Development of Eco-Friendly Techniques for Preparation of Porous Nano-/Micro-Size Hollow Silicate Particles

Raymond V.Rivera Virtudazo, Masayoshi Fuji*, Chika Takai, Takashi Shirai

Ceramics Research Laboratory, Nagoya Institute of Technology
3-101-1 Hon-machi, Tajimi, Gifu 507-0033, JAPAN

Developing an eco-friendly approach for the preparation of hollow particles (HP) of varied size/shape with tailored properties have been an immense scientific and technological importance. Hence, this review intend to mainly focus on the simple eco-approached done by CRL process group such as core-template, ammonia-hydrothermal template (AMT) and double emulsion approach for preparing porous novel–type hollow silicate particles (HSP). The our current eco-synthesis showed positive results in controlling the size, thickness, and permeability of HSP. Wherein, the potential applications of this porous HSP are also briefly discussed. The aim of this review is to provide synopsis for our alternative eco-approach for the development of nano-/micro-size hollow silicate particles (NMHSP).

1.Introduction

With the discovery/creation of fullerenes and carbon nano-tubes, a lot of research works in the last decade have been devoted for the development in preparation of micro/nanostructure hollow particles (M/NHP).[1), 2)] They have been attracted tremendous interest because of its unique properties compared to other solid counterparts, for instance higher specific surface area, lower density and better permeation/penetration. With the aid of modern science, it has been already a common knowledge that an exceptional properties may occur by downsizing the HP from micro to nano-size without changing their chemical composition which can be notably influence/affects the performance of the synthesized materials.[3)] A typical M/NHP process are usually suspended in a liquid medium which generally been the basis for having surprising array of material applications for technological scientific value. If then, functionalize the M/NHP (with facile processing), it can extend the impact of the M/NHP that may generate a novel synthetic implications.

This review paper initiates the simple preparation for the fabrication of M/NHP in an eco-friendly approach. Due to the broad scope of this topic, all research works about M/NHP in every eco-processing area cannot be treated in details. Instead, we focused/outlined our major existing research of M/NHP added with some current improvements in preparation of silicate and other inorganic M/NHP. A lot of excellent articles have been published for the progress of silicates and other inorganic M/NHP with respect to architectural design, synthesis and bio-related applications (drug release)[3), 4)] but only a few deals in establishing a route that would entail environmentally friendly. This is important task because taking good care of our environment is a major concern and if we can eliminate toxic waste by-products it would be good for human being. Also, a lot of studies involved in single-step or one-pot eco-synthesis approaches are becoming available and developing an eco-large–scale synthesis of HP would be a great challenge to eliminate environmental problems concerning fabrication of HP which can find a lot of commercial applications.

This reriew is organized as follows: Firstly, asses the basic fundamental process which is sol-gel. Then followed by, the general schematic approaches for M/NHP that our group has done and other significant reference papers about HP preparations such as solid-template (solid-cores template method), soft-template (double emulsion method), and facile process like ammonia-hydrothermal approach (AMT). After then, summarize common applications of NMHSP. This kind of approach primarily gears towards sol-gel process; a wet-chemical technique usually used for the fabrication of M/NHP which can create both glassy and ceramic materials.

2.Fundamental process: Sol-gel

Basically, the sol (or solution) evolves gradually towards the formation of a gel-like network containing both a liquid phase and a 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 on this section, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). A well studied alkoxide is TEOS. The chemical formula for TEOS is given by: $Si(OC_2H_5)_4$, or $Si(OR)_4$ where the alkyl group $R = C_2H_5$. This alkoxides are ideal chemical precursors for sol-gel synthesis because they react readily with water and some metal alkoxides (organometallic compounds). The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the silicon atom.[5] The process consists of a series of hydrolysis and condensation reactions of an alkoxide, which is shown in Fig. 1.

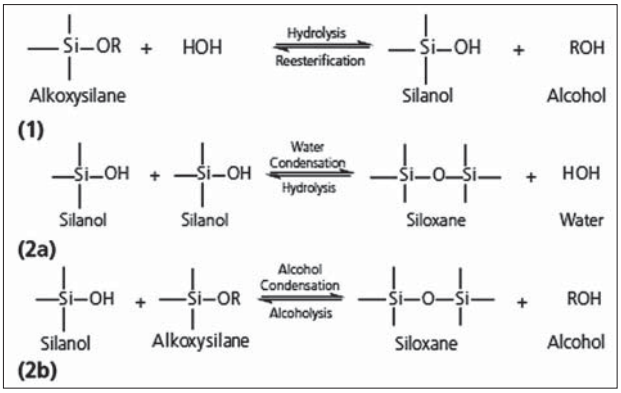

Fig. 1 Typical Sol-gel reaction scheme. [10]

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.[6), 7)] Hence, sol-gel process has been frequently employed in coating the colloidal core-templates followed by forming M/NHP or NMHSP by removing templates. This is a simple reaction that does not require unusual materials 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 removing the excess water/alcohol that the reaction generates. Also, the properties of the M/NHP prepared using sol gel approaches can easily be modify by utilizing an organically modified alkoxide or a variable metalloid (for example, an alkoxyborate instead of an alkoxysilane).

Mostly HPs are obtained through colloidal-template synthesis.[8), 9)] In template route, the inner diameter/ shape of HP is only determined by the dimensions of the kind of template (organic[10), 11)], inorganic[12), 13)] and biomolecules[14)]) used. Predominantly, these templates syntheses are divided into two parts namely hard and soft template syntheses in fabricating hollow particles with homogeneous, dense shell wall layers. The next section discuss on the preparation of NMHSP with some example of inorganic HP via solid-template (solid-cores template method), soft-template (double emulsion method) and facile route like AMT.

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

Extensive studies had been done to evaluate an ideal and convenient synthesis for M/NHP especially under mild eco-conditions. These common features such as the solid template, soft template and ammonia-hydrothermal approach (AMT) are basically discussed in this paper especially on our present eco-preparation in forming NMHSP.

3.1 Solid- Core Template Method

Colloid core-template particle is probably an effective and universal method for the preparation of HP, especially if required a narrow size distribution, for example, self-assembly and photonic crystals [15), 16)]. In the solid-template assisted synthesis, poly(styrene acrylic acid) (PSA), polystyrene (PS) latex, silica spheres and calcium carbonate ($CaCO_3$) particles are commonly used as colloidal core-templates because of their readily available in a wide range of sizes.[4), 17)] Technically, inorganic precursor (metal or non-metal alkoxides) is coated over the core-template either by physical or chemical reaction to provide an intermediate called core-shell (hybrid materials) may contain 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 M/NHP.[18), 19)] Majority of these M/NHP are formed on outer surfaces of core-templates through sol–gel, [20), 21)] hydrothermal treatment, [22)] layer-by-layer [2), 23)] and direct chemical deposition.[4)]

For instance, the research works done by Li et al[24)] use these surface-modified PS spheres as sacrificial template to fabricate silica-coated PS and titania-coated PS composites by co-condensation between hydroxyl groups with tetraethyl orthosilicate (TEOS) and titanium(IV) isopropoxide (TIPP) in a sol-gel process, respectively. The HSS and THS 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.

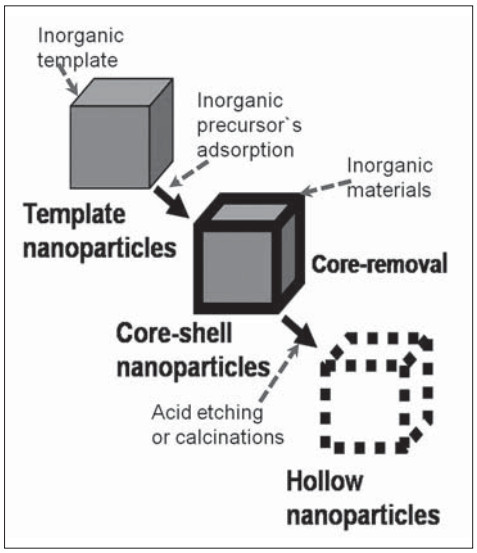

Fig. 2 General schematic illustration of anisotropic HP using inorganic template approach.

In this manner, simple eco-friendly step processes are needed for the synthesis of M/NHP. Our group have been successfully reported this process (Fuji et al.,[25), 26)]), via template sol-gel process by utilizing and removing the nano-core $CaCO_3$ particles through dissolution in acid etching followed by the formation of nano-size hollow silica particles (NSHSP). In this method, aqueous ammonia solution was used as the catalyst and medium. The naturally positively charged $CaCO_3$ nanoparticles were dispersed into the ethanol (EtOH) solution followed by sonicating for 10 min. Thus, ensures the generation of silicate sol from the hydrolysis and the condensation of TEOS. This rapidly captured by $CaCO_3$ particles via electrostatic interaction in aqueous ammonia solution either in room or elevated temperature. Under acid conditions, $CaCO_3$ particles were "dissolved" subsequently and even synchronously to directly formed NSHSP, as shown in Fig.2. The formation of the inorganic silicate shells and the dissolution of core template particle occurred during acid dissolution; neither additional toxic chemicals or calcination process was used to remove the $CaCO_3$ core.[26), 27)]

With this concept, we are able to utilized other inorganic core templates such as colloidal calcium rich-hydroxyapatite (Ca-HAp)[28)] nanoparticles and micro-size $CaCO_3$ particles for the formation of anisotropic NSHSP to micro-size hollow silicate particle (MSHSP).[29)] These core-templates are recyclable and only mild concentration of acid to dissolve the core templates. This is a facile eco-route in synthesizing nano-/micro-size hollow silicate particle (NMHSP) with tunable shell thickness and unique anisotropic hollow shape by employing inorganic particles (Ca-HAp and $CaCO_3$) as template in concurrence with the sol gel method. The results showed relatively stable anisotropic hollow shape with uniform silicate shell wall thickness. In addition, at relatively high concentration of silicate precursor (TEOS), the shell thickness and surface roughness increase. As expected, unique anisotropic shape and size of the NMHSP depend on the inorganic template used as illustrated in Fig. 3.

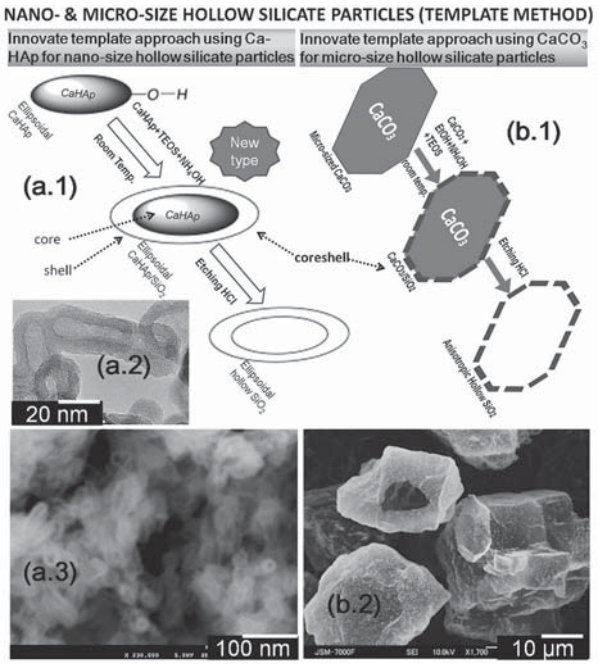

Fig. 3 Schematic illustration and typical images of the anisotropic template process to form NMHSP [36), 37)] using colloidal nano-size CaHAp (a.1, a.2, a.3) and micro-size $CaCO_3$ particles (b.1, b.2)

With solid template (hard), refilling the hollow interior with functional species or in situ encapsulations of quest molecules during the formation of shells, though possible, is still demanding. Thereby, fabricating a macroporous in the shell wall of hollow microsphere particles (HMP) is a remedy, but it is still tough. These difficulties have prompted to synthesize a more simple approach for producing HMP with macroporous shell that can easily encapsulate and release quest species. For instance, templating against soft (liquid or gaseous) template has been significant especially for the development of emulsion method. The next section will confer the essential concept of soft template and discuss the basic concept of the double emulsion method. The next section

re-established the potential of the soft template method to create an interior spaces and for a creating a functional shell structure through a one-pot synthesis.

3.2 Soft Template Method

The soft template synthesis is another simple and general method for obtaining hollow particles. Some hollow particles with nanometer to micrometer diameter have been successfully fabricated using double emulsion process usually composed of water-in-oil-in-water ($W_1/O/W_2$).[30)]

Generally, ($W_1/O/W_2$) 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. Because of their special internal structure, double emulsions have found significant applications in many areas, such as pharmaceuticals, foods, cosmetics and separation.[31), 32)] 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.[4), 32)] This is simply illustrated in Fig. 4.

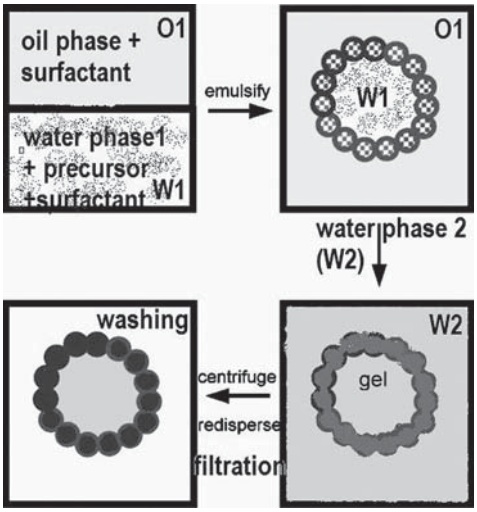

Fig. 4 Basic illustration of double emulsion method (W_1OW_2)

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 works of Fujiwara to fabricate macroporous hollow silicate microspheres (HSMSP) with addition of water soluble polymer and some innovation inters of 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 be controlled the micro-size through emulsion rate speed.

Basing from Fujiwara et al[33), 34)] in the case of hollow silicate microspheres (HSMP), the reaction of sodium silicate with a precipitant is utilized. W_1/O emulsion is made of W_1 (consist of water and sodium silicate) and O (oil phase) with surfactant for stabilizing emulsion. Then W_1/O is added to another aqueous solution of a precipitant W_2, forming $W_1/O/W_2$ emulsion system. During the elimination of the oil phase (O) between the two water phases (W_1 and W_2), these two aqueous solution are mixed to form silica precipitate along the emulsion interface. The sodium silicate of W1 was providing interfaces forming silicate particles (precipitate). After complete formation of the precipitate on the interfaces, all sodium silicate is consumed and the inside of the microcapsule was filled with only water. This water can be readily removed by drying treatment thru the pores of the silica shell. Finally HSMP with vacant inside are obtained. In this process no other process to remove the core compound are necessary.

With some innovations, water-soluble polymer (sodium polymethacrylate, Na-PA) was added into the aqueous solution of W_1, connotes as W_1P-X. Thereby, formed water$_1$+polymer/oil/water$_2$ (W_1P-X/O/W_2) emulsion system. Consequently, the parameters were controlled for instance emulsification rotational speed constant, fixed volume ratio, fixed surfactant ratio, modified (set-up) pressurized by N_2 filtration and calcination. Then, formed hollow silicate microspheres with meso/macroporous shell (HSMSP)[35)] were successfully prepared. The prepared HSMSP exhibits unique three-dimensional hierarchical architectures and demonstrated significantly improved physico-chemical properties as shown at the SEM images (inset) of Fig. 5.

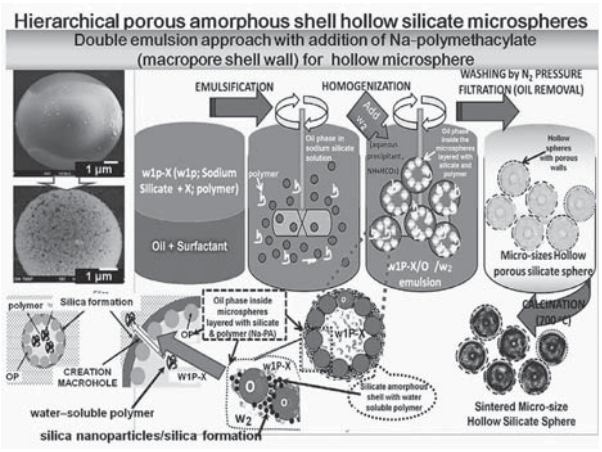

Fig. 5 Conceptual scheme of the porous hollow silicate microspheres (HSMSP) by W_1P-X/O/W_2 interfacial reaction upon addition of Na-PA and calcinations. Inset: SEM images of a usual HSMSP with macroporous shell.[46)]

Most of the double emulsions reported are macro-emulsions of which the inner and outer droplets are both in micron scale. But recently Deming et al.[36] reported a nano-scale double emulsion was formed, in which both oil droplet and internal aqueous droplet are in nano-meter size. The ultrasonic and micro-fluidic homogenization was utilized to induce the formation of nano-scale double emulsion, which was stabilized by specially designed amphiphilic diblock copolypeptide surfactants. This opens up the way to prepare double nano-emulsion. Another approach such as micro-fluidic device [37), 38)] and electric field [39), 40)] were also developed to make double emulsions.

Stability of the shell wall is generally the most common problems especially for template-sol-gel process. This is due to that template sol–gel process involves uncontrollable fast hydrolysis and condensation, and resulted to the formation of unstable shell wall of amorphous inorganic oxides.[41), 42)] Calcination of the core-shell is commonly done for this problem to stabilize the shell walls, generally above 500℃ usually required to transform amorphous oxides into crystalline ones. But, on the other hand, the high temperature thermal calcinations would seriously affect the particle size, surface structure and even would result in a collapse of the hollow structure.[8), 17)] Hence, next section briefly discussed our innovative method via ammonia-hydrothermal approach which is one way to eliminate this problem and enhances stability of the shell wall.

3.3 Ammonia-Hydrothermal-Template (AMT, facile approach)

Hybrid hollow particles of crystalline metal oxides can be synthesized in a simple one-pot synthesis via hydrothermal approach. 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 Fe_2O_3, Ni_2O_3, Co_3O_4, CeO_2, MgO, and CuO, were obtained.[43), 44)] But with ammonia-hydrothermal treatment (AMT) provides a facile and convenient method for refining the structural order and pore size uniformity. The AMT intensify transformation of silica wall (S)–interactions within the micro/nanostructure from a weaker (X) hydrogen bonding ($S^+X^-I^0$) to the stronger electrostatic (S^+I^-) interactions which can be illustrated in Figure 6d. This treatment resulted in an increase of both thermal and hydrothermal stability. Recently, our research group introduced AMT to improve the stability of template NSHSP using $CaCO_3$ nanoparticles while preserving the original morphology.[45)] The key determining factors involved in this treatment include hydrothermal temperature and aging time.[46), 47)] Then at elevated temperature (120℃), hollow calcium silicate hydrate nanoparticles (HCSHNP) formed. This simple process for the formation of a unique HCSHNP (< 100 nm), was successfully prepared via the hydrolysis and condensation of TEOS, ammonia water (NH_4OH) and $CaCO_3$ as template and then AMT. To appreciate the formation of HCSHNP, the temperature reaction was varied at room temperature (RT), 90 and 120℃ . Then each reaction temperature was varied in aging time for 3 h, 9 h, 24 h and 10 d.

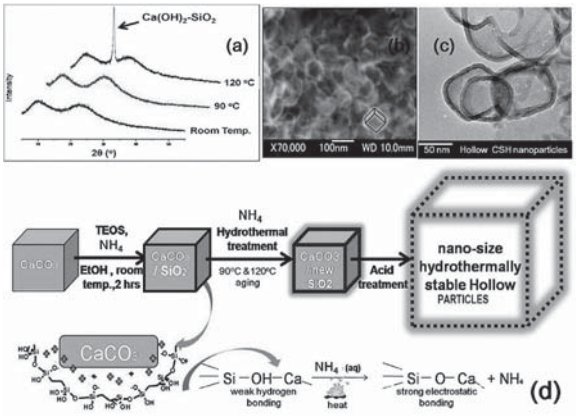

Fig. 6 General Illustration of stabilization and formation of hollow calcium silicate hydrate particles by ammonia-hydrothermal template process.[64)]

In Fig. 6 shows the typical (Fig. 6a) XRD pattern of semi-amorphous HCSHNP materials. The additional sharp peak at ~18.1 (2θ), corresponds to overlapped diffractions of $Ca(OH)_2$[48), 49)] and low crystalline CSH.[49)] While no visual peaks (amorphous phase) were observed for samples synthesize at room temperature and 90℃ . Hence, semi-amorphous CSH with $Ca(OH)_2$ may contained in the shell wall of the nano-size hollow particles (Fig. 6b and 6c). Thus, we successfully develop a simple-direct process via AMT, followed by acid etching; formed HCSHNP ranging from (60 to 100) nm. In future works, we can 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 material and coating additives as thermal insulating materials.

4. Developing a facile route and eco-innovative way for hollow silicate particles (HSP).

A lot of significant achievements have been made in this area, as reviewed in this paper. Nevertheless, there are still some challenges that need to be fulfilled. Syntheses of complicated structure such as controlling the size/shape, sphere-in-ellipsoidal and cage-like surfaces for HSP are just in its initial stage. It is anticipated that solid template and soft template/free template techniques will play a greater role in future eco-fabrication of complicated structure. As mention above, functional use of hollow structures is closely correlated with their morphological properties such as the exterior shape, the interior space, and the shell structure. To increase the permeability and create the ability to store bio-macromolecules and nanoparticles, it is desirable to build meso/macro-holes on the shells of inorganic hollow structures but needs proper proportioning inorder not to deteriorate the mechanical strength of the HSP. Thus, simultaneous achievement of a robust hollow architecture and improved large molecule permeability in a environmentally friendly approach is still remains a challenge

For this reason, NMHSP particles are interesting not only because of their superior interior void structures, but also for a few more important reasons as mention previously. Generally, the successful creation of these micro/nano-scopic materials itself is a proud representative of the advancement of modern synthetic technology. Thus, it is very helpful to deepen in the understanding the mechanism for the formation of micro/nanostructure HSP, which will encourage designing more and more novel structure. Also, compared with bulk micro/nano-material, the micro/nano-scopic hollow interior spaces with multiphase interfaces might cause a number of variations in the physico-chemical properties, reinforce interfacial effects and control the local chemical micro-environment that can bring a lot of potential applications.[50), 51)]

5. Potential applications of hollow inorganic/silicate particles

Since NMHSP possess characteristics such as low density, high surface-to volume ratio, low coefficient of thermal expansion and refractive index which makes it attractive for widespread potential applications ranging from chemical reactors, drug delivery, catalyst support, antireflection surface coating, lightweight materials, rechargeable batteries and various new application fields.[8)] Next section, will briefly summarized NMHSP common applications into four parts which simply illustrated in Fig. 7.

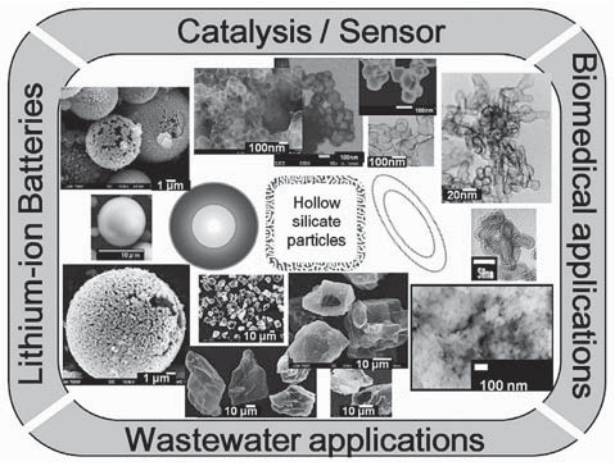

Fig. 7 Actual images of the typical-results of NMHSP fabricated via an eco-friendly process and basic summary of the potential application of the NMHSP.

5.1 Lithium-Ion Batteries (LIBs)

Macro-porous HSP is a fine example of good electrode materials for lithium ions.[52), 53)] Fundamentally, Silicon (Si) believed to be the highest known lithium storage capacity of 4200 mA h g-1, which makes it very attractive as a negative electrode materials for LIBs. But, Si nanoparticles based anodes are often found to have less satisfactory cycle life compared to other materials (e.g Sn-based anodes) again due to ultra large (>300%) volume changes during Li-Si alloying/dealloying processes. Recently, modified nestlike NSHSP exhibits much improved cycle life and rate capacity. These observations clearly verify the advantages of the NMHSP (nestlike Si hollow morphology)[54)] as compared for solid micro/nanoparticles of the same composition.

5.2 Biomedical Applications

With extensive development of NMHSP synthesis, it greatly helps tune the optical properties and superparamagnetic behaviour.[55)] As mention, NMHSP are good for storage and charge carriers.[56)] Since, silicate particles is an accepted materials for drug delivery, for the reason that of its non-toxicity. So, HSP has been extensively studied for biomedical applications technically because of its biocompatibility and well-established in terms of bioconjugation methods using silane chemistry.[57)] Generally, it has the ability for adsorption and release of sensitive materials such as fluorescent and drug markers aside from well-known catalytic applications.[51)] 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 amount rate of drugs by altering the pore dimensions and wall

structures.[58] Significantly, it was demonstrated that drug molecules can be stably encapsulated during the synthesis of HSP and the release can be triggered by ultrasound or controlling the pH.59), [60]

5.3 Waste treatment application

Wastewater is universally acknowledged as health and environmental problems. The complexity of wastewater composition led to intricate treatment process with high costs, which are impractically given the large volumes of waste produced by both domestic use and industry. Develop an effective and cheap decontamination method is urgent need. One remedy is for the using HSP as conventional adopted method for adsorption and ion exchanged. Some current studies confirm that these as prepared HSP showed an effective adsorbent; remove organic pollutants and removal of heavy metals ions in wastewater.[61), 62)]

5.4 Catalysis/sensor

Inorganic/silicate porous particles has been as used in extensively as catalysis, the scientific curiosity of this materials led to numerous applications. By only manipulating the particle range from nano- to microscale can directly represent a promising type of structures for enhancing their catalytic ability. The high surface-volume-ratio enhances the fraction of low coordination metal sites (e.g vertices, edges and kinks), and promotes adsorption of reactants. The accessible micro/meso/macropores at hollow surfaces afford ample channels between inner and outer surfaces, which facilitate diffusion of solvent, and reactants, thus accelerate chemical reactions.[63] Recently, a unique structure, in which the shell can effectively prevent the core particles from aggregation, hollow spheres incorporated with catalytic metal NPs (metal NP yolk/shell particles), has potential applications as nano-reactors for catalysis.[64] Taking Au/SiO_2 yolk/shell particles as an example, they have been widely tested for the catalytic reaction of p-nitrophenol by NaBH4.[65] In addition to their catalytic property, the confined growth and Oswald ripening of Au NPs in HSP have also been reported.[66] Greatly enhance photocatalytic activity and also by creating mesoporous silicates in the shell walls. Most importantly, the confined reaction on the surface of the core NPs, or transformation of the NPs themselves, provides an alternative mode for producing many other functional yolk/shell particles.

On the other hand, the high surface areas of NMHSP are also advantage for chemical/gas sensing. The HSP provide facile light guiding for quantum cascade laser (QCLs) over several meters and, hence can be used for remote gas sensing or IR light delivery in medical applications.[67] Chemical/gas sensors are also widely used for industrial process control and are experiencing growing use in security applications.[68] Sensing with these materials are performed through measurements of changes in electrical conductance produced by adsorption-desorption of a targeted analyte on the oxide surfaces.

6. Summary and Outlook

Considerable eco-synthesis of NMHSP has been made significantly for this past decade. In this review paper, eco-synthetic approach for the fabrication of micro/nano-size porous HSP was briefly summarize the basic concept base on the actual results done especially on the following: (1) core-templating (using nano-size CaHAp and micro-size $CaCO_3$ particles); (2) double emulsion method (using water soluble polymer as additive for (W_1OW_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, innovate way and an eco-friendly process for the formation of NMHSP.

Evidently, advantage of template using (solid) $CaCO_3$ particles and CaHAp are possibly the greenest approach, clearly effective, and most facile technique for synthesizing NMHSP. Aside from that $CaCO_3$ or CaHAp particles are technically abundant in nature and 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 on this approach rely on achieving high product yields from this simple synthetics process, difficulty in forming a uniform coating around surfaces with large variation of curvature and lack of structural robustness of the shells upon template removal. But these difficulties can be partly overcome by monitoring the acid concentration during acid etching, used of surfactant and exposed the core-shell particles through hydrothermal approach for structural stability.

While for double emulsion approach (W_1OW_2) for fabricating macroporous hollow microspheres (PHSM), a key advantage of using double emulsion method for the preparation of PHSM is that the core removal stage is very easily eliminated. The liquid template, liquid cores (W_1) can be easily removed by low-stress generating processes such as evaporation, filtration or dissolutions

with common solvent such as ethanol/water after the shell formation, final hollow product cannot be altered even it was calcined and has low parental toxicity because of the used of water–soluble polymer. However, the relatively low stability and the polydispersity of double emulsion approach may limit their application. Mostly controlling the microspheres, uniformity, and macroporous distribution into the shell still remain challenge. Moreover, the water-soluble polymer cannot be easily removed into the shell and liquid removal (W_1) is an energy-intensive process. But this problems can be partly overcome by calcination, pressure-filtration and controlling/monitoring the emulsion speed rate.

In our present results for the fabrications of NMHSP, we offer an innovative method for eco-synthetic strategy to form unique NMHSP with stable shell wall pore systems and also provide further understanding for the future mechanism on composite hollow materials which can be furtherly explained through extensive research works.

The core-template approach can be easily implemented. However, the capability of constructing complicated structure, 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.[20] Hopefully, based our innovate processes; another researcher can develop and synthesize hollow particles with more complicated structure in a simple eco-approach.

Finally based on the above findings, it is concluded that an eco-friendly approached in fabricating of NMHSP can be done. In general, by controlling the parameters enhance the surface morphology, porosity of the shell and stability of the HSP. The insights obtained from this non-toxic alternative mechanism will allow other researcher to gain better controls of the HSP especially in exploring the dispersion of the HSP. We are hopeful that a more versatile and powerful eco-method of preparation of HSP will be developed from both fundamental and practical viewpoints and develop more novel physicochemical properties. Thus, this sample eco-techniques presented in this review provides a good foundation for eco-synthesis of NMHSP especially for template and double emulsion approached and applications will be explored in the near future.

ACKNOWLEGEMENT

This research was partially supported by the Ministry of Education, Science, Sports and Culture, MONBUKAGAKUSHO Scholarship Program and Grant-in-Aid for Scientific Research (B), 22310066 "Clarification of mechanism of super-thermal insulation of hybrid thin film between nano-size hollow silica and polymer" 2010-2012.

REFERENCES

1) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, "One-Dimensional Nanostructures: Synthesis, Characterization, and Applications," *Advanced Materials,* **15**, 353-389 (2003).
2) F. Caruso, "Hollow Capsule Processing through Colloidal Templating and Self-Assembly," *Chemistry – A European Journal,* **6**, 413-419 (2000).
3) M.S. Fleming, T.K. Mandal, and D.R. Walt, "Nanosphere−Microsphere Assembly: Methods for Core−Shell Materials Preparation," *Chemistry of Materials,* **13**, 2210-2216 (2001).
4) X.W. Lou, L.A. Archer, and Z. Yang, "Hollow Micro-/Nanostructures: Synthesis and Applications," *Advanced Materials,* **20**, 3987-4019 (2008).
5) C.J. Brinker and G.W. Scherer, "Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing " pp. 912, Academic Press; , San Diego CA, USA,1990.
6) L.F. Francis, "Sol-Gel Methods for Oxide Coatings," *Materials and Manufacturing Processes,* **12**, 963-1015 (1997).
7) W.J. Elferink, B.N. Nair, R.M. de Vos, K. Keizer, and H. Verweij, "Sol–Gel Synthesis and Characterization of Microporous Silica Membranes: II. Tailor-Making Porosity," *J. Colloid Interface Sci.,* **180**, 127-134 (1996).
8) Y. Wang, A.S. Angelatos, and F. Caruso, "Template Synthesis of Nanostructured Materials via Layer-by-Layer Assembly†," *Chemistry of Materials,* **20**, 848-858 (2007).
9) F. Caruso, R.A. Caruso, and H. Möhwald, "Nanoengineering of Inorganic and Hybrid Hollow Spheres by Colloidal Templating," *Science,* **282**, 1111-1114 (1998).
10) A. Ahmed, R. Clowes, E. Willneff, H. Ritchie, P. Myers, and H. Zhang, "Synthesis of Uniform Porous Silica Microspheres with Hydrophilic Polymer as Stabilizing Agent," *Industrial & Engineering Chemistry Research,* **49**, 602-608 (2009).
11) Y. Chen, E.T. Kang, K.G. Neoh, and A. Greiner, "Preparation of Hollow Silica Nanospheres by Surface-Initiated Atom Transfer Radical Polymerization on Polymer Latex Templates," *Advanced Functional Materials,* **15,** 113-

117 (2005).

12) R.M. Anisur, J. Shin, H.H. Choi, K.M. Yeo, E.J. Kang, and I.S. Lee, "Hollow silica nanosphere having functionalized interior surface with thin manganese oxide layer: nanoreactor framework for size-selective Lewis acid catalysis," *Journal of Materials Chemistry,* **20**, 10615-10621 (2010).

13) W. Zhao, M. Lang, Y. Li, L. Li, and J. Shi, "Fabrication of uniform hollow mesoporous silica spheres and ellipsoids of tunable size through a facile hard-templating route," *Journal of Materials Chemistry,* **19**, 2778-2783 (2009).

14) K. Kamalasanan, S. Jhunjhunwala, J. Wu, A. Swanson, D. Gao, and S.R. Little, "Patchy, Anisotropic Microspheres with Soft Protein Islets," *Angewandte Chemie International Edition,* n/a-n/a (2011).

15) X. Xu and S.A. Asher, "Synthesis and Utilization of Monodisperse Hollow Polymeric Particles in Photonic Crystals," *Journal of the American Chemical Society,* **126**, 7940-7945 (2004).

16) R.A. Caruso, A. Susha, and F. Caruso, "Multilayered Titania, Silica, and Laponite Nanoparticle Coatings on Polystyrene Colloidal Templates and Resulting Inorganic Hollow Spheres," *Chemistry of Materials,* **13**, 400-409 (2001).

17) Z. Niu, J. He, T.P. Russell, and Q. Wang, "Synthesis of Nano/Microstructures at Fluid Interfaces," *Angewandte Chemie International Edition,* **49**, 10052-10066 (2010).

18) F. Caruso, A. Caruso, and H. ohwald, "Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating," *Science,* **282**, 1111 - 1114 (1998).

19) H. Xu and W. Wang, "Template Synthesis of Multishelled Cu2O Hollow Spheres with a Single-Crystalline Shell Wall," *Angewandte Chemie International Edition,* **46**, 1489-1492 (2007).

20) M. Darbandi, R. Thomann, and T. Nann, "Hollow Silica Nanospheres: In situ, Semi-In situ, and Two-Step Synthesis," *Chemistry of Materials,* **19**, 1700-1703 (2007).

21) S.-J. Ding, C.-L. Zhang, M. Yang, X.-Z. Qu, Y.-F. Lu, and Z.-Z. Yang, "Template synthesis of composite hollow spheres using sulfonated polystyrene hollow spheres," *Polymer,* **47**, 8360-8366 (2006).

22) R.V.R. Virtudazo, H. Watanabe, M. Fuji, and M. Takahashi, "A Simple Approach to form Hydrothermally Stable Templated Hollow Silica Nanoparticles," pp. 91-97, John Wiley & Sons, Inc.,2010.

23) F. Caruso, "Nanoengineering of Particle Surfaces," *Advanced Materials,* **13**, 11-22 (2001).

24) H. Li, C.-S. Ha, and I. Kim, "Facile Fabrication of Hollow Silica and Titania Microspheres Using Plasma-Treated Polystyrene Spheres as Sacrificial Templates," *Langmuir,* **24**, 10552-10556 (2008).

25) M. Fuji, C. Takai, Y. Tarutani, T. Takei, and M. Takahashi, "Surface properties of nanosize hollow silica particles on the molecular level," *Advanced Powder Technology,* **18**, 81-91 (2007).

26) R.V.R. Virtudazo, H. Watanabe, T. Shirai, M. Fuji, and M. Takahashi, "Direct Template Approach for the Formation of (Anisotropic Shape) Hollow Silicate Microparticles," ICC3, 2011.

27) H. Watanabe, M. FUJI, and M. TAKAHASHI, "Synthesis, characterization and application of nano-sized hollow silica particles," pp. 145-150 in Proceeding 9th Ceramic Materials and Components for Energy and Environmental Appliation and Lazer Ceramics Symposium Conference. Edited, China, 2008.

28) R.V. Rivera Virtudazo, H. Tanaka, H. Watanabe, M. Fuji, and T. Shirai, "Facile preparation in synthesizing nano-size hollow silicate particles by encapsulating colloidal-hydroxyapatite nanoparticles," *Journal of Materials Chemistry,* **21**, 18205-18207 (2011).

29) R.V.R. Virtudazo, H. Watanabe, T. Shirai, M. Fuji, and M. Takahashi, "Direct Template Approach for the Formation of (Anisotropic shape) Hollow Silicate Microparticles," *IOP Conference Series: Materials Science and Engineering,* **18**, 062014 (2011).

30) M. Fujiwara, K. Shiokawa, I. Sakakura, and Y. Nakahara, "Silica Hollow Spheres with Nano-Macroholes Like Diatomaceous Earth," *Nano Letters,* **6**, 2925-2928 (2006).

31) C. Ye, A. Chen, P. Colombo, and C. Martinez, "Ceramic microparticles and capsules via microfluidic processing of a preceramic polymer," *Journal of The Royal Society Interface,* **7**, S461-S473 (2010).

32) F. Gao, Z.-G. Su, P. Wang, and G.-H. Ma, "Double Emulsion Templated Microcapsules with Single Hollow Cavities and Thickness-Controllable Shells," *Langmuir,* **25**, 3832-3838 (2009).

33) M. Fujiwara, K. Shiokawa, K. Morigaki, Y. Zhu, and Y. Nakahara, "Calcium carbonate microcapsules encapsulating biomacromolecules," *Chemical Engineering Journal,* **137**, 14-22 (2008).

34) M. Fujiwara, K. Shiokawa, I. Sakakura, and Y. Nakahara, "Preparation of Hierarchical Architectures of Silica Particles with Hollow Structure and Nanoparticle Shells: A Material for the High Reflectivity of UV and Visible Light," *Langmuir,* **26**, 6561-6567 (2010).

35) R.V.R. Virtudazo, M. Fuji, and T. Shirai, "Fabrication of calcined hierarchical porous hollow silicate micro-size spheres via double emulsion process," *Materials Letters,* **65**,

3112-3115 (2011).

36) J.A. Hanson, C.B. Chang, S.M. Graves, Z. Li, T.G. Mason, and T.J. Deming, "Nanoscale double emulsions stabilized by single-component block copolypeptides," *Nature,* **455**, 85-88 (2008).

37) H.C. Shum, Y.-j. Zhao, S.-H. Kim, and D.A. Weitz, "Multicompartment Polymersomes from Double Emulsions," *Angewandte Chemie International Edition,* **50**, 1648-1651 (2011).

38) H.C. Shum, J.-W. Kim, and D.A. Weitz, "Microfluidic Fabrication of Monodisperse Biocompatible and Biodegradable Polymersomes with Controlled Permeability," *Journal of the American Chemical Society,* **130**, 9543-9549 (2008).

39) A.K. Tucker-Schwartz, Z. Bei, R.L. Garrell, and T.B. Jones, "Polymerization of Electric Field-Centered Double Emulsion Droplets to Create Polyacrylate Shells," *Langmuir,* **26**, 18606-18611 (2010).

40) Z.M. Bei, T.B. Jones, and A. Tucker-Schwartz, "Forming concentric double-emulsion droplets using electric fields," *Journal of Electrostatics,* **67**, 173-177 (2009).

41) M. Yang, J. Ma, C. Zhang, Z. Yang, and Y. Lu, "General Synthetic Route toward Functional Hollow Spheres with Double-Shelled Structures," *Angewandte Chemie,* **117**, 6885-6888 (2005).

42) M. Yang, J. Ma, Z. Niu, X. Dong, H. Xu, Z. Meng, Z. Jin, Y. Lu, Z. Hu, and Z. Yang, "Synthesis of Spheres with Complex Structures Using Hollow Latex Cages as Templates," *Advanced Functional Materials,* **15**, 1523-1528 (2005).

43) M.-M. Titirici, M. Antonietti, and A. Thomas, "A Generalized Synthesis of Metal Oxide Hollow Spheres Using a Hydrothermal Approach," *Chemistry of Materials,* **18**, 3808-3812 (2006).

44) J.H. Bang and K.S. Suslick, "Sonochemical synthesis of nanosized hollow hematite," *Journal of American Chemical Society,* **129**, 2242-2243 (2007).

45) R. V.Rivera-Virtudazo, H. Watanabe, M. Fuji, and M. Takahashi, "Hollow Silica Nanoparticles: Simple Template to Stabilize the Amorphous Silica Shell by Hydrothermal-Templated Process," pp. 83-84 in The 2nd Thailand-Japan International Academic Conference Integrated Research for Sustainable Development. Edited. Thai Students Association in Japan Under Royal Patronage (TSAJ), Kyoto, Japan, 2009.

46) X.-H. Li, D.-H. Zhang, and J.-S. Chen, "Synthesis of Amphiphilic Superparamagnetic Ferrite/Block Copolymer Hollow Supmicrosheres," *Journal of American Chemical Society,* **128**, 8382-8383 (2006).

47) J.-H. Sun and M.-O. Coppens, "A hydrothermal post-synthesis route for the preparation of high quality MCM-48 with a tailored pore size," *Journal of Materials Chemistry,* **12**, 3016-3020 (2002).

48) S.-H. Hong and J.F. Young, "Hydration Kinetics and Phase Stability of Dicalcium Silicate Synthesized by the Pechini Process," *Journal of the American Ceramic Society,* **82**, 1681-1686 (1999).

49) K. Yanagisawa, X. Hu, A. Onda, and K. Kajiyoshi, "Hydration of β-dicalcium silicate at high temperatures under hydrothermal conditions," *Cement and Concrete Research,* **36**, 810-816 (2006).

50) K. Hadinoto, P. Phanapavudhikul, Z. Kewu, and R.B.H. Tan, "Novel Formulation of Large Hollow Nanoparticles Aggregates as Potential Carriers in Inhaled Delivery of Nanoparticulate Drugs," *Industrial & Engineering Chemistry Research,* **45**, 3697-3706 (2006).

51) J. Liu, S.Z. Qiao, J.S. Chen, X.W. Lou, X. Xing, and G.Q. Lu, "Yolk/shell nanoparticles: new platforms for nanoreactors, drug delivery and lithium-ion batteries," *Chemical Communications,* (2011).

52) S.D. McAllister, S.N. Patankar, I.F. Cheng, and D.B. Edwards, "Lead dioxide coated hollow glass microspheres as conductive additives for lead acid batteries," *Scripta Materialia,* **61**, 375-378 (2009).

53) J.D. Newell, S.N. Patankar, and D.B. Edwards, "Porous microspheres as additives in lead-acid batteries," *Journal of Power Sources,* **188**, 292-295 (2009).

54) Y. Yao, M.T. McDowell, I. Ryu, H. Wu, N. Liu, L. Hu, W.D. Nix, and Y. Cui, "Interconnected Silicon Hollow Nanospheres for Lithium-Ion Battery Anodes with Long Cycle Life," *Nano Letters,* **11**, 2949-2954 (2011).

55) H.M. Chen and R.-S. Liu, "Architecture of Metallic Nanostructures: Synthesis Strategy and Specific Applications," *The Journal of Physical Chemistry C,* **115**, 3513-3527 (2011).

56) Y. Cheng, J. Guo, X. Liu, A. Sun, G. Xu, and P. Cui, "Preparation of uniform titania microspheres with good electrorheological performance and their size effect," *Journal of Materials Chemistry,* (2011).

57) W. Tong and C. Gao, "Multilayer microcapsules with tailored structures for bio-related applications," *Journal of Materials Chemistry,* **18**, 3799-3812 (2008).

58) X.-J. Wu, Y. Jiang, and D. Xu, "A Unique Transformation Route for Synthesis of Rodlike Hollow Mesoporous Silica Particles," *The Journal of Physical Chemistry C,* null-null (2011).

59) J. Yang, J. Lee, J. Kang, K. Lee, J.-S. Suh, H.-G. Yoon, Y.-M. Huh, and S. Haam, "Hollow Silica Nanocontainers as

Drug Delivery Vehicles," *Langmuir,* 24, 3417-3421 (2008).

60) Z.-Z. Li, L.-X. Wen, L. Shao, and J.-F. Chen, "Fabrication of porous hollow silica nanoparticles and their applications in drug release control," *Journal of Controlled Release,* **98**, 245-254 (2004).

61) J. Liu, S.B. Hartono, Y.G. Jin, Z. Li, G.Q. Lu, and S.Z. Qiao, "A facile vesicle template route to multi-shelled mesoporous silica hollow nanospheres," *Journal of Materials Chemistry,* **20**, 4595-4601 (2010).

62) H. Pu, X. Zhang, J. Yuan, and Z. Yang, "A facile method for the fabrication of vinyl functionalized hollow silica spheres," *J. Colloid Interface Sci.,* **331**, 389-393 (2009).

63) F. Caruso, R.A. Caruso, and H. Möhwald, "Production of Hollow Microspheres from Nanostructured Composite Particles," *Chemistry of Materials,* **11**, 3309-3314 (1999).

64) X.-J. Wu and D. Xu, "Soft Template Synthesis of Yolk/Silica Shell particles," *Advanced Materials,* **22**, 1516-1520 (2010).

65) J. Lee, J.C. Park, and H. Song, "A Nanoreactor Framework of a Au@SiO_2 Yolk/Shell Structure for Catalytic Reduction of p-Nitrophenol," *Advanced Materials,* **20**, 1523-1528 (2008).

66) M. Sanles-Sobrido, W. Exner, L. Rodríguez-Lorenzo, B. Rodríguez-González, M.A. Correa-Duarte, R.A. Álvarez-Puebla, and L.M. Liz-Marzán, "Design of SERS-Encoded, Submicron, Hollow Particles Through Confined Growth of Encapsulated Metal Nanoparticles," *Journal of the American Chemical Society,* **131**, 2699-2705 (2009).

67) B. Alfeeli, G. Pickrell, and A. Wang, "Sub-Nanoliter Spectroscopic Gas Sensor," *Sensors,* **6**, 1308-1320 (2006).

68) H.P. Martinez, Y. Kono, S.L. Blair, S. Sandoval, J. Wang-Rodriguez, R.F. Mattrey, A.C. Kummel, and W.C. Trogler, "Hard shell gas-filled contrast enhancement particles for colour Doppler ultrasound imaging of tumors," *MedChemComm,* **1**, 266-270 (2010).