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無機中空粒子の合成とその応用
―工学倫理の制約について―

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Application and Synthesis of Inorganic Hollow Particles

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近年，ナノからミクロンサイズの中空粒子の合成とその応用に強い関心が集まっている。特に，無機中空粒子は製紙・ドラッグデリバリー・光触媒・触媒などの幅広い分野で応用されている。その中空粒子の合成方法は２つのカテゴリーに分類される。１つはテンプレート法であり，有機ビーズテンプレート法，炭酸カルシウムテンプレート法，エマルジョンテンプレート法，そして界面活性剤テンプレート法などがあげられる。もう１つは，通常装置を必要とする噴霧熱分解法や静電噴霧法がある。本報では無機中空粒子の合成とその応用について我々の研究も含めて概説した。

Inorganic hollow particles are important fillers in the fields of papermaking, dyes, cosmetics and so on. Some hollow shells have been found extensive applications in catalysis, separations technology, drug delivery, optics, electronics, chemistry and coating system. Recently, many methods have been developed to prepare hollow particles. The applications and synthetic methods of inorganic hollow particles were reviewed in this paper. In the last part of this paper, the original work of our group has been summed up. [Received February 14, Accepted February 21, 2005]

1 Introduction

In recent years, there has been intense interest in the fabrication of micrometer- and nanometer-sized hollow particles. These hollow particles often exhibit special properties that are substantially different from dense particles, such as low density, large surface area, stability and surface permeability. Hollow oxide particles have been widely used for lightweight and thermally insulating fillers[1], composite materials[2], dyes and cosmetics[3]. Some hollow inorganic shells with controlled meso- and macro-porosity might find uses in catalysis, separations technology[4], capsule agents for drug delivery and protecting sensitive agents such as enzymes and proteins[5]. Besides, optically hollow shells have extensive applications in the fields of optics, electronics, chemistry and coating system due to a large refractive index contrast between the core and shell materials and can be used in photonic band gap materials, wavelength selective film and light scattering coating[6].

2 Applications

The followings are some applications of hollow particles.

2.1 Papermaking

One of the disadvantages of recycled paper when compared to paper from virgin pulp is difficulty to gain high brightness. To improve brightness, papermakers make efforts to develop recycling process such as introducing a strong surfactant in flotation and intensive bleaching. But, these process demand more water and energy, causing adversity to environment. Another possible idea is to hide gray appearance with an efficient coating or internal loading for high opacity. Hollow spheres made of calcium carbonate could be suitable for this purpose because hollow structure scatters more light result-ing in higher brightness and opacity.

Toshiharu Enomae and Koji Tsujino[7] have reported the preparation of spherical particles made of calcium carbonate by the interfacial reaction method[8]. When a potassium carbonate aqueous solution/benzene emulsion at a W/O ratio of 3:7 was poured in a sufficient volume of calcium chloride solution, spherical and sometimes hollow particles of calcium carbonate developed, maintaining the shape of emulsified droplets. The surfactant concentration and emulsifying conditions in dispersion and homogenization determined particles shape, size and distribution. Crystallographically, a portion of them was in vaterite form and the rest of it was in calcite form. When closely observed in a scanning electron microscope, individual particles appeared to have a rough surface, packed with fine primary particles 50nm in diameter. Prepared spherical particles were tried to be applied to papermaking as a filler and were compared with some kinds of ground calcium carbonate that are all of the commercial grade and of a similar particles size. Spherical particles were observed to disperse evenly while there were, though rarely, large particles 10 um in diameter for the commercial calcium carbonate, as shown in fig.1.

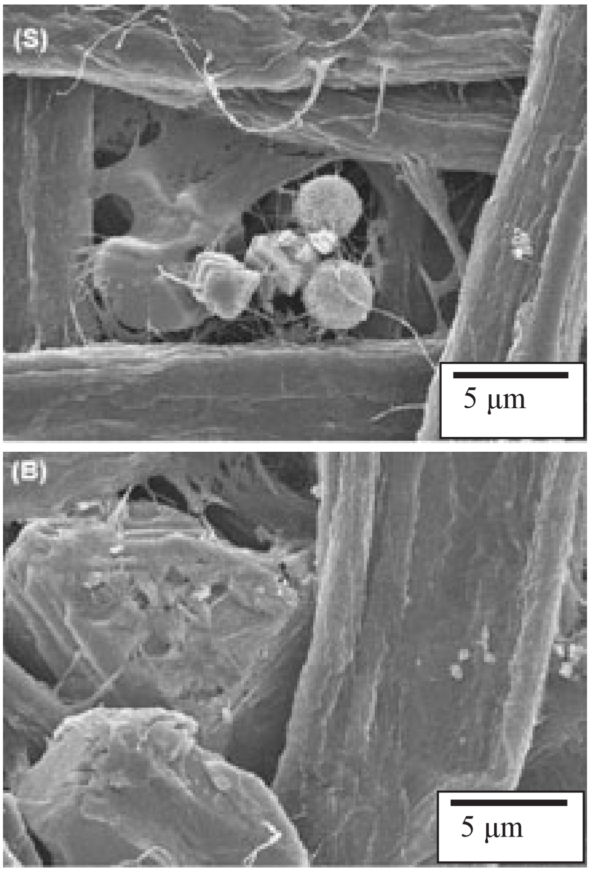

Fig. 1 SEM of a surface of a handsheet loaded with spherical particles (S) and ground calcium carbonate (B)

The density of paper loaded with the spherical particles was lower than that of the unloaded paper. This is often the case with filler loading because of acting as obstruction to interfiber bonding. The spherical particles increased surface smoothness presumably because the spherical particle trended to align with a flat surface due to their shape and no irregularly large particles protruding above the surface. The specific light scattering coefficient also increased with the spherical particles due to their porous structure. This finding suggests that the spherical particles are promising for coating use although attention must be paid to coating rheology. Besides, the possible thermal insulation due to the hollow structure is a unique feature to potentially enhance thermal wax-transfer printing. It was found that more addition of spherical hollow particles provided a larger area of wax ink transfer because efficient thermal insulation due to the porous structure maintained the temperature of the heated head and gave high ratios of wax ink transfer from ribbon to paper.

2.2 Drug deliveries

Silica is an important drug delivery media because its surface is rich in surface silanol groups that can easily react with alcohol and silane coupling agents to produce dispersions that are not only stable in non-aqueous solvents but also provide the ideal anchorage for covalent bounding of specific ligands. In addition, the silica surface confers high stability to suspensions of the particles at high volume fractions, change in pH or electrolyte concentration[9]

Jian Feng Chen et al.[10] prepared porous hollow silica nanoparticles by using $CaCO_3$ nano-particles as the inorganic template. The hollow particles were uniform spherical particles with a diameter of 60-70nm, wall thickness of approximately 10nm and a specific surface area of 867 m^2/g. The as-synthesized hollow particles were subsequently employed as drug carrier to investigate *in vitro* release behavior of cefradine in simulated body fluid. The preparation of drug carrying is illustrated as figure 2.

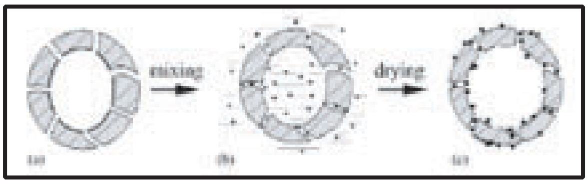

Fig. 2 Preparation of drug carrying for porous hollow calcium carbonate particles.
(a) hollow particles;
(b) suspension of cefradine and hollow particles;
(c) cefradine entrapped in hollow particles

First, cefradine (2.3% aq solution) and the as-synthesized hollow particles were mixed in a suspension with the weight ratio of cefradine/particles = 2:1, which was stirred vigorously for over 30h. After rinsed with acetone to remove unentrapped cefradine, the powder with the entrapped drug was dried in vacuum condition at 40 ℃ for 3h. *In vitro* release of cefradine was performed by immersing the prepared powder in simulated body fluid (SBF 0.1mol/l HCl solution), which was stirred at 100rpm and maintained at 25 ℃ via a thermostatic water bath. The aim of stirring was to ensure the uniform distribution of the drug molecules released into the solution. The release ratio of cefradine from powder was calculated by examining the concentration of cefradine in SBF at different time to evaluate the delayed release effects of cefadine entrapped in the hollow particles.

The vitro release of cefradine from the hollow carrier was depicted in Fig.3.

The release profile of cefradine could be divided into three stages roughly. The first stage was a rapid release of cefradine which reached near 74% within the initial 20 minutes. It was due to the delivery of the drug adsorbed on the surface of powder. The second stage saw a slow increase of cefradine release from 74% to near 82% within 10h, which might be explained as the release of the drug absorbed between the particles and entrapped in the pore channel of particles. The final stage reached a plateau where the release of cefradine had an insignificant increase from 10 to 12h. This might arise from the release of cefradine from the inside hollow part of carrier and can last a comparatively long time, leading to a delayed release of cefradine.

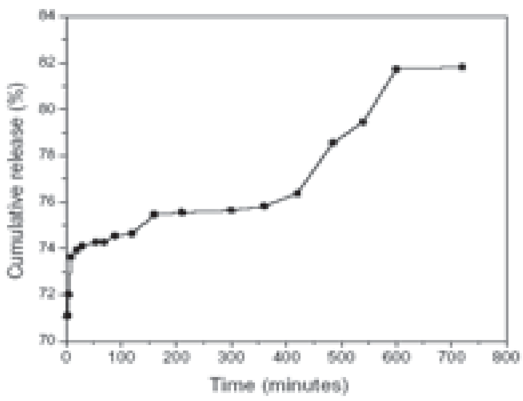

Fig. 3 In vitro release profile of cefradine from hollow particles

Recently, the use of magnetic particle for the delivery of drugs or antibodies to the organs or tissues altered by disease has become an attractive field of research. The process of drug localization using magnetic delivery system is based on the competition between force exerted on the particles by flood compartment and magnetic force generated from the magnet, i.e. applied field. When the magnetic force exceed the linear blood flow rates in arteries or capillaries, the magnetic particles are retained at the target site and maybe internalized by the endothelial cells of the target tissue. Tartaj P. et al.[11] have reported the preparation of silica coated Fe_2O_3 hollow spherical particles with an average size of 150nm by aerosol pyrolysis of methanol solution containing iron ammonium citrate and tetraethoxysilane (TEOS) at a total salt concentration of 0.25 M. It is worth mentioning that the small particles size of the composite renders these particles a potential candidate for their use in *in vitro* application.

2.3 Photocatalysis

Titanium dioxide (TiO_2) is a promising oxide that are able to degrade many kinds of organic pollutants in water with the production of hydrogen by photocatalysis. Although titania has been intesively investigated, its application in photocatalysis is limited because of its low efficiency in energy conversion. To enhance the efficiency, the absorption spectrum of titania is expected to extend to the visible range. Some researchers[12, 13] found that the hollow titania particle has a smaller band gap and obvious absorption shift towards longer wavelength. Fig.4[12] are the diffuse reflectance spectra of hollow titania which was prepared by surfactant-assisted templating method. The onset wavelength (λ_{onset}) of the spectra recorded from anatase is about

420nm, while the λ_{onset} of the hollow titania shift toward longer wavelength region. The effective band gap can be derived from the spectra by defining the energy necessary to create an electron (e^-) and hole (h^+) pair, and the excited electron-hole pair forms a bound state, i. e., Wannier exciton. The band gaps estimated from the spectra in Fig.4 give an evident reduction of the band gap for hollow titania compared with anatase, since a red shift of λ_{onset} was observed for hollow titania. This indicates that the present hollow TiO_2 microspheres should be efficient in photocatalysis applications.

Caixia Song et al.[13] have reported the preparation of silver-coated poly (methyl acrylic acid) (PSA) core-shell colloid particles by an in situ chemical reduction method. They prepared crystalline silver/titania composite hollow spheres by coating the as-prepared PSA/silver particles with an amorphous titania layer and subsequently calcinating in Ar atmosphere. UV-vis absorption spectra of the suspension of these composite particles are shown in Fig.5. As can be seen from curve b in fig.5, PSA/silver core-shell particles have a broad absorption at 400-500nm, which is the characteristic absorption of silver-latex composite. For the suspension of PSA/silver/TiO_2 particles, the absorption (curve c in fig.5) becomes weaker and broader, which may be the results of the scattering of the amorphous TiO_2 layers. The suspension of the silver/TiO_2 hollow spheres exhibits a UV-vis spectrum containing two peaks (curve d in fig.5), the weaker located at about 300nm can be assigned to Ag^{4+} cluster, and the stronger at about 500-600nm shows obvious red shifts with respect to the usual plasmon peak position of the silver nanoparticles. The obvious shift toward longer wavelengths in the present study might be related to the hollow structure of silver/TiO_2 particles, although the exact mechanism is not clear. The UV-vis investigation indicated that the as-prepared silver/TiO_2 hollow spheres showed broad and relatively strong absorption in visible region.

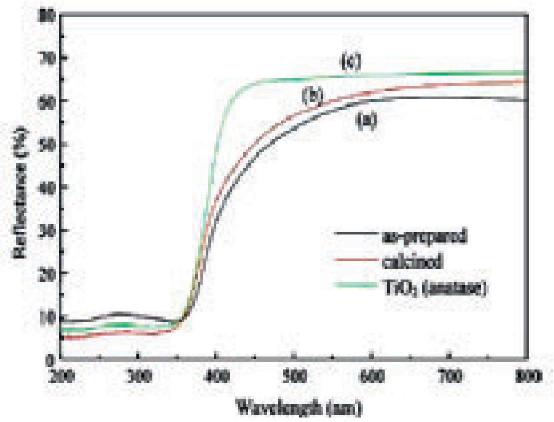

Fig. 4 UV-vis diffuse reflectance spectra of (a) as prepared, and (b) calcined hollow mesoporous TiO_2 microspheres, and (c) a well-crystalline TiO_2 sample of anatase phase

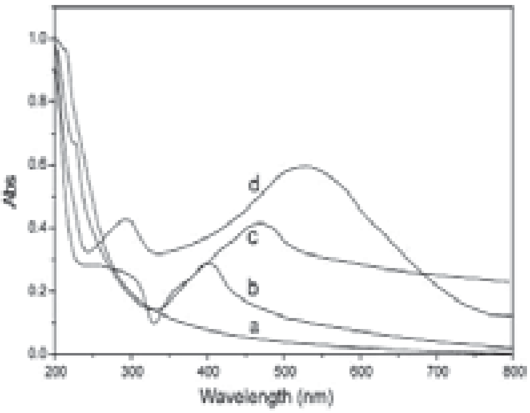

Fig. 5 UV-vis spectra of
(a) PSA,
(b) PSA/silver particles,
(c) PSA/silver/TiO_2, and
(d) silver/TiO_2 hollow spheres.

2.4 Catalysis

Palladium-catalyzed cross-coupling reactions of aryl halides with arylboronic acid, often referred as Suzuki coupling reactions, are versatile method for synthesizing unsymmetrical biaryls. The Suzuki coupling reactions have been applied extensively in the synthesis of natural products, nucleoside analogues, and pharmaceuticals. Many palladium complex have been used as homogeneous catalysis for these reactions. Song-Wook Kim et al[14] have reported the preparation of hollow palladium spheres by using the templates of uniform silica spheres. They have investigated the application of these hollow spheres to heterogeneous Suzuki coupling reactions. The results showed that the Pd hollow spheres are highly active for this reaction, in addition, the catalyst can be recycled and reused seven times without losing its catalytic activity. The high surface area of Pd spheres resulting from the nanoparticlar nature of the shell is responsible for the high catalytic activity. Earlier studies by other research groups reported the Pd nanoparticles used in Suzuki coupling reactions were agglomerated after one cycle, resulting in a loss of catalytic activity. Heterogeneous catalysts often suffer extensive leaching of the active metal species during

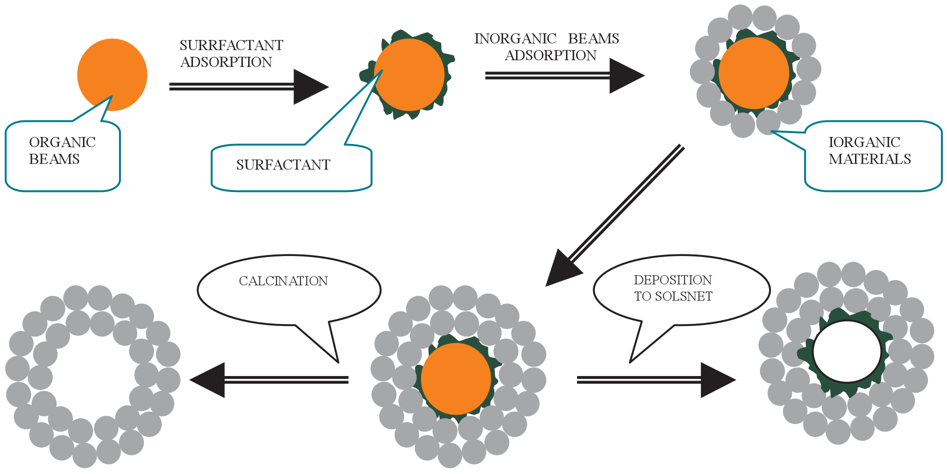

Fig. 6 Illustration for preparing inorganic hollow spheres with organic bean template

reactions and eventually lose their catalytic activities even after seven recycles. Elemental analysis of the filtrate after the reaction demonstrated to no leaching of Pd from the hollow spheres, which is very important when Pd catalysts are used for pharmaceutical production.

3 Synthesis methods

Inorganic hollow particles have been synthesized by different methods, such as organic bean template[5], emulsion method[24−27], surface-assisted method [32,33] and spray pyrolysis[34] or nozzle reactor process. Many interesting results have been reported as below.

3.1 Sacrificial cores method

3.1.1 Organic bean templating method

This method is designed to use some organic beams (polystyrene spheres) as the templates. The desired materials, such as silica[4, 5, 15], titania, zinic sulfide[6], CdS[16], are coated around the organic beams by deposition or electrostatic attraction[17]. After filtering and drying, the organic cores are removed by calcinations or decomposition to solvent. Fig.6 is the scheme illustration of this method.

Frank Caruso et al.[5] have reported their result on preparation of hollow silica and silica-polymer spheres by this method. Their first step involved the deposition of three-layer polymer film onto the negatively charged PS latex particles. This film provides a smooth and positively charged surface to aid subsequent adsorption of SiO_2. The SiO_2-PDADMAC multiplayer films were then formed by alternate adsorption of SiO_2 and PDADMAC. The templated PS latex cores were removed after the formation of multilayer film by calcinations (that is, by decomposition of the organic matter at 500℃). Alternatively, only the templated core was removed by decomposition in organic solvents. The TEM micrographs of hollow silica spheres were shown in fig.7.

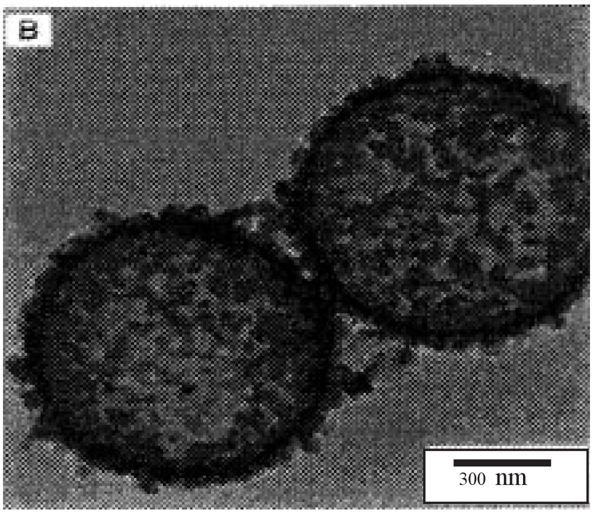

Fig. 7 TEM micrographs of PS (A) and hollow particle after calcinations (B)

Dominic Walsh et al.[18] have synthesized hollow porous shells of crystalline calcium carbonate using micrometer-sized polystyrene beads as the substrate (as shown in fig.8). They found that the thin cellular frameworks of either mesoporous or macroporous aragonite can be formed from oil-in-water micro emulsions which were supersaturated with calcium bicarbonate and coated around the PS beans. After drying and calcinations, hollow spherical shells with

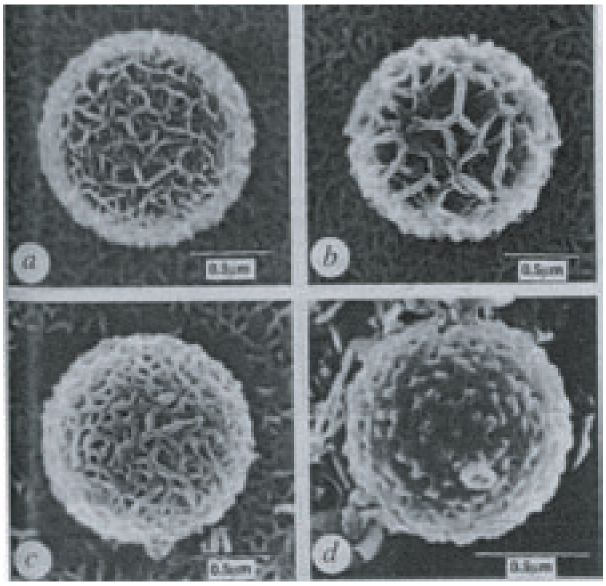

Fig. 8 SEM images of synthetic aragonite shells

honeycomb architecture were produced.

Kojima Yoshiyuki et al.[19] also synthesized hollow calcium carbonate with the organic template method. The hollow calcium carbonate was prepared by absorbing calcium carbonate onto the octane droplets surface dispersed in calcium chloride solution. This adsorption was based on -COOCa bonding formed by reaction of calcium ion of calcium carbonate and carboxylate ion of palmitic acid, which existed at the octane droplet surface. The modification of calcium carbonate adsorption on the octane droplet surface was calcite and the primary particle size was approximately 0.1-0.3 μm. And the particles have cavity inside after calcinations. Repeating numbers controlled the wall thickness of hollow calcium carbonate. In the case of repeating number of 5, its wall thickness was about 1.3μm. The average particle size of hollow calcium carbonate was adjusted from 7 to 8μm by changing concentration of octane.

Caixia Song et al.[13] have prepared silver/titania composite hollow spheres by coating the as-prepared PSA/silver particles with an amorphous titania layer and subsequently calcinating in Ar atmosphere. SEM and TEM investigation indicated that the silver/titania composite hollow particles were fairly uniform and the wall thickness of the hollow spheres was in the range of 40-80nm, as shown in fig.9.

Marcia C. Neves et al. [20, 21] synthesized hollow ZnO particles by the organic template method. Marcia C. Neves encapsulated the hollow particles with the $BiVO_4$ pigment and obtain a high performance pigment with the characteristics of low cost.

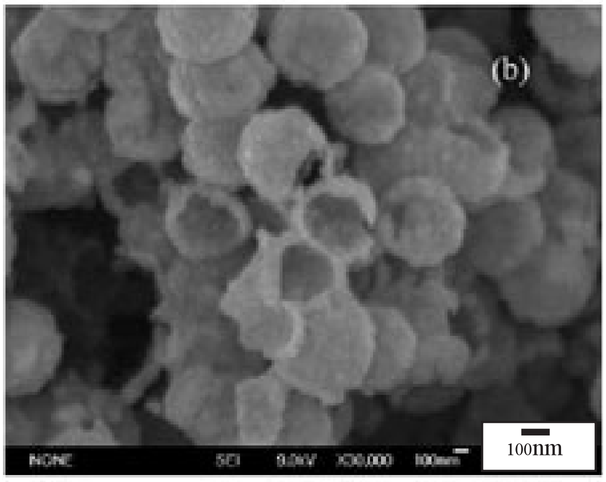

Fig. 9 SEM of silver/TiO_2 hollow spheres

3.1.2 $CaCO_3$ templating method

Recently, some researchers used nano-sized $CaCO_3$ as the sacrificial core to prepare hollow particles. They removed the $CaCO_3$ core by acid solution.

Jian Feng Chen et al.[22] prepared porous hollow silica nanoparticles with a diameter of 60-70nm using $CaCO_3$ nano-particles as the inorganic template. In their experiments, the sodium silicate (Na_2SiO_3 $9H_2O$) was added dropwise within 1h into nanosized calcium carbonate suspension, which was kept at 80℃ in a thermostatic water bath and adjusted pH at 9-10 by adding 10wt% HCl solution, to form a mixture with the molar ratio of $SiO_2/CaCO_3 = 1/10$. The mixture suspension was further stirred for another 2h at the above conditions and after-wards filtered, rinsed with distilled water and ethanol, dried at 100℃ and calcined at 700℃ for 5h to yield a core-shell composite of $CaCO_3$ and SiO_2. The composite was then dissolved into HCl dilute solution (10wt%) overnight to remove $CaCO_3$ template completely. The resulting gel was filtered and rinsed again, followed by calcined at 100℃ overnight to obtain porous hollow silica nanoparticles.

In the following, Jian Feng Chen et al.[23] developed this method to a double-template method, in which the calcium carbonate nanoparticles ($CaCO_3$) serve as core templates and the cetyltrimethylammonium bromide (CTAB) as wall structure-directing agents. The experimental results indicate that the as-prepared samples have an average external diameter of about 85nm and has occurrence of disordered mesopores in the walls.

3.2 Emulsion templating method

This method is designed to produce hollow structure by inheriting the emulsion template. An emulsion may be defined as a heterogeneous system, consisting of at least two immiscible liquids or phases. Emulsion are thermodynamically unstable, rearrangement from droplets into two bulk liquid will occur with a net reduction in interfacial area, and this is energetically favorable. So the surfactants or polymers, which can stabilize emulsions, are very important for this method.

Jae-hyung Park et al.[3] prepared hollow silica microspheres in W/O emulsions with polymers. In their experiments, to obtain hollow structures in silica particles, the viscosity of water droplets in W/O emulsion was controlled with polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP). To stabilize the emulsion structure, hydroxypropyl cellulose (HPC) was added to the oil phase. First, an external oil phase was prepared by dissolving HPC in octanol. Second, PEG or PVP dissolved in the water phase. Third, the water phase was added to the external oil phase and agitated to form a stable microemulsion. Then, the reagent TEOS was added into W/O emulsions. TEOS is soluble in the continuous phase of the W/O emulsion, but it becomes water-soluble after its hydrolysis. After the hydrolysis was completed, the samples were centrifuged and washed with ethanol. Then the particles were dried and calcinated to form the hollow structure. The hollow silicas produced by this method are shown in Fig.10.

Miguel Jafelicci Jr. et al.[24] prepared hollow silica particles from microemulsion. The micro-emulsion reactor is shown in fig.11, which shows the region that is chemically adequate for a precipitation reaction to take phase and form a silica inner shell in the acid region of water pool, i. e. on inter-face, consuming sodium silicate and hydroxonium ion. Their results suggested that silica preferably polymerize on microemulsion droplet interface where ionic strength of nitric acid aqueous solution is favorable for silica polymerization reaction.

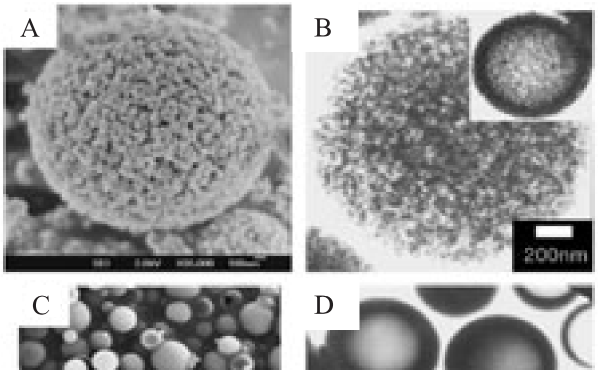

Fig. 10 SEM (A,C) and TEM (B,D) of silica particles

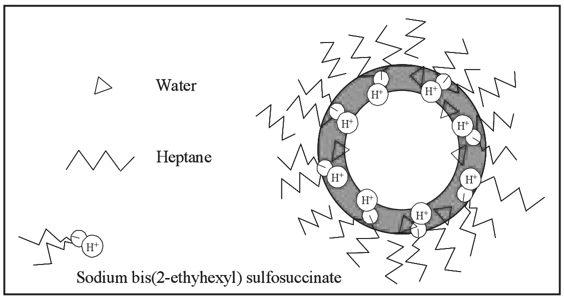

Fig. 11 Schematic representation of microemulsion model

Cheng Zhong Yu et al.[25] also synthesized siliceous hollow spheres using the emulsion template. The morphologies of prepared particles are shown in fig.12. The hollow spherical particles is about 200nm in thickness and the wall consists of uniform and hexagonally ordered ultra large mesoporous with the diameter of 50nm. The prepared particles have a high surface area ($674m^2$/g) and large pore volume ($1.25cm^3$/g).

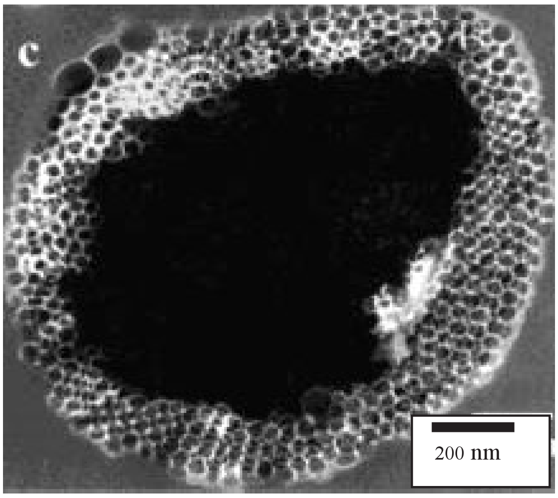

Fig. 12 SEM of hollow shell

Julie A. Thomas et al.[26] have prepared calcium carbonate microcapsules for the encapsulation of organic and inorganic substrates using a liquid emulsion membrane system. They prepared the emulsion by mixing a solution of 3.0M sodium carbonate which contains the materials to be encapsulated within the oil membrane phase. The oil phase contains surfactant mixture (sorbitan monostrearate/polyoxyethylene sorbitan monolaurate). The two phases were mixed together until a homogeneous macro-emulsion was formed. This water-in-oil emulsion was then added to a solution of 0.2M calcium chloride or calcium nitrate at 30℃. Based on work by Nakahara et al.[27], this method allow calcium ions to diffuse across the oil membrane into internal aqueous droplets that contains the materials to be encapsulated. Carbonate ions in the internal aqueous phase react with the diffused calcium ions at the oil-water interface and solid calcium carbonate in the metastable vaterite form precipitates at the interface encapsulating any materials dispersed in this phase. The vaterite spheres are prone to transformation to the more stable calcite polymorphy, a process that destroyed the capsules. In order to prevent this transformation, and stabilize the vaterite, L-glutamic acid, a known inhibitor of calcite crystallization was added to the aqueous phase prior to precipitation. Precipitation of the vaterite spheres decantated and centrifugated to recover the solid product, which was then washed with ethanol and water to remove excess oil and surfactant and then dried at 105℃.

Dominic Walsh et al.[28] have reported a facile one-step, high yield approach to produce the discrete spherical micrometer-sized particles of crystalline calcium carbonate (vaterite) with an elaborate sponge-like micro architecture, as shown in fig.13. They prepared the water-in-oil microemulsions by mixing octane with SDS ($CH_3(CH_2)_{11}OSO_3Na$) and a supersaturated $Ca(HCO_3)_2$ solution ([Ca]＝10mM, PH＝5.5-6.0). The microemultion was left partially uncovered at 25℃ to achieve slow evaporation of the volatile components in emuslion. They showed that the passive evaporation of water-in-oil microemulsions containing supersaturated droplets of calcium bicarbonate solution produces partterned mineral particles commensurate in size with the diameter of the water droplets. The spheroids are formed by nucleation of vaterite at the anionic head groups of sodium dodecylsulfate molecules present in the oil/water droplet interface, and patterned by microbubbles of CO_2 entrapped within and at the surface of the water droplets. The dependence of the particles size on the diameter of the droplets, rather than the concentration of the supersaturated solution, suggests that the nucleation and initial stages of mineral growth are preferentially located at the oil/water interface and not within the interior of the supersaturated water droplets. A possible mechanism of the formation of the vaterite microsponges is illustrated in Fig.14.

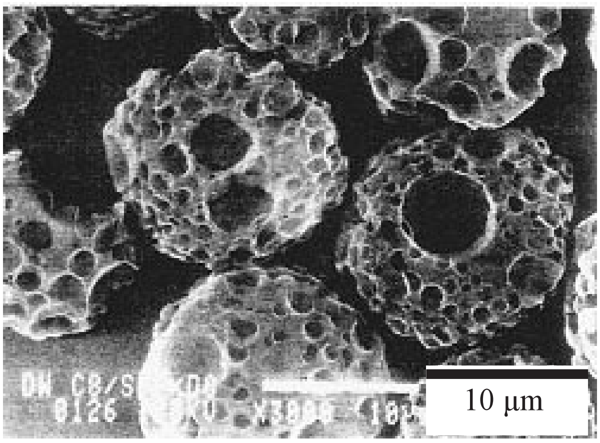

Fig. 13 SEM images of vaterite spheroids

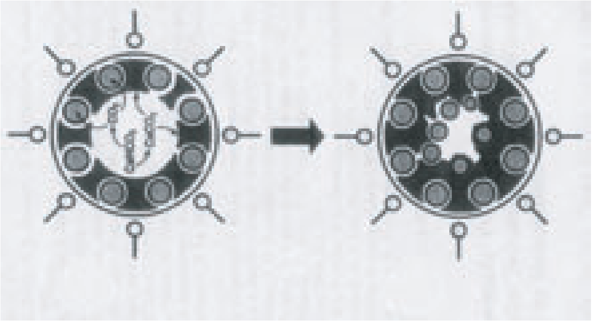

Fig. 14 Mechanism for the formation of vaterite microsponges

Besides, S. Schacht et al.[29] also prepared hollow silica by oil-water interface templating. A. D. Dinsmore et al.[30] reported a flexible approach to produce hollow elastic capsules, with size ranging from micrometers to millimeters. Their fabrication process used controlled self-assembly in three steps, as shown in Fig.15. First, aqueous solution is added to oil containing colloid particles that were then adsorbed on the surface of emulsion droplets. Second, particles are adsorbed automatically onto the surface of the droplet to reduce the total surface area. After the droplet surface is completely covered by particles, these particles are subsequently locked together by addition of polycations. Third, if required, the capsules are transferred to water by centrifugation. The resultant structures, which are called “colloidosome”, are hollow, elastic shells whose permeability and elasticity can be precisely controlled.

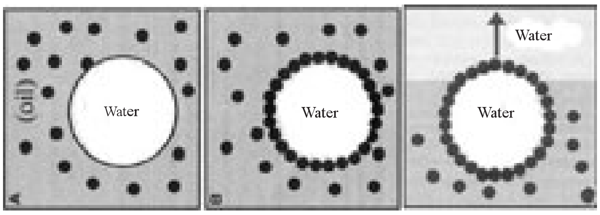

Fig. 15 Schematic illustration of the self-assembly process for colloidosome

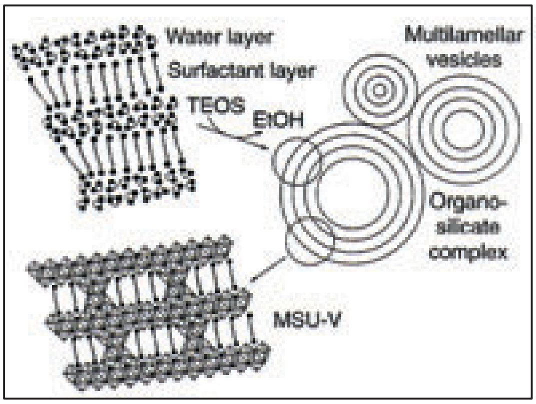

Fig. 16 Vesicular templating mechanism for the formation of porous lameller silica

3.3 Surfactant-assisted templating method

Templating process based on the hydrolysis and cross-linking of inorganic precursors at the surface of supramolecular surfactant assemblies have been used to prepare hollow particles. Peter T. Tanev and Thomas J. Pinnavaia[31] reported the preparation of porous lamellar silica that have vesicular structure, a high degree of thermal stability and framework cross-linking, very high specific surface area and pore volume. Their approach is based on the hydrolysis an cross-linking of a neutral inorganic alkoxide precursor in the interlayered regions of multilamellar vesiculars of a neutral bola-amphiphile surfactant that contains two polar head groups linked by a hydrophobic alkyl chain. Fig.16 is the illustration of the prepared vesicular templating process. The templating synthesis most likely occurs through the assembly of neutral diamine surfactants into multilamellar vesicles. The multilamellar regions of the vesicles are composed of closed packed layers of surfactant separated by water layers. The additions of TEOS penetrate the vesicle interface, diffuse into the multilamellar regions, and participate in H-bonding interactions with the lone electron pairs on the surfactant head groups. The simultaneous growth of the parallel silica layer leads to the formation of vesicular particles.

Tie-Zhan Ren et al.[12] prepared hollow TiO_2 microspheres with mesoporous crystalline shells with the assistance of non-ionic poly (alkylene oxide) surfactant molecules. The preparation of hollow microspheres of mesoporous titania was performed in a ethanol-surfactant system using Decaoxyethylene cetyl ether ($C_{16}(EO)_{10}$) surfactant as the template. At first a reaction process of alcoholysis of titanium alkoxide takes place slowly once the reactants are mixed. The formed partially hydrolysed alkoxides (titanium oxo cluster of nanosized Ti-O particles) are allowed to interaction with amphiphilic surfactant molecules through weak hydrogen bonding, forming mesostructured hybrid inorganic/organic precursor nanoparticles. These hydrophobic partially hydrolysed alkoxides can be emulsified as droplets in the reaction mixture, and stabilized by surfactant at droplets/ethanol interface. Further gelling under autoclaving follows the formation of -O-Ti-O-Ti- network by polycondensation between the nanoparticle precursors, resulting in the production of mesostructured spherical shells.

Michael S. Wong et al.[32] reported a room-temperature, wet chemical-based synthesis route in which silica and gold nanoparticles are cooperatively assembled with lysine-cysteine diblock copolypeptides into robust hollow spheres. Key determinants in the formation of the gold/silica hollow sphere (as shown in fig.17) are the ability of the sulfydryl group to form inter and intrachair disulfide bonds and the formation of the gold-

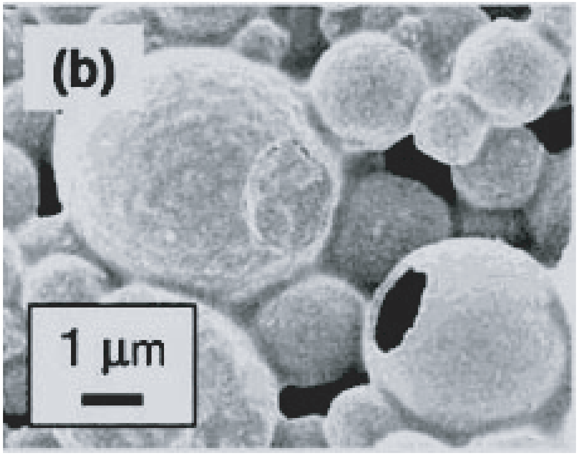

Fig. 17 SEM image of as-synthesized silicasomes

thiolate bonds. Hollow sphere did not form when the block copolypetide was reacted with n-SiO_2 and then with n-Au but formed only when the copolypetide was reacted with n-Au prior to reacting with n-SiO_2. The n-Au particles were thus found copolypeptide chains into the submicro/micro-sized aggregated around which n-SiO_2 attached. The scheme illustration of the assembly process is shown in fig.18.

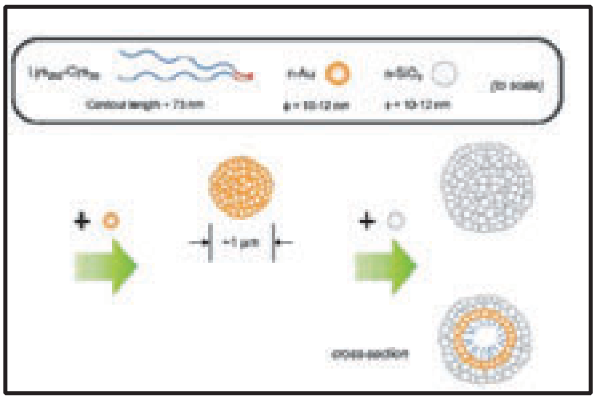

Fig. 18 Scheme of self-assembly of gold and silica nanoparticles

3.4 Others

Spray pyrolysis is a powerful tool to synthesize a variety of materials in power form including metals, metal oxides, superconducting materials, fullerenes, and nanophase materials. Messing G. L. et al.[34] reviewed the formation of particles with different morphology using a variety of spray pyrolysis techniques. The report showed that the spray pyrolysis techniques allow to produce dense (solid), hollow, porous or fibrous particles and even to deposit thin film, but the formation of hollow spherical particle is the most typical.

The general scheme of spray pyrolysis was shown in Fig.19[34].

First, the precursor solution is pumped into ultrasonic nebulizer operating at a frequency of 2.6MHz. Second, the obtained aerol is transported with inert, reducing or oxidizing gas ($Ar/Ar + H_2$, or air), respectively, into the quartz tube of the reactor that placed in a two-heat zone furnace. Hollow particles are formed by the surface precipitation because of rapid drying rate of droplet in thermal condition. The formed particles were separated from the gas phase using an electronic filter placed in the second zone of the furnace at a temperature of about 300℃.

K. T. Wojciechowski et al[34] prepared ultra-fine hollow spherical powders using ultrasonic spray pyrolysis (USP) method. The SEM images of prepared samples are shown in fig.20. The microscopic observations have shown that the powders consist of fine spheres with the diameter ranging from 100 to 300nm. Sphere thickness of various materials ranged form 8 to 50nm.

Hongyou Fan et al.[35] developed a rapid process to synthesize spherical particles, which relies on evaporation-induced interfacial self-assembly confined to spherical aerosol droplets. Their process

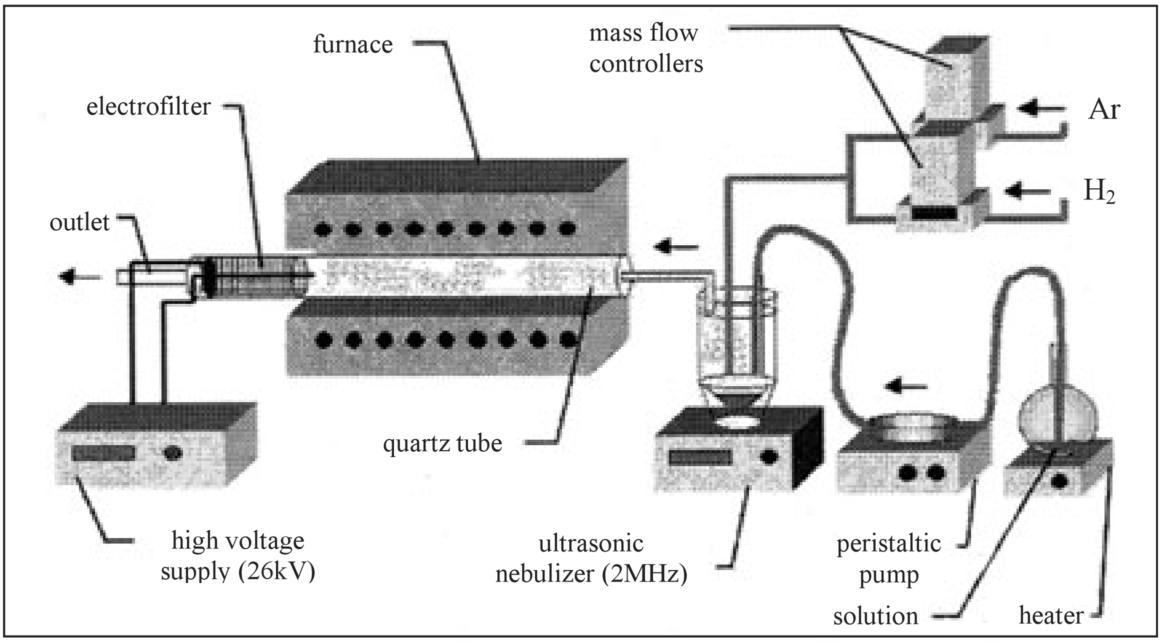

Fig. 19 Scheme of the ultrasonic spray pyrolysis

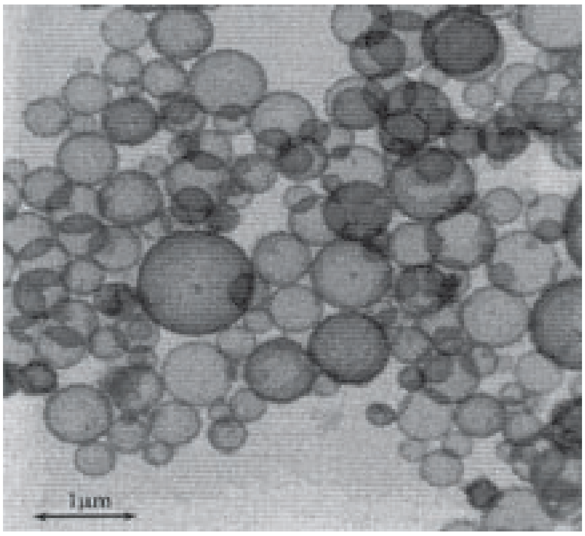

Fig. 20 TEM image of particles with nominal constitution 2CoO $3Sb_2O_3$

starts with a homogeneous solution of soluble silica plus surfactant prepared in an ethanol/water solvent with initial surfactant concentration co much less than the critical micelle concentration. Using the apparatus depicted in fig.21, they generated aerosol dispersion within a tubular reactor. In a continuous, the aerosol particles are dried, heated and collected. During drying, the preferential alcohol evaporation enriches the particles in surfactant, water and silica, inducing micelle formation. The resulting particles are commonly solid, with highly ordered hexagonal, cubic or vesicular mesostructures. However, the premature solidification usually results in the formation of hollow particles.

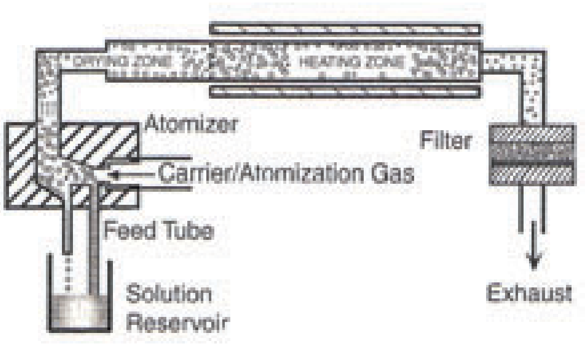

Fig. 21 Diagram of aerosol reactor

Besides, some researchers[36] proposed to prepare hollow particles using the electrostatic atomization combined with alcohol solidification. The scheme of this method is shown in fig.22.

The nozzle is composed of a stainless-steel hypodermic needle. The ground electrode is an aluminum plate with a hole at its center for the produced droplets to pass through. High voltage is applied between the nozzle and the ground electrode using a dc high voltage supply. The material in the sample vessel is pressurized by gas, and flows through the nozzle. The nozzle can control the particle size by adjusting voltage. The produced droplets immediately fall into an alcohol bath to dehydrate their surface. After filtered and dried, the hollow silica particles were produced, as shown in fig.23

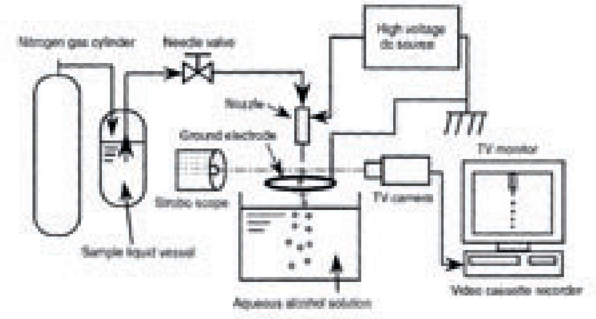

Fig. 22 Scheme of electrostatic atomization combined with alcohol solidification

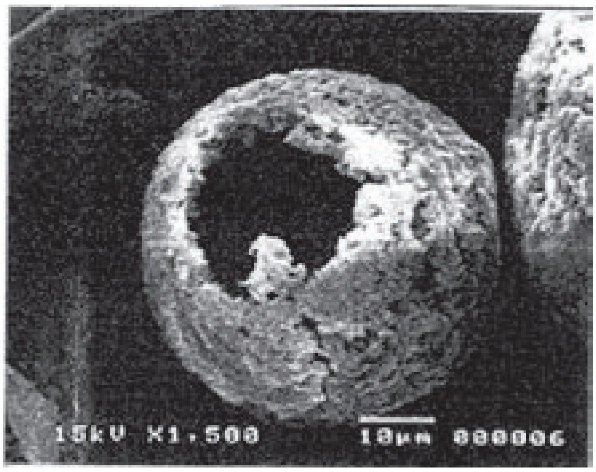

Fig. 23 SEM micrographs of hollow silica particle prepared by electrostatic

4 Our researches

Inorganic hollow particles have been intensively studied in recent years because of their potential application in industrial and biological fields. This paper has reviewed the synthetic method of inorganic hollow particles, including spray drying techniques, templating methods, and so on[37]. In a typical templating procedure, hollow particles are prepared by coating of the template with a thin layer of the precursor like a sol and a dispersion and subsequent removal of the template via a thermal decomposition or a chemical dissolution. This process has the advantage of preparing monodisperse hollow particles, while, unfavorably, it has a cumbersome procedure for removing the template. It is therefore, necessary to develop a simple and low-cost process for the preparation of hollow particles, especially for the industrial production. We proposed a new and simple process to prepare hollow calcium carbonate particles by using bubbles as templates[38, 39]. The advantage of this new approach is to simplify the synthesis of hollow particles by leaving out the removal of template.

We have successfully prepared hollow calcium carbonate particles by bubbling CO_2/N_2 mixed gas into $CaCl_2$ solution. The bubble is not only the reactive materials, but also the template for the formation of hollow particles. When the CO_2/N_2 bubbles were passed into $CaCl_2$ solution, the CO_2 gas dissolve into solution and react with calcium ion, forming calcium carbonate precipitation. The initial precipitation is the amorphous calcium carbonate that is unstable and quickly ransform to two crystalline phases, namely calcite and vaterite. The freshly crystalline particles with a nano-sized diameter are not stable because of its high surface area. The fine particles tend to aggregate to achieve a minimum of total surface free energy. Some fine particles attach to the N_2 bubbles and aggregate together, forming the hollow particles. So the formation mechanism of hollow particles can be depicted as Figure 24. It generally involves 3 steps. First is the formation of fine crystalline particles. Second is the attachment of fine particles to bubbles. Third is the aggregation of fine particles, forming the solid shell.

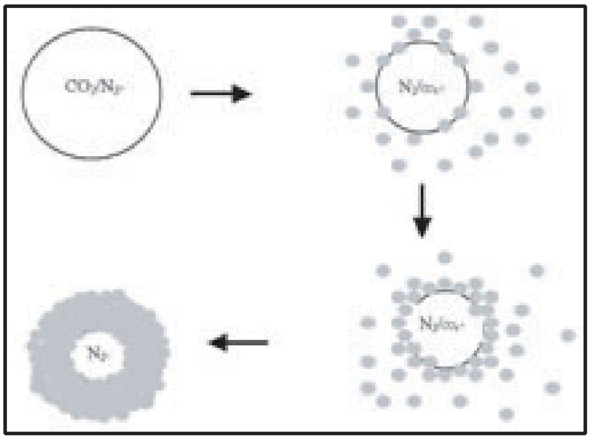

Fig. 24 Schematic mechanism for the formation of hollow $CaCO_3$

Fig.25 is the SEM image of prepared particles. Some broken particles were observed with void inside surrounding by solid shell with the thickness of several hundred nanometers. These particles were called hollow $CaCO_3$ particles. As far as our knowledge is concerned, the hollow $CaCO_3$ particles have not been reported in the carbonation of calcium solution. The formation of hollow particles in our experiments may attribute to the control of bubbles sizes, bubbles composition and other precipitation conditions[40,#41]. Figure 25c is a part of the hollow particles, indicating that the inside of hollow particles is porous. Figure 25d is another view of magnified hollow particles. It was found that the particles were formed by the aggregation of fine particles with the diameter of 20～30 nm.

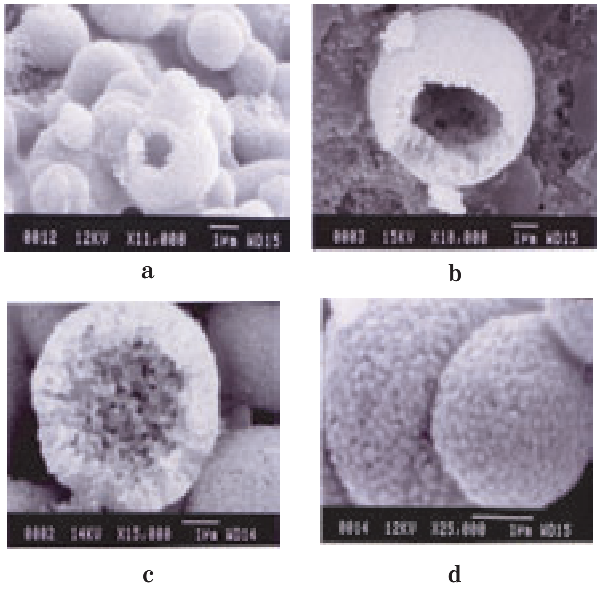

Fig. 25 SEM image of hollow calcium carbonate particles

Although the hollow calcium carbonate particles have been successfully synthesize by the bubble templating method, the yield of hollow particles is not so attractive. To improve the formation of hollow particles, it is necessary to modify the surfaces of particles and bubbles to make them ready for the attachment. In addition, the stability of bubbles is also important for the formation of hollow particles. The bubble that is stable and stay in the solution longer time provides more chances for the attachment of particles to bubble. And the small-sized bubbles are in favor of the formation of hollow particles. It can be speculated that nano-sized hollow particles will be prepared if the nano-sized bubbles are homogeneously supplied to the solution. Besides, the bubble templating method is a promising method to prepare some other hollow particles, such as hollow silica and hollow titania, by passing bubbles into their colloids or solutions.

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