for preparation of inorganic hollow spheres, the biggest advantage is that the polymer templates are easily prepared with controllable sizes and surface functional groups, thus many hollow spheres of nonmetallic oxides, metallic oxides, and even metals can be fabricated through this approach. However, the preparation processes can require a lot of energy and time. First, multi-step processes are required for the synthesis of core-shell composite particles, e.g., the surface-functionalization of templating particles and the exchange of solvent/coating reaction in the templating particle approach and repeated adsorption/centrifugation/washing/redispersion cycles in the LbL method. Second, in order to obtain hollow spheres from core-shell composite particles, removing the core particles by selective dissolution in an appropriate solvent or by calcination at elevated temperature in air is indispensable.

Recently, Wu et al. reported a one-step process of fabricating monodisperse hollow SiO2 and TiO2 spheres. This means the formation of the inorganic shells and dissolution of core polymer particles occurs in the same medium (Fig. 2).57–60 In this method, monodisperse, positively charged PS beads were prepared by dispersion polymerization using cationic monomer 2-(methacyrlolyl)ethyltrimethylammonium chloride as co-monomer, which ensures the resulting silica or titania nanoparticles from the hydrolysis and condensation of TEOS or tetra-n-butyl titanate could be rapidly captured by PS beads

![Fig. 1](image1.png)  
Illustration of the formation of double-shelled hollow spheres. (a) The sulfonated polymer hollow sphere templates; (b) titania composite hollow spheres; (c) doubled-shelled titania hollow spheres. Reprinted with permission from ref. 45. Copyright 2005 Wiley-VCH.

![Fig. 2](image2.png)  
Schematic illustrations of SiO2 (a), TiO2 (b) and ZnO (c) hollow spheres prepared via one-step process.
via electrostatic interaction in aqueous ammoniacal alcohol medium at 50 °C. Very interestingly, the PS beads are “dissolved” into PS macromolecule chains or their aggregates subsequently, even synchronously, in the same medium, and are further diffused out gradually through the silica or titania shells since the silica or titania shells prepared by the Stöber method are usually porous, directly forming hollow SiO₂ or TiO₂ spheres. Neither additional dissolution nor calcination processes are needed to remove the PS cores. If negatively charged PS beads are used as templates, then ZnO or even Ag/SiO₂ double-shelled hollow spheres could also be prepared based on the one-step method.⁶³,⁶⁴ If this coating process occurs under acidic circumstances, PS/SiO₂ hybrid hollow spheres and PS/rare-earth-doped nanocrystals (LaF₃: Eu³⁺, Tb³⁺, and YVO₄: Dy³⁺) hybrid hollow spheres could be directly obtained via a one-pot synthesis, in which the PS macromolecular chains diffused from core into the voids between inorganic nanoparticles driven by the strong capillary force to form hybrid shells. This organic–inorganic hybrid shell is expected to improve the mechanical properties of inorganic hollow spheres.⁶³,⁶⁴

2.2 Inorganic nonmetallic template-based methods

Inorganic nonmetallic templates mainly include carbon and silica particles. Carbon spheres appear to be particularly suitable for templating due to their rich reactive groups and ease of removal. Many uniform micro/nano-sized hollow spheres of metallic oxides such as VO₂,⁶⁵ Gd₂O₃: Ln (Ln = Eu³⁺, Sm³⁺), Ga₂O₃, NiO, MnO₂,⁶⁶ and so on,⁶⁷ have been fabricated using carbonaceous polysaccharide spheres as the templates. The surfaces of the carbonaceous microspheres, prepared from saccharide starting materials by dehydration under hydrothermal conditions, are hydrophilic and functionalized with –OH and C=O groups. Upon dispersal of the carbonaceous microspheres in metal salt solutions, the functional groups on the surface layer are able to bind metal cations through coordination or electrostatic interactions. In the subsequent calcination process, the surface layers incorporating the cationic metal ions are condensed and cross-linked to form oxide hollow spheres. For example, Yang and co-workers reported that hollow Gd₂O₃: Ln (Ln = Eu³⁺, Sm³⁺) microspheres with diameters of about 300 nm were successfully fabricated using carbon spheres as templates.⁶⁸ As shown in Fig. 3a, when the precipitation agent, urea, was dissolved in water, it decomposed into CO₂ and OH⁻, coupled with a large number of –OH bonds on the surfaces of the carbon spheres. In the coating process, Gd³⁺ and Ln³⁺ were easily precipitated on the surfaces of carbon spheres. Then the high crystallization of Gd₂O₃: Ln (Fig. 3b) was formed and the carbon spheres were removed at a calcination temperature of 700 °C. This fabrication process involves neither organic compounds nor etching agents.

Li and co-workers prepared Ga₂O₃ and GaN semiconductor hollow spheres, ranging from 100 nm to 1.5 μm in size, by adsorption of metal cations to the surface layer of hydrophilic carbon (carbonaceous polysaccharide) spheres with copious –OH groups, followed by calcination in air.⁶⁹,⁷⁰ They then extended this method to prepare hollow spheres from a wide range of metal oxides, including main group metal oxides (Al₂O₃, SnO₂), transition metal oxides (ZrO₂, TiO₂, CoO, NiO, Cr₂O₃, Mn₂O₃), and rare earth oxides (La₂O₃, Y₂O₃, Lu₂O₃, CeO₂).⁷¹ Suslick et al. reported a sonochemical fabrication of crystalline hollow hematite (R-Fe₂O₃) using carbon nanoparticles as a spontaneously removable template for nanosized hollow core formation.⁷²

In order to simplify the preparation of inorganic hollow spheres with carbon templates, Thomas et al. described a simple one-pot hydrothermal approach to the preparation of hollow spheres from crystalline metallic oxides such as Fe₂O₃, Ni₂O₃, Co₃O₄, CeO₂, MgO, and CuO.⁷³ As indicated in Fig. 4, various metal salts were dissolved in water with carbohydrates, and the mixtures were heated to 180 °C in an autoclave. During the hydrothermal treatment, carbon spheres were

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Fig. 3 (a) Schematic illustration of the formation of carbon spheres, the core-shell structured precursor and hollow Gd₂O₃: Ln spheres. (b) TEM image of hollow Gd₂O₃: Eu³⁺ spheres. Reprinted with permission from ref. 68. Copyright 2010 Royal Society of Chemistry.

Fig. 4 Schematic illustration of the synthesis of metal oxide hollow spheres from hydrothermally treated carbohydrate/metal salt mixtures. Reprinted with permission from ref. 73. Copyright 2006 American Chemical Society.
formed in situ with metal ions incorporated into their hydrophilic shell. The removal of carbon via calcination left behind hollow metallic oxide spheres. Following this method, ternary metal oxide hollow spheres (CoFe$_2$O$_4$) were also prepared.$^{74}$

In addition, the hollow shells of crystalline porous metal oxides such as γ-Al$_2$O$_3$, TiO$_2$, MgO–Al$_2$O$_3$, and MgTiO$_3$ have been nanocast using hollow spheres of mesoporous carbon as hard templates. The metal oxides are fabricated from alkoxide precursors within the pore channels of the carbon templates.$^{75}$

With the help of abundant hydroxyl groups on surfaces of the carbon nanospheres, a composite nanoreactor with mesoporous silica hollow spheres and palladium (Pd) nanoparticles inside was prepared in three steps.$^{76}$ As illustrated in Fig. 5, the Pd nanoparticles, about 5 nm in size, are uniformly distributed on the surfaces of the carbon nanospheres. Using TEOS as the silica source and cetyl trimethylammonium bromide (CTAB) as a soft template, a thin layer of mesoporous silica is coated onto the Pd/C spheres. Calcination of the precursor composite removes the carbon shell and CTAB, leaving only Pd nanoparticles inside the hollow spheres. Carbon spheres can be used not only as templates but also as the direct reagent, which can considerably simplify the fabrication process. Based on this idea, Chen et al. successfully fabricated SiC hollow spheres between solid carbon spheres (HCSs) with single shells, deformed shells, and N-doped shells using silica spheres as hard templates.$^{77}$ The SiC nanospheres had 18% shrinkage compared to the carbon nanospheres, which could be attributed to the direct reaction between the carbon-surface and the silicon-vapor.

Silica is another common inorganic metallic template to prepare hollow spheres because it is inexpensive, easily obtainable and controllable in size. There are several inorganic hollow spheres fabricated with silica particles as templates, such as nickel hydroxosilicate,$^{78-79}$ carbon,$^{80}$ and palladium.$^{81}$ The general procedure involves the coating of silica templates by surface precipitation of suitable inorganic precursors and the removal of the silica templates by etching using an alkaline or hydrogen fluoride. For example, Hyeon et al. successfully prepared Pd hollow spheres using mercaptopropylsiloxyl-functionalized silica particles as templates.$^{82}$ Pd precursor was adsorbed onto the surfaces of the functionalized silica spheres and then reduced by CO at 250 °C to produce Pd metal-coated spheres. Pd hollow spheres were yielded after the removal of the silica templates by etching. Zhao et al. reported the fabrication of graphitic carbon spheres (HCSs) with single shells, deformed shells, double shells, and N-doped shells using silica spheres as templates and benzene as a carbon precursor via chemical vapor deposition (CVD).$^{83}$ The microscopic features and shell thicknesses of the HCSs were found to depend on experimental conditions such as silica sphere diameter, CVD temperature, and duration.

In order to further expand the potential applications of hollow spherical structured materials, it is also important to design shells with unique structures, advanced chemical compositions, and built-in functionalities. For example, Wang et al. prepared a novel hierarchical structure of copper silicate (CuSiO$_4$) hollow spheres with nanotube assembled shells.$^{84}$ The silicon–oxygen bonds of SiO$_2$ colloidal spheres could be broken to form silicate ions under an alkaline condition. Ammonia was used as the source of OH$^-$ and coupled with Cu$^{2+}$ in the form of complex ions which homogeneously dispersed in solution. SiO$_4^{2-}$ was generated and reacted with Cu$^{2+}$ around the SiO$_2$ colloidal spheres at the high temperature, forming CuSiO$_4$ which preferentially deposited on the surface of SiO$_2$ colloidal spheres. With the reaction proceeding, the SiO$_2$ colloidal spheres were consumed and more CuSiO$_4$ was generated from the Cu–ammonia complex ions, causing CuSiO$_4$ hollow spheres with large specific surface areas and excellent adsorption capabilities (Fig. 6). They went on to develop a versatile method of synthesizing nickel silicate, silica, and silica–nickel composite porous hollow spheres by using silica spheres as templates.$^{85}$ Wan et al. synthesized Sn nanoparticle encapsulated elastic hollow carbon spheres (TNHCs)$^{86}$ Polycrystalline SnO$_2$ was first deposited on the templates of SiO$_2$ spheres to form uniform shells by the hydrolysis of Na$_2$SnO$_3$. Then SnO$_2$ spheres were obtained by etching SiO$_2$ cores with NaOH solutions. The carbon precursor layers were coated on the outer surface of the hollow SnO$_2$ spheres by the pyrolysis of glucose under hydrothermal conditions. TNHCs were prepared by the carbonization of the carbon precursor shell and the reduction of the inner SnO$_2$ shells.

Recently, Wang and Yamauchi fabricated Pt spheres with hollow interior and nanosponge shells with high surface areas by using SiO$_2$ particles functionalized with amino groups as templates.$^{87}$ During the process, the amino groups on the SiO$_2$ surface played a key role in forming attachment sites for initial Pt seeds and then acted as nucleation sites for the subsequent Pt growth. Furthermore, the average thickness of the Pt shells increased proportionally with increasing amounts of Pt (Fig. 7).
Mesoporous silica spheres are also often used as templates. Su et al. demonstrated a new versatile core-shell method of monodisperse crystalline semiconducting ZnS hollow microspheres employing CMI-1 mesoporous silica spheres as templates (2–5 μm in diameter).88 The reaction between mesoporous silica spheres functionalized with ethylenediamine molecules that chelated zinc ions and the sulfide reagent in an aqueous solution led to the formation of ZnS. Then ZnS hollow microspheres of around 1–2 mm in diameter were fabricated by etching the mesoporous silica core. Liu et al. also synthesized 200–300 μm zeolite hollow spheres with core/shell structures via in situ hydrothermal transformation of commercially available mesoporous silica spheres into ZSM-5 crystals of about 200 nm with the assistance of isopropylamine, a weak structure-directing agent for MFI zeolite.89

Alongside pure carbon or silica particles as inorganic nonmetallic templates, Cheng et al. fabricated SiC hollow spheres from a mesoporous SiO2–C nanocomposite by taking advantage of microphase separation in the mesoporous silica–carbon nanocomposite.90 The SiC shell grew through a carbothermal reduction between the two separated phases, the carbon spheres and the silica-rich matrix. Hollow SiC was formed after oxidation.

Because carbon and silica templates are hydrophilic and functionalized with –OH and other groups on their surfaces, they can provide the following advantages. (1) Cationic materials rather than alkoxides or metal oxide nanocrystals can be used as starting materials. This reduces preparation cost and saves time because alkoxides are sensitive to humidity and monodisperse nanoparticles are not readily accessible. (2) Agglomeration can be avoided because the cations are absorbed onto the surface layer to form a composite shell rather than forming a heterogeneous coating. In all, the carbon spheres are effective templates to prepare the metallic and metallic oxide hollow spheres, while the silica spheres are more used to fabricate metallic and nonmetallic salt hollow spheres.

In addition, the functional groups on the surfaces of the carbon spheres are inherited from the saccharide, so no surface modification or activation steps are required. This greatly reduces the processing steps and thus saves time. As the thickness of the functional surface layer is predetermined by hydrothermal synthesis, the integrity and uniformity of the shells of the final products can be assured.

As a whole, no matter whether inorganic nonmetallic or polymeric beads are used as templates, three steps are indispensable: (i) surface-functionalization/modification of the template particle to acquire favorable surface properties; (ii) coating the templates with designed ceramic shells or their precursors by various approaches; and (iii) selective removal of the templates to leave behind hollow structures by etching in appropriate solvents or by calcination at elevated temperatures. Theoretically, these template strategies can assure the expected monodisperse morphology and size of hollow spheres and can be used to fabricate various kinds of inorganic hollow spheres. Nonetheless, their inherent demerits are also obvious. Not only is the fabrication process complicated and tedious, but also special care must be taken to prevent shell collapse during template removal. For example, when using organic solvents to dissolve polymer templates, swelling of the polymer can rupture the hollow structure, causing shells with unpredictable shapes. When using high temperatures to burn off polymer templates or to crystallize shell particles, escape of gases produced by pyrolysis of the polymer templates and, possibly, shrinkage during the crystallizing or compacting process, often lead to defects such as holes in surfaces of the final hollow spheres. Post-calcination at high temperatures usually causes aggregation and hard dispersion of hollow spheres in media.

### 2.3 Metallic template-based methods

In contrast to the above mentioned polymer and inorganic nonmetallic templates, the key feature of metal-template-based methods is that the metal template itself can act as a reactant in the synthetic process. The template not only plays the role of scaffold and precursor for the shell, but it is also consumed completely during the coating process. This simplifies the preparation process. The morphology, void space, and wall thickness of the hollow structures are all determined directly by the metal templates. Generally, two formation mechanisms, the Kirkendall effect and galvanic replacement, have been used to understand the fundamentals of inorganic hollow spheres synthesized by metallic templates.

#### 2.3.1 Kirkendall effect

Originally, the term “Kirkendall effect” refers to the different atomic diffusive rates of binary elements in metals and alloys under thermally activated conditions. Due to this difference in metal diffusivities, the generation of porosity in the lower-melting component side of the diffusion couple near the interface could create hollow nanostructures.91,92 By introduction of oxidation or sulfidation reactions on the external surfaces of metallic nanocrystals, Alivisatos et al. first explained the formation of hollow nanocrystals of cobalt (Co) oxide and chalcogenides.93 The Co nanocrystals were chosen as a starting material to
synthesize the hollow nanocrystals through the reaction of Co colloidal solution with oxygen and either sulphur (S) or selenium (Se). The evolution of hollow morphology could be well illustrated by the reaction of Co nanocrystals with Se (Fig. 8). As the reaction proceeded, more Co atoms diffused out to the shell, and the accompanying transport of vacancies led to growth and merging of the initial voids. This resulted in the formation of bridges of material between the core (Co) and the shells (CoSe). These bridges persisted until the Co was completely consumed. After studying the physics of the nanoscale Kirkendall effect using the formation of cobalt sulfide hollow nanocrystals, they found that performing the reaction at temperatures greater than 120 °C led to fast formation of a single void inside each shell, whereas at room temperature multiple voids were formed within each shell. This could be attributed to strongly temperature-dependent diffusivities for vacancies. The void formation process was dominated by outward diffusion of Co$^{2+}$ cations. Because the final voids were smaller in diameter than the original Co nanocrystals, it could be inferred that significant inward transport of sulfur anions took place. The team then prepared hollow CdS$^{95}$ and $\gamma$-Fe$_3$O$_4$$^{96}$ spheres and found that the reaction conditions, such as the diffusion of equal species through an identical composite and the concentration and reactivity of the anion precursor, could have an impact on hollow structures.$^{97}$

Through similar strategies, other inorganic hollow spheres such as hollow CoSe nanoparticles from solution-phase selenization of Co nanoparticles,$^{98,99}$ hollow transition metal phosphide nanoparticles from reactions between metal nanoparticles and trioctylphosphine,$^{100,101}$ hollow magnetic iron oxide nanoparticles from gas-phase oxidation,$^{102}$ electron-beam irradiation,$^{103}$ and solution-phase synthesis,$^{104}$ have been fabricated. Recently, Peng and Sun reported a facile solution-phase synthesis of monodisperse hollow Fe$_3$O$_4$ nanoparticles by controlled oxidation of Fe-Fe$_3$O$_4$ nanoparticles.$^{105}$ The Fe nanoparticles were not chemically stable and oxidized easily when exposed to air, leaving core-shell Fe-Fe$_3$O$_4$ structures with both Fe and Fe$_3$O$_4$ in amorphous states. Controlled oxidation of these core-shell nanoparticles in the presence of the oxygen-transfer reagent trimethylamine N-oxide (Me$_3$NO) led to the formation of intermediate core-shell-void Fe-Fe$_3$O$_4$ and to hollow Fe$_3$O$_4$ nanoparticles.

A novel method for the synthesis of uniform hollow oxide nanoparticles was developed based on the Kirkendall effect. It involves a controlled nanoscale etching of MnO and iron oxide nanocrystals (Fig. 9) in the presence of trioctylphosphine oxide and alkylphosphonic acid.$^{106}$ In the early stage of the etching process, metal cations were dissolved into the solution by the coordination of alkylphosphonic acid, which increased the vacancy concentration near the surface of the particle. At the same time, phosphorus from the solution diffused to the surface of the particle, filling the vacancies. Continued dissolution of metal cations and supply of phosphorus transformed the outer shell of the nanocrystal from metal oxide to phosphor oxide. The outward diffusion of metal cations and the accumulation of vacancies inside the shell led to the formation of the void between the core and the shell. The diffusion of metal cations stopped when the composition of the particle became homogeneous. The final amorphous shell, composed of metal, phosphorus, and oxygen, was maintained by the balance of the inward diffusion of phosphorus and the outward diffusion of metal.

Note that the chemical transformation of nanoparticles accompanied by the Kirkendall effect often results in polycrystalline nanoparticle products, while single-crystal hollow structures are rarely obtained. Recently, Alivisatos’s group prepared parent-particle shape, single crystallinity and orientation of ZnS hollow nanoparticles through the heteroepitaxial anion exchange reaction with Kirkendall effect.$^{107}$ Thin layers of ZnS were grown epitaxially onto the ZnO core through a surface anion exchange reaction, which generated a highly strained interface between the ZnO core and the ZnS shell. To release this interface energy, the ZnO core spontaneously diffused into the ZnS shell, which was finally exchanged with sulfur precursors at the outer shell surface, forming fully converted hollow ZnS nanoparticles (Fig. 10).

To date, although the Kirkendall effect has achieved some success in the preparation of inorganic hollow compounds, it...
Galvanic replacement. Galvanic replacement reaction provides a remarkably simple and versatile route to metal nanostructures with controllable hollow interiors and porous walls. The key step of this process involves a replacement reaction between a suspension of more active metal templates and a salt precursor containing a relatively less active metal. Xia et al. first described a general approach to the generation of nanoscale hollow metal structures (Au, Pt, Pd) with well-defined void spaces and homogeneous, highly crystalline walls by reacting solutions of appropriate salt solutions with solid templates of a more reactive metal.108,109 The major steps involved in this process are shown in Fig. 11, with the gold/silver combination as an example. Silver nanoparticles could be oxidized to silver ions when mixed with an aqueous HAuCl₄ solution. The elemental gold should be confined to the vicinity of the template surface. Then they nucleate and grow into small clusters, and eventually evolve into a shell-like structure around the silver template. The thin shell formed in the early stage was incomplete, and so it was possible for HAuCl₄ and AgCl to diffuse across this layer until the silver template was completely consumed. When the reaction continued with refluxing at an elevated temperature, the wall of each gold shell would be consumed. When the reaction continued with refluxing at an elevated temperature, the wall of each gold shell would be consumed. When the reaction continued with refluxing at an elevated temperature, the wall of each gold shell would be consumed.

When comparing galvanic replacement reaction to the Kirkendall effect, galvanic replacement reaction does not require additional surface functionalization either, and moreover, it can be employed as a general route to fabricate hollow structures in a variety of shapes and sizes, but obviously, only for metallic hollow structures.

3. Soft template-based strategies

Soft template-based methods hold appeal because the templates are relatively easy to remove.116–120 However, the morphology and monodispersity of the as-prepared hollow products are usually poor due to the deformability of the soft templates. Controlling monodispersity and spherical morphology of the inorganic hollow structures is the most challenging part of this technique. Imhof et al. successfully synthesized monodisperse micrometre-sized SiO₂ hollow spheres by templating against low-molecular-weight polydimethylsiloxane (PDMS) silicone O/W emulsion droplets with diameters in the range of 0.6–2 μm.121,122 Feldmann et al. synthesized nanoscale La(OH)₃ hollow spheres exhibiting outer diameters of 11–30 nm and inner cavities of 2–17 nm in W/O microemulsion containing n-dodecane as the nonpolar oil phase, CTAB as the surfactant and 1-hexanol as the co-surfactant.123 Adjustment of the water to surfactant ratio of the underlying micellar system and the size of the relevant micelles influences the outer diameter and cavity size. Silver spheres of less than 50 nm in diameter with a wall thickness of 3–5 nm and an inner cavity of 10–15 nm were also realized in this way. More complex structural inorganic hollow spheres, such as hollow cage-like silica spheres loaded with superparamagnetic
iron oxide nanoparticles incorporated in their macroporous shells, have also been prepared via the oil-in-diethylene-glycol microemulsion method. Recently, Wu et al. successfully prepared monodisperse and size-tunable hollow Ag spheres with phase-transformable emulsions composed of natural beeswax as templates (Fig. 12). First, a mixture of beeswax and CTAB aqueous solution containing KBr was heated to 75 °C to produce molten-state beeswax, followed by an ultrasonic process to obtain monodisperse, stable emulsion droplets of beeswax. A small amount of AgNO₃ solution was added to form negatively charged AgBr “seeds” which were adsorbed onto the positively charged surfaces of droplets through electrostatic attraction. The AgBr seeds were then reduced to Ag nanoparticles and bound to the solidified beeswax particles. Because the Ag nanoparticles on the beeswax cores could act as catalysts and significantly accelerated the reduction process while the reduction of AgBr in continuous phase was metastable, and normally very slow, more Ag was deposited onto the surfaces of beeswax particles as more AgNO₃ solution was added. This led to dense, monodisperse Ag-coated beeswax spheres. Because natural beeswax has a relatively low phase-transformable temperature from solid to liquid (T_m = 62–67 °C), the beeswax cores were easily emigrated from inside to outside when heated to 70 °C, leaving behind well-defined hollow Ag spheres.

Han et al. fabricated hollow SiO₂ spheres using water/n-heptane/CTAB nanoemulsions and compressed CO₂ as a template. During the preparation process, heptane droplets with TEOS (oil phase) were dispersed in the aqueous phase with the aid of the surfactant. At the same time, there existed cylindrical micelles of the surfactant in the aqueous phase. Addition of the compressed CO₂ into the emulsion caused the dispersed oil droplets to become smaller and more uniform. The hydrolysis of TEOS occurred around the micelles near the oil/water interfacial region. The oil droplets formed the cores of the spheres, and the cylindrical micelles acted as templates for the formation of the mesopores in the SiO₂ shells. SiO₂ hollow spheres with ordered mesoporous shells were formed after removing the oil and surfactant by washing and calcination.

Surfactant molecules in aqueous solution can also self-assemble to form the micelles and closed-bilayer aggregates such as vesicles (also referred to as organized molecular assemblies) or dynamic nanostructures of surfactant molecules. These micelles or vesicles have been used as the templates to prepare hollow spheres, such as SiO₂, ZnO, GaS, and other materials. Wang and co-workers first successfully synthesized single-, double-, triple-, and quadruple-shelled GaO₂ hollow spheres with CTAB multilamellar vesicles as soft templates at 60 °C, as shown in Fig. 13. The concentration of the CTAB surfactant was found to be capable of adjusting the structures of these Cu₂O hollow spheres. Further, they simplified the process to synthesize Cu₂O hollow spheres with uniform double-wall structures at room temperature and without the addition of sodium hydroxide. The double-wall structure and size of Cu₂O hollow spheres was not found to change with increasing concentrations of CTAB.

This method can be extended to the utilization of poly(vinylpyrrolidone) as a vesicle template in the syntheses of various hollow structures such as VO₂, BaWO₄, SiO₂, Co₃O₄ and PbO₂ spheres. For example, based on the template of poly(vinylpyrrolidone), γ-Fe₂O₃ hollow spheres with multilevel interior structures were fabricated via the heterogeneous contraction approach by fast heating their gel precursors. The structure of the hollow spheres could be controlled for the formation of solid, hollow to core-in-hollow-wall, double-wall...
hollow, and core-in-double-hollow-wall spheres by adjusting the heating rate of the calcination as shown in Fig. 14.

Very recently, Che et al. successfully prepared novel SiO$_2$ mesoporous crystal spheres with polyhedral hollows and the reverse multiply twinned bicontinuous double diamond mesostructure as seen in Fig. 15. The hollow SiO$_2$ mesoporous crystal spheres were synthesized using amino acid-derived, anionic, amphiphilic N-stearoyl-L-glutamic acid as the template, 3-aminopropyltrimethoxysilane as a costructure directing agent, and TEOS as the silica source in the presence of the nonionic surfactant C$_{16}$H$_{31}$(OCH$_2$CH$_2$)$_{10}$OH. The formation of vesicles with low-curvature lamellar structure, which was self-assembled by amphiphilic carboxylic acid molecules in the presence of a nonionic surfactant and the lamellar-to-cubic shell transformation of vesicles, gave a reverse multiply twinned mesoporous shell while maintaining the hollow shape.

Soft templates include not only emulsion droplets, surfactants, other supramolecular micelles, and polymer vesicles, but also polymer aggregates and gas bubbles; more examples can be found in a previous review.

Compared to hard template-based methods, soft template-based methods not only eliminate the cores easily by gentle evaporation or dissolution in solvents, but also the liquid droplet templates still allow facile and efficient introduction of therapeutic and biologic active species inside the spheres. However, although some infusive progresses in controlling the size, uniformity and microstructure of the inorganic hollow spheres in the soft templates have been made in the past several years, this challenge is still serious and hard to overcome in most cases. This is attributed to the characteristics of soft templates. For example, the emulsion droplets are thermodynamically unstable, and the precursor of shell materials can initially exist in either the continuous phase or the droplet phase or both phases; the structure and stability of the supramolecular micelles/vesicles as soft templates are affected by many factors such as the solvent polarity, pH value, and the ionic strength of the solution.

4. Template-free strategy

As discussed above, although template methods are arguably the most effective and certainly the most common means of synthesizing hollow inorganic spheres on the micro and nano scales, some inherent disadvantages have proven very difficult to overcome. For example, in most hard template-based methods, removal of the template by either thermal or chemical means is very complicated and energy consuming. In soft template-based methods, the morphology and monodispersity of the hollow spheres are very difficult to control. Recently, the Ostwald ripening process has been proposed as a template-free strategy and is used more and more to fabricate inorganic hollow spheres. The basic principle of the inside-out Ostwald ripening process is that the larger crystals grow from those of smaller size, which have higher solubility than the larger ones. Within a colloidal aggregate, smaller, less crystallized, or less dense crystallites will dissolve into the liquid phase as a nutrient supply for the growth of larger, better crystallized, or denser ones. When the crystals grow in solution, the concentration of growth units varies across the mother solution, due to the size difference of resultant nanocrystals. With the driving force of the minimization of surface energy, metastable nanoparticle aggregates occur first due to the reduction of supersaturation in solution. Once the particles with different sizes are attached to each other, the large particles begin to grow, drawing from smaller ones. Voids gradually form and grow in the cores of large aggregates, and the shell thickness increases owing to the outward diffusion of solutes through the permeable shell.

The inside-out Ostwald ripening mechanism has been used to synthesize hollow spheres of a wide range of materials, such as, Fe$_2$O$_3$, SnO$_2$, Co$_3$O$_4$, Sb$_2$S$_3$, Bi$_2$WO$_6$, TiO$_2$, and other materials. For example, Zeng and coworkers reported a “one-pot” method of preparing

![Fig. 14](image-url) Illustration for the formation mechanism of solid (A), hollow (B), core-in-hollow-wall (C), double-wall hollow (D) and core-in-double-hollow-wall (E) spheres. Reprinted with permission from ref. 140. Copyright 2010 Royal Society of Chemistry.

![Fig. 15](image-url) (a and b) Cross-sectional SEM images of silica mesoporous crystal spheres with polyhedral hollows; (c) HRTEM image taken from the common [110] direction of the decahedron shape; (d) HRTEM image of a Wulff polyhedron taken from the [100] direction. Reprinted with permission from ref. 141. Copyright 2011 American Chemical Society.
hollow anatase TiO$_2$ spheres with diameters of 0.2–1.0 μm via the inside-out Ostwald ripening in TiF$_4$ solution.$^{163}$ The reduction of the overall surface energies could provide the driving force for Ostwald ripening within all the particles. With respect to hollowing, no apparent driving force could be easily identified.$^{164}$ Wang $et$ $al.$ prepared a hierarchical structure of Ni(OH)$_2$ hollow microspheres with β-Ni(OH)$_2$ nanosheets as the in situ building units (Fig. 16a–d).$^{165}$ NiO hollow spheres were successfully synthesized by thermal decomposition of the as-synthesized Ni(OH)$_2$ hollow spheres at 600 °C for 2 h. The formation process of Ni(OH)$_2$ hollow microspheres could be divided into three obvious stages. In the first stage, the precipitated Ni(OH)$_2$ crystals assembled into loosely attached aggregates with diameters of 800–900 nm. With increasing reaction time, the aggregates continuously grew in size and density to form spheres with solid cores. Finally, an interior cavity was gradually formed via a core evacuation process, through a mechanism similar to Ostwald ripening (Fig. 16e–g). Wang $et$ $al.$ further reported a hierarchical and porous structure of Ni hollow microspheres with Ni nanoparticles as the in situ formed building units which were fabricated by a novel, hydrothermal redox method with Ni(OH)$_2$ as the precursor.$^{166}$

Also, the hollow spheres produced from the self-templated formation have recently been further elaborated.$^{167,168}$ The term “localized Ostwald ripening” is used to describe the preferential dissolution of the particle interior. Yu $et$ $al.$ prepared a wide range of hollow spheres including calcium carbonate, strontium tungstate, TiO$_2$, SnO$_2$, CuO/Cu$_2$O and so on.$^{169-171}$ With increasing reaction time, the surface layer first transformed to a thermodynamically more stable form (e.g., crystallization), as the supersaturation fell in the surrounding solution. Thus an ultrathin shell of less-soluble crystalline phase was formed on the amorphous solid spheres. As a result, the amorphous core would have a strong tendency to dissolve and diffuse out through the shell because it remained out of equilibrium with the surrounding solution. Furthermore, they prepared mesoporous anatase-phase TiO$_2$ hollow spheres with high photocatalytic activity by hydrothermal treatment and self-transformation of amorphous TiO$_2$ solid spheres in an NH$_4$F aqueous solution.$^{172}$ Initially (0 min), the precursors were solid spheres with smooth surfaces (Fig. 17a) and in the amorphous state (Fig. 17b). After hydrothermal reaction for 30 min, the diffraction peaks for the crystalline TiO$_2$-anatase appeared in the XRD pattern of the product (Fig. 17d). The product was still solid spheres and the surfaces of the spheres, which contained nano-sized crystalline particles, became rough (Fig. 17c). Extending the reaction time to 60 min resulted in an increase in the crystallinity of the samples (Fig. 17f), and the hollowing interiors took place around the centers of the solid spheres (Fig. 17e).

Complex structures, such as core-shells and binary and ternary composite hollow spheres can also be prepared via Ostwald ripening.$^{173-176}$ Zeng and Liu synthesized hollow core-shell oxide and sulhide semiconductor particles.$^{177}$ While the original shape of a crystallite aggregate forms the exterior appearance, the route of preorganization of crystallites determines the ultimate interior space structure of the aggregate upon Ostwald ripening. They demonstrated that Ostwald ripening could also be used as a facile wet chemical route to synthesize binary metal oxide nanospheres with additional architecture of interior spaces. The high-quality Sn-doped TiO$_2$ hollow spheres were prepared with the hydrolysis of
fluoride salts of both TiF$_4$ and SnF$_4$ (Fig. 18). The formation of the hollow sphere was ascribed to an Ostwald ripening process (steps 1–4). The surface-adsorbed fluoride anions prevented the nanospheres from the agglomeration via negative repulsive interaction (steps 5 to 6). Furthermore, the fluoride anion overlayer also served as a diffusion boundary to restrain rapid crystal growth and prevent direct fusion among the nanospheres during the ripening. The content of Sn$^{4+}$ in the solid solution obviously influenced the hollowing degree of these nanospheres.

Wu et al. first reported the successful synthesis of superparamagnetic fluorescent Fe$_3$O$_4$/ZnS hollow spheres of under 100 nm in size using corrosion-aided Ostwald ripening. The synthetic procedure was very easy and straightforward. When the monodisperse FeS particles were dispersed in a mixture containing zinc acetylacetonate (ZA), PVP, ammonium nitrate, glycol and water, and reacted at 150 $^\circ$C for 10 h, Fe$_3$O$_4$/ZnS hollow spheres were directly obtained. As demonstrated in Fig. 19, ZA hydrolysis at pH 6–9 generated Zn(NH$_3$)$_4$(OH)$_2$ which further eroded the FeS particles (Fig. 19a) to cause supersaturated Fe$_3$O$_4$ and ZnS phase. This phase underwent consequent nucleation and growth around the entire surface stabilized by PVP (Fig. 19b). As time went on, FeS, ZA and water were consumed gradually and the resultant ZnS and Fe$_3$O$_4$ molecules decreased in number. The growth rate also decreased, due to the narrowing concentration gap between the molecules in the medium and the equilibrium value needed for growth. The Fe$_3$O$_4$ and ZnS formed around the surface of FeS particles, and small particles grew into larger particles, which then coalesced and formed shells (Fig. 19c). Etching did not cease until the FeS core had vanished, finally leaving Fe$_3$O$_4$/ZnS hollow spheres (Fig. 19d and e).

Ostwald-ripening-based template-free methods can both resolve the problem of the template removal in hard template-based strategies and provide uniform hollow spheres both in morphology and size that are so difficult to attain via soft template-based strategies. However, to date, this strategy has only focused on some special compounds, and no copious fundamental evidences are available in support of this mechanism. More mechanistic studies on the fabrication of inorganic hollow spheres are required to provide deeper fundamental understanding of Ostwald ripening. The representative inorganic spheres and their preparation methods are summarized in Table 1.

5. Applications

The most attractive characteristics of inorganic hollow spheres are their well-defined morphology, their large specific surface area, low density, and the optical, electric, and magnetic properties of their inorganic components. All of these make inorganic hollow spheres superior to other similar materials in applications such as catalysis, lithium-ion batteries, biomedical applications, and gas sensors. We will now introduce some important applications of not only the inorganic hollow spheres themselves (0D), but also the 2D and 3D arrays of inorganic hollow spheres, since more and more much higher-grade assemblies of inorganic hollow spheres have been reported recently.

5.1 Hollow spheres (zero-dimensional, 0D)

Hollow spheres or so called 0D hollow structures have been extensively investigated in their potential applications, especially in catalysts, lithium-ion batteries, biomedical materials and gas sensors. As catalysts, except for Suzuki coupling reactions, heterogeneous hydrogenation reactions, Sonogashira reactions, aerobic oxidation, many inorganic hollow spheres such as ZnS, C, WO$_3$, TiO$_2$, CuO/Cu$_2$O, ZnO-SnO$_2$, and others occupy photocatalytic
or electrocatalytic properties. For example, Pt hollow nanospheres with an average diameter of 24 nm and discrete Pt nanoparticles, display twice the electrocatalytic activity of the solid Pt nanoclusters in the oxidation of methanol.\textsuperscript{111} The hierarchical flower-like Bi\textsubscript{2}MoO\textsubscript{6} hollow spheres exhibited excellent visible-light-driven photocatalytic efficiency for the degradation of Rhodamine B, up to 95\% within 2 h, which was much higher than that of solid-state Bi\textsubscript{2}MoO\textsubscript{6} and TiO\textsubscript{2} (P25).\textsuperscript{176} By designing specific hollow structures, one can improve the catalytic property. For example, the rattle-structured hollow Au@ZrO\textsubscript{2} was used as a model high-temperature-stable catalyst for CO oxidation, in which the Au nanoparticles were effectively separated but still highly accessible to gas molecules.\textsuperscript{191} The rattle-type TiO\textsubscript{2}@void@SiO\textsubscript{2} particles, with commercial TiO\textsubscript{2} particles encapsulated into hollow SiO\textsubscript{2} shells, showed high photocatalytic activity and UV-shielding performance without decomposing the supporting organic materials, as well an increasing photocatalytic activity with an increasing thickness of void space.\textsuperscript{192}

In lithium-ion batteries, hollow nanomaterials made of Sn,\textsuperscript{193–195} and some transition metal oxides\textsuperscript{196,197} have recently been the focus of research into high-energy electrode materials for novel lithium-ion batteries. Archer \textit{et al.} used the SnO\textsubscript{2} hollow nanoparticles as anode materials for lithium-ion batteries, demonstrating a surprisingly large initial discharge capacity of 1140 mA h g\textsuperscript{-1}, more than 75\% greater than that of pristine SnO\textsubscript{2} nanoparticles (ca. 645 mA h g\textsuperscript{-1}).\textsuperscript{198} Rattle-type structures with other functional cores in the interior void space exhibited excellent electrochemical properties in lithium storage capacities.\textsuperscript{199} Uniform a-Fe\textsubscript{2}O\textsubscript{3}@SnO\textsubscript{2} nanorattles with large void spaces were found to improve lithium storage capabilities. Their first discharge capacities were 1544 mA h g\textsuperscript{-1}, and corresponding charge capacities were 865 mA h g\textsuperscript{-1}.\textsuperscript{200} The same authors reported that complex hollow spheres assembled from anatase TiO\textsubscript{2} nanosheets with exposed (001) facets displayed the excellent cyclic retention even at high current rates.\textsuperscript{201,202}

Wang \textit{et al.} used the complicated Co\textsubscript{3}O\textsubscript{4} multishelled hollow spheres, including single shelled (S-Co), double shelled (D-Co) and triple shelled (T-Co) spheres composed of oriented self-assembled nanosheets as the anode material in lithium-ion batteries.\textsuperscript{203} These hollow microspheres exhibited excellent cycle performance and enhanced lithium storage capacity in contrast to the commercial Co\textsubscript{3}O\textsubscript{4} as shown in Fig. 20. Double-shelled hollow structures in particular delivered an

<table>
<thead>
<tr>
<th>Structure</th>
<th>Composition</th>
<th>Synthesis methods</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-shelled hollow sphere</td>
<td>SiO\textsubscript{2}</td>
<td>LbL self-assembly method based polymer spheres</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>TiO\textsubscript{2}</td>
<td>One step method against polymer template</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polymer template method</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O/W emulsion droplets template method</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amphiphilic carboxylic acid template method</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>SnO\textsubscript{2}</td>
<td>Templating against colloidal crystals</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>Silica template method</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Au, Pt, Pd</td>
<td>Galvanic replacement reaction</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>Ga\textsubscript{2}O\textsubscript{3}, GaN</td>
<td>Carbon template method</td>
<td>69, 70</td>
</tr>
<tr>
<td></td>
<td>CoO, CoS</td>
<td>Kirkendall effect</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>ZnS, Co\textsubscript{3}O\textsubscript{4}</td>
<td>Ostwald ripening</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>Fe\textsubscript{2}O\textsubscript{3}, Ni\textsubscript{2}O\textsubscript{3}, Co\textsubscript{3}O\textsubscript{4}, CeO\textsubscript{2}, MgO, CuO</td>
<td>In situ formed carbon template</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>Fe\textsubscript{3}O\textsubscript{4}</td>
<td>Kirkendall effect</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>Phase-transformable emulsion method</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>ZnS</td>
<td>Silica template method</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>Gd\textsubscript{2}O\textsubscript{3}: Ln (Ln = Eu\textsuperscript{3+}, Sm\textsuperscript{3+})</td>
<td>Carbon template method</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>NiPt</td>
<td>Wet chemical process combined with galvanic replacement</td>
<td>115</td>
</tr>
</tbody>
</table>

| Multi-shelled hollow sphere | TiO\textsubscript{2} | Polymer template method | 45 |
| | Carbon, Carbon/N | Silica template method | 83 |
| | CuO | CTBA vesicles template method | 134 |
| | CoO | Self-aggregation combined with Ostwald ripening | 203 |

| Hierarchical hollow sphere | Ni(OH)\textsubscript{2} | Inside-out Ostwald ripening | 165 |
| | CuSiO\textsubscript{4} | Silica template method | 84 |
| | WO\textsubscript{3} | Template-free method | 186 |
| | Bi\textsubscript{2}MoO\textsubscript{4} | Self-aggregation combined with Ostwald ripening | 176 |

| Binary composite hollow sphere | Sn–TiO\textsubscript{2} | Ostwald ripening | 178 |
| | Fe\textsubscript{3}O\textsubscript{4}–ZnS | Corrosion-aided Ostwald ripening | 179 |
| | NiO–SnO\textsubscript{2} | Ni template method | 213 |

| Rattle-type hollow sphere | TiO\textsubscript{2}@void@SiO\textsubscript{2} | LbL combined with photocatalytic method | 192 |
| | a–Fe\textsubscript{2}O\textsubscript{3}@SnO\textsubscript{2} | Inside-out Ostwald ripening | 200 |
| | Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2} | Carbon template method | 208 |

| Nanoparticles encapsulated in hollow sphere | SnO\textsubscript{2}@carbon | Silica template method | 86 |
| | Sn@Carbon | Silica template method | 199 |
| | Pd@SiO\textsubscript{2} | Carbon template method | 76 |
exceptional capacity of 866 mA H g⁻¹ over 50 cycles at a current rate of \( C/5 \) (completing the charge or discharge process in 5 h; 1 \( C = 890 \) mA g⁻¹).

In biomedical materials, the most important application of inorganic hollow spheres is drug loading and delivery.²⁰⁴–²⁰⁶ Magnetic and fluorescent hollow spheres are particularly preferred for this purpose.²⁰⁷ Combinations of mesoporous SiO₂ with magnetic particles to form magnetic mesoporous composites have great advantages for cancer therapy. SiO₂ hollow spheres with rattle-type magnetic cores and mesoporous shells not only enable high drug loading and magnetically targeted delivery but also facilitate drug molecules to diffuse into or out of the shells.²⁰⁸ Mesoporous and luminescence-functionalized CaF₂: Ce³⁺/Tb³⁺ hollow spheres have been used as drug carriers.²⁰⁹ Wu et al. reported that the Fe₃O₄/ZnS hollow spheres synthesized via corrosion-aided Ostwald ripening, displayed not only superparamagnetism and fluorescence but also high drug loading capacity and a comparable release rate to conventional silica drug carriers, releasing more than 50 and 90% of the drug within 10 and 65 h, respectively.²¹⁰

Hollow spheres of semiconducting metal oxides can still find other uses such as gas sensing, because their large surface-to-volume ratios significantly enhance gas diffusion and mass transport in the sensing layers.²¹⁰,²¹¹ For example, Au-studded porous SnO₂ hollow spheres could obviously improve sensor response. With ethanol, the responses to 10, 50, 100, 200, and 600 ppm were about 9.3, 21.2, 76.9, 129.8, and 147.8 times higher for Au-studded spheres than for SnO₂ hollow spheres alone. With acetone, the responses were about 5.8, 11.9, 24.5, 34.5, and 47.8 times higher than its original value.²¹² The ethanol sensors based on nanoscale SnO₂ hollow spheres with NiO-functionalized inner walls exhibited ultra-fast response and recovery. As shown in Fig. 21, the gas responses \( (R_a/R_g, R_c) \): resistance in air, \( R_c \): resistance in gas) to 20, 50, and 100 ppm ethanol were 1.75, 2.58, and 3.54, respectively. The times to reach 90% variation in resistance upon exposure to ethanol and air were defined as the 90% response time \( (t_{res}) \) and the 90% recovery time \( (t_{recov}) \), respectively. The \( t_{res} \) values upon exposure to 20, 50, and 100 ppm ethanol were 5, 2, and 2 s, respectively. These fast responses and recovery characteristics can be attributed to rapid gas diffusion through the less agglomerated porous shells and the promotion of surface reaction by the NiO inner layers.²¹³

In addition, inorganic hollow spheres with large specific surface areas, such as those made from MgSiO₃,²¹⁴ Mn₂O₃,²¹⁵ and CeO₂²¹⁶ can be used as absorbents to remove organic molecules and heavy-metal ions from waste water. Recently, the interesting optical properties of hollow silica nanoparticles showed potential applications as optical devices. When particle size was adjusted from 333 to 642 nm, the color of powders created by resonant Mie scattering turned from blue to violet (Fig. 22).²¹⁷

### 5.2 Two-dimensional (2D) arrays

Another important potential application of inorganic hollow spheres is their 2D ordered structures. These arrays display special magnetic properties,²¹⁸ optical properties,²¹⁹ photocatalytic properties,²²⁰ gas sensing properties,²²¹ and surface-enhanced Raman scattering (SERS).²²² In this field, Cai and...
his colleagues prepared a series of 2D arrays of inorganic hollow spheres from such substances as Si, CdS, NiO, Ni, and Ni(OH)\textsubscript{2} through deposition of hollow spheres onto conductive substrates combined with thermal treatment and subsequent solution-dipping, electrochemical deposition, or electrophoresis, and obtained some encouraging results. For example, the 2D array of Ni hollow spheres showed excellent magnetic properties.\textsuperscript{225} The coercivity values were 104 Oe for the applied field parallel to the film and 87 Oe for the applied field perpendicular to the film. These are larger than those of bulk Ni and hollow Ni submicrometer-sized spheres. The hierarchical Ni(OH)\textsubscript{2} monolayer hollow-sphere arrays also demonstrated a tunable optical transmission stop band in the visible-near-IR region from 455–1855 nm, depending on the size and fine structure of the hollow sphere (Fig. 23). Very interestingly, they unveiled a nearly incident-angle-independent position of the stop band, which 3D photonic crystals do not possess. This should be of great significance to applications in optical devices, photonic crystals, nanoscience, and nanotechnology.\textsuperscript{226}

2D ordered hollow sphere arrays have also been shown to be good candidates for the SERS-active substrates due to the periodic characteristics and the nano-sized structures. The hierarchically micro/nanostructured rough Au particle arrays exhibited a strong SERS effect using Rhodamine 6G as probe molecules.\textsuperscript{222} The SERS intensity at 1362 cm\textsuperscript{-1} for the porous Au nanostructured film was about 2.5 times higher than that for the Au/Ag-coated silica film, and the SERS performance of such ordered porous nanostructured films could be stable for at least 3 months. Hollow SnO\textsubscript{2} hemisphere arrays fabricated via sputtering thin films of SnO\textsubscript{2} onto PMMA colloidal templates on alumina or Si substrates displayed a three-fold enhancement in sensitivity to NO\textsubscript{2} relative to non-templated counterparts. This ratio comes close to the geometric enhancement in their surface area (compared to flat films), which stands at 3.6 for an ideal 2D hexagonal close packed array of hemispheres.\textsuperscript{227}

In addition, 2D structured porous films of SiO\textsubscript{2} hollow spheres on substrates prepared by a facile layer-by-layer dip-coating approach showed unique superhydrophilic and anti-fogging properties, attributable to both its surface roughness and surface porosity.\textsuperscript{228} The immediate water contact angle of this hollow sphere film was about 0°. The first water droplet spread flat in less than 0.033 s. When a control glass slide and a glass slide with superhydrophilic film after cooling at about -18 °C for 3 h were exposed to humid laboratory air (ca. 50% RH), the former glass fogged immediately and many dewdrops were observed on the glass surface. In contrast, the slide glass with the superhydrophilic film remained clear (Fig. 25).

### 5.3 Three-dimensional (3D) arrays

In addition to the above applications, inorganic hollow spheres can be self-assembled into 3D crystals, since 3D colloidal crystals have attracted great interest for their stability and potential applications in catalysis, anti-reflection coating, lithium ion batteries, and photonic materials such as optical filters, optical switches, and low-threshold lasers.\textsuperscript{229–232} For example, the 3D crystal film of TiO\textsubscript{2} hollow spheres exhibited higher photocatalytic activity compared to the
The hollow SiO₂ nanoparticles were LbL-assembled on both PMMA and glass substrates to produce anti-reflection (AR) coatings. Single-index AR coatings can be made with optimized AR performance at any wavelength between 300 and 650 nm. In this case, reflection near the targeted wavelength was reduced from 7 to 0% and transmission was increased from 92 to 97% (Fig. 26). Although 3D-ordered hollow sphere arrays should be relevant to many applications, there are still many difficulties in controlling their size and morphology and preventing agglomeration.

Interestingly, close-packed-array photonic crystals (PCs) of SiO₂ shells were fabricated via the shrinkage of SiO₂ shell/poly(N-isopropylacrylamide) (PNIPAm) core particles during solvent evaporation and calcination for core removal. Compared to dry SiO₂ shell PCs, the Bragg diffraction peak wavelength of SiO₂ shell PCs in water only increased 5% in refractive index. This showed that these SiO₂ shells were impervious to water because the process of making them resulted in a continuous shell of silica without holes (Fig. 27).  

6. Summary and outlook

This review highlights the most important synthetic methods and applications of inorganic hollow spheres. The relative advances in the synthesis and properties of these particles have paved the way to a huge range of new materials with many potential applications. In this article, we have reported selected examples of inorganic hollow spheres prepared either using template strategies against (i) polymeric, (ii) inorganic nonmetallic, (iii) metallic particles, (iv) soft compounds, or from template-free strategies. We have also reported the potential applications of 0D, 2D, and 3D arrays.

Templating against polymeric colloids and inorganic nonmetallic particles such as silica and carbon is incontrovertibly the most efficient and common strategy of fabricating inorganic hollow spherical micro/nanomaterials. This is due to the controllable morphology and uniform size of the hollow spheres and theoretical universality for various kinds of ceramic shells. Its complicated process is nonetheless unsatisfactory. In particular, removal of these templates by etching or calcination is not only time-consuming but can also cause collapse or deformation of the shell. Metallic template-based syntheses have been embraced by many researchers in recent years due to the lack of additional operating costs, such as functionalization and core template removal, but this technique is only used to prepare spheres from a few metals and metallic compounds.

The soft-template approach provides advantages such as easy template removal and efficient encapsulation of therapeutic and biologically active molecules. However, obtaining monodisperse size and spherical morphology is difficult because soft templates are usually thermodynamically unstable and can be influenced by factors such as the solvent polarity, pH value, and the ionic strength of the solution. Template-free strategies such as the Ostwald ripening process can overcome the demerits of template strategies,
and obviously is becoming one of the most useful methods. However, this strategy is only useful for the synthesis of hollow spheres from certain special compounds.

Inorganic hollow spheres have many potential applications in catalysts, lithium-ion batteries, biomedical materials, gas sensors, mini-reactors, and other tools. Recent studies indicate that the 2D and 3D arrays of some inorganic hollow spheres have preferable and even novel characteristics.

Many fabrication methods and their related hollowing mechanisms have been proposed over the past ten years, but each approach has its pros and cons. This in turn provides us important research opportunities. In particular, we believe that the following aspects should be paid more attention in the future research and development of inorganic hollow spheres:

(i) As there is no single method that works well for every situation, the exploration of synergistic features and interconnections of two or more methods will be very interesting. It is foreseeable that one will be able to prepare the desired inorganic hollow spheres with controllable composition and properties and even more complex hollow architectures. In particular, researchers should explore universal, simple, and scalable methodologies for the fabrication of various commercial-scale, high-quality inorganic hollow spheres.

(ii) The Kirkendall effect and Ostwald ripening process can work very well under circumstances that confound polymer and nonmetal template approaches. However, these methods provide only certain prototypes. More comprehensive investigations should be carried out into the mechanism and process by which hollow spheres are formed via the Kirkendall effect and Ostwald ripening process. This may allow the community to expand the scope of these methods.

(iii) More practical applications may be envisioned by the integration of two or more performances, such as superparamagnetism, fluorescence, spectrum selectivity, biocompatibility, photocatalysis, mechanical properties, electrical properties, stimulus response, and dispersibility in media into hollow spheres through the assembly of different inorganic and organic components.

(iv) Although the properties and applications of inorganic hollow spheres themselves have been widely studied, the investigations themselves are relatively new. More importantly, the properties and potential applications of 2D and 3D arrays of inorganic hollow spheres are still new ground. New and even unprecedented properties should be expected for both fundamental research and applications. For example, 2D arrays of semiconducting hollow spheres are promising candidates for the key sensing of elements in optoelectronic devices due to their high area coverage ratios and large surface-to-volume ratios. 3D arrays of alternative inorganic hollow spheres and solid particles may enhance the bandwidth and reflectivity, which has great potential in reflective mirrors for microlasers.

We hope that the general preparation procedures and principles of each method, the selected samples reviewed in this article, and our personal opinions can provide readers with the necessary background and ideas to develop deeper expertise and more effective fabrication methods. We are confident that more versatile and powerful methods of preparation of inorganic hollow spheres will be developed from both fundamental and practical viewpoints and that novel physicochemical properties and applications will be explored in the near future.

Acknowledgements

The National Natural Science Foundation of China (No. 21074023), National “863” Foundation, Science and Technology Foundation of Shanghai (0952nm01000, 10JC1401900), the innovative team of the Ministry of Education of China (IRT0911), and Shanghai Chenguang Foundation (10CG60) are thanked for their financial support.

Notes and references


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