Hollow particles as controlled small space to functionalize materials

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Molecules indicate a particular property by obeying a special characteristic in small space in some cases. It was discovered for a liquid phase such as decreasing the melting point in a nano-sized pore. A special phenomenon may also occur in the gas phase in a small space. To demonstrate this prediction, I have begun trying to fabricate a small space. A nano-sized hollow structure is very attractive for obtaining a small space. An inorganic template using inorganic particles is a facile technique to obtain hollow particles with various shapes, sizes, from nano to micron, and also different shell microstructures. This paper describes the sol–gel synthesis that is useful to form the shell structure of hollow particles and then how to control the particle structure using various templating routes. The hollow particles are used for the fabrication of air/solid composites with a controlled small space. These structure controls provide wide applications such as superior thermal insulation films, anti-corrosion films, and unexpected “easy-to-grip” volleyball coatings, etc. In addition to our achievements using hollow silica nanoparticles, the development of applications such as the lithium ion battery, biomedical products, catalysts, etc., will be outlined.

Key-words : Hollow particle, Inorganic template, Structure control, Shell microstructure, Small space

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1. Introduction

There is the possibility that a small space made from pores or hollow structures leads to special properties. The property is known as the frozen point decreasing in a small pore. Also, the micropore filling of a pore for gas adsorption is a special property of a small space. If a special property were initiated into a solid-state material, a new possibility of material design would become available. Both the pores and hollow structures are very attractive for material functionalization. This review paper deals with only hollow particles due to space limitations.

Many research studies in the last decade have been devoted to the development of preparing nano/micro-sized hollow particles.1–6 They have attracted tremendous interest because of their unique properties compared to other dense materials, for instance, a high specific surface area, low density, and excellent permeation and penetration abilities. With the aid of modern science, it is already common knowledge that exceptional properties may occur by downsizing the hollow particle from micro to nano-size without changing their chemical composition which can significantly affect the performance of the synthesized materials.5 In a typical process for applications, nano/micro-sized hollow particles are dispersed in a liquid medium which is generally been the basis for having a surprising array of material applications for technological scientific value. The functorialization of the nano/micro-sized hollow particles (with facile processing) can then extend the impact of the nano/micro-sized hollow particles that may generate a novel synthetic implication.

The hollow interior of the hollow particles is said to be the second-generation two-level structural micro/nano-material which exhibits a complex chemical composition, but relatively simple structures and hierarchically constructed that can show superior physico-chemical properties.7,8 Whereas, the third-generation nano/micro-sized hollow particles with multilevel porous shell wall structures or having a complex interior architecture, have also spurred interest in the field of nano-material science applications. Just for the purpose of discussion, the first generations are said to be a one-level structure with solid interiors (solid particles). In this case, this paper mainly focuses on the second and third generation micro/nano-material fabrications.

This review paper describes the simple preparation procedures for the fabrication of nano/micro-sized hollow particles with an eco-friendly approach. Due to the broad scope of this topic, all research studies about nano/micro-sized hollow particles in every eco-processing area cannot be treated in detail. Instead, we focused our major existing research on nano/micro-sized hollow particles by adding some current improvements for the preparation of silicate and other inorganic nano/micro-sized hollow particles. Many excellent articles have been published for the advancement of silicates and other inorganic nano/micro-sized hollow particles with respect to the architectural design, synthesis and bio-related applications such a drug release,7–9 but only a few deals with establishing a route that would be environmentally friendly. This is an important task because taking good care of our environment is a major concern, and if we can eliminate toxic waste byproducts, it would be good for humans. Also, many studies involving single-step or one-pot eco-synthesis approaches would become available, and developing an eco-large–scale synthesis of hollow particles would be a great challenge to eliminate environmental problems concerning the fabrication of hollow particles which would provide many commercial applications.

This review paper is organized as follows: First, the basic fundamental process which is the sol–gel method is assessed. This is followed by the general schematic approaches for nano/micro-sized hollow particles that our group has done and other significant reference papers about hollow particle preparations such as the solid-core template method, soft-core template (double emulsion method), and facile process like the ammoni-
hydrothermal approach. The common applications of nano/micro-sized hollow particles are then summarized. This kind of approach is primarily geared towards the sol–gel process; a wet-chemical technique usually used for the fabrication of nano/micro-sized hollow particles which can create both glassy and ceramic materials.

2. Fundamental of sol–gel process

Basically, the sol (or solution) gradually evolves towards the formation of a gel-like network containing both a liquid phase and solid phase. The precursors used in sol–gel processing consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides, such as aluminates, titanates and zirconates, are the most popular precursors because of their high reactivity towards water. The most widely used non-metal alkoxides are alkoxysilanes which is mostly discussed in this section, such as TEOS (tetraethoxysilane) and TMOS (tetramethoxysilane). Although ethyl groups are the most common alkoxide groups, methoxy, propoxy, butoxy and other long-chain hydrocarbon alkoxide groups are also used in alkoxysilanes. Organometallic compounds (metal alkoxides) are used in the sol–gel process either alone or in combination with non-metal alkoxides such as TEOS or alkoxysiloxanes. The basic structure or morphology of the solid phase can range anywhere from discrete colloidal particles to a continuous chain-like polymer network.10,11 A well-studied alkoxide, TEOS, whose chemical formula is given by Si(OC2H5)4 or Si(OR)4 where the alkyl group R = C2H5. These alkoxides are ideal chemical precursors for the sol–gel synthesis because they readily react with water. This reaction is called hydrolysis, because a hydroxyl ion becomes attached to the silicon atom.13 The process consists of a series of hydrolysis and condensation reactions of an alkoxide, which proceed according to the reaction scheme shown in Fig. 1. The alkoxysilanes are used as an example but all of the metal alkoxides similarly react. Wherein hydrolysis and condensation reactions of most metal alkoxides can be carried out without a catalyst because of the extremely fast rates of reaction, alkoxysilanes hydrolyze much more slowly, requiring the addition of either an acidic or basic catalyst. Hydrolysis is initiated by the addition of water to the silane solution under acidic, neutral, or basic conditions. Thus, the polymerization is associated with the formation of a dimensional network of siloxane Si–O–Si=Si bonds accompanied by the production of H2O and R–OH species.

By definition, condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build large silicon-containing molecules by the process of polymerization. Thus, a polymer is a huge molecule (or macromolecule) formed from hundreds or thousands of units called monomers. The number of bonds that a monomer can form is called its functionality. The polymerization of silicon alkoxide, for instance, can lead to the complex branching of the polymer, because of fully hydrolyzed monomeric Si(OH)4 is tetrafunctional (can branch or bond in 4 different directions). Alternatively, under certain conditions (e.g., low water concentration) fewer than 4 of the OR or OH groups (ligands) can be capable of condensation, so relatively little branching would occur. The mechanisms of hydrolysis and condensation, and the factors that bias the structure toward linear or branched structures are the most critical issues of sol–gel science and technology.10,11,13,14

Therefore, the sol–gel process has been frequently employed in coating the colloidal core-templates followed by forming nano/micro-sized hollow particles by removing the templates. This is a simple reaction that does not require unusual materials, catalysts or expensive deposition equipment. Likewise, sol–gel reactions do not employ extreme reaction conditions. The reactions can take place at room temperature and require only moderate temperatures to ‘cure’ the gel which can easily remove the excess water/alcohol that the reaction generates. Also, the properties of the nano/micro-sized hollow particles prepared using sol gel approaches can be easily modified by utilizing an organically modified alkoxide or a variable metalloid (for example, an alkoxysilicate instead of an alkoxysilane).

Hollow particles are typically obtained through self-assembly using surfactants because it provides superior control over the nucleation and crystal growth. However, it is not very popular because of its poor control over the phase purity and morphology.

Thereby, an alternative treatment of hollow particles is performed by a colloidal-template synthesis.3,15 In the template route, the inner diameter/shape of the hollow particles is only determined by the dimensions of the template type (organic, inorganic and biomolecules) that is used. These template syntheses are mostly divided into two parts, namely hard and soft-core template syntheses, in fabricating hollow particles with homogeneous, dense shell wall layers. The next section discusses the preparation of the nano/micro-sized hollow particles with some examples of inorganic hollow particles via the solid-core template, soft-core template (double emulsion method) and facile route like the ammonia-hydrothermal approach.

3. Fabrication and common approaches for forming hollow inorganic/silicates particles

Extensive studies have been done to evaluate the ideal and convenient synthesis for nano/micro-sized hollow particles especially under mild eco-conditions. These common features, such as the solid template, soft template and ammonia-hydrothermal approach, are basically discussed in this paper, especially regarding our recent eco-preparation of nano/micro-sized hollow particles.

3.1 Solid-core template method

A template in a colloid core-particle is probably an effective and universal method for the preparation of hollow particles, especially if a narrow size distribution, for example, self-assembly and photonic crystals, is required.12,13,21,22,23 In the solid-template assisted synthesis, poly(styrene acrylic acid), poly(styrene (PS) latex, silica spheres and calcium carbonate (CaCO3)
particles are commonly used as colloidal core-templates because they are readily available in a wide range of sizes. Technically, an inorganic precursor (metal or non-metal alkoxide) is coated over the core-template either by a physical or chemical reaction to provide an intermediate, called the core–shell, that may contain an organic–inorganic or inorganic–inorganic core shell structure. The core-template particles were subsequently removed by selective dissolution in an appropriate solvent or by calcination at elevated temperature in air to generate the nano/micro-sized hollow particles. The majority of these nano/micro-sized hollow particles are formed on the outer surfaces of the core-templates through a sol–gel, hydrothermal treatment, layer-by-layer or direct chemical deposition.

As an example, Tissot et al. worked on the synthesis of composite particles with PS as the core and silicate as the shell via an ammonia-catalyzed sol–gel process. Hollow silica spheres were obtained by the subsequent step of thermal degradation of the PS cores at 600°C. Similarly, Zhong et al. prepared titania-coated PS beads by templating the sol–gel precursor solution against crystalline PS beads. This was immersed in toluene to dissolve the PS template to obtain the mesoscale titanina hollow spheres. The group of Imhof et al. reported a one-step method to coat cationic polystyrene spheres with titania precipitated during the hydrolysis of a titanium alkoxide. This core particle turned into titanina hollow spheres by dissolution of the polystyrene cores in a suspension or by calcination of the dried particles in a furnace. Also, by means of a plasma technique, the surfaces of the monodispersed PS colloids have been modified with hydroxyl groups. The research studies done by Li et al. used these surface-modified PS spheres as a sacrificial template to fabricate silica-coated PS and titania-coated PS composites by co-condensation between the hydroxyl groups with TEOS and TIPP [titanium(IV) isopropoxide] in a sol–gel process, respectively. The hollow silica spheres and titanina hollow spheres can be generated by the subsequent removal of the PS core using tetrahydrofuran. Although the above mentioned research studies were very interesting, the preparation processes seem to be time-consuming, expensive and not eco-friendly.

In this respect, simple eco-friendly step processes are needed for the synthesis of nano/micro-sized hollow particles. Our group has successfully reported this via a template sol–gel process by utilizing and removing the nano-core CaCO₃ particles through dissolution by acid treatment followed by the formation of nanosize hollow silica particles. In this method, an aqueous ammonia solution was used as the catalyst and medium. The naturally positively charged CaCO₃ nanoparticles were dispersed in an ethanol (EtOH) solution followed by sonication for 10 min. This ensures the generation of a silicate sol from the hydrolysis and the condensation of TEOS. This is rapidly captured by the CaCO₃ particles via an electrostatic interaction in an aqueous ammonia solution either at room or elevated temperature. Under acid conditions, the CaCO₃ particles were subsequently “dissolved” and even subsequently to directly form the nano hollow silica particles, as shown in Fig. 2. The formation of the inorganic silicate shells and the dissolution of the core template particle occurred during the acid dissolution; neither additional toxic chemicals nor a calcination process was used to remove the CaCO₃ core.

Based on this concept, we were able to utilize other inorganic core templates, such as colloidal calcium rich-hydroxyapatite nanoparticles and micro-size CaCO₃ particles, for the formation of anisotropic nano to micro-sized hollow silicate particles. These kinds of core-templates are recyclable and do not need a sophisticated mechanism to dissolve the core-templates; a mild concentration of acid is needed to dissolve the core templates. This is a facile eco-route for synthesizing a nano-/micro-size hollow silicate particle with a tunable shell thickness and unique anisotropic hollow shape by employing inorganic particles (calcium rich-hydroxyapatite and calcium carbonate) as the template along with the sol gel method. The results showed a relatively stable anisotropic hollow shape with a uniform silicate shell wall thickness. In addition, at a relatively high concentration of the silicate precursor (TEOS), the shell thickness and surface roughness increased. As expected, the unique anisotropic shape and size of the ano-/micro-size hollow silicate particles depend on the type of inorganic template used, which was clearly shown in Fig. 3.

With a solid-core template, refilling the hollow interior with functional species or in-situ encapsulations of guest molecules during formation of the shells, though possible, is still required. Thereby, fabricating a macroporous shell wall of hollow microsphere particles is a remedy, but it is still difficult to do. These difficulties have prompted us to propose a more simple approach for producing hollow microsphere particles with a macroporous shell that can easily encapsulate and release guest species. For instance, templating against a soft-core (liquid or gaseous) template has been significant especially for the development of the emulsion method. The next section will discuss the essential concept of a soft-core template and the basic concept of the double emulsion method. The next section re-established the potential of the soft template method to create interior spaces and for creating a functional shell structure through a one-pot synthesis.

3.2 Soft-core template method

The soft-core template synthesis is another simple and general method for obtaining hollow particles. Some hollow particles with a nanometer to micrometer diameter have been successfully fabricated using the double emulsion process usually composed of water-in-oil-in-water (W₁/O/W₂). Generally, the (W₁/O/W₂) double-emulsion system consists of individual oil globules that contain smaller droplets of the
internal aqueous phase and are dispersed in an external aqueous phase. Due to their special internal structure, double emulsions have found significant applications in many areas, such as pharmaceuticals, foods, cosmetics and separation.41–45) Double emulsions are typically formed through two-emulsification processes, i.e., by first emulsifying the inner droplets in the middle fluid, and then by undertaking a second emulsification step for the dispersion.8),44),45)

To develop simple, effective, controllable, and environmentally benign methods to form hollow microspheres by double emulsions remains challenging and is of great importance. In this section, the researcher utilized the results of Fujiwara to fabricate macroporous hollow silicate microspheres with the addition of a water soluble polymer and some innovative pressure filtration for faster processing. This method has some unusual advantages, such as, it is very simple, green, and the formation of double emulsions can control the micro-size through the emulsion rate.

Based on Fujiwara et al.40),46),47) for the hollow silicate microspheres, the reaction of sodium silicate with a precipitant is utilized. The W1/O emulsion is made of W1 (consists of water and sodium silicate) and O (oil phase) with a surfactant for stabilizing the emulsion. W1/O is then added to another aqueous solution of a precipitant W2, thus forming the W1/O/W2 emulsion system. During the elimination of the oil phase (O) between the two water phases (W1 and W2), these two aqueous solutions are mixed to form the silica precipitate along the emulsion interface. The sodium silicate of W1 provided the interfaces forming the silicate particles as the precipitate. After complete formation of the precipitate at the interfaces, all the sodium silicate is consumed and the inside of the microcapsule was filled with only water. This water can be readily removed by a drying treatment thru the pores of the silica shell. Finally, the hollow silicate microspheres are obtained. With this process, no other process to remove the core compound is necessary.

With some innovations, a water-soluble polymer (sodium polyacrylate) was added to the aqueous solution of W1, and denoted W1P-X. Thereby, the water1-polymer/oil/water2 (W1P-X/O/W2) emulsion system was formed. The controlled parameters included the emulsification rotational speed constant, fixed volume ratio, fixed surfactant ratio, modified (set-up) pressurized by N2 filtration and calcination. The formed hollow silicate microspheres with a meso/macroporous shell48 were then successfully prepared. The prepared hollow silicate microspheres exhibited unique three-dimensional hierarchical architectures as shown in the SEM images of Fig. 4 along with a conceptual scheme.

Most of the reported double emulsions are macro-emulsions of which the inner and outer droplets are both of micron scale. Recently, Deming et al.49),50) reported a nano-scale double emulsion, in which both the oil droplet and internal aqueous droplet are of nanometer size. An ultrasonic and micro-fluidic homogenization was utilized to induce the formation of the nanoscale double emulsion, which was stabilized by specially designed amphiphilic diblock copolymer surfactants. This opened up the way to prepare a double nano-emulsion. Another approach, such as using a micro-fluidic device51–53) and electric field,54),55) were also developed to make the double emulsions.

The stability of the shell wall is generally the most common problem especially for the template-sol-gel process. This is due to the fact that the template sol–gel process involves an uncontrollable fast hydrolysis and condensation, resulting in the formation of an unstable shell wall of amorphous inorganic oxides.56),57) Calcination of the core–shell is commonly utilized for this problem to stabilize the shell walls, and above 500°C is usually required to transform the amorphous oxides into crystalline ones. On the other hand, thermal calcinations at high temperature would seriously affect the particle size, structure and even result in a collapse of the hollow structure.3),15),24) Hence, the next section briefly discusses our innovative method via an ammonia-hydrothermal approach which is one way to eliminate this problem and enhance the stability of the shell wall.

3.3 Ammonia-hydrothermal-approach

Hollow particles of crystalline metal oxides can be synthesized in a simple one-pot process via a hydrothermal approach. By adding metal salts directly to the carbohydrate solutions in water, followed by a hydrothermal treatment and then calcination, hollow particles of various metal oxides, such as Fe2O3, Ni2O3, Co3O4, CeO2, MgO, and CuO, were obtained.58),59) The ammonia-hydrothermal approach provides a facile and convenient method for partial crystallization of the dissolved precursor ions that can refine a structural ordering with the possibility of pore-size uniformity. For instance, the ammonia-hydrothermal approach can intensify the formation of a stronger electrostatic interaction (Si–O–Ca) from the weaker electrostatic contact composed of a silicate wall-calcium hydroxide forming a thin semi-amorphous calcium silicate hydrate shell wall which is schematically illustrated in Fig. 5(c). This treatment resulted in an increase in both the thermal and hydrothermal stabilities. Recently, our research group introduced the ammonia-hydrothermal approach to improve the stability of the template nano hollow silica particles using CaCO3 nanoparticles while preserv-
The key factors involved in this treatment include the hydrothermal temperature and aging time. At elevated temperature (120°C), hollow calcium silicate hydrate nanoparticles are then formed. This simple process for the formation of a unique hollow calcium silicate hydrate nanoparticle (particle size is less than 100 nm) was successfully prepared via the hydrolysis and condensation of TEOS, ammonia water (NH₄OH) and inorganic CaCO₃ as the template and then the ammonia-hydrothermal approach. To appreciate the formation of hollow calcium silicate hydrate nanoparticles, the temperature reaction was varied at room temperature, 90 and 120°C. At each reaction temperature the aging time was then varied for 3, 9, 24 h and 10 days.

Figure 5 shows the typical XRD pattern of the semi-amorphous hollow calcium silicate hydrate nanoparticles. The additional sharp peak at ~18.1° (2θ) corresponds to the overlapped diffractions of Ca(OH)₂ and low crystalline calcium silicate hydrate. No visual peaks (amorphous phase) were observed for the samples synthesized at room temperature and 90°C. Hence, the semi-amorphous calcium silicate hydrate with Ca(OH)₂ may be contained in the shell wall of the nano-size hollow particles. Thus, we successfully developed a simple-direct process via the ammonia-hydrothermal approach, followed by acid etching; the formed hollow calcium silicate hydrate nanoparticles ranged from 60 to 100 nm. In future studies, we will further functionalize this to allow more dispersed particles and fabricate hollow hybrid bio-glass particles. Due to its exceptional physico-chemical properties, it may find wide use for nano-cement materials, nano-biomedical materials and coating additives as thermal insulating materials.

4. Developing a facile route and eco-innovative method for hollow silicate particles

Many significant achievements have been made in this area as reviewed in this paper. Nevertheless, there are still some challenges that need to be fulfilled. The syntheses of complicated structures such as controlling the size/shape, sphere-in-ellipsoidal and cage-like surfaces for hollow silicate particles are just in their initial stages. It is anticipated that solid template and soft template/template-free techniques will play a greater role in the future to achieve the eco-fabrication of complicated structures. As already mentioned, the functional use of hollow structures is closely correlated with their morphological properties such as the exterior shape, the interior space, and the shell structure. In the proposed inorganic template method, the shape of the obtained hollow particle can be a copy of the template. By choosing different crystal templates (vaterite, calcite, and aragonite), hollow particles with different morphologies such as spherical, cubic, and tube can be prepared. The size of the CaCO₃ is controllable on a nano-scale, therefore, the size of the hollow particles can be controlled. On the other hand, considering the affinity between CaCO₃ and the silica coating can provide a unique shell structure as a “skeleton” which has twelve cubic silica frames with six square windows as shown in Fig. 6. When CaCO₃ adsorbed with an organic acid was used as the template and dispersed in a poor solvent for the acid, silanol as hydrolyzed TEOS and the organic acid undergo adsorption on the CaCO₃ surface. This exchange adsorption could occur only on the edge and vertex of the cubic CaCO₃ depending on the template size, acidity strength of the silanol compared to the organic acid, and poor dissolving power of the solvent for the organic acid. The sol–gel reacting conditions can provide different silica frame widths and thicknesses and the obtained structure will be utilized in many application fields.

To increase the permeability and create the ability to store biomacromolecules and nanoparticles, it is desirable to build nano/meso/macro-holes on the shells of inorganic hollow structures, but proper proportioning is needed in order not to decrease the mechanical strength of the hollow silicate particles. Thus, simultaneous achievement of a robust hollow architecture and improved large molecule permeability in an environmentally friendly approach still remains a challenge.

Previously, the surface characterization of hollow silica nanoparticles was based on the gas adsorption isotherm. The shell
characteristics were estimated from the adsorption isotherm and Brunauer–Emmett–Teller (BET) specific surface area. From the adsorption isotherm of nitrogen gas on the hollow particles, there are no mesopores in the shell wall. There is a small number of micropores in the shell wall by which nitrogen gas can penetrate from the outside to the inside. Therefore, the specific surface area for the hollow particles would be the sum of both surfaces of the shell wall. In addition, the surface structure of the hollow silica nanoparticles was characterized in order to compare it with that of dense nanoparticles using the gas adsorption isotherm. It can be estimated from the water vapor adsorption that surface free silanol groups on the hollow particles have the same characteristics as on the dense particles.35)

Based on these results, definition of the shell microstructure as the apparent shell density has been proposed. Three typical types of hollow silica nanoparticles were selected using transmission electron microscopy (TEM) observations such as (A) the thickness of the silica shell is relatively thin and the spherical shape of the stacked particulates is clearly identified in the shell, (B) the thickness of the silica shell has the same thickness as the type A, but the shape of the stacked particulates is identified as half-round, and (C) the thickness of the silica shell is greater and the stacked particulates are not recognized in the shell as shown in the illustration of Fig. 7. The apparent shell density of the hollow particles was defined using the BET specific surface area and shell thickness measured by the TEM images. Based on the graph in Fig. 7, it appeared between 1.4 and 2.2 g/cm³ and increased in the order of type A, B, and C. The experimental conditions of the suspension pH and reaction time could lead to a major difference in their apparent shell density even though they have similar shell microstructures estimated by the TEM.69)

For this reason, the nano/micro-sized hollow particles are interesting not only because of their superior interior void structures, but also for a few more important reasons as previously mentioned. Generally, the successful creation of these micro/nanoscale materials themselves is a significant representation of the advancement in modern synthetic technology. Thus, it is very helpful to deepen the understanding of the mechanism for the formation of the micro/nanostructure hollow silicate particles, which will encourage the designing of more novel structures. Also, compared to the bulk micro/nanomaterial, the micro/nanoscale hollow interior spaces with multiphase interfaces might provide a number of variations in the physicochemical properties, reinforce interfacial effects and control the local chemical microenvironment that can produce many potential applications.3),7),8),70)

5. Potential applications of hollow inorganic/silicate particles

Since nano/micro-sized hollow particles possess characteristics, such as a low density, high surface-to-volume ratio, low coefficient of thermal expansion and refractive index, makes them attractive for widespread potential applications ranging from chemical reactors, drug delivery, catalyst support, antireflection surface coatings, lightweight materials, rechargeable batteries and various new application fields.71),72) Our group developed a thermal insulation film in which hollow nanoparticles were dispersed in a polymer film. The thermal conductivity of the composite film was 0.025 W/mK and the transparency in the visible wavelength range is high enough for use as a window film. Excellent properties were achieved by adjustment of the shell microstructure and particle dispersibility in the film.73) While an anti-corrosion coating for aluminum products was produced on a commercial basis using the low electric insulation of the hollow nanoparticles. Unlike the conventional anti-corrosion coating, it is said to be an environmental friendly material due to being chrome-free, just only one-tenth the thickness is needed, etc. During the research of the coating, a distinguishing texture appeared on some coatings. Surprisingly, an excellent anti-slipping performance occurred when the coating was applied on a volleyball’s leather surface. The volleyball players feel the effect during a high impact spike and receiving even with sweaty hands when the outer cover of the ball is coated by the hollow silica nanoparticles dispersed in a resin. This easy-to-grip volleyball received official recognition by the Fédération International de Volleyball (FIVB) as shown in Fig. 8. It was first introduced in the Beijing summer Olympic game in 2008 and is subsequently used in various megaevents such as the world cup competition. FIVB has extended and agreed to use this as the official volleyball in the London summer Olympic game in 2012. Even today, this ball is used in all official games. The effect of anti-slippering is a one of the mysterious effects caused by the hollow nano-sized particles and appeared in Nature.

In the following sections, other possible applications using hollow nanoparticles will be described.
5.1 For use in a lithium-ion battery

The macroporous hollow silicate particle is a fine example of a good electrode material for lithium ions.\(^\text{75-77}\) Fundamentally, silicon (Si) is believed to have the highest known lithium storage capacity of 4200 mA h g\(^{-1}\), which makes it very attractive as a negative electrode material for the lithium-ion battery. However, Si nanoparticles-based anodes are often found to have a less than satisfactory cycle life compared to other materials (e.g., Sn-based anodes) due to the ultrahigh (>300%) volume changes during the Li-Si alloying/dealloying processes. Recently, modified nestlike nanosilica hollow particles exhibited a much improved cycle life and rate capacity. These observations clearly verified the advantages of the nano/micro-sized hollow particles (nestlike Si hollow morphology)\(^\text{77,79-78}\) as compared to solid micro/nanoparticles of the same composition.

5.2 For Biomedical use

With extensive development of the nano/micro-sized hollow particles synthesis, it significantly helps to optimize the optical properties and superparamagnetic behavior.\(^\text{9,24,57,73,76}\) As already mentioned, nano/micro-sized hollow particles are good for storage and charge carriers.\(^\text{40,77-82}\) Silicate particles are accepted materials for drug delivery due to their non-toxicity. Therefore, hollow silicate particles have been extensively studied for biomedical applications because of its biocompatibility and well-established in terms of bioconjugation methods using silane chemistry.\(^\text{9,81,83-85}\) Generally, it has the ability for the adsorption and release of sensitive materials, such as fluorescent and drug markers, aside from its well-known catalytic applications.\(^\text{9,70,72,73}\) Moreover, drug molecules can be loaded into the cavity and on the surface of the hollow structure and typically release over living cells wherein it can control the rate of drug release by altering the pore dimensions and wall structures.\(^\text{9,24,41,73,86}\) It was significantly demonstrated that drug molecules can be stably encapsulated during the synthesis of hollow silicate particles and the release can be triggered by ultrasound or controlling the pH.\(^\text{81,87,88}\)

5.3 For waste treatment use

Wastewater is universally acknowledged as a health and environmental problem. The complexity of the wastewater composition has led to an intricate treatment process with high costs, which are impractical given the large volumes of waste produced by both domestic use and industry. Development of an effective and cheap decontamination method is urgently needed. One remedy is using hollow silicate particles as a conventional adopted method for adsorption and ion exchange. Some current studies have confirmed that these as prepared hollow silicate particles acted as an effective adsorbent; they can remove organic pollutants and heavy metal ions from wastewater.\(^\text{90-91}\)

5.4 For catalysis or sensor use

Inorganic/silicate porous particles have been extensively used in catalysis; the scientific curiosity of these materials has led to numerous applications. By only manipulating the particle range from nano- to microscale, one can directly provide a promising type of structure for enhancing their catalytic ability. The high surface-to-volume ratio enhances the fraction of low coordination metal sites (e.g., vertices, edges and kinks) and promotes the adsorption of reactants. The accessible micro/meso/macropores in the hollow surfaces afford ample channels between the inner and outer surfaces, which facilitate the diffusion of solvent and reactants, thus accelerates the chemical reactions.\(^\text{92}\) Recently, a unique structure, in which the shell can effectively prevent the core particles from aggregation, of hollow spheres incorporated with catalytic metal nanoparticles (metal nanoparticles yolk/shell particles), has potential applications as nanoreactors for catalysis.\(^\text{93,94}\) Taking the Au/SiO\(_2\) yolk/shell particles as an example, they have been widely tested for the catalytic reaction of p-nitrophenol by NaBH\(_4\).\(^\text{95}\) In addition to their catalytic property, the confined growth and Ostwald ripening of Au nanoparticles in hollow silicate particles have also been reported.\(^\text{95,96}\) The photocatalytic activity is greatly enhanced by creating mesoporous silicates in the shell walls. Most importantly, the confined reaction on the surface of the core nanoparticles, or transformation of the nanoparticles themselves, provides an alternative mode for producing many other functional yolk/shell particles.

On the other hand, the high surface areas of the nano/micro-sized hollow particles are also an advantage for chemical/gas sensing. The hollow silicate particles provide a facile light guide for a quantum cascade laser over several meters and, hence, can be used for remote gas sensing or IR light delivery in medical applications.\(^\text{93-99}\) Chemical/gas sensors are also widely used for industrial process control and are experiencing growing use in security applications.\(^\text{100,101}\) Sensing with these materials is performed through measurements of the changes in electrical conductance produced by the adsorption–desorption of a targeted analyte on the oxide surfaces.

6. Summary

Considerable eco-synthesis of nano/micro-sized hollow particles has been significantly made over this past decade. In this review paper, the eco-synthetic approach for the fabrication of micro/nano-size porous HSP briefly summarized the basic concept based on the actual results done especially in the following areas: (1) core-templating (using nano-size CaHAp and micro-size CaCO\(_3\) particles); (2) double emulsion method (using water soluble polymer as an additive for (W\(_1\)/O/W\(_2\)); and (3) ammonia-hydrothermal templating (using coreshell-CaCO\(_3\)/SiO\(_2\) nanoparticles for fabricating HCSHNP). This review is likely to contribute/re-evaluate the fabrication of HSP, which presents a simple, innovative way and an eco-friendly process for the formation of nano-/micro-sized hollow particles.

Evidently, the advantage of a template using (solid) CaCO\(_3\) particles and CaHAp are possibly the greenest approach, clearly effective, and the most facile technique for synthesizing nano/micro-sized hollow particles. Aside from the fact that CaCO\(_3\) or
CaHAp particles are technically abundant in nature and a low cost material, they generally require no or minimal addition of surface functionalization, and shell formation is guaranteed by chemical reactions. However, the general disadvantages of this approach rely on achieving high product yields from this simple synthesis process, difficulty in forming a uniform coating around surfaces with large variations in curvature and lack of structural robustness of the shells upon template removal. However, these difficulties can be partly overcome by monitoring the acid concentration during acid etching, use of a surfactant and exposing the core–shell particles through a hydrothermal approach for structural stability.

Regarding the double emulsion approach (W1/O/W2) for fabricating macroporous hollow microspheres, a key advantage of using the double emulsion method for the preparation of the macroporous hollow microspheres is that the core removal stage is very easily eliminated. The liquid template, i.e. the liquid cores of the double emulsion, has a low parental toxicity because of using a water-soluble polymer. However, the relatively low stability and the poly-dispersion of the double emulsion approach may limit their application. Controlling the microspheres, uniformity, and macroporous distribution into the shell still remain a challenge. Moreover, the water-soluble polymer cannot be easily removed from the shell, and liquid removal (W1) is an energy-intensive process. However, these problems can be partly overcome by calcination, pressure-filtration and controlling/monitoring the emulsion speed rate.

Based on our present results for the fabrication of nano/micro-sized hollow particles, we offer an innovative method for the eco-synthetic strategy to form unique nano/micro-sized hollow particles with stable shell wall pore systems and also provide a further understanding for the future mechanism of composite hollow materials which can be further explained through extensive research studies.

The core-template approach can be easily implemented. However, the capability of constructing complicated structures, such as macro-through-holes connecting the inner and outer spaces of hollow structures, is limited by the availability of a template. As an alternative, it is important to develop a range of comprehensive template-free methods, confidently having the same flexibility as the existing template-assisted techniques, to meet new technological requirements. Hopefully, based on our innovative processes; another researcher may be able to develop and synthesize hollow particles with a more complicated structure using a simple eco-approach.

Finally, based on these findings, it is concluded that an eco-friendly approach in the fabricating of nano/micro-sized hollow particles can be done. In general, by controlling the parameters, one can enhance the surface morphology, porosity of the shell and stability of the hollow silicate particles. The insights obtained from this non-toxic alternative mechanism will allow other researchers to gain better control of the hollow silicate particles especially in exploring the dispersion of the hollow silicate particles. We are hopeful that a more versatile and powerful eco-method for preparing hollow silicate particles will be developed from both fundamental and practical viewpoints and develop more novel physicochemical properties. Thus, these several eco-techniques presented in this review provide a good foundation for the eco-synthesis of nano/micro-sized hollow particles, especially for the template and double emulsion approach, and applications will be explored in the near future.

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